Chemical analysis of oils, fats, waxes and of the commercial products derived therefrom : founded on Benedikt's second ed. of 'Analyse der fette,' / by Dr. J. Lewkowitsch.

Contributors

Lewkowitsch, J. 1857-1913.
Benedikt, Rudolf, 1852-1896. Analyse der fette.

Publication/Creation

London : Macmillan and co., limited ; New York, The Macmillan company, 1898.

Persistent URL

https://wellcomecollection.org/works/czbkewg9

License and attribution

This work has been identified as being free of known restrictions under copyright law, including all related and neighbouring rights and is being made available under the Creative Commons, Public Domain Mark.

You can copy, modify, distribute and perform the work, even for commercial purposes, without asking permission.

wellcome collection

Wellcome Collection
183 Euston Road
London NW1 2BE UK
T +44 (0)20 7611 8722
E library@wellcomecollection.org
https://wellcomecollection.org

N VII. e 20

EX LIBRIS



WELLCOME

CHEMICAL RESEARCH

LABORATORIES

LONDON

22900367896

C.R. 7054

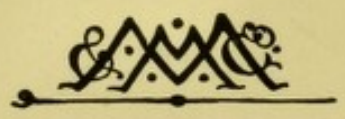
Med
K1183

THE
WELLCOME
RESEARCH LABORATORIES.

CHEMICAL ANALYSIS

OF

OILS, FATS, AND WAXES



CHEMICAL ANALYSIS

OF

OILS, FATS, WAXES

AND OF THE

COMMERCIAL PRODUCTS DERIVED THEREFROM

FOUNDED ON BENEDIKT'S SECOND EDITION OF 'ANALYSE DER FETTE'

BY

DR. J. LEWKOWITSCH, F.I.C., F.C.S.

CONSULTING AND ANALYTICAL CHEMIST, AND CHEMICAL ENGINEER; EXAMINER IN SOAP MANUFACTURE, AND IN FATS AND OILS, INCLUDING CANDLE MANUFACTURE, TO THE CITY AND GUILDS OF LONDON INSTITUTE

SECOND THOROUGHLY REVISED AND ENLARGED EDITION

London

MACMILLAN AND CO., LIMITED

NEW YORK: THE MACMILLAN COMPANY

1898

All rights reserved

12598

135250?

First Edition, 1895; *Second Edition*, 1898.

WELLCOME INSTITUTE LIBRARY

Coll.	welMOmec
Call No.	QP

PREFACE TO THE SECOND EDITION

THE gratifying fact that the First Edition has been exhausted in so comparatively short a time could but act as an incentive to me to increase, as far as possible, the usefulness of this work.

The daily use of the book in the laboratory showed me the necessity for a more logical exposition, and accordingly the subject-matter of Chapters i.-viii. has been entirely rearranged, and to some extent amplified and rewritten. Separate chapters have been assigned to the Saponification of Fats and Waxes, and to the Chemistry of Resin, the importance of the matter fully justifying this step. Special attention has been paid to the Chapters ix. to xii., and nearly all the tables have been either re-cast or enlarged.

This Second Edition claims, therefore, to be a thoroughly revised one. The new matter—not always consisting of abstracts of recently published papers—has been worked into and amalgamated with the context. I believe that no paper published on our subject during the last few years has escaped my attention; but in accordance with the principles laid down in the Preface to the First Edition, I have excluded matter which seemed to me of doubtful value, and relegated to footnotes those publications that appeared to be of minor importance.

I hope that my criticism may meet with the approval of my professional brethren, for, in my opinion, the reader of a work of this kind does not merely want a compilation of facts, but also desires opinion for guidance.

Where new methods or new lines of research have appeared likely to lead to an extended knowledge, I have taken care to point this

out, and I hope that such hints may help to swell the ranks of workers, whose lines have been sadly thinned by the premature deaths of such eminent investigators as Benedikt and Alder Wright.

The footnotes refer for more detailed information in the first instance to the pages of the *Journal of the Society of Chemical Industry*, it being assumed that this review is in the hands of every reader. Wherever that journal does not give an abstract of the original paper, other journals are used as reference in the order of easy accessibility to the majority of chemists.

I have some doubts as to the advisability of adding a chapter on reagents and a series of tables frequently required in the laboratory, but the book being out of print, the consideration of this matter must be left for a subsequent edition.

J. LEWKOWITSCH.

December 1897.

PREFACE TO THE FIRST EDITION

THERE has not hitherto been any English work dealing exclusively with the chemical analysis of Oils, Fats, and Waxes. I was on the point of writing one, in compliance with a wish expressed to me by several friends, when I was asked by Professor Benedikt to render his German work, *Die Analyse der Fette und Wachsarten*, into English, with such alterations as I thought necessary. As his book is undoubtedly the best on that subject, I thought, instead of adding to the number of text-books, it would be more useful to found on it an English edition, and to increase its usefulness as far as I was able.

My task has therefore been a threefold one, to wit—to translate, revise, and enlarge the German work.

Little can be said under the first head. A literal translation of the text, as far as it was retained, was, of course, out of the question. Especially when describing analytical processes the almost epic breadth in which our Continental brethren indulge made it necessary to leave out many details which would be found wearisome by English chemists.

The *revising* of the work was the most important part of my task. I have often asked myself the question whether the writer of a book of this kind should not have himself tested all the methods he puts before his readers. But, on the one hand, it is impossible to personally examine every little modification or process, the description of which helps to swell the literature of our subject, whilst on the other hand to neglect this lays one open to the charge of hasty and presumptuous criticism. In revising I had to be guided by such experience as I have gained during many years devoted to the chemistry of Fats and Oils

in the laboratory, as well as in the works which it has been my lot to manage both in this country and on the Continent. If this experience has led me to criticise somewhat freely, I trust I have not transgressed the limits which ought to be observed; but I consider that criticism is decidedly necessary in this branch of applied chemistry, abounding as it does with papers and communications, the contents of which can only have been new to their writers. Therefore the reader is constantly referred to the pages of the *Journal of the Society of Chemical Industry*—our own *Jahresberichte*—and other easily accessible journals.

No useful purpose would be served by pointing out at length the numerous additions that have been made and the alterations which have been found necessary; of these every page bears evidence. It may, however, be stated briefly that obsolete processes have been abridged or entirely left out, and that the arrangement of the subject-matter has been altered so as to suit practical requirements. A special feature is the tabular form adopted for the constants of the individual oils, fats, and waxes. In Chapters ix.-xii. large portions have been entirely re-written, and differ so widely from the original, that they may be regarded as substantially new, and in Chapter xi. a system of classification has been given which appeared to me the most natural one, at any rate in the present state of our knowledge.

The *enlarging* has consisted, in the first instance, in devoting more space to the work of English and American chemists than would naturally be the case in a German publication. The new work in fat analysis published during the last four years has been embodied in the text, and all information up to the last weeks whilst the book has been in the press has been included. A large number of my own experiments and observations have been extracted from my note-books and published here for the first time. Thus the bulk of the book has been almost doubled notwithstanding extensive abridgments.

The responsibility for these alterations and additions rests with me. My object has been throughout to place a book before my colleagues, containing in a handy and easily accessible form all the information which is required in the practice of the analytical and technical chemist,—in short, a compendium such as I should have wished to have beside me for my own reference in the laboratory.

Great as the temptation has been to the contrary, the description of technical processes has been compressed within the narrowest limits,

and only those points have been emphasised which are required to give the analyst the necessary clue as to the lines to be adopted in the course of analysis.

I trust also that the scientific aspect of the subject has not been lost sight of, as indeed it ought not to be, for, to quote from Benedikt's preface, "The analysis of fats presents an almost complete system, such as is found in no other branch of technical organic analysis,—a system which will admit of application in the examination of ethereal oils, resins, balsams, and substances of a similar nature. For these reasons the analysis of fats and waxes may serve the student as the best introduction to the study of organic technical analysis."

It is hoped that, through the amalgamation of scientific accuracy with practical knowledge, a work has been produced that by its completeness may prove useful to the analytical, technical, and scientific chemist, as well as to the teacher of chemistry.

In conclusion, I wish to acknowledge my great indebtedness to my friend, Mr. William McDonnell Mackey, who has carefully read both the MS. and the proofs, with a view to making corrections in the language and freeing the text from any idiomatic harshness

J. LEWKOWITSCH.

February 1895.

CONTENTS

CHAPTER I

PHYSICAL AND CHEMICAL PROPERTIES OF FATS AND WAXES

PAGE

1. Fats (Liquid and Solid) 1
   Chemical constitution of fats. Preparation and properties of pure glycerides 1
   Monostearin, 2. Distearin, 3. Triacetin, 3. Tributyrin, 3. Triisovalerin, 4. Trilaurin, 4. Trimyristin, 4. Tripalmitin, 4. Tristearin, 4. Triarachin, 4. Tricerotin, 5. Trimelissin, 5. Triolein, 5. Trielaïdin, 5. Trierucin, 5. Tribrassidin, 5. Triricinolein 5
   Foreign substances in fats 6
   Free fatty acids in fats 7
   Properties of fats and fatty oils 8
   Rancidity of fats 11
   Behaviour with reagents 13

2. Waxes (Liquid and Solid) 14
   Chemical constitution of waxes. Preparation and properties of pure waxes 14
   Cetyl palmitate, 15. Octodecyl palmitate, 15. Ceryl palmitate, 15. Myricyl palmitate, 15. Cetyl stearate, 15. Ceryl cerotate, 15. Cocceryl coccerate, 15. Cholesteryl palmitate, 16. Cholesteryl oleate, 16. Cholesteryl stearate, 16. Isocholesteryl stearate . 16
   Foreign substances in waxes 16
   Free fatty acids and free alcohols in waxes 16
   Properties of waxes 17

CHAPTER II

SAPONIFICATION OF FATS AND WAXES

Saponification of fats 18
Purification of alcohol 19
Cold saponification 20
Saponification of waxes 22

CHAPTER III

CONSTITUENTS OF FATS AND WAXES

PAGE

A. ACIDS 26

Occurrence of fatty acids 26

Properties of fatty acids 27

Melting points, 27. Boiling points, 30. Solubility, 30. Action on indicators, 31. Methylorange, 31. Phenolphthalein, 32. Litmus, 33. Lacmoïd, 33. Viscosity of fatty acids, 33. Salts of fatty acids, 33. Salts of the alkali-metals, 33. Hydrolysis of soaps, 35.

Metallic soap 41

I. *Acids of the Acetic Series*, $C_nH_{2n}O_2$ 42

Acetic acid, 42. Butyric acid, 42. Isovaleric acid, 43. Isobutylacetic acid, 43. Caprylic acid, 44. Capric acid, 44. Umbellulic acid, 44. Lauric acid, 44. Myristic acid, 45. Isocetic acid, 45. Palmitic acid, 46. Daturic acid, 47. Margaric acid, 47. Stearic acid, 47. Arachidic acid, 49. Behenic acid, 49. Lignoceric acid, 49. Carnaübic acid, 50. Hyænic acid, 50. Cerotic acid, 50. Melissic acid 51

II. *Acids of the Oleic Series*, $C_nH_{2n-2}O_2$ 52

Tiglic acid, 53. Acids $C_{12}H_{22}O_2$ and $C_{14}H_{26}O_2$, 53. Hypogæic acid (Gaïdic acid), 53. Physetoleic acid, 53. Lycopodic acid, 54. Asellic acid, 54. Oleic acid, 54. Elaïdic acid, 57. Iso-oleic acid, 57. Rapic acid, 58. Doeglic acid, 58. Jecoleic acid, 59. Erucic acid, 59. Brassidic acid, 59. Iso-erucic acid 60

III. *Acids of the Linolic Series*, $C_nH_{2n-4}O_2$ 60

Elæomargaric acid, 60. Linolic acid, 60. Tariric acid, 61. Millet oil acid 61

IV. *Acids of the Linolenic Series*, $C_nH_{2n-6}O_2$ . . . 62

Linolenic acid, 62. Isolinolenic acid, 62. Jecoric acid . . 62

V. *Acids of the Series* $C_nH_{2n-8}O_2$ 63

Isanic acid, 63. Therapic acid 63

VI. *Hydroxylated Acids*, $C_nH_{2n}O_3$ 63

Lanopalmic acid, 63. Acid $C_{21}H_{42}O_3$, 64. Cocceric acid . . 64

VII. *Acids of the Ricinoleic Series*, $C_nH_{2n-2}O_3$ . . . 64

Ricinoleic acid, 64. Ricinisoleic acid, 64. Ricinelaïdic acid, 65. Ricinic acid 66

VIII. *Acids of the Series* $C_nH_{2n}O_4$ 66

Dihydroxylated acids, 66. Dihydroxystearic acid, 66. Lanoceric acid 66

Appendix to the Fatty Acids 67

I. Hydroxylated Acids 68

1. Monohydroxylated acids, $C_nH_{2n}O_3$ 68

β-Hydroxystearic acid, 68. α-Hydroxystearic acid, 69. Stearolactone 69

PAGE

I. Hydroxylated Acids—*continued.*

2. Dihydroxylated acids, $C_nH_{2n}O_4$ 69
Tigliceric acid, 69. Dihydroxypalmitic acid, 70. Dihydroxyasellic acid, 70. Dihydroxystearic acid, 70. Dihydroxystearidic acid, 70. p-Dihydroxystearic acid, 70. Dihydroxyjecoleic acid, 70. Dihydroxybehenic acid, 70. Isodihydroxybehenic acid, 71. Paradihydroxybehenic acid 71

3. Trihydroxystearic acids, $C_{18}H_{33}O_2(OH)_3$ . . . 71
Trihydroxystearic acid, 71. α-Isotrihydroxystearic acid, 71. β-Isotrihydroxystearic acid . . . 71

4. Tetrahydroxystearic acid, $C_{18}H_{32}O_2(OH)_4$ (Sativic acid) . 72

5. Hexahydroxystearic acids, $C_{18}H_{30}O_2(OH)_6$ . . . 72
Linusic acid, 72. Isolinusic acid 72

II. Dibasic Acids 72
Suberic acid, 73. Azelaic acid 73

B. ALCOHOLS 73

I. *Alcohols of the Ethane Series*, $C_nH_{2n+2}O$ . . . 73
Cetyl alcohol, 74. Octodecyl alcohol, 74. Carnaübyl alcohol, 74. Alcohol $C_{24}H_{50}O$, 75. Ceryl alcohol, 75. Isoceryl alcohol, 75. Myricyl alcohol (Melissyl alcohol) 75

II. *Alcohols of the Allylic Series*, $C_nH_{2n}O$ . . . 75
Lanolin alcohol, 76. Alcohols $C_{15}H_{30}O$ and $C_{36}H_{72}O$, 76. Psyllostearyl alcohol 76

III. *Alcohols of the Glycolic Series*, $C_nH_{2n+2}O_2$ . . . 76
Alcohol $C_{25}H_{52}O_2$, 76. Cocceryl alcohol 76

IV. *Alcohols of the Series* $C_nH_{2n+2}O_3$ 77
Glycerol, 77. Ethers of glycerol, 80. Reactions of glycerol, 80. Isoglycerol 83

V. *Alcohols of the Aromatic Series* 83
Cholesterol, 83. Isocholesterol, 85. Phytosterol . . 86

CHAPTER IV

DETERMINATION OF FOREIGN MATTERS OF A NON-FATTY NATURE, AND PREPARATION OF THE FATTY SUBSTANCE FOR ANALYSIS

1. Sampling 87
2. Estimation of water 88
3. Determination of foreign matters of a non-fatty nature in fats . . 88
4. Determination of fat 90
5. Preparation of the fat for examination 92
6. Determination of inorganic substances in the fatty matter . . 95
Sulphur, 95. Phosphorus, 97. Chlorine, 97. Metals, 97. Copper, 98. Lead, 98. Iron 99
7. Preparation of the insoluble fatty acids of a fat for examination . . 99
8. Weighing of the fat for analysis 101

CHAPTER V

PHYSICAL METHODS OF EXAMINING FATS AND WAXES

PAGE

1. Consistency and viscosity 102
   Viscosimeters, 105. Redwood's viscosimeter, 107. Saybolt's, 109. Engler's 109
2. Spectroscopical examination 113
3. Determination of the refractive power 113
   Abbe's refractometer, 115. Butyro-refractometer, 116. Pulfrich's refractometer, 117. Oleo-refractometer 119
4. Rotatory power of the plane of polarisation 120
5. Microscopical appearance 121
6. Electrical conductivity 121
7. Critical temperature of dissolution 122
8. Determination of the specific gravity 123
   Sprengel's picnometer, 125. Specific gravity of solid fats . . 128
9. Melting and solidifying points 130
   Solidifying points of fats, 132. Solidifying points of fatty acids, 133. Solidifying or freezing points of oils, 135. Freezing mixtures . 136

CHAPTER VI

CHEMICAL METHODS OF EXAMINING FATS AND WAXES

1. Ultimate Analysis of Fats and Waxes 137

2. Qualitative Examination of Fats of known Origin by strictly Scientific Methods 138
   A. Examination of the acid constituents 139
   Examination of the volatile acids, 139. Examination of the non-volatile acids, 140. Fractional crystallisation, 140. Oxidation of the liquid acid, 141. Fractional distillation . . . 144
   B. Examination of the basic constituents. 146

3. General Methods of Quantitative Analysis of Fats, or Mixed Fats and Waxes 147
   A. *Quantitative Reactions* 147
   i. The acid value 148
   ii. The saponification value (Köttstorfer value), 151. Saponification equivalent 153
   iii. The ether value 154
   iv. The Reichert-Meissl value, 154. Baryta value . . . 159
   v. The Hehner value 160
   vi. The acetyl value. 162
   vii. The (bromine or) iodine value, 167. (*a*) Bromine value, 167. (*b*) Iodine value 170

PAGE

B. *Quantitative Determination of some Constituents of Fats and Waxes* . 181

i. Free fatty acids and neutral fat; mean molecular weight of the fatty acids 182

ii. Diglycerides 190

iii. Soluble (volatile) and insoluble (non-volatile) fatty acids . 191

iv. Saturated and non-saturated fatty acids—Proportion of liquid and solid acids in the insoluble fatty acids . . . 192

v. Mixed palmitic, stearic, and oleic acids, other non-volatile fatty acids being absent, 196. Determination of oleic acid, 197. Determination of stearic acid, 198. Determination of palmitic acid, 199. Determination of oleic, palmitic, and stearic acids 201

vi. Approximate determination of liquid fatty acids—oleic and linolic 202

vii. Hydroxy acids 204

viii. Lactones—Inner anhydrides 206

ix. Glycerol, 207. Determination of glycerol by titration with caustic potash, 208. Determination of glycerol by oxidation processes, 208. Determination of glycerol by the acetin process 213

x. Higher aliphatic alcohols 213

CHAPTER VII

DETECTION AND QUANTITATIVE DETERMINATION OF UNSAPONIFIABLE MATTER IN FATS AND WAXES

1. Detection of Unsaponifiable Matter. 217

2. Quantitative Determination of Unsaponifiable Matter . . 218

i. Gravimetric methods 218

ii. Volumetric methods 222

3. Detection of Small Quantities of Fat in Mineral Oils . . 223

4. Examination of the Unsaponifiable Matter. 224

i. Liquid unsaponifiable substances, 224. Mineral oils, 224. Tar oils, 225. Resin oils, 225. Discrimination between mineral, resin, and tar oils 225

ii. Solid unsaponifiable substances 229

CHAPTER VIII

DETECTION AND QUANTITATIVE DETERMINATION OF RESIN IN FATS OR FATTY ACIDS

i. Properties of resin 234

ii. Detection of resin when admixed with fats, fatty acids, and waxes . 238

iii. Quantitative determination of resin in neutral fats . . . 239

iv. Quantitative determination of resin acids in admixture with fatty acids . 240

PAGE

1. Barfoed's method, 240. 2. Gladding's method, 241. 3. Twitchell's method 244
v. Quantitative determination of resin in admixture with fats or fatty acids and unsaponifiable matter 249
vi. Separation of resin from fatty matter 250

CHAPTER IX

APPLICATION OF PHYSICAL AND CHEMICAL METHODS TO THE SYSTEMATIC EXAMINATION OF FATTY OILS AND LIQUID WAXES

Organoleptic Methods 252

A. Application of Physical Methods in the Identification of Individual Oils and Recognition of their Purity . . . 254
i. Specific gravities of fatty oils and liquid waxes . . . 254
ii. Solidifying points of fatty oils, 259. Melting and solidifying points of some fatty acids 260
iii. Optical methods of examination 261
Spectroscopical examination 261
Refractometric examination 261
Polarimetric examination 267
iv. Viscosimetric examination 268
v. Difference in the solubility of oils as a means of identification . 269
Solubility in alcohol 269
Solubility in acetic acid, Valenta's test 270
Solubility in carbolic acid 274
vi. Other physical properties 274
Cohesion figures 274
Pattern test 275
Electrical conductivity 275
vii. Critical temperature of dissolution 276

B. Application of Chemical Methods in the Identification of Individual Oils and Recognition of their Purity . . . 277
Liquid waxes 277. Fish, liver, and blubber oils, 278. Drying and non-drying oils 279
1. Elaïdin test 280
2. Sulphur chloride test 282
3. Oxygen absorption test. Livache test 285
4. Thermal tests 291
Thermal reaction with sulphuric acid: Maumené test . . 291
Thermal reaction with sulphur chloride 298
Thermal reaction with bromine 300
5. Quantitative reactions 302
Saponification values 302
Hehner values 306
Reichert (Meissl) values 306
Iodine (and Bromine) values 307
Acetyl values 313
6. Qualitative reactions 313
Colour reactions 314
Distinction between animal and vegetable oils 317

CHAPTER X

APPLICATION OF PHYSICAL AND CHEMICAL METHODS TO THE SYSTEMATIC EXAMINATION OF SOLID FATS AND WAXES

PAGE

1. Specific gravities of solid fats and waxes 321
2. Melting and solidifying points of solid fats and waxes . . . 323
3. Melting and solidifying points of the mixed fatty acids from fats and waxes 325
4. Behaviour with solvents 328
5. Hehner values 328
6. Reichert-Meissl values 329
7. Saponification values 329
8. Iodine (and Bromine) values 329
9. Acetyl values 333
   Thermal tests 333
   Sulphur chloride test 333
   Refractive index 333

CHAPTER XI

DESCRIPTION OF NATURAL FATS AND WAXES: METHODS OF EXAMINING THEM AND DETECTING ADULTERATIONS

A. OILS AND FATS. GLYCERIDES 336

I. Oils or Liquid Fats 336

1. *Vegetable Oils* 336

(1) *Drying Oils* 336

Linseed oil 336
Japanese wood oil 345
Lallemantia oil 347
Hemp seed oil 348
Walnut oil—Nut oil 350
Poppy seed oil 352
Niger seed oil 354
Sunflower oil 356
Fir seed oil 358
Madia oil 360
Candle nut oil 362
Isano (Ungueko) oil 362
Mohamba oil 363
Garden rocket oil 363
Henbane seed oil 365
Celosia oil 365
Indian laurel oil 365
Tobacco seed oil 365
Weld seed oil 366

PAGE

(2) *Semi-drying Oils* 366

a. Cotton seed oil group 366

Cameline oil (German Sesamé oil) . . . 367
Soja bean oil 369
Pumpkin seed oil 371
Maize oil—Corn oil 372
Kapok oil 375
Cotton seed oil 375
Sesamé oil (Gingili oil, Teel oil) . . . 385
Basswood oil 393
Beechnut oil 393
Brazil nut oil 395

β. Rape oil group 397

Garden cress oil 397
Hedge mustard oil 399
Rape oil [Colza oil] 399
Black mustard oil 407
White mustard oil 409
Radish seed oil 411
Jambo oil 413

γ. Castor oil group 413

Croton oil 414
Curcas oil (Purging nut oil) 416
Grape seed oil 418
Castor oil 420

(3) *Non-drying Oils* 426

Cherry kernel oil 426
Cherry laurel oil 428
Apricot kernel oil 428
Plum kernel oil 430
Peach kernel oil 432
Wheat-meal oil 434
Acorn oil 434
Almond oil 435
Sanguinella oil 440
Californian nutmeg oil 441
Arachis oil (Peanut oil, Earthnut oil) . . . 441
Rice oil 447
Tea seed oil 447
Pistachio oil 449
Hazelnut oil 449
Olive oil 451
Olive kernel oil 464
Coffee berry oil 465
Ungnadia oil 466
Ben oil 467
Strophantus seed oil 467
Secale oil 468

PAGE

2. *Animal Oils* 468

(1) *Marine Animal Oils* 469

α. Fish oils 470

Menhaden oil 470

Sardine oil. Japan fish oil 472

β. Liver oils 474

Cod liver oil. Cod oil. Coast cod oil . . . 475

Shark liver oil. Haddock liver oil. Skate liver oil . 489

γ. Blubber oils 490

Seal oil 490

Whale oil 492

Dolphin oil (Black fish oil) 495

Porpoise oil 497

(2) *Terrestrial Animal Oils* 499

Sheep's foot oil 499

Horses' foot oil 501

Egg oil 503

Neat's foot oil 504

II. Solid Fats 506

1. *Vegetable Fats* 506

Cotton seed stearine 506

Chaulmoogra oil 508

Carapa oil (Crab wood oil) 509

Laurel oil 509

Mowrah seed oil (Mahwah butter) 511

Shea butter (Galam butter) 513

Vegetable tallow (of China) 515

Palm oil 517

Macassar oil 520

Sawarri fat 521

Mafura tallow 521

Nutmeg butter (Mace butter) 523

Rambutan tallow 526

Mkanyi fat 526

Cacao butter 527

Kokum butter, Goa butter, Mangosteen oil . . . 531

Borneo tallow 533

Dika oil (Oba oil) 533

Mocaya oil 534

Palm nut oil 535

Cocoa nut oil 537

Myrtle wax 542

Ucuhuba fat 544

Japan wax 546

Malabar tallow (Piney tallow) 549

Wild olive fat 550

PAGE

2. *Animal Fats* 550

Blackcock, wild duck, domestic duck, starling, pigeon, turkey, fox, badger, pine marten, chicken, polecat, dog, wild cat, domestic cat, elk, roebuck, fallow buck, chamois . . 551
Horse fat 552
Horse marrow fat 555
Hare fat 555
Rabbit fat 557
Goose fat 559
Human fat 562
Lard 563
Lard oil 584
Beef marrow fat 586
Bone fat 587
Tallow 591
Tallow oil 591
Beef tallow 592
Mutton tallow 598
Butter fat 601
Stag fat 641

B. WAXES 643

I. Liquid Waxes 643

Sperm oil 643
Arctic sperm oil (Bottlenose oil) 647

II. Solid Waxes 649

1. *Vegetable Waxes* 649

Carnaüba wax 649

2. *Animal Waxes* 651

Wool wax (Wool grease) 651
Beeswax 655
Spermaceti (Cetin) 669
Insect wax (Chinese wax) 672

CHAPTER XII

TECHNICAL AND COMMERCIAL ANALYSIS OF THE RAW MATERIAL AND PRODUCTS OF THE FAT AND OIL INDUSTRIES

A. Oleaginous Seeds and Oil Cakes 673

B. Fats and Oils 676

1. Synthetical fats. Acetine 676
2. Edible fats and oils 678
(*a*) Edible fats 678
Butter substitutes 678
Lard substitutes 682
(*b*) Edible oils. Salad oils (Sweet oils) 684
3. Burning oils 685
4. Paint oils 685

PAGE

C. Waste Fats 686

1. Wool fat, Wool grease (Recovered grease, Brown grease) . . 686
(*a*) Pure (Anhydrous) wool fat. Adeps Lanæ . . . 689
(*b*) Lanoline 689
(*c*) Distilled grease 690
2. Cotton seed foots 692
3. Fuller's grease—"Seek oil" 693
4. Black oil 693
5. Sod oil—Dégras 693

D. Wool Oils—Cloth Oils 704

E. Lubricating Oils 712

1. Fatty oils and liquid waxes 718
2. Mineral oils 719
3. Mixtures of fatty and mineral oils 722
4. Solid lubricants—Greases 726

F. Turkey-red Oils 726

G. Oxidised Oils 733

1. Blown oils, Base oils, Thickened oils, Soluble castor oil . . 733
2. Boiled oil 735
3. Lithographic varnish 739
Linoleum 741

H. Vulcanised Oils. Rubber Substitutes 742

I. Candles 745

1. Tallow candles 745
2. Stearine candles 745
3. Wax candles 755
4. Sperm candles 756
5. Paraffin wax candles 757
6. Cerasin candles 763

K. Commercial Oleic Acid. Oleine, Elaïne 765

L. Soaps 769

I. Soaps of the alkali metals 769
II. Insoluble soaps (Metallic soaps) 785

M. Glycerin 786

1. Chemically pure glycerin 786
2. Dynamite glycerin 802
3. Crude glycerin 805

CHAPTER XIII

EXAMPLES

1. Tournant oil 811
2. Commercial acetine 812
3. Composition of butter fat 812
4. Product obtained by the action of zinc chloride on oleic acid . . 812
5. "Recovered grease" 816
6. Distilled grease 820

CHAPTER I

PHYSICAL AND CHEMICAL PROPERTIES OF FATS AND WAXES

UNDER the term natural fats and waxes (liquid and solid) we comprise all those substances that are formed in animals and plants, and consist mostly of glycyl,—or other ethers of the higher members of the several series of fatty acids, sometimes in conjunction with the free fatty acids themselves.

A systematic classification of the fats and waxes is not yet possible, all attempts at establishing different classes or groups based on physical differences having hitherto failed.

Thus the consistency has been made the basis of a classification into oils, lards, and solid fats; and some authors have tried to differentiate the fats into several groups by making use of some chemical properties of the fats, as the drying properties, etc.; but the old adage "*natura non facit saltum*" has proved too strong for these artificial classifications, inasmuch as there exist a number of intermediate fats which might be classified under two or more heads.

A distinct difference, however, can be established between fats and waxes on chemical grounds.

Considered chemically the fats are the neutral glycerides of fatty acids, whilst the waxes are ethers formed by the union of fatty acids and alcohols of the ethane (and perhaps also of the allylic) series. This chemical difference, however, does not always find a ready expression in common parlance. Thus, *e.g.* Japan wax consists chiefly of glycerides, whilst on the other hand sperm oil, according to its chemical constitution, must be classed amongst the waxes.

For the sake of convenience we subdivide in this work the fats and waxes into liquid and solid ones. The liquid fats are also termed fatty oils or, in short, oils.

1. FATS (LIQUID AND SOLID)

Chemical Constitution of Fats. Preparation and Properties of Pure Glycerides

The fats are the product of the combination of glycerol and fatty acids. Glycerol being a trihydric alcohol, and consequently deporting

itself like a trihydric base, is able to combine with three radicles of fatty acids, as expressed by the following equation, in which R represents the acid radicle of any fatty acid :—

$$\begin{matrix} O.H \\ C_3H_5\ O.H \\ O.H \end{matrix} + 3R.OH = \begin{matrix} O.R \\ C_3H_5\ O.R \\ O.R \end{matrix} + 3H_2O.$$

The resulting compounds are called "triglycerides" or "neutral glycyl ethers," and they may be compared to neutral salts; therefore the triglycerides are also called *neutral fats*, and their nomenclature is similar to that of salts. Thus we speak of glyceryl stearate or stearic glyceride, etc. This constitution of the fats has been established by the classic researches of *Chevreul* (*Les Corps Gras d'origine animale.* Paris, 1815-1823. Reprinted 1889), *Berthelot*, and *Wurtz*. Adopting this constitution of the neutral fats, theory predicts the possible existence of diglycerides and monoglycerides corresponding to the formulæ

$$\begin{matrix} O.R \\ C_3H_5\ O.R \\ O.H \end{matrix} \text{ and } \begin{matrix} O.R \\ C_3H_5\ O.H \\ O.H. \end{matrix}$$

In nature only the triglycerides occur, the monoglycerides and diglycerides are apparently not met with in freshly rendered fats. *Allen's* conjecture that Japan wax contains the diglyceride of palmitic acid,

$$\begin{matrix} O.R \\ C_3H_5\ O.R \\ O.H \end{matrix}$$

($R = C_{16}H_{31}O$), has not been confirmed. *Will* and *Reimer*, however, have found in old rape oil the diglyceride of erucic acid, $C_3H_5(O.C_{22}H_{41}O)_2OH$, but this exception to the general rule is only an apparent one, as it is most likely that the rape oil in question had become rancid with formation of free erucic acid, whilst dierucin separated as a solid mass.

The mono- and diglycerides can be prepared synthetically by heating fatty acids with glycerol (*Berthelot*).

Thus, on heating equal parts (by weight) of stearic acid and glycerol in a sealed tube for twenty-six hours at 200° C., part of the contents is converted into *monostearin*[1] according to the following equation—

$$C_3H_5(OH)_3 + C_{18}H_{35}O.OH = C_3H_5(O.C_{18}H_{35}O)(OH)_2 + H_2O.$$

The monostearin is isolated by separating off the fatty substance floating on the unchanged part of the glycerol, dissolving it in ether, adding slaked lime to convert the unchanged stearic acid into its calcium salt, warming a little and finally extracting with boiling ether.

Monostearin crystallises in microscopic needles, melting point 61° C. It distils unchanged *in vacuo*. It dissolves with some difficulty in cold ether, but readily in hot ether and hot alcohol.

Distearin is prepared by heating equivalent quantities of mono-

[1] The spelling "acetin," "stearin," etc., denotes in this work the pure triglycerides, whilst under "acetine," "stearine," etc., the commercial products are understood.

stearin and stearic acid in a retort up to 150°-180° C., and at-last from 180° to 200° C., until one molecule of water has passed over. It crystallises from alcohol in needles, melting point 76·5° C. It is very slightly soluble in cold alcohol, readily so in 150 parts of boiling alcohol; it is easily soluble in warm ether, petroleum ether, chloroform, and benzene.[1]

A great many fats may be considered as mixtures of the triglycerides of the several fatty acids, say of tripalmitin, tristearin, and triolein. It may be noted in favour of this assumption, that from the liquid oils tripalmitin and tristearin separate out on cooling either in their pure state or as a mixture. It is, however, not unlikely that there exist fats which consist of mixed ethers of glycerol, *i.e.* ethers containing in one molecule the acid radicles of several different fatty acids combined with glycerol. Thus, experiments by *Bell* have rendered probable the existence of an oleo-palmito-butyrate, of the formula $C_3H_5(O.C_{18}H_{33}O)(O.C_{16}H_{31}O)(O.C_4H_7O)$, in cow butter (cp. Butter Fat, chap. xi. p. 605). Recently *Heise* stated that oleodistearin occurs in Mkanyi fat and in Kokum butter[2]) (cp. p. 526).

The most important of the triglycerides, because most largely occurring in nature, are tripalmitin, tristearin, and triolein.

The following triglycerides have been prepared in a state of purity :—

Triacetin, *Acetin*, $C_3H_5(O.C_2H_3O)_3$, is prepared by heating 20 c.c. of glycerol with 10 c.c. of acetic anhydride and 50 grms. of finely powdered hydrogen potassium sulphate. As soon as a violent reaction sets in 20 c.c. more of acetic anhydride are added and the mixture boiled for some time. The cooled mass is exhausted by means of ether, and thus a mixture of triacetin and diacetin is obtained, which can be separated into its components by fractional distillation.

Triacetin boils at 258°-259° C. under ordinary pressure; at 171° C. under 40 mm. pressure. Its specific gravity is 1·1603 at 15° C. (water 15° C. = 1).[3] It is miscible with alcohol, ether, chloroform, benzene; it is, however, insoluble in carbon bisulphide and petroleum ether.[3]

Tributyrin, *Butyrin*, $C_3H_5(O.C_4H_7O)_3$, is obtained on boiling one molecule of glycerol with three molecules of butyric acid for sixty hours. It is a butter-like mass, distilling unchanged at 285° C. Its specific gravity is 1·056 at 8° C., 1·052 at 22° C. Butyrin when boiled with strong alcohol and a quantity of caustic potash insufficient for complete saponification yields ethyl butyrate.

[1] Monocerotin, dicerotin, monomelissin, and dimelissin have been prepared synthetically by *Marie* (*Jour. Chem. Soc.* 1896, Abstr. i. 347).

[2] *Arbeiten aus dem Kaiserlichen Gesundheitsamte*, 1896, xii. 540; xiii. 302, Oleodistearin, $C_3H_5(O.C_{18}H_{35}O)(O.C_{18}H_{35}O)_2$, obtained by precipitating with alcohol the ethereal solution of these fats, is stated to melt at 44°-44·5° C., and to solidify at 40·8°. If the melted glyceride is cooled rapidly, the melting point is 27°-28° C., and rises gradually, on keeping at the ordinary temperature, to 37°-38° C. Its specific gravity at 70° C. is 0·8928, and at 98° C. 0·8547. Although *Heise* has no doubt as to the individuality of the oleodistearin, it appears (to me) strange that the mixed fatty acids, consisting roughly of 33 per cent oleic acid and 66 per cent stearic acid, should have as high a melting point as 60°-62° C. (cp. Dalican's table, chap. xii. p. 750).

[3] 100 c.c. of water at 15° C. dissolve 7·17 grms. Geitel, *Jour. praktische Chemie*, 1897 [55], 420.

Triisovalerin, Valerin, $C_3H_5(O.C_5H_9O)_3$, is formed by heating synthetical divalerin with 8-10 parts of isovaleric acid to 220° C. It is soluble in alcohol and ether.

Trilaurin, Laurostearin, Laurin, $C_3H_5(O.C_{12}H_{23}O)_3$, has been isolated by boiling pichurim beans or laurel oil with alcohol. It is stated to occur in the liver fat of a crustacean.[1] It crystallises in needles, melting point 45° C. Sparingly soluble in cold absolute alcohol, it dissolves readily in ether.

Trimyristin, Myristin, $C_3H_5(O.C_{14}H_{27}O)_3$, has been found in nutmeg butter, and in the wax from cochineal. It crystallises from its ethereal solution in laminæ, melting point 55° C. When melted trimyristin is heated to 57°-58° C. it solidifies into a porcelain-like mass, melting at 49° C. Heated again for a very short time to 50° C. it solidifies and regains the original melting point, viz. 55° C. Trimyristin is easily soluble in ether, benzene, and chloroform.

Tripalmitin, Palmitin, $C_3H_5(O.C_{16}H_{31}O)_3$, has been obtained synthetically by heating either dipalmitin with palmitic acid, or a mixture of glycerol and palmitic acid, when mono- and dipalmitin are formed simultaneously. The tripalmitin is isolated by dissolving the mixture in alcohol and allowing it to crystallise, when small nacreous crystals of the triglyceride are obtained. They dissolve with very great difficulty in cold alcohol, more easily in hot alcohol, separating from this solution in flocks. Ether dissolves tripalmitin in every proportion. The crystals melt at 62° C., also 63°-64° C., solidifying at 45·5° C., also 45°-47° C.; this change in the melting and solidifying points seems to depend on slight differences of manipulation, such as the rapidity of heating the crystals, and on the temperature they have been cooled down to.

Tristearin, Stearin, $C_3H_5(O.C_{18}H_{35}O)_3$, is obtained by heating monostearin with 15-20 parts of stearic acid for three hours at 275° C. It is a crystalline substance, still less soluble in cold alcohol than palmitin; solutions of tristearin in boiling alcohol deposit the dissolved substance nearly completely on cooling. Judging from the melting points, there exist two modifications of stearin, one melting at 71·6° C., the other at 55° C.

The stearin obtained by crystallisation from ether melts at 71·6° C., and solidifies at 70° C. to an indistinctly crystalline mass; this, when heated above its melting point—by at least four degrees—solidifies at about 52° C. to a wax-like mass, melting at 55° C.; and on heating this modification a few degrees above its melting point, the former substance, having the melting point 71·6° C., is again obtained. The specific gravity of a (not quite pure) specimen of stearin in the melted state was found to be 0·9235 at 65·5° C. Stearin distils unchanged *in vacuo*.

Tristearin is partially converted into ethyl stearate by boiling with a solution of sodium in absolute alcohol (*Duffy*), or by heating with small quantities of alcoholic potash (*Bouis*). On substituting amyl alcohol for ethyl alcohol, amyl stearate is obtained.

[1] *Chem. Zeit.* 1895, 651.

Triarachin, *Arachin*, $C_3H_5(O.C_{20}H_{39}O)_3$, prepared by *Berthelot* from diarachin and arachidic acid, is very slightly soluble in ether.

Tricerotin, *Cerotin*, $C_3H_5(O.C_{25}H_{49}O)_3$, has been prepared by *Marie*[1] from dicerotin. It crystallises in slender needles, melting at 76·5°-77° C.

Trimelissin, *Melissin*, $C_3H_5(O.C_{30}H_{59}O)_3$, was obtained from dimelissin by *Marie*.[1] It resembles cerotin; its melting point is 89° C.

Cerotin and melissin apparently do not occur in nature.

Triolein, *Olein*, $C_3H_5(O.C_{18}H_{33}O)_3$. This glyceride[2] has been obtained by heating glycerol with an excess of oleic acid at 240° C. Olein is a liquid substance which has not been obtained hitherto in the solid state; it distils *in vacuo* without decomposition. Its specific gravity at 15° C. is 0·900.

Olein dissolves easily in ether; in absolute alcohol it is more readily soluble than either palmitin or stearin; it is insoluble in dilute alcohol.

Olein combines with concentrated sulphuric acid to form a saturated compound having the formula $(C_3H_5)_2(O.C_{18}H_{34}O.SO_4.C_{18}H_{34}O.O)_3$;[3] this substance is very unstable, and is partly dissociated on treatment with water or alcohol into H_2SO_4 and α-hydroxystearic acid.

Just as oleic acid is converted by nitrous acid into elaïdic acid (p. 57), so olein is converted under the same conditions into elaïdin.

Trielaïdin, *Elaïdin*, $C_3H_5(O.C_{18}H_{33}O)_3$, crystallises in warts, melting point 32° C. (*Mayer*), 38° C. (*Duffy*). It dissolves readily in ether, but is nearly insoluble in alcohol.

Trierucin, *Erucin*, $C_3H_5(O.C_{22}H_{41}O)_3$, is prepared like olein. It is a crystalline mass, of the melting point 31° C. Nearly insoluble in alcohol, it dissolves very readily in ether, benzene, and petroleum ether. Nitrous acid converts trierucin into tribrassidin.

Tribrassidin, *Brassidin*, $C_3H_5(O.C_{22}H_{41}O)_3$, is a crystalline powder, melting point 47° C. When heated above its melting point it solidifies, on cooling, into another modification (?), melting at 36° C.

Triricinolein, *Ricinolein*, $C_3H_5(O.C_{18}H_{33}O)_3$, has been synthetised by heating ricinoleic acid with glycerol at 120°-130°, unchanged glycerol and ricinoleic acid being removed by water and petroleum ether respectively.[4] If *Berthelot's* method be employed, *i.e.* pressure and high temperature, condensation products of mono- and di-ricinolein are formed, the simplest of which is isomeric with triricinolein, and has the formula $OH.C_{17}H_{32}.COO.C_{17}H_{32}.COO.C_3H_5(C_{17}H_{32}.COOH)_2$.

When triricinolein is boiled with toluene, either alone or in presence of zinc chloride, it is condensed to various ethers, such as that represented by the formula $[(OH.C_{17}H_{32}.COO)_2C_3H_5.C_{17}H_{32}.CO]_2O$, which differ from triricinolein by their sparing solubility in alcohol and petroleum ether.

H. Meyer[5] describes triricinolein (prepared by heating ricinoleic

[1] *Jour. Chem. Soc.* 1896, Abstr. i. 347.
[2] Coula oil is stated to consist of almost pure olein (*Jour. Soc. Chem. Ind.* 1895, 493).
[3] Cp. also Juillard, *Jour. Soc. Chem. Ind.* 1894, 820.
[4] Juillard, *Jour. Chem. Soc.* 1895, Abstr. i. 500.
[5] *Jour. Soc. Chem. Ind.* 1897, 633, 684.

acid and glycerin to 280°-300° C.) as a colourless oil, soluble in 96 per cent alcohol, and in methyl alcohol, having the specific gravity 0·959-0·984, and $[\alpha]_D = +5·16°$. Unlike castor oil it does not form ricinelaïdin on treating with nitrous acid. On keeping, the molecule becomes doubled or trebled, the specific gravity being increased to 0·988-1·009 and the iodine number decreasing from 71-84 to 44-57.

Foreign Substances in Fats

In consequence of the mode of preparation adopted, the fats are generally found to contain impurities of one kind or another, such as remnants of animal or vegetable tissue, or other foreign substances. These, for the most part, can be got rid of by washing with water (the solid fats must be washed in a melted state), with subsequent drying and filtering.

The fats purified as described above still contain small quantities of foreign substances, such as minute traces of colouring matters (causing the colour reactions which are characteristic of some fats), albuminoid substances [1] occurring in fats of animal origin, or cellulose, found in fats and oils prepared from seeds. These substances are dissolved in the fats, and appear after saponification, on decomposing the soaps with acid, as flocculent matter between the aqueous and the fatty acid layers.

According to *Allen* and *Thomson's* [2] researches, all the fats contain traces of unsaponifiable substances, either hydrocarbons (?) or higher alcohols. The occurrence of the latter may be explained by assuming the presence of minute quantities of wax-like substances in the fats.

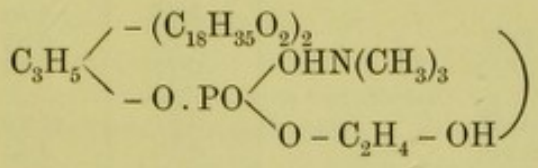
Allen and *Thomson* have examined the following fats quantitatively :—

Fat.	Unsaponifiable. Per cent.
Olive oil	0·75
Rape oil (German)	1·00
Cotton seed oil	1·64
Lard	0·23
Cod liver oil	0·46-1·32
Japan wax	1·14

In the case of some of the fats the unsaponifiable substance consists of cholesterol, isocholesterol, or phytosterol. *Fahrion* [3] found in the course of an examination of thirty samples of various liver and blubber oils percentages of unsaponifiable matter (cholesterol) varying between 0·49 and 5·27. A specimen of egg oil contained 1·5 per cent of cholesterol.

[1] Yssel de Schepper and Geitel, *Dingl. Polyt. Jour.* 245, 295.
[2] *Chemical News*, 43. (1881), 267. [3] *Jour. Soc. Chem. Ind.* 1893, 607.

The fats from seeds of *Leguminosæ* and *Graminaceæ*, and also some fats of animal origin, as egg oil, contain not inconsiderable quantities of lecithin, $C_{44}H_{90}O_9PN$. This substance is split up, on saponification, into fatty acids, glycerolphosphoric acid and choline. (*Hoppe-Seyler* gives the following formula for lecithin :



The following table contains the proportion of lecithin found in a few fats :—

Fat from	Phosphorus. Per cent.	Corresponding to Lecithin. Per cent.	Observer.
Peas . .	1·17	30·5[1]	Töpler
Wheat . .	0·25	6·5[1]	,,
Egg Yolk .	—	0·2	Kitt

Schulze and *Likiernik*,[2] have also shown that lecithin is widely distributed in seeds (though absent from the husks), and that it passes to a considerable extent into their ethereal extracts.

Free Fatty Acids in Fats

Animal fats, when freshly prepared, contain but infinitesimal quantities of free fatty acids, and may therefore, for practical purposes, be considered as consisting of absolutely neutral glycerides.

Fats of vegetable origin, however, mostly contain notable amounts of free fatty acids. Experiments made by *Rechenberg*[3] have shown that unripe seeds contain considerably larger quantities of free acids than ripe ones. In the seeds, which have been gathered in the unripe state, chemical changes take place, resulting in a diminution of free fatty acids with formation of neutral fats.

Archbutt[4] has found in 151 samples of olive oil from 0·5 to 25·2 per cent of free fatty acids calculated to oleic acid.

Nördlinger[5] has determined the amount of free fatty acids in the oils mentioned in the subjoined table ; the percentages have also been calculated for oleic acid.

[1] These numbers appear to the writer extraordinarily high. As it seems probable that the potassium hydrate used in converting the phosphorus into phosphoric acid contained considerable quantities of alumina, these figures should be accepted with reserve.

[2] *Berichte*, 1891, 71.

[3] *Ibid.* 1881, 2217.

[4] *Jour. Soc. Chem. Ind.* 1889, 685.

[5] *Ibid.* 1889, 806.

Oils and Fats.	Percentage of Free Fatty Acids.		
	Minimum.	Maximum.	Mean.
A. Oils.			
Rape—Salad oil	0·53	1·82	1·19
Commercial oil	0·52	6·26	2·88
Extracted oil	0·77	1·10	0·93
Olive—Salad oil	...	...	1·66
Commercial oil	3·87	27·16	12·97
Poppy seed—Salad oil	0·70	2·86	1·92
Commercial oil	12·87	17·73	15·37
Extracted oil	2·15	9·43	4·72
Arachis—Salad oil	0·85	3·91	1·94
Commercial oil	3·58	10·61	6·52
Extracted oil	0·95	8·85	4·02
Sesamé—Salad oil	0·47	5·75	1·97
Commercial oil	7·17	33·13	17·94
Extracted oil	2·62	9·71	4·89
Cotton seed—Salad oil [1]	...	...	0·15
Commercial oil	0·42	0·50	0·46
Mustard—Expressed oil	0·68	1·02	0·85
Castor—Expressed oil	0·62	18·61	9·28
Extracted oil	1·18	5·52	2·78
Linseed—Commercial	0·41	4·19	1·57
Candle nut—Commercial	...	...	56·45
B. Solid Fats.			
Palm nut—Commercial, expressed	3·30	17·65	6·91
Extracted	4·17	11·42	8·49
Palm (old sample)	...	...	50·82
Cocoa nut—Commercial, expressed	3·03	14·35	7·92
Extracted	1·00	6·31	4·26
Mowrah seed—Commercial	...	...	28·54
Illipé—Extracted	14·40	34·72	24·56
Ucuhuba—Expressed	...	...	18·55
Japan wax	...	...	9·25

The amount of free fatty acids in vegetable fats increases on keeping. This is specially noticeable in the case of palm oil, which gradually decomposes, on standing for some time, into free fatty acids and glycerol.

Properties of Fats and Fatty Oils

The glycerides that occur naturally and that are free from fatty acids, or have been freed therefrom by chemical operations, are either liquid at ordinary temperature, or at least may be melted below 100° C. without decomposition. In the cold the solid fats become harder, whilst most of the liquid fats solidify.

Liquid fats easily penetrate into the pores of dry substances. If dropped on paper they leave a transparent spot—grease-spot—which cannot be removed by washing with water and subsequent drying. (Difference from glycerol spots.)

[1] Fresh cotton seed oil is entirely free from fatty acids, owing to its being refined by means of caustic alkalis.

A curious effect caused by fats, which may be used for the detection of the minutest quantities, has been described by *Lightfoot*. Camphor, crushed between layers of paper without having been touched with the fingers, rotates when thrown on water, but a trace of fat on the surface of the water causes the rotation to cease immediately; it is sufficient to touch the water with a needle which has been passed previously through the hair.

For analytical purposes the fats may be considered as completely insoluble in water, although traces are dissolved when the liquid fats are shaken with large quantities of water. On allowing the emulsions, thus obtained, to become clear by standing, separating the fat, filtering the aqueous layer, and shaking the latter with ether, a minute quantity of fat passes into that solvent, and may be recovered by evaporating the ether. On the other hand fats dissolve a little water; on heating, however, the last trace of moisture is expelled.

With the exception of castor oil, croton oil, and olive kernel oil, all fats dissolve but very sparingly in cold *alcohol*. Thus, according to *Jüngst*, 100 parts of alcohol, specific gravity 0·83, dissolve at 15° C.: 0·534 parts of rape oil, 0·642 parts of linseed oil, and 0·561 parts of grape seed oil. Boiling alcohol, however, dissolves somewhat larger quantities of fats, especially of the liquid ones; but, on cooling, nearly all the dissolved fat separates completely. The solubility is considerably increased by the presence of a large amount of free fatty acids (cp. chap. ix. p. 272).

The fats dissolve very readily in *ether*, *carbon bisulphide*, *chloroform*, *carbon tetrachloride*, *benzene*, *petroleum*, and *petroleum ether*. Castor oil, however, is insoluble in the two last-mentioned solvents. Pure stearin alone is but sparingly soluble in ether, one part of the triglyceride requiring 200 parts of ether; in the presence of other glycerides, however, the solubility of stearin in ether is much increased.

The solutions of the neutral fats are without action on indicators, provided, of course, that the solvents used have been completely freed from traces of acids.

In their pure state the fats and oils are odourless, colourless, and tasteless; and what is usually regarded as characteristic in these respects of the different oils and fats is really due to the presence of small quantities of foreign substances. On exposure to sunlight (and to air) even strongly coloured oils are gradually bleached, some oils becoming almost colourless.

The specific gravity of the fats and oils is less than that of water; it varies between the limits of 0·910 to 0·970.

Fats and oils dissolve sulphur and phosphorus at the ordinary temperature[1] to a slight extent.[2]

Soaps are also somewhat soluble in fats. Notable quantities of soaps, however, are dissolved by solutions of fats in ether or petroleum ether.

[1] At temperatures above 100° C. sulphur interacts with fats (cp. p. 14).

[2] On the solubility of indigo in fats and oils cp. *Jour. Soc. Chem. Ind.* 1895, 1027. Iodine is stated to be soluble in liver oils to the extent of 20 per cent, and in neat's foot oil up to 33 per cent (Focke, *Pharm. Zeit.* 1896, 616).

The fats can be heated up to about 250° C. without undergoing any change. When further heated, decomposition sets in owing to the destruction of the glycerol, with formation of volatile products, the most characteristic of which is acrolein. The intense odour of acrolein, which all fats emit on heating above 250° C., is one of the most characteristic criterions to distinguish fats and fatty oils from mineral or ethereal oils.

Amongst the volatile products obtained on heating the fats and fatty oils to high temperatures are found hydrocarbons, the quantity of which is considerably increased when the heating and the destructive distillation takes place under pressure. This fact lends strong support to the theory that the hydrocarbons of petroleum owe their origin to the destruction of animal fats.

On exposure to the atmosphere the fats and oils gradually undergo certain changes. The change is most marked in the case of the so-called *drying oils* (linseed oil, walnut oil, hemp seed oil, poppy seed oil, etc.) They thicken and dry with absorption of oxygen, and if exposed in sufficiently thin layers, *e.g.* spread on wood or glass, they are converted finally into a transparent, yellowish, flexible substance, insoluble in water and alcohol. This substance is called *varnish*. The change is attended by an increase in weight (*Livache's* test, see chap. ix. p. 285), and it takes place all the more readily if the oils have been mixed previously with certain metals or metallic compounds ("driers"), as lead, copper, or litharge, manganese borate, etc. The "drying" oils differ from the "non-drying" oils chemically in that they contain large amounts of the glycerides of linolic and linolenic acids, or other acids belonging to the same series.

The *non-drying* oils remain unchanged at the ordinary temperature (cp. p. 279) when absolutely pure and protected from light and air. The commercial oils, however, acquire, on exposure to air, a disagreeable smell and an acrid taste, at the same time becoming slightly thicker and acid to litmus; they turn "rancid," as the term runs. In the course of this alteration small quantities of volatile acids (butyric, isobutylacetic, and other acids) are formed, and the glycerol is also partially decomposed. At the same time the amount of free, non-volatile fatty acids increases considerably; in some cases, as in palm oil, the fats are split up into their components, fatty acids and glycerol. Rancidity is, however, not due, as is generally believed, to the liberation of free acid; for, as *Ballantyne*[1] has shown, in many instances (olive oil, castor oil, etc.) rancidity sets in and continues for some time without the liberation of any free acid whatever, whilst in other instances free acid is liberated long before the fat has turned rancid (cotton seed oil, linseed oil). *Heyerdahl*[2] (before him) had proved for cod liver oil, that addition of its free fatty acids (from 2 per cent downwards) to samples of oil free from rancidity did not impart to the oil a rancid character, although it certainly produced a

[1] *Jour. Soc. Chem. Ind.* 1891, 29.

[2] *Ibid.* 1889, 54. Cp. also Besana, *Chem. Zeit.* 1891, 410, and v. Klecki, *Zeit. f. analyt. Chemie*, 1895, 633.

sharp taste; thus no connection could be traced between rancidity and the proportion of free fatty acid.[1]

Therefore fats cannot be called "rancid" because of the presence of free fatty acids alone; this term must be reserved rather for those fats containing an excess of free fatty acids due to the action of air (*Nördlinger*), and, it should be added, exhibiting the peculiar taste of rancid fats.

The changes accompanying rancidity have been described by some authors as due to the action of certain foreign substances which are supposed to act as ferments. Others, again, point to a possible action of micro-organisms, a theory which seemed to have been supported by the discovery of living micro-organisms in poppy seed oil (*Kirchner*[2]). But *Duclaux*[3] has shown in an investigation of butter fat that micro-organisms play no such part,[2] the fat, being insoluble in water, not affording any nutriment to the protoplasma of the cells; rancidity is rather due to slight hydrolysis and the subsequent action of the oxygen in the air assisted by light, the influence of which is enhanced the larger the surface of the exposed fat is. *Ritsert*,[4] who has recently instituted an exhaustive examination into the causes of rancidity, has summed up his results in the following propositions: Pure lard is not turned rancid by bacteria, either aërobic or anaërobic, the bacteria introduced into the fat dying quickly. The action of ferments must also be excluded, sterilised fat, heated to a temperature of 140° C. (whereby ferments are destroyed), having become rancid on subsequent exposure to light and air. Nor can a certain amount of moisture be considered a necessary factor, experiments having shown that dried fats are more liable to turn rancid than such as contain a small quantity of moisture. Rancidity must, therefore, be considered due to *direct oxidation* by the oxygen of the air, this action being intensified by exposure to light.[5] Both oxygen and light must act simultaneously on fats and oils in order to produce rancidity, either of these agents alone being unable to cause any alteration in that respect. Nitrogen and hydrogen do not act on fats; nor does carbonic acid cause them to turn rancid. [The last-mentioned gas, however, seems to have some action on lard, imparting to it a tallow-like taste.]

Solid fats, especially those of animal origin, are less liable to turn rancid than liquid fats; the former resist better the action of light and air; indeed, it may be taken as a rule that the higher the proportion of stearin and palmitin, and the smaller the percentage of olein in a fat, the less will be its liability to become rancid.

[1] *Scala* (*Le Stazione sperimentale agric. ital.* 28, 733) proposes to measure the rancidity of fats other than butter by their proportion of free volatile acids.

[2] *Berichte der deutsch. botan. Gesellschaft*, 1888, 101; cp., however, p. 617. *Zopf*, *Schmidt*, *Ritthausen*, and *Baumann* have collected several kinds of fungi which consume fats, but it is very likely that in these cases an enzyme or similar body is the cause of the disappearance of the fats.

[3] *Annales de l'Institut Pasteur*, 1887; *Compt. rend.* 102, 1077.

[4] *Untersuchungen über d. Ranzigwerden der Fette.* Inaug. Diss. Berlin, 1890.

[5] Mjöen (*Forschungsberichte über Lebensmittel*, etc., 1897, 201), states that light is not necessary, and that the chemical change taking place in presence of air and under action of light differs from that occurring in absence of light.

The properties of rancid fats differ in some respects from those of neutral fats (see further below). It has generally been assumed that it is principally oleic acid that is set free on fats becoming rancid. Experiments, however, made by *Thum*,[1] with palm oil and olive kernel oil in order to ascertain if palmitic, stearic, and oleic acids are liberated in the same or in a different proportion to that in which they exist in those two fats, have proved that the ratio between oleic and the solid fatty acids is the same in the free as in the combined state. This fact was confirmed by *Spaeth* in the case of rancid lards.

A few data regarding the rancidity of some fats may be recorded here.

Lenz has found that a specimen of horse fat, exposed to the atmosphere for two years, increased by 3·5 per cent in weight. Afterwards the weight remained constant. The ultimate analysis showed that the percentages of carbon and hydrogen had decreased (from 76·72 per cent C to 71·05, and from 12·17 per cent H to 10·95 per cent) whilst the oxygen had increased. The insoluble fatty acids decreased by 5 per cent, the amount of soluble fatty acids having at the same time been increased.

Whilst it has been found by general experience (and confirmed by *Allen's* and *Ritsert's* researches) that fats kept in closed vessels remain unchanged for an indefinitely long time, *Langbein*[2] states that several animal fats which had been kept in corked bottles for ten years had acquired a rancid smell with formation of free fatty acids. He concludes from an "acetyl value" (cp. chap. vi. p. 162) he has found that *hydroxy acids* had been formed. The same conclusion has been arrived at by *Wachtel*[3] when examining very old samples of fat; and also by *Heyerdahl*,[4] who states that cod liver oil prepared with exclusion of air was free from hydroxy acids, whereas the oil heated in contact with air gave distinct "acetyl values." These experiments, however, cannot be looked upon as conclusive, the method of examination employed leaving room for doubt (compare Acetyl Value, chap. vi. p. 164), and the statement frequently met with in papers published by German analysts that hydroxy acids are formed when fats become rancid must be accepted with due reserve.

In contrast with these statements, and supported by ample evidence gained from experiments extending over four years, *Gröger*[5] has found for six kinds of fat that they suffer but little change if air be excluded, with one exception, viz. palm oil. An examination of the fatty acids isolated from the fats thus exposed showed, without an exception, that a splitting up of the fatty acids into acids of a lower molecular weight had taken place, instead of their undergoing change by mere additive absorption of oxygen. (This excludes the formation of hydroxy acids.) Further evidence in that direction was afforded by the isolation of azelaic and suberic acids in that portion of the rancid fat that was soluble in water. As to the glycerol,

[1] *Jour. Soc. Chem. Ind.* 1891, 70.
[2] Muspratt's *Chemie von Stohmann und Kerl III.* (1891), 505.
[3] *Jour. Soc. Chem. Ind.* 1890, 979.
[4] *Cod Liver Oil and Chemistry* by P. Möller, p. 93.
[5] *Jour. Soc. Chem. Ind.* 1889, 202.

Gröger concludes that it must suffer oxidation as well as the fatty acids, since free glycerol could not be found.

On blowing *air*—or, better still, *oxygen*—through fatty oils heated to the temperature of boiling water, oxidation takes place with evolution of heat sufficient to allow the oxidation process to continue without further heating. The most notable change is a large increase in the density, and the oils thus obtained, especially those from cotton seed oil, resemble very much castor oil in their density and viscosity, but differ from it in that they are soluble in petroleum ether. These oils are known in commerce under the name of *blown oils*, *oxidised oils*, *base oils*, or *soluble castor oil*, and are used for lubricating purposes (cp. chap. xii. p. 733). The *drying oils* subjected to this oxidising process yield jelly-like masses. The *blown oils* are characterised by a large amount of soluble non-volatile acids and triglycerides of hydroxy acids.

On mixing a fatty oil with *concentrated sulphuric acid* a considerable rise in temperature takes place with evolution of sulphurous acid (see chap. ix. p. 291, *Maumené* test). If the oil be mixed very gradually with the acid, and at a low temperature, glycerides of a complex constitution are formed. Thus on treating olive oil with concentrated sulphuric acid a compound has been obtained which may be regarded as a triglyceride of oleic acid, stearic sulphuric acid, and hydroxy-stearic acid,[1] possessing the formula

$$C_3H_5[O \cdot C_{18}H_{33}O] \cdot [O \cdot C_{18}H_{34}(SO_4H) \cdot O] \cdot [O \cdot C_{18}H_{34}(OH)O].$$

Concentrated nitric acid attacks the fats, acting on them violently and with copious evolution of red fumes. Hot dilute nitric acid oxidises the fats gradually.

Fahrion[2] concludes from some experiments that all glycerides of unsaturated acids when acted on with nitric acid give rise to the formation of hydroxy acids, which on further treatment with nitric acid are said to be converted into nitro-derivatives of hydroxy acids. This statement, however, being of a preliminary nature, stands in need of confirmation.

On treatment with *nitrous acid* the non-drying oils become solid, or acquire the consistency of butter according to the proportion of triolein (trierucin, etc.) they contain; the triolein (trierucin, etc.) being converted into the solid isomeride trielaïdin (trierucin, etc.) (cp. chap. ix. p. 281). Drying oils, on the other hand, remain liquid when similarly treated, although at the same time their chemical and physical properties are considerably modified. *Lidoff*[3] states that their specific gravity increases as also their viscosity and saponification value, whereas the iodine and the Hehner values decrease. All oils, after treatment with nitrous acid, contain, according to the same author, nitrogen varying in amount from 1 to 2·5 per cent. These substances may be reduced, yielding new compounds, which probably contain the NH_2 group. The free unsaturated acids yield no such compounds.

On passing *chlorine* through fats hydrochloric acid is evolved, and

[1] Geitel, *Jour. Soc. Chem. Ind.* 1888, 219. [2] *Zeitsch. f. angew. Chemie*, 1891, 74.
[3] *Jour. Chem. Soc.* 1893, Abstr. ii. 559.

similarly on treating with *bromine* hydrobromic acid, with formation of glycerides of chloro- or bromo-substitution products of the fatty acids. If triglycerides of the unsaturated acids are treated in this manner, the fatty acids may also absorb chlorine or bromine with formation of additive products.

Iodine does not yield substitution products, and is but slowly absorbed when mixed with a solution of a fat. The absorption, however, takes place readily if, following *Hübl's* process (chap. vi. p. 170), an alcoholic solution of iodine and mercury bichloride is allowed to act on a chloroformic solution of the fats. The glycerides of the unsaturated acids most likely absorb in that case one atom of iodine and one atom of chlorine for each pair of doubly-linked carbon atoms. Thus oleic acid is converted into chloro-iodo-stearic acid (oleic chloro-iodide), $C_{18}H_{34}ClIO_2$, a colourless compound of lard-like consistency, becoming brown with separation of iodine. The products obtained by the interaction of the alcoholic iodine and mercury bichloride solution and fats are viscous or varnish-like substances.

Sulphur does not act in the cold on fats and oils. At higher temperatures, however, from 120° to 160° C., all oils assimilate sulphur, and it would appear that the sulphur is absorbed much in the same manner as iodine is absorbed by oils. Experiments made by *Altschul*[1] have demonstrated that stearic acid is hardly acted upon by sulphur at a temperature of about 130° C., whereas oleic acid treated with 10 per cent of sulphur at 130°-150° C. absorbs the sulphur without any evolution of sulphuretted hydrogen. In a similar manner fatty oils (as containing glycerides of the unsaturated fatty acids), notably linseed oil, castor oil, rape oil, cotton seed oil, and marine animal oils, absorb sulphur at 120°-160° C.

On cooling, the sulphur does not separate out, and on saponifying the sulphurised oils in the cold,[2] sulphurised fatty acids are obtained, whilst very little sulphuretted hydrogen is evolved.[3]

The action of *sulphur chloride* on fats and oils will be described further on (chap. ix. p. 282).

2. Waxes (Liquid and Solid).

The waxes occur in both the vegetable and animal kingdoms, carnaüba wax and common beeswax being the best-known representatives of both types.

Chemical Constitution of Waxes. Preparation and Properties of Pure Waxes

The most essential point of difference between fats and waxes has been already explained. The fats are the glycyl ethers of the

[1] *Jour. Soc. Chem. Ind.* 1896, 282.

[2] On heating the sulphurised fatty acids to 130°-200° C., however, sulphuretted hydrogen escapes in large quantities, substitution of hydrogen in the molecule of the fatty substance taking place.

[3] Henriques, *Jour. Soc. Chem. Ind.* 1896, 282.

higher fatty acids, whilst the waxes proper must be considered as ethers formed by the combination of mono- or dihydric alcohols with higher fatty acids. Thus cetin, or cetyl palmitate, is obtained from cetyl alcohol and palmitic acid by abstraction of water, according to the following equation—

$$C_{16}H_{33}.OH + C_{15}H_{31}.CO.OH = C_{16}H_{33}.O.CO.C_{15}H_{31} + H_2O.$$

Therefore, whilst the fats and fatty oils have one common constituent in their basis—viz. the trihydric alcohol: glycerol—the waxes are characterised by their basic constituents being monohydric and dihydric alcohols. The alcohols hitherto identified in waxes belong to both the aliphatic and aromatic series; the former being represented by alcohols of the ethane, allylic, and glycolic series, the latter by the cholesterols.

The fatty acids of the waxes are either liquid or solid; no acid of a lower number of carbon atoms than myristic acid has been found hitherto. The fatty acids of wool wax are remarkable for the ease with which they are converted into lactones.[1]

The following pure "waxes" have been isolated:—

Cetyl Palmitate, Cetin, $C_{16}H_{33}.O.CO.C_{15}H_{31}$, occurs largely in spermaceti, being its chief constituent. It is prepared by repeatedly re-crystallising spermaceti from ether. Cetin forms white crystals, melting at 55° C., easily soluble in boiling alcohol, but nearly insoluble in cold alcohol. In a vacuum cetin can be distilled unchanged. When distilled under ordinary pressure, or even under a pressure of 300 to 400 mm., it is split up into palmitic acid and the hydrocarbon hexadecylene (cetene), according to the following equation—

$$C_{16}H_{33}.O.CO.C_{15}H_{31} = C_{16}H_{32}O_2 + C_{16}H_{32}.$$

Octodecyl Palmitate, $C_{18}H_{37}.O.CO.C_{15}H_{31}$. This wax forms crystals, melting at 59° C.

Ceryl Palmitate, $C_{27}H_{55}.O.CO.C_{15}H_{31}$, is the chief constituent of opium wax. It crystallises from boiling alcohol in small prisms, having the melting point 79° C. The melted substance solidifies at 76° C.

Myricyl Palmitate, Myricin, $C_{30}H_{61}.O.CO.C_{15}H_{31}$, is the chief constituent of that part of beeswax which is insoluble in alcohol. It forms feather-like crystals, melting at 72° C.

Cetyl Stearate, $C_{16}H_{33}.O.CO.C_{17}H_{35}$, forms large scales resembling those of spermaceti. Its melting point is 55°-60° C.

Ceryl Cerotate, $C_{27}H_{55}.O.CO.C_{26}H_{53}$, occurs in Chinese wax, which consists almost exclusively of this ether. It has also been found in opium wax, and very likely occurs in wool fat. Ceryl cerotate forms snow-white, lustrous scales (from chloroform), melting at 82·5° C.

Cocceryl Coccerate, Coccerin, $C_{30}H_{60}(O.C_{31}H_{61}O_2)_2$, has been found in the wax from cochineal. It is obtained as nacreous, thin laminæ (from benzene), melting point 106° C. Coccerin is nearly insoluble

[1] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1892, 132; 1896, 14.

in cold alcohol or ether, and dissolves with great difficulty in cold benzene and glacial acetic acid.

Cholesteryl Palmitate, $C_{26}H_{43} . O . CO . C_{15}H_{31}$, occurs in blood-serum ;[1] it forms snow-white plates, melting at 77°-78° C.

Cholesteryl Oleate, $C_{26}H_{43} . O . CO . C_{17}H_{33}$, has been found conjointly with the palmitate in blood-serum.[2] It crystallises in long, thin needles, melting at about 41° C., soluble in ether, chloroform, and benzene, but only sparingly so in alcohol; the rotatory power is $[\alpha]_D = 18° 48'$.

Cholesteryl Stearate, $C_{26}H_{43} . O . CO . C_{17}H_{35}$, has been prepared synthetically by heating one part of cholesterol with 8-10 parts of stearic acid to a temperature of 200° C. (*Berthelot*). It has been stated to occur in wool wax conjointly with the wax described next (compare wool wax, chap. xi. p. 652). It crystallises in small needles, melting at 65° C. This wax is nearly insoluble in alcohol, and but slightly soluble in ether.

Isocholesteryl Stearate, $C_{26}H_{43} . O . CO . C_{17}H_{35}$, has also been obtained by synthetical methods. It crystallises in fine needles, melting point 72° C., and is but very slightly soluble in boiling alcohol.

Liquid waxes occur in sperm oil. They most probably represent a combination of unsaturated alcohols, $C_nH_{2n}O$, with unsaturated fatty acids.[2]

Foreign Substances in Waxes

With the exception of carnaüba wax and beeswax, the waxes have not been examined yet so thoroughly that general statements can be made under this head.

In the case of these two waxes, however, the occurrence of hydrocarbons has been placed beyond doubt. The hydrocarbons of beeswax belong to the ethane series, and their melting points are high. The hydrocarbon found in carnaüba wax is very likely a member of the same series.

Free Fatty Acids and Free Alcohols in Waxes

Whereas in the case of animal fats at least it is proved that the occurrence of free fatty acids must be considered as an indication of decomposition having taken place, the same cannot be said with certainty of the waxes—at any rate, in our present state of knowledge.

A certain proportion of free fatty acids is characteristic of carnaüba wax, beeswax, and (natural) wool fat, whilst the liquid waxes and spermaceti are neutral in their fresh state.

Perhaps the conjecture is permissible that the occurrence of free fatty acids is due to a secondary action if we bear in mind that in the

[1] Hürthle, *Jour. Chem. Soc.* 1896, Abstr. ii. 485.
[2] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1892, 135.

waxes containing free fatty acids simultaneously free alcohols are present. [Glycerol being so easily soluble in water, it is evident that in the case of fats the "alcohol" escapes detection.] Therefore these waxes contain notable amounts of unsaponifiable matter (partly due to presence of hydrocarbons).

Properties of Waxes

In their physical properties the liquid and solid waxes resemble very much the fatty oils and fats. When melted together they mix in all proportions. Their behaviour to solvents is similar; and, like fats, the waxes in a liquid condition or in solution leave a grease-spot on paper.

It will, therefore, suffice to emphasise the points of difference.

The liquid waxes are readily distinguished from fatty oils by their lower specific gravity,—from 0·875 to 0·881.

On heating, the waxes do not emit the odour of acrolein, glycerol being absent; nor do they turn rancid on keeping for a long time, owing to the stability of their ethers (and the stability of their fatty acids).

Although insoluble in water, the solid waxes have the property of forming emulsions with water, so much so that large quantities of water can be incorporated with them (cp. p. 690), yielding salve-like substances.

CHAPTER II

SAPONIFICATION OF FATS AND WAXES

THE chemical change taking place on boiling fats with strong bases and resulting in the formation of glycerol and of the alkali salts of the higher fatty acids has been termed "saponification." In a wider sense, however, every chemical process by which fats or waxes are split up into their constituents—glycerol and fatty acids in the case of the fats, and higher alcohols and fatty acids in the case of waxes—is called saponification, even if no bases be used to effect the reaction.

The term "saponification" is almost exclusively used in practice, its scientific synonym "hydrolysis" being confined to papers of a scientific character.

The **fats** are decomposed on a very large scale by various chemical operations; they are "saponified" either by strong bases (caustic soda, caustic potash, lime), or by strong sulphuric acid, or by water alone, under a pressure of fifteen atmospheres (corresponding to 200° C.), or when distilled in a current of superheated steam. These methods will be detailed below (chap. xii. p. 745). In all these processes the fats undergo a perfectly definite chemical change, being split up into their constituents with the absorption of the elements of water. Thus, taking tristearin as an example, the following equation expresses the chemical change:[1]—

$$C_3H_5(O \cdot C_{18}H_{35}O)_3 + 3H_2O = 3C_{18}H_{36}O_2 + C_3H_5(OH)_3.$$

For *analytical* purposes the saponification is effected by means of strong bases only. The recently—somewhat needlessly—proposed process of saponifying butter by means of sulphuric acid will be discussed further on under "Butter Fat" (chap. xi. p. 635). For many purposes, especially for the subsequent estimation of glycerol, it would be most convenient to use such bases as form insoluble salts with the fatty acids, *e.g.* lead oxide, lime, and baryta. Careful examination, however, has proved[2] that with these bases saponification of many fats (tallow, cacao butter) is not complete, part of the neutral fat escaping decomposition. Therefore, in the analysis of fats the saponification

[1] Geitel has since shown (*Jour. prakt. Chemie*, 1897 [55], 418) that the saponification takes place in three stages, diglycerides being formed first, then monoglycerides, which are ultimately broken up into glycerol and fatty acids.

[2] v. d. Becke, *Zeitsch. f. analyt. Chemie*, 19. 291.

must be effected by means of caustic potash or caustic soda, if reliable results are to be obtained.

All triglycerides are not saponified with the same facility. Thus, olein is acted upon with greater difficulty than palmitin and stearin, a fact which has led to the statement (and patent) that on mixing olive oil, which consists essentially of the glycerides, olein (stearin ?), and palmitin, with cold caustic soda, and shaking the mixture occasionally during twenty-four hours, olein only remains unchanged. It has, however, been shown by *Thum*[1] that there is no marked difference between oleic and commercial stearic acids in their behaviour with caustic alkalis. On adding to a mixture of oleic and crude stearic acids an amount of caustic potash, insufficient to completely neutralise the acids, it was found that the composition of the acids that had been converted into soaps was almost the same as that of the acids that had remained free. Hence it is impossible to effect a separation of solid fatty acids from liquid ones by partial saturation with alkalis.

The carbonates of the alkalis do not act like the caustic alkalis. Alcoholic solutions of the caustic alkalis saponify more readily than aqueous.

Therefore, in the laboratory alcoholic soda and alcoholic potash are chiefly used for effecting saponification. If aqueous alkalis are employed for some special reason, saponification is completed only by prolonged boiling or by heating under pressure.

As commercial alcohol is seldom free from traces of acid, it should be tested, and, if necessary, it must be neutralised with decinormal caustic alkali, using phenolphthalein as indicator, or it may be distilled over lime or baryta. For the purpose of fat analysis rectified spirits of wine will, as a rule, be pure enough. It should be tested by boiling a few c.c. with several drops of concentrated caustic potash ; pure alcohol will not become brown, a slight yellow colour may, however, be allowed to pass. The appearance of a brown colour would point to the presence of aldehyde or acetone.

If the cost of spirits of wine preclude its use, recourse may be had to methylated spirit. This alcohol may be purified for analytical purposes by the following method, proposed by *Waller* :[2] The alcohol is shaken with powdered potassium permanganate until it assumes a distinct colouration. It is allowed to stand for some hours until the permanganate has been decomposed and hydrated manganese peroxide is deposited. A pinch of calcium carbonate is then added, and the alcohol distilled from a flask provided with a *Wurtz* tube or a *Le Bel-Henninger* fractionating column at a rate of about 50 c.c. in 20 minutes. The distillate is tested frequently until 10 c.c. of it, when boiled with 1 c.c. of a strong (syrupy) solution of caustic potash, gives no yellow colouration on standing for 20 or 30 minutes. What distils after that is preserved for use ; care, however, has to be taken not to distil to dryness. The alcohol thus prepared is completely neutral, and is

[1] *Jour. Soc. Chem. Ind.* 1891, 70.

[2] *Jour. Amer. Chem. Soc.* 1889, 124 ; *Analyst*, 1890, 50.

especially suitable for the preparation of alcoholic potash solution; even on standing for a long time alcoholic potash made from such alcohol does not become discoloured.[1]

It should be noted that alcohol is methylated at present (General Order as to Methylated Spirit, July 20th, 1891) by mixing with it mineral naphtha of a specific gravity of not less than 0·800. The admixed hydrocarbons are not got rid off by the foregoing processes of purification, but will pass over into the distillate with the alcohol. In estimations of "unsaponifiable" matter in fats this source of error must be specially guarded against.

The following are convenient proportions for saponifying fats: To 10 parts (by weight) of the fat in a flask are added 30 to 40 parts of alcohol by volume, and 4 to 6 parts of solid caustic potash previously dissolved in 20 parts of water. The flask is then connected with an inverted condenser, and the contents are kept gently boiling for half an hour or an hour.

These proportions may be varied within very wide limits. Thus *Yssel de Schepper* and *Geitel* recommend 20 grms. of fat, 40 c.c. of caustic potash of specific gravity 1·4, and 40 c.c. of alcohol, whilst *Dalican* proposes to pour into 50 grms. of tallow, heated to 200° C., a mixture of 40 c.c. caustic soda, specific gravity 1·33, and 33 c.c. of 95 per cent alcohol with constant shaking.

Yssel de Schepper and *Geitel*,[2] in order to accelerate the process of saponification, add some ether, thus ensuring a readier contact of the particles of fat and alkali. The same proposal has also been made by *Hehner*[3] and others; but it is not recommended, as the presence of ether necessarily demands a lower temperature than would be required in many cases.

Another method to saponify in the *cold* was recently proposed by *Henriques*.[4] His process consists in dissolving the fat in petroleum

[1] Another method has been recommended by *J. Carter Bell* (*Jour. Soc. Chem. Ind.* 1893, 236), and is carried out as follows: 500 c.c. of methylated alcohol, about 85 or 90 per cent, are placed in a flask of about 1000 c.c. capacity, containing 25 grms. of stick potash. When the latter has been dissolved, 250 grms. of melted lard, or of some other saponifiable fat, are added. The flask is then connected with an inverted condenser and heated on the water-bath, when the fat is readily saponified, especially if the flask be shaken repeatedly. After the condenser has been inverted, about 450 c.c. of alcohol are distilled off. According to *Carter Bell*, the alcohol thus obtained will not turn brown on the addition of potash after several days, and when the solution is kept in a strong light only a slight yellow colour may be developed. This property of soap, to retain the impurities of methylated spirit, is well known to manufacturers of transparent soap from stock soaps by dissolving them in boiling methylated spirit. The commercial methylated spirit when *first* used for this process yields a distillate which has a much less unpleasant smell than the crude spirit. At each subsequent time of using the methylated spirit a further improvement of the quality of the alcohol takes place; ultimately a spirit is obtained which is quite free from the rank odour of the commercial article.—*Kadel* (*Pharm. Jour. and Transactions*, 1894, 356) distils impure alcohol first over caustic soda—30 grms. for 5 litres—after allowing to stand for a few days. The distillate is next treated with permanganate and distilled off again. If necessary the latter operation is repeated and followed by filtration over charcoal.

[2] *Dingl. Polyt. Journal*, 245, 295. [3] *The Analyst*, 1893.

[4] *Jour. Soc. Chem. Ind.* 1896, 299, 476. The objections raised by Henriques to the usual method of saponification are groundless (cp. Holde, *Jour. Soc. Chem. Ind.* 1896, 476).

ether and mixing with alcoholic soda ; on standing for 12 hours complete saponification takes place. Besides having the disadvantage, that an operation which can be easily finished in half an hour is unduly protracted, this method has the further drawback that the solution of alkali must be prepared with strongest alcohol, as it is essential to obtain a homogeneous liquid on mixing the alcoholic soda with petroleum ether. For these reasons, but chiefly because, on the author's own showing,[1] wool wax is not saponified completely, this method cannot be recommended as one to replace the usual method. In the case of sulphurised (vulcanised) fats and oils, however, the cold saponification process may be used with advantage, as otherwise sulphur is eliminated from the fatty substance by boiling alcoholic potash to a far greater extent than in the cold.

Those fats which are not saponified readily are best heated with the alcoholic potash under pressure. *Becker* heats the fat with twelve times its quantity of half-normal or normal alcoholic potash in a flask on the water-bath for half an hour, the flask being closed by a cork, fitted with a safety tube containing mercury. The flask is heated until the pressure equals 5 cm. mercury. The writer[2] uses for these purposes a copper bottle with a screwed stopper ; the bottle may be immersed in water, and is not liable to breakage as seltzer-water bottles are.

Kossel and *Obermüller*[3] recommend sodium ethoxide (prepared by dissolving 5 grammes of metallic sodium in 100 c.c. of absolute alcohol) as the most readily acting reagent for saponification of fats. It is, however, difficult to see what advantages this method offers. The high price of metallic sodium and absolute alcohol, and the inconvenience of having to prepare the reagent afresh for each series of experiments, are not compensated for by the somewhat shorter time required for saponification. Furthermore, as the reaction proceeds according to the following equation—

$$C_3H_5(O.C_{18}H_{35}O)_3 + 3C_2H_5.ONa = C_3H_5(ONa)_3 + 3C_{18}H_{35}O.O.C_2H_5,$$

with formation of sodium glyceroxide and the ethyl ethers of the fatty acids, the reacting masses must be heated, as in other processes, in order to allow the alcohol to absorb sufficient moisture from the air for the decomposition of the sodium glyceroxide into glycerol and sodium hydrate, which latter saponifies ultimately the ethylic ethers of the fatty acids. It will, therefore, be found preferable to use alcoholic potash for the saponification of **oils and fats.**

An easy calculation will show that, theoretically, for the saponification of 1 grm. of fat from 0·2-0·3 grm. of caustic potash are required at most ; but in order to obtain complete saponification *an excess of the alkali must be used.* On using a small quantity of caustic potash and strong alcohol all the glycerol may be split off ; but

[1] In a later paper *Henriques* maintains that wool wax *is* completely saponified, but his contention does not appear to be sufficiently substantiated.

[2] *Jour. Soc. Chem. Ind.* 1892, 137. [3] *Zeitsch. f. physiolog. Chemie*, 15. 321-330.

still part of the fatty acids are obtained as ethyl ethers. Thus *J. Bell* has found that on boiling cow butter with half the quantity of alcoholic potash required for complete saponification a light oil is obtained, solidifying at 43° C. This oil was looked upon by him as a diglyceride of the following composition—$C_3H_5(OH)(OC_{16}H_{31}O)(OC_{18}H_{33}O)$; but it is actually a mixture of ethyl ethers of fatty acids. *Allen*[1] found similarly that, on heating acetin with the fiftieth part of alcoholic potash required for complete saponification, 39 per cent out of the theoretically possible quantity of ethyl acetate had been formed, whilst three-fiftieth parts of potash converted 85 per cent into acetic ether. A larger proportion of alkali diminished the yield of acetic ether; thus with sufficient caustic soda to saponify 39·8 per cent of the acetin used, the amount converted into acetic ether was 52·4 per cent.

Kossel and *Krüger*[2] state that in their experiments with the sodium ethoxide method saponification was complete if the theoretical quantity of sodium was employed. If, however, the proportion of alcohol used for dilution was large, considerable quantities of ethyl stearate and palmitate were formed, and saponification could only be completed by boiling on the water-bath. Judging from their experiments, supported and amplified by *Obermüller*,[3] the sodium ethoxide appears to form sodium glyceroxide and ethylic salts of the fatty acids, as explained by the equation given above. The traces of water that adhere to the absolute alcohol decompose the sodium glyceroxide, and the caustic soda thus formed is enabled to saponify the more readily saponifiable ethylic salts. Considering that 1 grm. of fat requires no more than 0·06 grm. of water, the small quantities of water found in absolute alcohol, conjointly with the amount absorbed from the atmosphere during the operation, may suffice to decompose the sodium glyceroxide. As the operation is usually completed on the water-bath there is ample occasion for the absorption of water to take place. Moreover, experiments with carefully dried alcohol, whilst moisture from the atmosphere was rigidly excluded, proved that, even after boiling continued for half an hour, about 30 per cent of the fat remained unsaponified.

The **waxes** are decomposed by saponification into fatty acids and higher alcohols. Thus, myricin is split up into its constituents, palmitic acid (resp. its potassium salt) and myricyl alcohol, according to the following equation—

$$C_{15}H_{31}CO \cdot O \cdot C_{30}H_{61} + KOH = C_{15}H_{31}CO \cdot OK + C_{30}H_{61} \cdot OH.$$

On diluting the alcoholic solution of a saponified wax with water, the higher alcohols, being insoluble in water, separate out and rise to the surface of the liquid, or remain suspended in it as a turbid mass. They are separated from the soap by shaking with ether,

[1] *Chem. News*, 1891, 64. 179.
[2] *Zeitsch. f. phys. Chemie*, 1891, 15. 322. [3] *Ibid.* 1891, 16. 154.

or by evaporating the solution and precipitate to dryness and exhausting with petroleum ether (cp. chap. vii., "Unsaponifiable Matter"). In practice these substances, being insoluble in water and alkalis, are termed "unsaponifiable."

The saponification of some of the waxes, as Chinese wax and especially wool wax, is effected with great difficulty under the conditions stated above for fats and oils. Wool wax must be boiled with an excess of alcoholic potash for at least twenty hours. It is, however, easily saponified by sodium ethoxide, according to *Kossel* and *Obermüller's* method. *Lewkowitsch*[1] has shown that equally satisfactory results are obtained by saponifying with double normal alcoholic potash under pressure. *Henriques* is of opinion that in the last-mentioned method action of alkali on the (unsaponifiable) alcohols takes place, whereas by his method of "cold saponification" such further action of the alkali is excluded. The proof, however, for this statement is still wanting (cp. footnote 1, p. 21).

The difficulty met with in the saponification of waxes is no doubt due to the fact that the soaps formed are less readily soluble than those usually obtained on saponifying fats. [In the case of wool wax *Lewkowitsch* has proved the formation of soaps that are very sparingly soluble in water.] Such soaps would naturally envelop unsaponified wax, thus protecting it from contact with alkali.

Although the theoretical aspect of the saponification process lies beyond the scope of this work, it may be pointed out that *V. Meyer's*[2] rule:—Ethers that are formed readily are readily saponifiable, and *vice versa*—is fully borne out by the facts given in the preceding pages. Thus ethyl stearate is more easily prepared, and also saponified, than glyceryl stearate.

[1] *Jour. Soc. Chem. Ind.* 1892, 137. [2] *Berichte*, 1895, 1263.

CHAPTER III

CONSTITUENTS OF FATS AND WAXES

THE fats and waxes are resolved into their constituents, viz. into fatty acids and glycerol on the one hand, and into fatty acids and alcohols on the other, by being heated with bases or acids, or by being treated with superheated steam; they are thus hydrolysed or "saponified." By means of these saponification processes the following acids and alcohols have been prepared from fats and waxes :—

A. Acids

I. Acids of the series $C_nH_{2n}O_2$. Acids of the Acetic Series.

$C_2H_4O_2$	Acetic acid	$C_{16}H_{32}O_2$	Palmitic acid
$C_4H_8O_2$	Butyric acid	$C_{17}H_{34}O_2$	Daturic acid
$C_5H_{10}O_2$	Isovaleric acid	$C_{18}H_{36}O_2$	Stearic acid
$C_6H_{12}O_2$	Isobutyl acetic acid (Caproic acid)	$C_{20}H_{40}O_2$	Arachidic acid
		$C_{22}H_{44}O_2$	Behenic acid
$C_8H_{16}O_2$	Caprylic acid	$C_{24}H_{48}O_2$	Lignoceric acid
$C_{10}H_{20}O_2$	Capric acid	$C_{24}H_{48}O_2$	Carnaübic acid
$C_{11}H_{22}O_2$	Umbellulic acid	$C_{25}H_{50}O_2$	Hyænic acid
$C_{12}H_{24}O_2$	Lauric acid	$C_{26}H_{52}O_2$	Cerotic acid
$C_{14}H_{28}O_2$	Myristic acid	$C_{30}H_{60}O_2$	Melissic acid
$C_{15}H_{30}O_2$	Isocetic acid		

II. Acids of the series $C_nH_{2n-2}O_2$. Acids of the Arcylic or Oleic Series.

$C_5H_8O_2$	Tiglic acid	$C_{18}H_{34}O_2$	Elaïdic acid
$C_{12}H_{22}O_2$	not named	$C_{18}H_{34}O_2$	Isooleic acid
$C_{14}H_{26}O_2$	not named	$C_{18}H_{34}O_2$	Rapic acid
$C_{16}H_{30}O_2$	Hypogæic acid	$C_{19}H_{36}O_2$	Doeglic acid
$C_{16}H_{30}O_2$	Physetoleic acid	$*C_{19}H_{36}O_2$	Jecoleic acid
$C_{16}H_{30}O_2$	Lycopodic acid [1]	$C_{22}H_{42}O_2$	Erucic acid
$*C_{17}H_{32}O_2$	Asellic acid	$C_{22}H_{42}O_2$	Brassidic Acid
$C_{18}H_{34}O_2$	Oleic acid	$C_{22}H_{42}O_2$	Isoerucic acid

[1] Aldepalmitic acid $C_{16}H_{30}O_2$ (Wanklyn, *Jour. Soc. Chem. Ind.* 1891, 212) has not been admitted to the above list on account of its doubtful existence.

* The existence of the acids marked with an * has been inferred from derivatives of such hypothetical acids.

III. Acids of the series $C_nH_{2n-4}O_2$. Acids of the Linolic Series.

$C_{17}H_{30}O_2$ Elæomargaric acid	$C_{18}H_{32}O_2$ Tariric acid
$C_{18}H_{32}O_2$ Linolic acid	$C_{18}H_{32}O_2$ Millet oil acid

IV. Acids of the series $C_nH_{2n-6}O_2$. Acids of the Linolenic Series.

$C_{18}H_{30}O_2$ Linolenic acid	*$C_{18}H_{30}O_2$ Jecoric acid
$C_{18}H_{30}O_2$ Isolinolenic acid	

V. Acids of the series $C_nH_{2n-8}O_2$.

$C_{14}H_{26}O_2$ Isanic acid	*$C_{17}H_{26}O_2$ Therapic acid

VI. Acids of the series $C_nH_{2n}O_3$. Hydroxylated Acids.

$C_{16}H_{32}O_3$ Lanopalmic acid	$C_{31}H_{62}O_3$ Cocceric acid
$C_{21}H_{42}O_3$ not named	

VII. Acids of the series $C_nH_{2n-2}O_3$. Acids of the Ricinoleic Series.

$C_{18}H_{34}O_3$ Ricinoleic acid	$C_{18}H_{34}O_3$ Ricinisoleic acid

VIII. Acids of the series $C_nH_{2n}O_4$. Dihydroxylated Acids.

$C_{18}H_{36}O_4$ Dihydroxystearic acid	$C_{30}H_{60}O_4$ Lanoceric acid

B. Alcohols

I. Alcohols of the series $C_nH_{2n+2}O$. Alcohols of the Ethane Series.

$C_{16}H_{34}O$ Cetyl alcohol (Ethal)	$C_{26}H_{54}O$ Ceryl alcohol
$C_{18}H_{38}O$ Octodecyl alcohol	$C_{27}H_{56}O$ Isoceryl alcohol
$C_{24}H_{50}O$ Carnaübyl alcohol	$C_{30}H_{62}O$ Myricyl (Melissyl) alcohol
$C_{24}H_{50}O$ or $C_{25}H_{52}O$ not named	

II. Alcohols of the series $C_nH_{2n}O$. Alcohols of the Allylic Series.

$C_{12}H_{24}O$ Lanolin alcohol	$C_{33}H_{66}O$ Psyllostearyl alcohol
$C_{15}H_{30}O$ not named	

III. Alcohols of the series $C_nH_{2n+2}O_2$. Alcohols of the Glycolic Series.

$C_{25}H_{52}O_2$ not named	$C_{30}H_{62}O_2$ Cocceryl alcohol

IV. Alcohols of the series $C_nH_{2n+2}O_3$.

$C_3H_8O_3$ Glycerol

V. Alcohols of the Aromatic Series.

$C_{26}H_{44}O$ Cholesterol
$C_{26}H_{44}O$ Isocholesterol

$C_{26}H_{44}O$ Phytosterol

A. ACIDS

Occurrence of Fatty Acids

The fatty acids enumerated above by no means occur in the fats in anything approaching equal quantities. Those fatty acids which contain an uneven number of carbon atoms (isovaleric, umbellulic, isocetic, daturic, hyænic, tiglic acid, etc.) are of comparatively rare occurrence and mostly confined to some one individual fat. Indeed, some of those enumerated will not, perhaps, bear the light of modern investigation with its improved methods of research, and may have to share the fate of medullic,[1] moringic, theobromic,[2] crotonoleic[3] acids, which must be considered as definitely removed from the list of fatty acids. The fatty acids of by far the greater number of fats contain exclusively an even number of carbon atoms. Amongst the latter palmitic, stearic, and oleic acids predominate (in some fats linolic and ricinoleic acids) to such an extent that the chief part of most fats consists of a mixture of the glycerides of these three acids. Glycerides of the lower fatty acids may occur conjointly with them, but in that case they are present in smaller quantities. Therefore a *large percentage* of a fatty acid other than palmitic, stearic, or oleic acid in a fat may always be looked upon as being characteristic of that fat, as will readily be seen from the following short summary :—

Acetic acid is found as a glyceride (triacetin) in small quantities in the seeds of the spindle-tree[4] (*Evonymus europæus*, L.)

Butyric acid occurs as a glyceride (butyrin) in cow butter to the extent of about 6 per cent.

Isovaleric acid occurs as a glyceride in porpoise and dolphin oils.

Isobutylacetic (Caproic) acid has been proved to form part of butter fat and cocoa nut oil, as the glyceride caproin, in conjunction with the glycerides of caprylic and capric acids (caprylin and caprin). If butyrin, caproin, caprylin, and caprin conjointly exist to the extent of at least 1 to 2 per cent in a fat, that fat will be characterised by these glycerides. Thus, butter fat and cocoa nut oil are specially

[1] *Berichte*, 23. Ref. 493.
[2] *Ibid.* 16. 1103.
[3] *Jour. Soc. Chem. Ind.* 1895, 985.
[4] *Jahresberichte*, 1851, 444.

remarkable for containing 8, and 4 to 5 per cent of those glycerides respectively.

Umbellulic acid has been shown to occur as a glyceride in the seeds of the Californian bay-tree (*Umbellularia californica*).

The glyceride of *lauric* acid, laurin or laurostearin, is the chief constituent of the tangkallah fat from the Javanese tree *Cylicodaphne sebifera*, Bl.; it occurs also in large quantities in laurel oil.

Myristic acid is found as a glyceride in nutmeg butter, liver fat, and, as a wax, in wool wax, *isocetic* acid in the seeds of the purging nut (*Jatropha curcas*, L.); *daturic* acid in the oil of *Datura Stramonium*, and perhaps among the solid fatty acids of palm oil; *arachidic* acid in arachis (earth nut) oil; *behenic* acid in ben (behen) oil; and *lignoceric* acid in arachis oil.

Carnaübic acid occurs in carnaüba wax, and in wool wax; *cerotic* and *melissic* acids are found in the free state in beeswax, and the former, as ceryl cerotate, also in Chinese wax and most likely also in wool wax.

Hyænic acid has been detected in the glandular pouches of the striped hyæna, occurring there as a glyceride.

Of the rarer acids belonging to the oleic series the following occur as glycerides; *tiglic* (or *angelic*) acid in croton oil, and, passing over the two unnamed acids $C_{12}H_{22}O_2$ and $C_{14}H_{26}O_2$ which have been found in the fat of cochineal, *physetoleic* acid in sperm oil, *doeglic* acid in Arctic sperm (bottlenose) oil, and *erucic* and *rapic* acids in rape oil.

Whilst *elæomargaric* acid has been found hitherto as a glyceride in the seeds of *Elæococca vernicia* only, large quantities of the glyceride of *linolic* acid are characteristic of the so-called drying oils, and it is generally associated with the glycerides of *linolenic* and *isolinolenic* acids. *Tariric* acid has been recently found as a glyceride in the seeds of a Guatemalan shrub, *Picramnia*.

Of the acids of the series $C_nH_{2n-8}O_2$—*isanic* acid—too little is known as yet.

The hydroxylated acids *lanopalmic* acid, the acid $C_{21}H_{42}O_3$, and *cocceric* acid, are constituents of wool wax, carnaüba wax, and of the wax of cochineal respectively. Finally, the glycerides of *ricinoleic* and *ricinisoleic* acids constitute the principal part of castor oil.

The first natural dihydroxylated acid, *dihydroxystearic* acid, has been detected in castor oil; another dihydroxylated acid, *lanoceric* acid, occurs in wool wax.

Properties of Fatty Acids

Melting Points of Fatty Acids.—The lower members of the acetic acid series, including caprylic acid, and further oleic, rapic, doeglic, linolic, and ricinoleic acids, are liquid at the ordinary temperature, all the others are solid. The following table contains the melting points of the more important acids:—

Acid.	Melting Point. °C.
Capric	31·3
Lauric	43·6
Myristic	53·8
Palmitic	62·0
Stearic	71-71·5
Arachidic	77·0
Behenic	83-84
Lignoceric	81·0
Carnaübic	72·5
Cerotic	78·0
Melissic	90·0
Tiglic	64·5
Hypogæic	33·0
Physetoleic	30·0
Isooleic	44-45
Elaïdic	51-52
Erucic	33-34
Isoerucic	54-56
Brassidic	65·0
Elæomargaric	48·5
Lanopalmic	87-88
Lanoceric	104-105

The melting point of a mixture of two fatty acids cannot be calculated from the melting points of the constituents. As a rule, the melting point lies considerably below the calculated one, sometimes even below the melting point of the lowest melting acid. The following tables will clearly illustrate this fact:—

Melting Points of Mixtures of Lauric Acid with Myristic, Palmitic, and Stearic Acid (Heintz)

Lauric Acid. Per cent.	Myristic Acid.		Palmitic Acid.		Stearic Acid.	
	Per cent.	Melting Point.	Per cent.	Melting Point.	Per cent.	Melting Point.
		°C.		°C.		°C.
100	0	43·6	0	43·6	0	43·6
90	10	41·3	10	41·5	10	41·5
80	20	38·5	20	37·1	20	38·5
70	30	35·1	30	38·3	30	43·4
60	40	36·7	40	40·1	40	50·8
50	50	37·4	50	47·0	50	55·8
40	60	43·0	60	51·2	60	59·0
30	70	46·7	70	54·5	70	62·0
20	80	49·6	80	57·4	80	64·7
10	90	51·8	90	59·8	90	67·0
0	100	53·8	100	62·0	100	69·2

Melting Points of Mixtures of Myristic Acid with Palmitic and Stearic Acid (Heintz)

Myristic Acid. Per cent.	Palmitic Acid.		Stearic Acid.	
	Per cent.	Melting Point.	Per cent.	Melting Point.
		°C.		°C.
100	0	53·8	0	53·8
90	10	51·8	10	51·7
80	20	49·5	20	47·8
70	30	46·2	30	48·2
60	40	47·0	40	50·4
50	50	47·8	50	54·5
40	60	51·5	60	59·8
30	70	54·9	70	62·8
20	80	58·0	80	65·0
10	90	60·1	90	67·1
0	100	62·0	100	69·2

Melting Points of Mixtures of Palmitic Acid with Stearic Acid

Palmitic Acid. Per cent.	Stearic Acid. Per cent.	Melting Point.	
		Heintz.	Hehner and Mitchell.
		°C.	°C.
100	0	62·0	61·8
90	10	60·1	59·0
80	20	57·5	56·5
70	30	55·1	54·2
67·5	32·5	55·2	54·5
60	40	56·3	55·5
50	50	56·6	55·6
40	60	60·3	59·4
30	70	62·9	61·5
20	80	65·3	64·2
10	90	67·2	66·5
0	100	69·2	68·5[1]

Melting Points of Mixtures of Palmitic and Cerotic Acids (Lewkowitsch)

Palmitic Acid. Per cent.	Cerotic Acid. Per cent.	Melting Point. °C.
100	0	60·0
90	10	56·0
85	15	56·5
75	25	60·5
60	40	65·5
50	50	68·6
40	60	70·0
0	100	78·5

[1] The different melting point of the stearic acid used by these observers will satisfactorily explain the discrepancies ; pure stearic acid melts, however, at 71° to 71·5° C.

Boiling Points of Fatty Acids.—Of the more frequently occurring fatty acids only the following can be distilled under ordinary pressure without undergoing decomposition :—

Acid.	Boiling Point. °C.
Butyric	162·3
Isobutylacetic . . .	about 200
Caprylic	236
Capric	268-270

All the others, when distilled at ordinary pressure, undergo partial decomposition, and amongst the products of the destructive distillation hydrocarbons of the ethane series are found, a fact which forms the main chemical argument in favour of *Höfer-Engler's* theory of the formation of petroleum from the fats of marine animals.

Under diminished pressure, however, and also by the use of superheated steam, many fatty acids may be distilled without suffering decomposition. In practice, the latter method is largely used for the preparation of the distilled fatty acids. More recently the two methods have been combined.

At a pressure of 100 mm., 15 mm., and *in vacuo*, the following boiling points have been found :—

Acid.	Boiling Point at 100 mm. Pressure. °C.	Boiling Point at 15 mm.[1] Pressure. °C.	Boiling Point *in vacuo*.[1] °C.
Lauric . . .	225	176	102
Myristic . .	250·5	196·5	121-122
Palmitic . .	271·5	215	138-139
Stearic . . .	291	232·5	154·5-155·5
Hypogæic[2] .	...	236	...
Oleic . . .	285·5	232·5	153
Elaïdic . . .	287·8-288	234	154
Erucic . . .	...	264	179
Brassidic . .	...	265	180

The fatty acids boiling at ordinary pressure without undergoing destructive distillation are called *volatile fatty acids*, in contradistinction to the *non-volatile acids*.

Solubility of Fatty Acids.—The lowest members of the acetic series are miscible with water in every proportion ; isobutylacetic acid is soluble in water, but no longer miscible with it. The solubility in water decreases rapidly with the increase of the number of carbon atoms in the molecule. Caprylic acid requires for its solution 400 parts of boiling water ; on cooling, the acid separates out nearly completely. Capric and lauric acids are very slightly soluble in boiling water ; the higher acids are altogether insoluble in water. Taking the solubility as a basis for classification, we may subdivide

[1] Krafft and Weilandt, *Berichte*, 1896 (29), 1324.
[2] Bodenstein, *ibid.* 1894, 3399.

the fatty acids for analytical purposes into *soluble* and *insoluble* fatty acids. The acids up to capric acid are called *soluble* fatty acids; the higher fatty acids from myristic acid upwards are the *insoluble* fatty acids. Lauric acid has an intermediate position between the soluble and the insoluble acids.

On distilling aqueous solutions of the volatile fatty acids, especially if care be taken to replace the water as it boils away, the whole amount of acid present can be obtained in the distillate; the higher the boiling point of a fatty acid the easier is this process carried out. Therefore, from a mixture of butyric and isobutylacetic acids dissolved in water the latter acid will pass over first (cp. chap. vi. p. 139).

All the fatty acids without exception are soluble in hot alcohol.

Action of Solutions of Fatty Acids on Indicators.—In the commercial analysis of fats the fatty acids are frequently estimated by titration with alkalis, and it is therefore important to know their behaviour towards the indicators used in volumetric analysis.

From the large number of indicators which have been proposed from time to time, we select for the analysis of fats and its components methylorange and phenolphthalein, which, in conjunction with tincture of litmus (the place of which has lately been taken by lacmoïd), will be found quite sufficient for all analyses.

Methylorange[1] is prepared from diazobenzene sulphonic acid $C_6H_4 \begin{matrix} -N=N \\ -SO_3 \end{matrix}\!\!\diagdown$ and dimethylaniline. It is the ammonium salt of dimethylaniline-azobenzenesulphonic acid, the constitution of which is expressed by the formula—

$$C_6H_4 \begin{matrix} -SO_3NH_4 \\ -N=N- \end{matrix} C_6H_4N(CH_3)_2 .$$

Methylorange dissolves in water to a yellow liquor, which on the addition of a strong acid turns crimson, appearing yellowish-red in deep layers, a salt being formed with the acid. If hydrochloric acid has been used the following salt is obtained—

$$C_6H_4 \begin{matrix} -SO_3H \\ -H=N- \end{matrix} C_6H_4N(CH_3)_2 . HCl.$$

The change from the yellowish colour of the neutral solution to the red is especially sharp in very dilute solutions. Weak acids, as carbonic acid, do not change the colour; therefore, it is possible to titrate carbonates, using methylorange as an indicator, without requiring to drive off the liberated carbonic anhydride by boiling. The acid carbonates of the alkalis are alkaline to methylorange (difference from phenolphthalein). This indicator is specially suitable for the estimation of mineral acids.

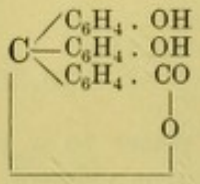
[1] According to *Lunge*, tropæolin 00 or 000 is often sold as methylorange. I have occasionally met with methylorange having such strong alkaline reaction, that four drops of a $\frac{1}{10}$ per cent solution required 0·1 c.c. of normal acid for neutralisation. Methylorange should, therefore, always be examined before use.

An excess of the soluble fatty acids also reddens a solution of methylorange, but on titrating with normal alkali the end-reaction is not sharp, and the red colour has disappeared when considerable quantities of free fatty acids are still in the solution; therefore methylorange cannot be used in this case. The insoluble fatty acids, however, as stearic or oleic, do not affect this indicator at all in their alcoholic solution, nor do they act on it when shaken in the liquid state with an aqueous solution of methylorange. It is, therefore, possible to titrate mineral acids in presence of higher fatty acids by using this indicator, and it offers the further advantage, that it can be employed along with another indicator. Thus the mineral acid may be estimated first, using methylorange as the indicator, and subsequently phenolphthalein having been added, the higher fatty acids may be titrated.

The solution of the indicator is prepared by dissolving 1 grm. in 1000 c.c. of water. Four drops of this solution are sufficient for every 100 c.c. of the liquid to be titrated.

Phenolphthalein.—This is prepared by heating to 115°-120° C., for ten to twelve hours, a solution of 250 grms. of phthalic anhydride $C_6H_4 \begin{matrix} -CO \\ -CO \end{matrix} \!\!>\!O$ in 200 grms. of concentrated sulphuric acid, with 500 grms. of phenol $C_6H_5 . OH$. The hot melt is poured into boiling water, and washed with boiling water until the odour of phenol has disappeared. The residue is of sufficient purity to be at once used as an indicator.

The chemical constitution of phenolphthalein is expressed by the formula—



To prepare the solution required for volumetric analysis 1 grm. is dissolved in 100 c.c. of 95 per cent alcohol. Two drops of this indicator will be found sufficient for every 100 c.c. of solution. The alcoholic solution of phenolphthalein is yellowish, and turns pink on the addition of the slightest quantity of a fixed alkali owing to the formation of a salt. These salts are decomposed completely even by weak acids, therefore the insoluble fatty acids may be titrated in their alcoholic solutions by means of this indicator. Ammonia does not affect phenolphthalein in alcoholic solution, and for this reason is unsuitable for the titration of fatty acids. Phenolphthalein may also be used for the titration of the soluble fatty acids in the same way as litmus, which is, however, preferred by some chemists. Due regard should be paid to the sensitiveness of phenolphthalein to carbon dioxide, and to the fact that the acid carbonates of the alkalis do not affect phenolphthalein; it is therefore absolutely necessary to remove the carbonic dioxide by boiling. When standard-

ising acids and alkalis with the aid of phenolphthalein this possible source of error should especially be guarded against.

Litmus.—Tincture of litmus may be used in the analysis of fats for titrating the volatile fatty acids, mineral acids, caustic alkalis, carbonates, etc. The statement made by *Rechenberg*,[1] that the salts formed by the union of volatile fatty acids with alkalis and alkaline earths—especially those of butyric acid—show in their aqueous solution strongly alkaline reaction, has not been confirmed by the author's experience. It is quite possible to titrate butyric acid, using litmus as an indicator. The change is rather gradual, but perfectly distinct.

Lacmoïd.[2]—This colouring matter is prepared by heating 100 parts of resorcinol, 5 parts of sodium nitrate, and 5 parts of distilled water in an oil bath to 110° C. The melt is dissolved in water and precipitated by salting out. Its chemical constitution is unknown. *Thomson*[3] found that it can be used for the titration of fixed alkalis, ammonia, alkaline earths, and mineral acids. It is, however, useless for the titration of fatty acids, as their neutral salts themselves produce the blue colour.

Viscosity of Fatty Acids.—Since viscosimetric methods have been proposed for the examination of fats and oils, it may be found useful to record here the following viscosimetric constants. From the values given in the table it is evident that the viscosity increases with the molecular weight.

Viscosimetric Constants of Fatty Acids (Pribram and Handl).

Fatty Acid.	Molecular Weight.	Specific Viscosity at		
		10° C.	30° C.	50° C.
Propionic . .	74	70·3	51·5	49·9
Butyric . . .	88	110·2	77·4	57·6
Valerianic . .	102	152·4	103·3	71·5
Capronic . .	116	222·2	139·7	97·8

With regard to other physical constants *Guillot's*[4] pamphlet should be consulted.

Salts of Fatty Acids.—The metallic salts of the non-volatile acids are called SOAPS. In common parlance, however, we understand under the term "soap" the alkali salts of the non-volatile acids.

Salts of the Alkali-Metals

The normal salts of the saturated acids have the general formula $C_nH_{2n+1}CO.OM$, where M stands for Na or K. In alcoholic solution

[1] *Jour. prakt. Chemie*, 1884, 519. [2] *Jour. Soc. Chem. Ind.* 1884, 296.
[3] *Chem. News*, 52. 18, 29.
[4] A. Guillot, *Propriétés Physiques des Acides de la Série Grasse.* Paris, Baillière et fils, 1895.

these salts are neutral to phenolphthalein. There are also in existence acid salts of the formula $C_nH_{2n+1}CO.OM$, $C_nH_{2n}O_2$; dissolved in hot alcohol they show acid reaction to phenolphthalein.

The alkali-salts of the fatty acids are remarkable in their behaviour to water.

The salts of the lowest members of the series are easily soluble in water. Thus the alkali salts of butyric acid are deliquescent, and those of capric acid are still very easily soluble in water at the ordinary temperature. But the solubility in water decreases as the molecular weight of the fatty acids increases; thus the alkali salts of palmitic or stearic acid are no longer soluble in cold water. They dissolve, however, when boiled with not too large a quantity of water, to a clear solution, which solidifies, on cooling, to a mucilaginous mass, representing the normal salts of the fatty acids, or at any rate approximately so.

On diluting the clear hot solutions with water they become turbid, and, on shaking, a lather is produced which persists for some time. The turbidity is due to the dissociation of the normal salt into caustic alkali and free fatty acid. This dissociation, termed *hydrolysis of soap*, is a very gradual one, depending on the amount of water present and also on the temperature.

The free alkali remains in solution, and the free fatty acid combining with non-hydrolysed salt separates, forming an acid salt, *i.e.* a salt containing more than one equivalent of acid for one equivalent of alkali, presumably in association with some undissociated salt.

Chevreul, who first studied this question, found that a solution of one part of neutral potassium stearate, $C_{18}H_{35}O.K$, in 20 parts of boiling water, treated with additional 1000 parts of boiling water yields, on cooling, an acid salt of the composition $C_{18}H_{35}O_2K.C_{18}H_{36}O_2$, *potassium bistearate*, whilst free alkali and an infinitesimal quantity of stearic acid remain in solution. Similarly, neutral sodium stearate dissolved in 2000 to 3000 parts of boiling water yields, on cooling, an acid salt of the composition $C_{18}H_{35}O_2Na.C_{18}H_{36}O_2$, *sodium bipalmitate*. Neutral oleate, however, requires a very large quantity of water and a low temperature to become dissociated; the difference between oleic acid on the one hand, and palmitic and stearic on the other hand, is so marked that an approximate method of separation may be based on this property.

The potassium bistearate can be further dissociated by treatment with water into a more acid salt, presumably of the composition of a quadro-stearate.

The amount of alkali thus set free under given conditions can be determined quantitatively by salting out the "curd," filtering off and washing with brine, dissolving the curd in absolute alcohol, and determining the acidity by titration with alkali, using phenolphthalein as indicator.

Alder Wright and *Thompson*[1] derived from a series of observations the results contained in the following table. I have arranged the fatty acids in the order of their molecular weights:—

[1] *Jour. Soc. Chem. Ind.* 1885, 630.

Fatty Acids.	Mean Molecular Weight.	Hydrolysis brought about by x Molecules of Water.				
		$x=150$	$x=250$	$x=500$	$x=1000$	$x=2000$
Crude lauric . .	195	3·75	4·5	5·4	6·45	7·1
(Cotton seed oil acids .	250[1]	2·25	3·0	5·0	7·5	9·5)
Nearly pure palmitic .	256	1·45	1·9	2·6	3·15	3·75
(Palm-oil-tallow soap .	271	1·1	1·55	2·6	4·1	5·3)
Pure oleic . . .	282	1·85	2·6[2]	3·8	5·2	6·65
Pure stearic . .	284	0·7	1·0	1·7	2·6	3·55

The numbers represent the quantities of Na_2O set free by hydrolysis, calculated for 100 parts of Na_2O contained in the soap in combination with fatty acid, x molecules of water being used for one of anhydrous soap.

If we look at the numbers given for lauric, palmitic, and stearic acids only, it would appear that the sodium salts of the fatty acids are decomposed with greater ease, the *lower* their molecular weight. But on the one hand the behaviour of oleic acid does not conform with this rule, and on the other hand *Thomsen*[2] has shown that sodium acetate is not measurably dissociated by water. (Cp., however, p. 38.)

Rotondi[3] explained the action of water on soap in the following manner: The neutral (commercial) soaps, on being dissolved, are decomposed into basic and acid salts; the latter are insoluble in cold and only slightly soluble in hot water. The acid salts are not dialysable, and can, therefore, be separated from the former which are readily so. The basic soaps are completely soluble in cold and hot water, and are entirely precipitated by sodium chloride without loss of alkali; their solutions dissolve acid soaps on heating, but become turbid on cooling.

These views have been shown by *Krafft* and *Stern*[4] to be erroneous. They repeated *Chevreul's* experiment with pure sodium palmitate (2 grms.), and obtained the following result:—

1 Part of Sodium Palmitate containing 8·27 per cent Na	
Boiled with parts Water	yielded, on cooling, salt containing Na.
	Per cent.
200	7·01
300	6·84
400	6·60
450	6·32
500	6·04
900	4·20

[1] This appears to be somewhat low.
[2] *Thermochemische Untersuchungen*, i. 372.
[3] *Jour. Soc. Chem. Ind.* 1885, 601.
[4] *Berichte*, 1894, 1747.

To get an insight into the approximate composition of the separated salts the following table may be consulted :—

Salts of the formula	Containing Na. Per cent.
$C_{16}H_{31}O_2Na$	8·27
$3C_{16}H_{31}O_2Na + C_{16}H_{32}O_2$	6·33
$C_{16}H_{31}O_2Na + C_{16}H_{32}O_2$	4·31
$C_{16}H_{31}O_2Na + 3C_{16}H_{32}O_2$	2·20

Similar experiments with pure sodium stearate gave the following result :—

1 Part of Sodium Stearate containing 7·52 per cent Na		
Boiled with parts Water	yielded, on cooling, salt containing Na.	
	Per cent.	
	I.	II.
200	6·34	6·27
300	5·81	5·71

Sodium bistearate $C_{18}H_{35}O_2Na + C_{18}H_{36}O_2$ contains 3·89 per cent Na.

From these experiments the conclusion must be drawn that hydrolysis increases with the molecular weight of the fatty acids; this is in direct opposition to the conclusions derived from *Alder Wright* and *Thompson's* more complete series of observations detailed above (p. 35).

As shown above, oleic acid occupies an exceptional position as regards hydrolysis of its salts. This has been confirmed by *Krafft* and *Stern*, according to whose observation pure neutral sodium oleate dissolves to a *clear* solution in about 10 parts of *cold* water, which does not yield a sensibly turbid solution even on dilution with 900 parts of water, whereas the sodium bioleate, $C_{18}H_{33}O_2Na + C_{18}H_{34}O_2$, is immediately dissociated by cold water. In order to hydrolyse oleates by far larger quantities of water are required, at the same time the temperature must be lowered considerably.

The solid elaïdic acid, however, simulates stearic acid in its behaviour, as the following observations prove :—

1 Part of Sodium Elaïdate containing 7·56 per cent Na	
Boiled with parts water	yielded, on cooling, salt containing Na.
	Per cent.
300	5·80
1500	3·24

In the light of these experiments, the commercial soaps, consisting of palmitates, stearates, and oleates, would yield, on treatment with large quantities of water, acid palmitates and stearates as precipitates,

whereas free alkali and oleates would remain in solution. The solution would thus contain soap *plus* free alkali, a fact which has been taken by *Rotondi* as a proof for the existence of basic soaps in solution. Besides, direct experiments made with a view to preparing synthetically basic salts from oleic acid failed completely, and on hydrolysing pure sodium palmitate with 900 parts of water not a trace of palmitic acid could be detected in the cold supernatant solution.

The direct proof that free fatty acid and free alkali co-exist in a dilute solution in the hot was given by extracting a solution of not completely hydrolysed normal sodium palmitate with toluene, when free palmitic acid was obtained.

The hydrolysis of soaps becomes complete according to *Krafft* and *Wiglow*,[1] if the one of the two components of the normal salt—say, fatty acid—is removed, as by shaking out repeatedly with toluene.[2]

It is apparent from the foregoing notes that oleates behave differently from the solid fatty acids and even from elaïdic acid, with which it is isomeric. This difference, however, disappears if not only the one factor, which has been considered hitherto exclusively, viz. the proportion of water, is taken into account, but if proper regard is had to the temperature. For *Krafft* and *Wiglow*[1] observed that the temperature at which the separation of acid salts commences always lies below the melting point of the corresponding fatty acid. The following table reproduces their experiments, in which a one per cent solution of the sodium salt was examined :—

Sodium Salt of	Temperature of Separation.	Melting Point of Acid.	Difference.
	°C.	°C.	
Stearic Acid	60	69·2	9·2
Palmitic ,,	45	62·0	17·0
Myristic ,,	31·5	54·5	23·0
Lauric ,,	11	43·6	32·6
Elaïdic	35	51·0	16·0
Oleic	0	14·0	14·0

From these numbers the following rule has been derived: The temperature of crystallisation of the soaps always lies below the melting point of the free fatty acid, and the difference between both temperatures increases on descending the homologous series.

It will thus be seen that oleic acid falls in line with the other acids, and that, *e.g.*, a hot solution of sodium palmitate behaves like a cold solution of sodium oleate.

From a series of observations undertaken by *Krafft* and *Wiglow*[3] with a view to determining the molecular weight of soaps by the

[1] *Jour. Soc. Chem. Ind.* 1896, 206.

[2] This observation, however, is not consistent with the fact that free alkali (p. 38) causes a diminution of the amount of hydrolysis, and one would accordingly expect that an equilibrium would be established, so that for the *same amount of* water no more than a certain quantity, but not the whole quantity, of fatty acid could be extracted. (J. L.)

[3] *Berichte*, 1896, 1329.

ebullioscopic method, it appears that the sodium salts of the lower fatty acids raise the boiling point of water by twice the normal value; this is explained by assuming that each molecule is hydrolysed into free fatty acid and sodium hydroxide, as indicated by the following equation :—

$$\underset{\text{Sodium Acetate.}}{C_2H_3O_2Na} + H_2O = C_2H_4O_2 + NaOH.$$

The sodium salts of the higher fatty acids, however, do not raise the boiling point of water at all; the solutions solidify on cooling to gelatinous masses, and thus show the characteristic behaviour of colloids.

The observations referred to are reproduced in the following table :—

Sodium Salts of Acid.	Formula.	Parts of Salt in 100 parts of Water.	Molecular Weight.		Apparent Mol. W. / Normal Mol. W.
			Apparent.	Normal.	
Acetic	$C_2H_3O_2Na$	0·9	50·5	82	0·6
		25·2	40·3		0·5
Propionic	$C_3H_5O_2Na$	3·8	51·7	96	0·6
		19·8	46·2		0·5
Caproic	$C_6H_{11}O_2Na$	3·5	72·8	138	0·52
		20·6	77·9		0·56
Nonylic	$C_9H_{17}O_2Na$	3·4	144·1	180	0·8
		20·4	285·5		1·58
Lauric	$C_{12}H_{23}O_2Na$	3·3	474	222	2·13
		16·1	507		2·28
Palmitic	$C_{16}H_{31}O_2Na$	16·4	about 1060	278	about 4
		25·0	approaching ∞		approaching ∞
Stearic	$C_{18}H_{35}O_2Na$	abt. 16·0	about 1500	306	about 5
		27	approaching ∞		approaching ∞
Oleic	$C_{18}H_{33}O_2Na$	26·5	approaching ∞	304	approaching ∞

The numbers given in the last column are a measure of the dissociation brought about, and they show in a general way that the salts of the lowest fatty acids are hydrolysed in the hot, those of the higher acids already in the cold, whereas laurates occupy an intermediate position.

The hydrolytic action of water is retarded by the addition of **free alkali**. The following table due to *Alder Wright* and *Thompson*, which should be compared with the one given above, p. 35, clearly points out this fact.

Fatty Acids.	Extra Na_2O added to solution per 100 as combined soap.	Hydrolysis brought about by x Molecules of Water.		
		$x=150$	$x=250$	$x=2000$
Crude Lauric	11·0	1·1	1·6	2·0
Cotton seed oil acids . .	15·0	nil	nil	6·5
Stearic and Oleic (from tallow)	20·0	nil	nil	nil

An equally retarding influence is exercised by **alcohol**. Absolute alcohol, as also alcohol of 95 to 90 per cent, dissolve neutral soaps without dissociation. If, however, water be added to an alcoholic soap solution, hydrolysis is brought about more or less, according to the quantity of water added. (This is easily demonstrated by adding a drop of phenolphthalein solution.) From concentrated alcoholic solutions the soaps mostly separate on cooling in a jelly-like mass, which, however, becomes crystalline on standing for some time.

Also **glycerol** causes a diminution of the amount of hydrolysis brought about by water.

Presence of **salts** diminishes the solubility of soaps in water; in sufficiently concentrated solutions of common salt, sodium sulphate, also caustic alkalis, soaps are insoluble, they are therefore thrown out of their aqueous solutions by adding salt, etc. (*soap-making*). The laurates and ricinoleates are remarkable for the large quantity of salt required to throw them out of their solutions, or, as the term goes, for "salting out."

The commercial soaps, containing potash as alkali, constitute the "soft soaps," those containing soda the "hard."

The affinities of fatty acids, such as occur ordinarily in most glycerides, to **caustic soda and potash** are sensibly the same; so that if a mixture of caustic soda and potash be brought into contact with fatty acids, insufficient in quantity to neutralise the total alkali present, a mixture of soda and potash soaps results with excess of the caustic alkalis, the ratio between free caustic soda and potash being approximately the same as that of the combined alkalis. The following table, due to *Alder Wright* and *Thompson*,[1] expresses this clearly; in each experiment for a given amount of fatty acid two equivalents of alkali, one of caustic soda and one of caustic potash, were present:

Fatty Acid.	Percentage of Total Fatty Acid converted into	
	Soda Soap.	Potash Soap.
Pure Stearic	51·2	48·8
Pure Oleic	50·8	49·2
Crude Stearic and Oleic (tallow) .	51·5	48·5
Crude Stearic Palmitic and Oleic (palm oil and tallow) . . .	48·2	51·8
Crude Lauric (cocoa nut oil) . .	49·7	50·3
Mean .	50·3	49·7

Practically, in every case half the caustic alkali was present as soap and the other half as uncombined hydroxide (cp. also chap. ii. p. 19). The logical postulate, that a soda soap on treatment with as

[1] *Jour. Soc. Chem. Ind.* 1885, 626.

much caustic potash as is equivalent to the soda present, and conversely, a potash soap with the equivalent of caustic soda, should yield a soap containing half the fatty acid in combination with potash and the other half combined with soda, is thus borne out by experiments.

The **carbonates** of soda and potash behave in a very different manner. Experiments carried out in a similar fashion to those described in the case of the caustic alkali proved that the prevailing tendency is towards the formation of potash soap and sodium carbonate, whether potassium carbonate was intermixed with soda soap in equivalent proportions of the basis, or sodium carbonate was intermixed with potash soap; in the latter case, even if the quantity of sodium carbonate was largely in excess of the amount equivalent to the potash present, only a comparatively small proportion of soda soap was formed. The following table, due to the same authors, gives the actual figures obtained :—

Fatty Acid.	Soda Soap fused with CO_3K_2. Percentage of total Fatty Acids present.		Potash Soaps fused with CO_3Na_2. Percentage of total Fatty Acids present.	
	Equivalent to the CO_3K_2 added.	Actually converted into Potash Soap.	Equivalent to the CO_3Na_2 added.	Actually converted into Soda Soap.
Stearic and Oleic (tallow) . .	10·4	8·0	...	...
,, ,,	45·7	34·4	...	...
,, ,,	100·0	97·95	100·0	4·3
,, ,,	104·2	99·00	1000	15·0
Stearic, Palmitic, and Oleic (palm oil and tallow) . . .	57·2	52·1	...	...
Stearic, Palmitic, and Oleic (palm oil and tallow) . . .	108·0	90·8	177·0	9·5
Crude Lauric (Cocoa nut oil) .	52·8	46·4	...	...
,, ,,	114·8	87·9	197·0	6·2
Crude Ricinoleic acid (Castor oil)	50·0	48·4	...	...
,, ,, ,,	100·0	93·8	205·0	8·2

The **chlorides** of the alkalis behave in the opposite manner to the carbonates; the prevailing tendency being towards the formation of soda soap and potassium chloride; at any rate, these salts are formed in preference to potash soap and sodium chloride when the relative masses of the two alkalis are nearly equal. (*Old method of making hard soap from wood ashes.*) On repeating the same operation, the exchange of the metals may become a complete one.

The results obtained by *Alder Wright* and *Thompson* in experiments when using 10 molecules of KCl and 10 molecules of NaCl for 1 molecule of soap consisting of one-half molecule of potash soap and one-half molecule of soda soap are reproduced in the following table :—

Fatty Acid.	Percentage of Fatty Acid contained		Molecular Ratio of Soda Soap to Potash Soap.
	As Potash Soap.	As Soda Soap.	
Pure Oleic	38·0	62·0	1·63 : 1
Crude Ricinoleic (from castor oil)	17·8	82·2	4·6 : 1
Stearic, Oleic, and Resin (from tallow-resin soap) . .	17·2	82·8	4·8 : 1
Crude Lauric Acid (from cocoa nut oil soap) . .	15·1	85·9	5·7 : 1

By modifying, however, the relative masses, potash soap and sodium chloride can be produced. The experimental proof is given by the figures in the following table, where in the case of columns (*a*) potash soaps dissolved in M molecules of water were salted out by N molecules of sodium chloride for 1 molecule of soap, and in the case of columns (*b*) soda soaps dissolved in M molecules of water were salted out by adding N molecules of potassium chloride for 1 molecule of soap.

Fatty Acid.	M	N	(*a*) Potash Soaps salted out with NaCl. Percentage of Fatty Acid in Curd as		(*b*) Soda Soaps salted out with KCl. Percentage of Fatty Acid in Curd as	
			Potash Soap.	Soda Soap.	Potash Soap.	Soda Soap.
Stearic and Oleic (from tallow)	100	5	10·5	89·5	79·1	20·9
,, ,,	200	20	5·1	94·9	82·1	17·9
Stearic Palmitic and Oleic (from palm oil and tallow)	200	20	3·8	96·2	95·8	4·2
Crude Lauric (from cocoa nut oil)	200	20	5·4	94·6	74·8	25·2

Salts of the Alkaline Earths and of the Heavy Metals

These salts of the lowest members of the fatty acids are soluble in water, easily forming basic salts which separate out on boiling the solutions.

As the solubility of the free acids, starting from butyric acid, decreases with the increase of the number of carbon atoms in the molecule, so likewise the solubility of the salts decreases. The figures for the solubility of the calcium salts given in the following table demonstrate this very clearly :—

Calcium Salt of	Soluble in parts of Water.	At Temperature. °C.
Butyric acid . . .	3·5	14
Isovaleric acid . .	4·9	20
Isobutyl acetic acid .	11·1	19
Caprylic acid . .	more than 160·0	20
Capric acid . . .	large quantity of water	100
Lauric acid . . .	about 2000	100

The barium salts of the volatile acids (see *Knight*, chap. vi. p. 161), as also the lead salts of the volatile acids (*Asbóth*), are stated to be soluble in water, so that the solubility of the volatile acids themselves corresponds to the solubility of their barium, or lead, salts.

The salts are best obtained by precipitating alcoholic solutions of the acids with solutions of the acetates of the metals. The salts of the higher acids are even insoluble in alcohol.

The lead salts of the higher saturated acids are nearly insoluble in ether, whereas lead oleate, lead linoleate,[1] lead ricinoleate,[1] in short, the lead salts of the higher unsaturated acids, are soluble in this menstruum.

More information will be found under the headings of the individual acids and in chap. xii. p. 785.

I.—Acids of the Acetic Series, $C_nH_{2n}O_2$

Acetic Acid, $C_2H_4O_2 = CH_3 . COOH$

The glyceride of this acid has been found in the seeds of the spindle-tree—*Evonymus europæus*, L. The occurrence of acetic acid as a component of a fat being limited, according to our present knowledge at least, to this one case, the properties of this acid need not be detailed here, inasmuch as every text-book of qualitative analysis supplies the necessary information.

Butyric Acid, $C_4H_8O_2 = CH_3 . CH_2 . CH_2 . COOH$

The glyceride of butyric acid occurs in ordinary butter—as butyrin—to the extent of about 6 per cent.

Butyric acid at ordinary temperature is a colourless liquid. When freshly distilled its odour resembles that of acetic acid; diluted with water it has a smell resembling that of rancid butter. It solidifies at $-19°$ C.; the crystals melt between $-2°$ and $+2°$ C. The acid boils at 162·3° C., and has the specific gravity 0·9746 at 0° C.; 0·958 at 14° C.; 0·9587 at $\frac{20°}{4°}$ C., and 0·8141 at $\frac{161·5°}{4°}$ C.

Butyric acid is miscible with water, alcohol, and ether in all proportions; it can be separated from its aqueous solution in the form of oily drops on adding calcium chloride or common salt.

Solutions of butyric acid have a sour burning taste; they redden tincture of litmus, and discharge the pink colour of slightly alkaline solutions containing phenolphthalein. Methylorange turns red in solutions of butyric acid free from butyrates.

On distilling a dilute aqueous solution of butyric acid it all passes

[1] By linoleate and ricinoleate is meant the salt of the mixed fatty acids from linseed and castor oils.

over into the distillate. If the solution is too weak it will be found preferable to neutralise with caustic soda and concentrate by evaporation. The concentrated solution is then acidified by means of dilute sulphuric acid and distilled.

On warming an alcoholic solution of butyric acid with concentrated sulphuric acid, ethyl butyrate is formed, the smallest quantity of which may be recognised by its pleasant odour, resembling that of pine-apples. Butyric acid is detected by means of this reaction in dilute solutions by neutralising with caustic soda, evaporating to dryness, and warming the residue gently with alcohol and sulphuric acid.

It should be noted that ethyl butyrate is also formed to some extent on saponifying fats, containing butyrin, by means of strong alcohol and caustic potash; this occurs especially if the quantity of alkali is not sufficient to effect complete saponification.

The metallic salts of butyric acid are—with the exception of the silver, mercurous, and lead salts—*easily* soluble in water; the salts of the alkalis are deliquescent.

The calcium salt, $Ca(C_4H_7O_2)_2 + H_2O$, is remarkable on account of its solubility decreasing with the increase of temperature. At 14° C. the saturated solution contains 1 part of the salt dissolved in $3\frac{1}{2}$ parts of water. On warming to 30° C. a precipitate is obtained, and on boiling the salt separates, nearly completely redissolving on cooling. The calcium salt is also soluble in alcohol.[1]

Silver butyrate, $AgC_4H_7O_2$, dissolves in 200 parts of water at 14° C. It crystallises according to the concentration in needles or monoclinic prisms, and is obtained on adding silver nitrate to the solution of the butyrate of any alkali.

Isovaleric Acid, $C_5H_{10}O_2 = (CH_3)_2 . CH . CH_2 . COOH$

This acid occurs as a glyceride—triisovalerin—in porpoise and dolphin oils, the blubber oils from *Delphinus phocæna* and *Delphinus globiceps*. *Chevreul* discovered the acid when examining the oil of the former animal, and termed it phocenic acid.

The odour of isovaleric acid is like that of valerian root or putrid cheese.

The acid is a colourless liquid; its boiling point is 173·7° C. at 760 mm.[2]; its specific gravity is 0·9467 at 0° C., 0·931 at 20° C. It dissolves in 23·6 parts of water at 20° C., and is separated from this solution on adding calcium chloride.

Isobutylacetic Acid (Caproic acid), $C_6H_{12}O_2 = (CH_3)_2 . CH . CH_2 . CH_2 . COOH$

Isobutylacetic acid occurs in combination with glycerol as the glyceride caproin in cow butter and in cocoa nut oil. The acid is not miscible with water, although to some extent soluble in it. It

[1] With regard to the barium salt, cp. Wilcox, *Proceed. Chem. Soc.* 1895, 202.

[2] The melting point lies at −51° C., its solidifying point −57° C. Massol, *Jour. Soc. Chem. Ind.* 1895, 828.

does not crystallise when cooled to -18° C.; it boils at 199·7° C. at 732 mm., and its specific gravity is 0·925 at 20° C. Its odour is like that of sweat.

Caprylic Acid, $C_8H_{16}O_2 = CH_3 . (CH_2)_6 . COOH$

Caprylic acid exists as a glyceride in cow butter, in human fat, and notably in cocoa nut oil. At the ordinary temperature liquid, it crystallises on cooling to 12° C. in the shape of laminæ, melting at 16·5° C.; it boils at 236°-237° C. at 761 mm. pressure. Its specific gravity is 0·9270 at 0°, and 0·9139 at 20° C. One part dissolves in 400 parts of boiling water, and on cooling it separates out nearly completely. The acid possesses an intense odour of sweat.

Capric Acid, $C_{10}H_{20}O_2 = CH_3 . (CH_2)_8 . COOH$

The butter fat of the cow and goat contains this acid combined with glycerol as the glyceride *caprin*; the same glyceride is also found in cocoa nut oil in association with the glycerides of the two preceding acids. As a potassium salt it occurs in wool yolk.

Capric acid crystallises in fine needles, having the melting point 31·3°-31·4° C., and boiling point 268°-270° C.

The specific gravity of the acid at 37° C. is 0·930.

Nearly insoluble in cold water, it dissolves in about 1000 parts of boiling water.

The acid has a goat-like smell, which becomes more distinct at the temperature of its melting point.

Of the metallic caprates, the salts of the alkalis only are easily soluble in water.

Umbellulic Acid, $C_{11}H_{22}O_2$[1]

The glyceride of this acid is said to exist to the extent of about 60 per cent in the nuts of the Californian bay-tree—*Umbellularia californica*; it is also stated to occur in Chaulmoogra oil.

The acid is crystalline, and melts at 21°-23° C.; it can be distilled at 275°-280° C. without undergoing decomposition. It possesses a faint odour and has a disagreeable and irritating taste.

Lauric Acid, $C_{12}H_{24}O_2$

Lauric acid is found as a glyceride in laurel oil, cocoa nut oil, pichurim beans, spermaceti, and tangkallah fat, the fat from the fruit of *Cylicodaphne sebifera*.

The acid is solid at ordinary temperature, and crystallises from alcohol in needles, melting point 43·6° C. Lauric acid is the first acid of the acetic series that cannot be distilled at ordinary pressure without undergoing slight decomposition. Its boiling point is 225°

[1] Stillman and O'Neill, *Jour. Soc. Chem. Ind.* 1883, 124.

C. at 100 mm., 176° C. at 15 mm., 102° C. *in vacuo*. The specific gravity is 0·883 at 20° C., and 0·875 at 43·6° C.

Lauric acid is slightly soluble in large quantities of boiling water; on distilling such a solution it passes over to an appreciable extent with the vapours.

The laurates of the alkali-metals require very large quantities of salt for "salting out." (Cocoa nut soaps, marine soaps.)

The solubilities of a number of metallic salts of lauric acid in water and alcohol are given in the following table due to *Oudemans*:—

Name of Salt.	Formula.	1000 parts of Water dissolve		1000 parts of Alcohol dissolve	
		At the Boiling Point.	At 15° C.	At the Boiling Point.	At 15° C.
Magnesium laurate	$Mg\bar{A}_2+3H_2O$	0·411	0·230	126·0	15·25
Calcium laurate .	$Ca\bar{A}_2+H_2O$	0·547	0·039	22·02	0·719
Strontium laurate .	$Sr\bar{A}_2+H_2O$	0·360	0·272	3·59	9·598
Barium laurate .	$Ba\bar{A}_2$	0·698	0·054	1·009	0·187
Zinc laurate . . .	$Zn\bar{A}_2+H_2O$ (?)	0·189	0·103	8·78	0·134
Lead laurate . .	$Pb\bar{A}_2$	0·011	...	2·35	0·047
Manganese laurate .	$Mn\bar{A}_2+xH_2O$	0·401	0·011	3·82	0·481
Cobalt laurate . .	$Co\bar{A}_2+H_2O$	0·376	0·072	18·01	0·174
Nickel laurate . .	$Ni\bar{A}_2+H_2O$ or $3H_2O$	0·390	0·197	6·68	0·640
Copper laurate . .	$Cu\bar{A}_2$	0·029	0·023	6·53	0·775
Silver laurate . .	$Ag\bar{A}$	0·405	0·001	0·824	0·323

Myristic Acid, $C_{14}H_{28}O_2$

The glyceride of myristic acid occurs in wool wax, nutmeg butter (from *Myristica moschata*), and in otoba fat (from *Myristica otoba*); further, it has been found in large quantities in dika oil, and to a small extent also in cocoa nut oil and the wax of cochineal. It occurs also as cetyl myristate in spermaceti. In very small quantity it has been recently found in the gall of oxen.

Myristic acid crystallises in laminæ of the melting point 53·8° C., and boiling point 350·5° C. at 100 mm., 196·5° C. at 15 mm., 121°-122° C. *in vacuo*. The specific gravity is 0·8622 at 53·8° C.

The acid is completely insoluble in water; when boiled with water very slight quantities of the acid are carried away with the vapours. It dissolves with difficulty in cold alcohol and ether.

Isocetic Acid, $C_{15}H_{30}O_2$

The oil from the seeds of *Jatropha curcas* (purging nut oil, curcas oil) contains the glyceride of isocetic acid. The acid crystallises in laminæ, having the melting point 55° C. An examination of this acid is very desirable.

Palmitic Acid, $C_{16}H_{32}O_2$

Palmitic acid occurs, as a glyceride—palmitin—in most animal and vegetable fats; and notably in large quantities in palm oil, vegetable tallow (from *Stillingia sebifera*), and Japan wax. It occurs also in spermaceti as cetyl palmitate, in beeswax as myricyl palmitate, and in opium wax as ceryl palmitate.

The synthesis of palmitic acid from oleic acid is commercially[1] important, and is brought about by melting the latter with caustic alkali, whereby acetates are obtained as by-product according to the following equation:—

$$C_{18}H_{34}O_2 + 2KOH = KC_{16}H_{31}O_2 + KC_2H_3O_2 + H_2.$$

Pure palmitic acid forms tufts of finely crystallised needles; the melted acid solidifies on cooling to a nacreous, scaly, crystalline mass. The acid is free from smell or taste. The melting point is 62° C. It distils between 339° and 356° C. with slight decomposition; it boils under a pressure of 100 mm. at 271·5° C., under a pressure of 15 mm. at 215° C., and *in vacuo* at 138°-139° C. The specific gravity of the acid is 0·8527 at $\frac{62°\text{ C.}}{4°}$.

Melted palmitic acid dropped on paper causes a grease-spot; this is also obtained when an alcoholic or ethereal solution of palmitic acid is allowed to evaporate.

Palmitic acid is not readily soluble in cold alcohol; 100 c.c. of (methylated) alcohol, specific gravity 0·8183 (containing 94·4 per cent of alcohol by volume), dissolve the following quantities after being kept the number of hours stated at 0° C.:[2]—

Hours.	Grms.
12	1·298-1·320
36	1·244
60	1·211
84	1·134
108	1·086
132	1·044
156	1·028

100 parts of absolute alcohol dissolve at 19·5° C. 9·32 parts only. It dissolves very readily in boiling alcohol, and therefore this menstruum is conveniently used for purifying palmitic acid.

Dilute acids have no action on palmitic acid; it dissolves, however, in concentrated sulphuric acid. On diluting with water, the palmitic acid separates from this solution unchanged. Boiling concentrated nitric acid attacks it very slowly. Oxidised in alkaline solution by means of potassium permanganate, it gives rise to the formation of acetic, butyric, caproic, oxalic, succinic, adipic, and hydroxylated acids.

[1] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1897, 390.
[2] Hehner and Mitchell, *Analyst*, 1896, 323.

Concentrated solutions of permanganate yield lower members of the fatty acid series than dilute solutions.

The metallic salts of palmitic acid resemble very much those of stearic acid (see p. 48), but they possess a somewhat greater solubility. The silver palmitate can be obtained in a crystalline form by adding an alcoholic solution of silver nitrate to an alcoholic solution of ammonium palmitate; silver palmitate separates from the solution in the shape of small, lustrous laminæ. Lead palmitate is almost insoluble in absolute ether, 50 c.c. of the latter dissolving 0·0092 grm. of the lead salt.

A quantitative determination of palmitic acid may be effected by precipitating it from the solution of palmitates by means of hydrochloric acid, washing the precipitate with water, dissolving it in absolute alcohol, evaporating to dryness, and finally drying in a desiccator over sulphuric acid.

Daturic Acid, $C_{17}H_{34}O_2$

The glyceride of daturic acid has been recently discovered in the oil from the seeds of *Datura Stramonium* (thorn-apple).[1] The acid dissolves more easily in cold alcohol than palmitic acid, and crystallises from it in fine needles, melting point 55° C. *Nördlinger*[2] claims to have found the same or an isomeric acid amongst the solid fatty acids of palm oil to the amount of 1 per cent; this acid melts at 57° C., and boils between 223° and 225° C. under a pressure of 15 mm.

Margaric acid is an obsolete commercial term for a mixture of palmitic and stearic acids, for which, in older text-books, the formula $C_{17}H_{34}O_2$ is assumed. The butter substitute "margarine" derives its name from this acid.

Stearic Acid, $C_{18}H_{36}O_2$

Stearic acid occurs largely as a glyceride in most natural fats, especially in the harder ones, such as tallow. The higher the melting point of a fat the greater will be found the percentage of stearin—the glyceride of stearic acid.

Pure stearic acid forms white, nacreous laminæ melting between 71° and 71·5° C. to a perfectly colourless liquid, which on cooling solidifies to a crystalline transparent mass at 69·3° C. It boils at about 360° C. under ordinary pressure with slight decomposition; under a partial vacuum, however, it distils unchanged. The boiling point for 100 mm. pressure is 291° C., for 15 mm. 232° C., and *in vacuo* the acid boils at 154·5°-155·5° C. The acid may also be distilled in a current of steam without fear of partial destruction.

The specific gravity of stearic acid is 0·8454 at its melting point.

[1] Gérard, *Jour. Soc. Chem. Ind.* 1890, 1137. [2] *Ibid.* 1892, 444.

At 11° C. its specific gravity is exactly that of water; at more elevated temperatures it floats on water, expanding more quickly than the latter.

Like palmitic acid it possesses neither smell nor taste; it is greasy to the touch, and produces a grease-spot on paper under the same conditions as palmitic acid.

Insoluble in water, it dissolves easily in hot alcohol. It is less soluble in absolute alcohol than palmitic acid, one part of stearic acid requiring 40 parts of this solvent. 100 c.c. alcohol (methylated), of specific gravity 0·8183 (containing 94·4 per cent of alcohol by volume), dissolve at 0° C. 0·155 to 0·158 grm. after 12 hours' standing, and 0·145 to 0·153 grm. after 36 hours' standing.[1] Stearic acid dissolves easily in ether; at 23° C. 1 part of benzene dissolves 0·22 parts of the acid, and 1 part of carbon bisulphide 0·3 parts. On oxidising stearic acid with potassium permanganate *Carette* obtained dibasic acids (succinic, adipic). *Marie*[2] has found amongst the products of oxidation normal valeric acid (and not iso-valeric acid, contrary to previous statements).

Stearates of the Alkali-Metals.—These stearates are prepared by adding stearic acid to aqueous solutions of potassium or sodium carbonates, whereby carbonic acid is expelled. A better method, however, is to add the boiling aqueous solution of the carbonates to an alcoholic solution of stearic acid, and to evaporate to dryness; the excess of the carbonate is then removed by exhaustion of the residue with alcohol. From the alcoholic solution the salts deposit on cooling. The alkali salts crystallise when quite pure.

In ether, petroleum ether, carbon bisulphide, and chloroform, the stearates are insoluble (difference from oleic acid).

Potassium stearate, $KC_{18}H_{35}O_2$, forms crystals possessing a greasy lustre; they dissolve in 6·6 parts of boiling alcohol. On diluting the hot aqueous solution of the potassium stearate with a large proportion of water, pearly laminæ of an acid stearate separate, possessing the formula $KC_{18}H_{35}O_2 . C_{18}H_{36}O_2$.

Sodium stearate, $NaC_{18}H_{35}O_2$, resembles very much in its properties the potassium salt; the crystals are lustrous laminæ. The acid salt has the formula $NaC_{18}H_{35}O_2 . C_{18}H_{36}O_2$.

Ammonium stearate, $(NH_4)C_{18}H_{35}O_2$, on being warmed in aqueous solution loses some of its ammonia, and changes into the acid salt. The same change takes place when the ammonia soap is allowed to stand over concentrated sulphuric acid in a desiccator.

The other metallic salts of stearic acid are obtained by double decomposition from sodium stearate, or, better still, by precipitating alcoholic solutions of stearic acid with solutions of the acetates of the metals. The stearates thus obtained are insoluble in water.

Calcium, *strontium*, and *barium stearates* form crystalline precipitates insoluble in alcohol. The *magnesium* salt crystallises in microscopical laminæ; it is nearly insoluble in cold alcohol, but so far soluble in boiling alcohol that it can be crystallised from it.

[1] Hehner and Mitchell, *Analyst*, 1896, 323. [2] *Jour. Soc. Chem. Ind.* 1896, 362.

The stearates of the heavy metals, as the *silver*, *copper*, and the *lead* salts, are mostly amorphous; the last-mentioned salt melts at 125° C. without undergoing decomposition. The *lead* salt is very sparingly soluble in ether (difference from oleic acid), and less still in petroleum ether (*Twitchell*). 50 c.c. of absolute ether dissolve 0·0074 grm. of lead stearate (*Lidoff*).

The insoluble salts of stearic acid are partly decomposed on washing with water. Thus barium stearate loses thereby barium oxide, and with the undissociated residue there remains some free stearic acid which can be extracted by alcohol. This is of importance for the quantitative determination of stearic acid (also of palmitic and oleic acids), as has been shown by *Chittenden* and *Smith*. In accurate estimations the salts cannot be employed; the free acids must be separated and weighed as such.

Arachidic Acid, $C_{20}H_{40}O_2$

The glyceride of arachidic acid has been found in very small quantities in cow butter. It occurs in larger quantities in arachis oil and in Rambutan tallow, the oil from the seeds of *Nephelium lappaceum*, L., in smaller quantities in rape oil, cacao butter, etc. Arachidic acid crystallises in small, lustrous scales having the melting point 77° C. The acid is soluble in cold alcohol with great difficulty, but dissolves easily in boiling alcohol. Part of the acid is, however, transformed into ethylic arachidate during this operation; to avoid loss in recrystallising, the acid should, therefore, only be boiled until the arachidic acid has passed into solution; 100 parts of 90 per cent alcohol dissolve at 15° C. 0·022 parts of arachidic acid, and at 20° C. 0·045 parts. The acid is therefore much less readily soluble than stearic acid. The metallic salts of arachidic acid are not unlike those of stearic acid.

Behenic Acid, $C_{22}H_{44}O_2$

The oil of ben (or behen), expressed from the seeds of *Moringa oleïfera*, contains the glyceride of this fatty acid. The melting point of behenic acid is 80°-82° C., its solidifying point 79°-76° C.[1] Synthetical behenic acid from erucic acid[2] melts at 83°-84° C., and solidifies at 79°-77° C. The acid crystallises in needles; it is less soluble in alcohol than in ether.

Lignoceric Acid, $C_{24}H_{48}O_2$

The glyceride of this acid has been shown to occur in arachis oil, in association with arachidic acid. The melting point of lignoceric acid is 80·5° C.; the melted acid solidifies on cooling into a mass possessing radiated structure; when cold, this mass becomes brittle. The acid crystallises from alcohol in white flocks of silky lustre, which,

[1] *Jour. für prakt. Chemie*, 1894 (64), 61. [2] *Ibid.* 1895 (50), 71-73.

on pressing between filter-paper, become scaly and show nacreous lustre. In cold alcohol but very sparingly soluble, lignoceric acid dissolves readily in benzene, ether, and carbon bisulphide.

Carnaübic Acid, $C_{24}H_{48}O_2$

This acid, isomeric with lignoceric acid, occurs as an ether combined with higher alcohols in carnaüba wax; it has been discovered recently in wool wax.[1] It is sparingly soluble in cold methyl alcohol, but easily soluble in boiling alcohol, ether, benzene, petroleum ether, and glacial acetic acid. The melting point is 72·5° C., the solidifying point 69°-67° C. The ammonium salt is insoluble in water and alcohol; the potassium salt is sparingly soluble in these menstrua in the cold, more readily so at higher temperatures. The lead salt melts at 109°-111° C.

Hyænic Acid, $C_{25}H_{50}O_2$

The glyceride of this acid has been shown to occur in the anal glandular pouches of the striped hyæna. Its melting point is between 77° and 78° C. An examination of this acid is very desirable.

Cerotic Acid, $C_{26}H_{52}O_2$ ($C_{25}H_{50}O_2$ or $C_{27}H_{54}O_2$)

Cerotic acid exists in the free state in beeswax and in carnaüba wax. Combined with ceryl alcohol, as cerylic cerotate, it has been shown to be present in Chinese wax, opium wax, and in wool wax.

Crude cerotic acid is prepared from beeswax by exhausting it with boiling alcohol, and is a wax-like mass, melting between 78° and 82° C. It separates from its alcoholic solution on cooling in thin, straight or curved needles. The separation is so complete in the course of a few hours, that the addition of water to the filtrate produces no precipitate, but only a milky turbidity. This constitutes an essential difference from palmitic and stearic acids. *Marie* states that the crystals deposited from alcohol vary according to the purity of the acid. Pure cerotic acid crystallises from alcohol in stellate, microscopic needles, melting point 77·8° C. (corr.); from benzene in dense laminæ, and from ether in tabular masses consisting of large aggregated needles. (The crystals deposited from alcohol, if the acid contains neutral substances, form a gelatinous mass consisting of microscopic needles, and containing a large proportion of alcohol; if the impurity is melissic acid, short granular crystals separate.)

When boiled with sodium carbonate or dilute aqueous caustic soda, the acid does not pass into solution; it dissolves, however, in boiling alcoholic potash; on cooling, the potassium cerotate solidifies into a mucilaginous mass (*Barfoed*).

[1] *Jour. Soc. Chem. Ind.* 1896, 460; *Berichte*, 29. 618; 2892.

Cerotic acid can be estimated volumetrically in its alcoholic solution by caustic potash, phenolphthalein serving as the indicator.

Some doubt has been thrown on the existence of an acid of the composition of cerotic acid by *Schalfejeff*;[1] but its existence has been confirmed by *Nafzger*,[2] by *Zatzek*,[3] and by *Marie*.[4] The formula of cerotic acid has not yet been definitively ascertained. The ultimate analyses of cerotic acid and its esters agree with the formula $C_{26}H_{52}O_2$, or $C_{25}H_{50}O_2$.[5] It would appear, however, to the writer that no definite information can be gained from ultimate analysis, as a glance at the following little table will show :—

	C	H	O
	Per cent.	Per cent.	Per cent.
$C_{27}H_{54}O_2$.	79·02	13·17	7·81
$C_{26}H_{52}O_2$.	78·80	13·12	8·08
$C_{25}H_{50}O_2$.	78·53	13·09	8·38

It would certainly be safer to determine the acid value (cp. p. 148), as the differences between the acids of various formulæ are larger than the errors inherent to the method.[6]

	Molecular Weight.	Acid Value.
$C_{27}H_{54}O_2$ . .	410	136·8
$C_{26}H_{52}O_2$ . .	396	141·7 [7]
$C_{25}H_{50}O_2$ . .	382	146·8

However, whether cerotic acid has the composition $C_{26}H_{52}O_2$, or is a mixture of different acids, the estimation of the free acids in waxes is not affected thereby.

Pure cerotic acid in 1 per cent boiling alcoholic solution gives no precipitate with magnesium acetate, the salt separating on cooling to 50° C.; but if the cerotic acid contain melissic acid, there is an immediate precipitate.

Melissic Acid, $C_{30}H_{60}O_2$

Melissic acid occurs, also in the free state, in beeswax. It crystallises in scales possessing silky lustre, and melting at 90° C. *Schwalb*[8] has prepared, from beeswax-myricyl alcohol, a melissic acid crystallising from petroleum ether in small, fine needles, to which he ascribes the

[1] *Berichte*, 9. 278 ; 1688.
[2] *Annalen*, 224. 256.
[3] *Berichte*, 15. 2625.
[4] *Jour. Soc. Chem. Ind.* 1894, 1207 ; 1895, 599.
[5] *Ibid.* 1896, 362.
[6] Lewkowitsch, *Proc. Chem. Soc.* 1890, 92.

[7] Lewkowitsch found for a sample of pure cerotic acid from beeswax the acid value 142·1. Henriques, on repeating this experiment quite recently obtained 141·4 for cerotic acid from Chinese wax.

[8] *Annalen*, 235. 135.

formula $C_{31}H_{62}O_2$, and the melting point 88·5°-89° C. The melissic acid, $C_{30}H_{60}O_2$, is readily soluble in warm alcohol, chloroform, carbon bisulphide, and petroleum ether, but sparingly soluble in ether.

II.—Acids of the Oleic Series, $C_nH_{2n-2}O_2$

The acids belonging to the oleic, or acrylic (from acrylic acid, the lowest member) series are so-called unsaturated compounds, and possess therefore the property of absorbing, under certain conditions, chlorine, bromine, iodine, and the hydrogen acids of these halogens. They assimilate two atoms of the halogens, or one molecule of the hydrogen acids, being converted thereby into derivatives of the acids belonging to the acetic series. Some of these unsaturated acids also take up hydrogen when acted upon with sodium amalgam in alkaline solution, and thus become, in a direct way, reduced to acids of the saturated series. Oleic acid, however, does not take up hydrogen,[1] and cannot be converted into stearic acid by this reaction, but on being treated with fuming hydriodic acid, in presence of phosphorus, at a temperature of 200°-210° C., stearic acid is formed. The following equation illustrates the chemical change, which, however, is by no means a quantitative one :—

$$C_{18}H_{34}O_2 + 2HI = C_{18}H_{36}O_2 + I_2.$$

The lower members of this series volatilise without undergoing decomposition, and are miscible with water in every proportion. With the increase of the number of carbon atoms the boiling points become higher and the solubility in water decreases. The specific gravity also diminishes.

The higher acids of this series cannot be distilled under ordinary pressure ; they pass over unchanged in a current of superheated steam or *in vacuo*.

Some of the higher acids, when treated with a small quantity of nitrous acid at the ordinary temperature, or with sulphurous acid or bisulphites at high temperatures and under pressure, are changed into crystallisable isomerides. A characteristic property of the lead salts of the higher acids is their solubility in ether, by which reaction they may be separated from the corresponding acids of the acetic series.

The unsaturated acids are far more readily soluble in alcohol than the saturated acids having the same number of carbon atoms.

Oxidised by means of a dilute solution of potassium permanganate in alkaline solution, the unsaturated acids are converted into hydroxylated acids (see p. 67). When melted with caustic alkalis they are broken up into two acids possessing together a number of carbon

[1] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1897, 390.

atoms equal to the decomposed acid; thus oleic acid yields palmitic and acetic acids.

Wanklyn and *Johnstone*[1] claim to have discovered several acids having the general composition $C_nH_{2n-2}O_2$, and possessing remarkable properties. The existence of these so-called alde-acids stands in need of confirmation.

Tiglic Acid, $C_5H_8O_2 = CH_3 . CH : C(CH_3) . COOH$

The glyceride of tiglic acid occurs in croton oil. This acid, an isomeride of angelic acid, crystallises in triclinic columns; melting point 64·5° C. The acid boils at 198·5° C. Sodium amalgam has no effect on the acid. On melting with caustic potash, acetic and propionic acids are produced. By oxidation with potassium permanganate, dihydroxytiglic (tigliceric acid) is formed.

Fittig's[2] researches prove that tiglic acid occurs in croton oil as such, and is not formed from angelic acid under the influence of the caustic soda used in saponifying the oil, as has been assumed repeatedly, for on prolonged boiling of angelic acid with caustic soda hardly 5 per cent of tiglic acid was obtained.

Acids $C_{12}H_{22}O_2$ and $C_{14}H_{26}O_2$

These acids are said to occur in combination with glycerol in the fat of cochineal.[3]

Hypogæic Acid, $C_{16}H_{30}O_2$ (Gaïdic Acid, $C_{16}H_{30}O_2$)

The glyceride of this acid has been stated to occur in arachis oil by *Gössmann* and *Scheven*, and by *Schröder*. *Schoen*, however, could not find any hypogæic acid in this oil, and although his statement is confirmed by *Bodenstein*,[4] yet the hypogæic acid prepared by the latter synthetically has the properties of the acid obtained by *Schröder* from arachis oil.

Hypogæic acid crystallises in needles, melting at 33°-34° C., boiling 236° C. under a pressure of 15 mm., and at 230° C. under a pressure of 10 mm. On passing nitrous acid fumes through hypogæic acid, its stereometrical isomeride, *gaïdic acid*, melting at 39° C., is formed.

Physetoleic Acid, $C_{16}H_{30}O_2$

This acid is said to occur as an ether in sperm oil. It differs from hypogæic acid, which has the same composition, by its not being transformed into a stereometrical isomeride by nitrous acid. Further, it does not yield sebacic acid on distillation, like hypogæic acid. The melting point of physetoleic acid is stated to be 30° C.

[1] *Chem. News*, 65. 75.
[2] *Liebig's Annalen*, 283. 65.
[3] Raymann, *Monatshefte für Chemie*, 6. 895.
[4] *Berichte*, 1894, 3397.

Lycopodic Acid, $C_{16}H_{30}O_2$

The glyceride of this fourth acid, having the composition $C_{16}H_{30}O_2$, has been discovered in the spores of lycopodium.[1] It differs from the above described isomerides by being liquid at the ordinary temperature. Potassium permanganate transforms it into dihydroxypalmitic acid; melting caustic potash splits it up into isobutyric and lauric acids.

Asellic Acid, $C_{17}H_{32}O_2$

This acid is assumed to exist as a glyceride in sardine oil (see p. 472), inasmuch as dihydroxyasellic acid (p. 70) was obtained by oxidising the fatty acids of that oil.

Oleic Acid

$$C_{18}H_{34}O_2 = C_8H_{17} - C - H \text{ [2]}$$
$$\|$$
$$H - C - (CH_2)_7COOH;$$

or
$$CH_3 - (CH_2)_{13} - C - H \text{ [3]}$$
$$\|$$
$$H - C - CH_2COOH$$

(Elaïdic acid, $C_{18}H_{34}O_2$; Isooleic acid, $C_{18}H_{34}O_2$)

Oleic Acid occurs very largely in nature. It is found in most animal and vegetable fats, especially in the liquid ones, in combination with glycerol.

Large quantities of oleic acid are prepared commercially as a by-product in the manufacture of candles (see chap. xii. p. 752). The chemically pure product can only be obtained with difficulty, and, in this state, it forms a colourless liquid free from smell, solidifying at 4° C., and melting at 14° C. The specific gravity at 14° C. is 0·898; and at 100° C. 0·876. Under ordinary pressure oleic acid cannot be distilled without undergoing decomposition; in a current of superheated steam, however, it passes over unchanged at a temperature of about 250° C. The following boiling points have been found by *Krafft* and *Nördlinger*,[4] and *Krafft* and *Weilandt*,[5] for the pressures given in the table:—

Boiling Point. °C.	Pressure. mm. Mercury.
153·0	0
223·0	10
232·5	15
249·5	30
264·0	50
285·5-286·0	100

[1] *Jour. Chem. Soc.* 1889, Abstracts, 741; 1059.
[2] Baruch, *Berichte*, 1894 (27), 173. Cp. also Lewkowitsch, *Jour. Soc. Chem. Ind.* 1897, 391.
[3] Saytzeff, *Berichte*, 1894 (27), Ref. 577.
[4] *Jour. Chem. Soc.* 1889, Abstracts, 691.
[5] *Berichte*, 1896, 1324.

The chemically pure acid is said to have no action on blue litmus, but it discharges the colour of an alkaline solution made pink with phenolphthalein.

On exposure to the air oleic acid turns yellowish or yellow, acquires a rancid smell, and reddens blue litmus paper.

Oleic acid is insoluble in water, but dissolves readily in cold alcohol, even if the alcohol is diluted. On adding large quantities of water to its alcoholic solution the acid is thrown out. On this greater solubility of oleic acid in mixtures of water, alcohol, and acetic acid, compared with that of the solid fatty acids (palmitic and stearic), *David* has based a method of separating the several acids (see chap. vi. p. 197).

Oleic acid is converted into elaïdic acid when acted upon with nitrous acid at the ordinary temperature[1] (see p. 57). The same change takes place when it is treated with sodium bisulphite under pressure at 175°-180° C., or with sulphurous acid under pressure at 200° C.

On passing air through oleic acid, previously heated to 200° C., oxygen is absorbed and large quantities of hydroxyoleic acid are formed.[2] Similarly on digesting oleic acid with sulphur at a temperature between 130° and 150° C. the sulphur is absorbed, without evolution of sulphuretted hydrogen, apparently forming an addition-product (see chap. xii. p. 744). At higher temperatures, however, say from 200° to 300° C., sulphuretted hydrogen is evolved.

If bromine be dropped into oleic acid, using molecular proportions (4 : 7 parts), with constant shaking, or, better still, if solutions of bromine and oleic acid in carbon bisulphide, or another solvent, be used, all the bromine is absorbed with formation of dibromostearic acid (or dibromide of oleic acid) according to the following equation :—

$$C_{18}H_{34}O_2 + Br_2 = C_{18}H_{34}Br_2O_2.$$

The product forms, in its pure state, a heavy yellow oil. On reduction with zinc and hydrochloric acid, oleic acid is regenerated. Oleic acid absorbs iodine and chlorine when acted upon by an alcoholic solution of iodine and mercury bichloride (Hübl's method ; see chap. vi. p. 170).

When heated with melted caustic potash oleic acid is split up into palmitic and acetic acids (see p. 46, Palmitic Acid).

Oleic acid dissolves in cold concentrated sulphuric acid, forming sulphostearic acid, $C_{18}H_{35}(SO_4H)O_2$; on boiling this product with water, sulphuric acid is split off, and hydroxystearic acid is formed conjointly with a small quantity of stearolactone (see Turkey-red Oil, chap. xii. p. 727).[3] A similar transformation takes place on heat-

[1] According to Lidoff (*Analyst*, 1895, 178), by the action of nitrous oxides on oleic acid at 80°-85° C. an increase of weight takes place, and the iodine value of the product is only 9 per cent. Experiments made by the writer show, however, that elaïdic acid is formed and the apparent low iodine value is due to the action of nitrous acid, left in the fatty acid, on potassium iodide (*Jour. Soc. Chem. Ind.* 1897, 390).

[2] Benedikt and Ulzer, *Zeitsch. Chem. Industrie*, 1887, 246.

[3] Cp. also *Jour. Soc. Chem. Ind.* 1897, 390.

ing oleic acid with zinc chloride to 185° C. (see Commercial Stearic Acid, chap. xii. p. 747).

Dihydroxystearic acid is formed when potash permanganate is allowed to act on oleic acid in dilute alkaline solution.

The reduction of oleic acid to stearic acid by means of hydriodic acid and phosphorus has been mentioned already. *P. de Wilde* and *Reychler*[1] tried to convert oleic acid into the more valuable stearic acid by heating the former, mixed with 1 per cent of iodine, in autoclaves up to 270°-280° C. A mixture of fatty substances results, melting from 50°-55° C., which they separated by distillation in a current of superheated steam into a residue insoluble in alcohol, a distillate containing stearic acid, and a liquid, which cannot be converted into stearic acid by repeating the process. The yield of stearic acid only reaches 70 per cent, and but one-third of the iodine can be recovered. Thus the costliness of the process prevents its introduction into candle-works.

The metallic oleates behave with water in much the same way as the metallic salts of palmitic and stearic acids. Only the salts of the alkali-metals are soluble in water, under the conditions described above for the corresponding stearates.

The salts of the alkali-metals—oleic acid soaps—are thrown out from their aqueous solution by adding strong alkali, common salt, or other soluble mineral salts.

All these oleates are considerably softer than the corresponding salts of palmitic and stearic acids; most of them melt without decomposition.

Sodium oleate, $NaC_{18}H_{33}O_2$, is prepared by crystallisation from absolute alcohol, not from dilute alcohol. It dissolves in 10 parts of water at 12° C., or in 20·6 parts of alcohol, specific gravity 0·821, at 13° C., or in 100 parts of boiling ether.

Potassium oleate, $KC_{18}H_{33}O_2$, forms a transparent jelly-like mass, far more readily soluble in water, alcohol, and ether than the sodium salt, 1 part of the salt requiring 4 parts of water, or 2·15 parts of alcohol, or 29·1 parts of boiling ether.

All the other metallic oleates are soluble in alcohol; some are also dissolved by ether.

Barium oleate, $Ba(C_{18}H_{33}O_2)_2$, is a crystalline powder insoluble in water, and but sparingly soluble in boiling alcohol. At the temperature of 100° C. it conglutinates without, however, becoming liquid.

Aluminium oleate, $Al(C_{18}H_{33}O_2)_3$, forms a jelly-like mass slightly soluble in hot ether and petroleum ether. In the arts it is used as an "oil-thickener."

Silver oleate, $AgC_{18}H_{33}O_2$, is nearly insoluble in ether. (Difference from silver salt of resin acids.)

Lead oleate, $Pb(C_{18}H_{33}O_2)_2$, is a white powder, melting at 80° C. to a yellow oil. It is soluble in ether, and may thus be separated (as in general the liquid acids of the unsaturated series) from the saturated acids (palmitic, stearic, etc.) This separation, however, is not a

[1] *Jour. Soc. Chem. Ind.* 1889, 466.

complete one.[1] Lead oleate is also soluble in petroleum ether, but only slightly soluble in absolute alcohol (*Twitchell*).

Elaïdic Acid is obtained by allowing nitrous acid fumes, or a nitrite and nitric acid, to act on oleic acid at the ordinary temperature; after a short time the oleic acid is changed into its stereometrical isomeride, elaïdic acid. The separation of elaïdic acid from unchanged oleic acid is readily effected by crystallisation from ether. The rational formula of elaïdic acid is

$$\begin{array}{r} C_8H_{17}-C-H \\ \| \\ CO_2H-(CH_2)_7-C-H \end{array} \quad \text{or} \quad \begin{array}{r} CH_3-(CH_2)_{13}-C-H \\ \| \\ CO_2H-CH_2-C-H. \end{array}$$

The acid crystallises from alcohol in plates melting at 51°-52° C.; it solidifies at 44°-45° C.[2] Elaïdic acid distils almost unchanged. The following boiling points have been ascertained by *Krafft* and *Nördlinger*:—

Boiling Point. °C.	Pressure. mm. Mercury.
154	0
225	10
234	15
251·5	30
266	50
287·8-288·0	100

Elaïdic acid can be converted in its turn into ordinary oleic acid by boiling iodostearic acid, prepared from elaïdic acid, with alcoholic potash; simultaneously some iso-oleic acid is formed.[3]

Acted on by potassium permanganate in alkaline solution, elaïdic acid yields dihydroxystearidic acid.[4] Heated with melted caustic potash it yields, like ordinary oleic acid, palmitic acid.

Isooleic (Para-oleic), Solid Oleic Acid, $\begin{array}{l} CH_3-(CH_2)_{14}-C-H \\ \quad\quad\quad\

Isooleic acid is then separated from its zinc salt by sulphuric acid and purified by repeated crystallisation from ether.

Isooleic acid is also formed, when iodostearic acid, obtained by the action of hydriodic acid on ordinary oleic acid or elaïdic acid, is heated with alcoholic potash in a flask connected with an inverted condenser. The resulting product contains isooleic acid, together with unchanged oleic acid.

Isooleic acid occurs in considerable quantities in commercial stearic acid obtained by "acid saponification" and subsequent distillation (cp. chap. xii. p. 746).

Isooleic acid forms transparent, rhombic plates (from ether), melting from 44° to 45° C. It is very easily soluble in alcohol, considerably less so in ether. It absorbs, like ordinary oleic acid, two atoms of bromine or iodine, and undergoes the same change as oleic acid when treated with melted potash. With permanganate of potash a dihydroxystearic acid is obtained which differs from that obtained from ordinary oleic acid by the same reaction (cp. p. 70).

On treating isooleic acid with concentrated sulphuric acid, and subsequently boiling the product with water, two isomeric hydroxystearic acids are formed (see p. 68), differing by their behaviour when subjected to distillation *in vacuo*.

The lead salt of isooleic acid is considerably less soluble in ether than lead oleate.

Rapic Acid, $C_{18}H_{34}O_2$

The glyceride of rapic acid occurs, according to *Reimer* and *Will*,[1] in rape oil. Rapic acid does not solidify on cooling, and does not yield a solid isomeride when acted upon by nitrous acid. The sodium salt forms a gelatinous mass easily soluble in water; the zinc salt is crystalline, dissolves easily in alcohol and ether, and melts at 78° C.

Reimer and *Will* assigned to the acid the formula $C_{18}H_{34}O_3$, but rapic acid cannot be an hydroxylated acid, as the acetyl value of the crude rape oil acids found by *Benedikt* and *Cantor* corresponds to but 3·8 per cent of a hydroxylated acid. Again, as the iodine absorption of rape oil is very high, rapic acid must be an unsaturated acid, and cannot be a ketonic acid; besides, it does not form a compound with phenylhydrazine.

Recently *Zellner*[2] has shown that rapic acid has the composition $C_{18}H_{34}O_2$, as he was able to convert it into an iodo-compound yielding stearic acid on subsequent reduction with zinc and hydrochloric acid. The analysis of zinc rapate confirms the formula $C_{18}H_{34}O_2$. Rapic acid must therefore be looked upon as an isomeride of oleic acid.

Doeglic Acid, $C_{19}H_{36}O_2$

The existence of this acid is somewhat doubtful, and it may possibly

[1] *Jour. Soc. Chem. Ind.* 1887, 732. [2] *Ibid.* 1896, 661.

be identical with oleic acid. It has been stated by *Scharling*[1] to occur in Arctic sperm oil as a dodecatyl ether of doeglic acid (cp. Arctic Sperm Oil, chap. xi. p. 647).

Jecoleic Acid, $C_{19}H_{36}O_2$

An acid of this composition is assumed by *Heyerdahl* to occur in cod liver oil,[2] inasmuch as he has obtained a dihydroxyjecoleic acid (cp. p. 70), by oxidising the cod liver oil fatty acids with potassium permanganate. Jecoleic acid is stated to form at least 20 per cent of the liquid fatty acids of cod liver oil.

Erucic Acid

$$C_{22}H_{42}O_2 = C_8H_{17} - C - H \text{ [3]}$$
$$\|$$
$$H - C - C_{11}H_{22} - COOH;$$

or

$$CH_3 - (CH_2)_{17} - CH$$
$$\|$$
$$CH - CH_2 - CO_2H.\text{ [4]}$$

The glyceride of this acid occurs in rape oil, and in black and white mustard oils.[5] The acid crystallises from alcohol in long, fine needles, melting from 33° to 34° C. The following boiling points have been found by *Krafft* and *Nördlinger*:—

Boiling Point. ° C.	Pressure. mm. Mercury
179	0
254·5	10
264	15
281	30

In its properties it very much resembles oleic acid. Thus it absorbs two atoms of bromine or iodine; nitrous acid and sulphurous acid under pressure at high temperatures (cp. oleic acid, p. 55), as also bisulphites, convert it into its stereometrical isomeride, *brassidic acid*, $C_{22}H_{42}O_2$; heated with hydriodic acid and phosphorus it is reduced to behenic acid; melting caustic potash splits it up into acetic and arachidic acids; oxidised with potassium permanganate it yields dioxybehenic acid. On oxidation with nitric acid, nonylic and brassylic acids are obtained. The lead salt of erucic acid is but sparingly soluble in ether, differing in this respect from oleic acid.

Brassidic acid,

$$C_8H_{17} - C - H \qquad \text{or} \qquad CH_3 - (CH_2)_{17} - C - H$$
$$\| \qquad\qquad\qquad\qquad\qquad\qquad \|$$
$$CO_2H \,.\, C_{11}H_{22} - C - H, \qquad\qquad CO_2H - CH_2 - C - H$$

[1] *Jour. prakt. Chemie*, 43. (1848), 257. [2] *Cod Liver Oil and Chemistry*, p. xcviii.
[3] Liebermann, *Berichte*, 1893, 1869.
[4] Alexandroff and Saytzeff, *Jour. für prakt. Chemie*, 49. (1894), 63.
[5] The occurrence of erucic acid in grape seed oil (Fitz, *Berichte*, 1871, 444) is doubtful (cp. Grape Seed Oil).

crystallises from alcohol in laminæ, having the melting point 65° C., and solidifying point 56° C.; it boils *in vacuo* at 180° C., and under a pressure of 15 mm. at 265° C.

Iso-erucic acid, $CH_3 - (CH_2)_{17} - CH_2 - CH = CH - CO_2H$),[1] is obtained from iodo-behenic acid by boiling with alcoholic potash. The iodo-behenic acid may have been prepared from either erucic or behenic acid[2] (cp. iso-oleic acid, p. 58).

Iso-erucic acid crystallises from alcohol in plates, melting at 54°-56° C., solidifying at 52°-51° C.

III.—Acids of the Linolic Series, $C_nH_{2n-4}O_2$

The acids belonging to this series are characterised, for analytical purposes at least, by their capability of absorbing four atoms of bromine or iodine, and by the solubility of their lead salts in ether. They are not affected by nitrous acid. Their property of absorbing oxygen on exposure to the air is very important in the arts (drying oils).

Isomeric with the acids described below are the solid palmitolic, stearolic, and behenolic acids.

Elæomargaric Acid, $C_{17}H_{30}O_2$

The glyceride of this acid has been found in Japanese wood Oil, the oil from the seeds of *Aleurites cordata* (*Elæococca vernicia*) (p. 346). The free acid crystallises in rhombic plates, melting point 48° C. It readily absorbs oxygen from the atmosphere and becomes resinous. Protected from light, the alcoholic (or ethereal) solution of the acid remains unchanged; on exposure to light, however, crystals are deposited from the alcoholic solution, melting at 71° C. These are crystals of the isomeric acid **elæostearic acid.** Exposure of the Japanese wood oil to light is said to change the glyceride of the elæomargaric acid into that of elæostearic acid.

Linolic Acid, $C_{18}H_{32}O_2$

The glyceride of linolic acid occurs in linseed oil and other drying oils. It has been found in the fat from hares, Caspian sea seals, sturgeons, and shad-fishes, and is most likely the less saturated acid in lard and other animal fats having high iodine values. *Reformatzky*[3] claims to have prepared the pure acids by hydrolising pure ethyl linolate; but according to *Hazura's* researches it is quite possible

[1] Saytzeff, *Jour. für prakt. Chemie*, 1892 (45), 301.
[2] Alexandroff and Saytzeff, *ibid.* 1894 (49), 58. Saytzeff, *ibid.* 1894 (50), 65.
[3] *Jour. Soc. Chem. Ind.* 1890, 744.

that *Reformatzky's* linolic acid is a mixture of the unsaturated acids occurring in linseed oil, and containing chiefly acids of the formula $C_{18}H_{30}O_2$ (cp. Linseed Oil, chap. xi. p. 337).

Linolic acid is a slightly yellowish oil, which remains fluid even at a temperature of − 18° C.; its specific gravity is 0·9206 at 14° C. It has a slight acid reaction, and dissolves readily in alcohol and ether.

Nitrous acid does not produce a solid acid from linolic acid (important difference from acids of the oleic series). Linolic acid absorbs oxygen rapidly from the atmosphere, and when exposed in thin films to the air it is converted within a few days into a solid resinous substance named oxyoleic acid; and after a more prolonged exposure it forms a neutral body insoluble in ether. The latter compound is the so-called "linoxyn."[1]

Linolic acid absorbs four atoms of bromine, forming the tetrabromide $C_{18}H_{32}O_2Br_4$, melting point 114°-115° C., which can be reduced to linolic acid by means of zinc and alcoholic hydrochloric acid. By oxidation with a dilute solution of potassium permanganate, tetrahydroxystearic or sativic acid $C_{18}H_{36}O_6$ (cp. p. 72) is formed. By heating linolic acid with phosphorus and hydriodic acid to 200° C. we obtain stearic acid. The two last-mentioned reactions definitely exclude the older formula $C_{16}H_{28}O_2$ given in text-books for linolic acid.

The metallic salts of linolic acid are amorphous, with the exception of the zinc salt. Barium and calcium linolates are soluble in boiling alcohol; the calcium, barium, zinc, copper, and lead salts also dissolve in ether. The linolates absorb oxygen more readily than the free acid. ("Driers," chap. xii. p. 737.)

Tariric Acid, $C_{18}H_{32}O_2$

This isomeride of linolic acid has been found[2] combined with glycerol in the fat from the seeds of a Guatemalan *Picramnia* (Tariri), and also in the fat from *Picramnia Camboita*.[3]

Tariric acid melts at 50·5° C. It absorbs four atoms of bromine forming a tetrabromide, melting point 125° C. The potassium salt is only slightly soluble in 98 per cent alcohol, 100 parts of the latter dissolving 2·48 parts of tariric acid at 15° C.

On treating tariric acid with hydriodic acid and amorphous phosphorus, it is reduced to stearic acid.[4]

Millet Oil Acid, $C_{18}H_{32}O_2$

The existence of this acid, assumed by *Kassner*[5] to occur as a glyceride in millet oil, is somewhat doubtful.

[1] *Jour. Soc. Chem. Ind.* 1888, 680.
[2] *Ibid.* 1892, 916.
[3] Grützner, *Chem. Zeit.* 1893, 1851.
[4] Arnaud, *Compt. rend.* 122, 1000.
[5] *Jour. Chem. Soc.* 1888, Abstr. 673.

IV.—Acids of the Linolenic Series, $C_nH_{2n-6}O_2$

The acids of the linolenic series assimilate six atoms of bromine or iodine, and absorb oxygen readily. Their lead salts are easily soluble in ether. Nitrous acid does not produce solid isomerides.

Linolenic Acid, $C_{18}H_{30}O_2$

The glyceride of this acid occurs in large quantities in the drying oils, especially in linseed oil. The free acid has been prepared by *Hazura*[1] from a hexabromide, which he obtained on brominating the crude liquid acids of linseed oil. This hexabromide, having a melting point of 177° C., yielded on reduction with zinc and alcoholic hydrochloric acid the linolenic acid. Potassium permanganate oxidises linolenic acid to hexahydroxystearic or linusic acid (cp. p. 72). *Reformatzky*[2] considers *Hazura's* hexabromide to be a dibromo- (substitution product) derivative of the tetrabromide of linolic acid, and throws doubt on the existence of linusic acid, which he considers to be a product of oxidation of tetrahydroxystearic acid. In *Reformatzky's* opinion linolenic acid does not exist, and is identical with linolic acid. It must, however, be pointed out in support of *Hazura's* views, that his acid was found by him to absorb 245 per cent of iodine, theory requiring for an acid of the formula $C_{18}H_{30}O_2$ 274 per cent, whilst linolic acid is only able to assimilate 181 per cent (cp. Linseed Oil). The physical properties of linolenic acid resemble those of linolic acid with the exception of its odour, which is similar to that of fish oils.

Isolinolenic Acid, $C_{18}H_{30}O_2$

This acid has not been yet isolated, but its existence, as a glyceride in linseed oil, is inferred by *Hazura*[3] from the fact that he obtained isolinusic acid, an isomeride of linusic acid, on oxidising linseed oil acids with potassium permanganate.

Jecoric Acid, $C_{18}H_{30}O_2$

Fahrion[4] assumes the existence of this acid in sardine oil from the analyses of the barium, calcium, and magnesium salts. Other analytical data, however, as ultimate analysis, acid value, iodine value, do not agree with those required by theory. The existence of this acid is therefore somewhat doubtful. This acid does not conform to *Hazura's* rule, inasmuch as it does not yield a hydroxy acid on oxidation, only volatile acids and carbonic dioxide being obtained.

[1] *Jour. Soc. Chem. Ind.* 1888, 506.
[2] *Ibid.* 1890, 744.
[3] *Ibid.* 1888, 506.
[4] *Ibid.* 1893, 938.

V.—Acids of the Series $C_nH_{2n-8}O_2$

Isanic Acid, $C_{14}H_{20}O_2$

This acid [1] has been isolated from the oil from the seeds of I'Sano or Ungueko (a large tree of the *Oleaceæ* family, growing in the French Congo), forming about 10 per cent of the fatty acids of the oil.

The acid forms foliated crystals (from ether), melting at 41° C.; it is readily soluble in strong alcohol, ether, chloroform, benzene, acetone, methyl alcohol, and petroleum ether.

It possesses a peculiar odour, which it imparts to the seeds, and is extremely susceptible to change of colour on exposure to air, thereby turning rose-red, the tinge deepening with the increased absorption of oxygen. Ether leaves the oxidised rose-coloured substance undissolved.

The formula given above seems doubtful, although derived from analyses of the acid and the silver and barium salts. The cryoscopic determination of the molecular weight gave 217 ($C_{14}H_{20}O_2 = 220$), but the acid absorbed about 2 molecules of bromine only. Endeavours to reduce the acid by means of hydriodic acid did not lead to positive results.

Therapic Acid, $C_{17}H_{26}O_2$

The occurrence of an acid of this formula is inferred by *Heyerdahl* [2] from a bromine product $C_{17}H_{26}Br_8O_2$ he obtained on brominating the cod liver oil fatty acids. It is stated to occur in cod liver oil to the extent of 20 per cent. The name has been chosen by *Heyerdahl* to express his opinion that this acid plays the most important part in the therapeutical action of cod liver oil.

VI.—Hydroxylated Acids, $C_nH_{2n}O_3$

Lanopalmic Acid, $C_{16}H_{32}O_3$

Lanopalmic acid has been isolated from that portion of the wool wax acids which forms potash-soaps readily soluble in cold alcohol (chap. xii. p. 654).

On decomposing the magnesium salt, by means of which it is isolated, not the free acid, but an anhydride (or perhaps its ethylate) is precipitated.

The acid crystallises from dilute alcohol in radiated crystals, melting at 87°-88° C., and solidifying at 85°-83° C. It is insoluble in

[1] *Jour. Soc. Chem. Ind.* 1896, 660. [2] *Cod Liver Oil and Chemistry*, p. xcv.

water, but dissolves in it in the presence of very little alcohol on boiling, and separates on cooling as a white crystalline magma. The usual organic solvents dissolve it readily.

Treated with aqueous alkalis it does not pass into solution, but on adding a little alcohol and heating, the alkali salts are readily formed. The alkali salts exist in aqueous solution only in the hot, but on cooling they are dissociated into acid salts, which separate, and free alkali.

The magnesium salt is insoluble in hot alcohol; the calcium salt dissolves easily in boiling absolute alcohol, but sparingly in 95 per cent alcohol.

An acid of the formula $C_{21}H_{42}O_3$ occurs, combined with alcohols, in carnaüba wax.[1] The free acid does not appear to exist, the inner anhydride, or lactone, of the acid being precipitated, whenever the latter itself might be expected.

Cocceric Acid, $C_{31}H_{62}O_3$

Cocceric acid occurs in the wax of cochineal[2] combined with cocceryl alcohol. The acid forms a crystalline powder (from alcohol), melting point 92°-93° C., and dissolves sparingly in cold alcohol, ether, benzene, petroleum ether, and glacial acetic acid.

VII.—Acids of the Ricinoleic Series. Hydroxylated Acids, $C_nH_{2n-2}O_3$

Ricinoleic Acid, $C_{18}H_{34}O_3 = CH_3 - (CH_2)_5 - CH\,.\,OH - CH_2 - CH = CH - (CH_2)_7 - CO_2H$[3]

(Ricinisoleic Acid, $C_{18}H_{34}O_3$; Ricinelaïdic Acid, $C_{18}H_{34}O_3$; Ricinic Acid, $C_{18}H_{34}O_3$)

Ricinoleic acid occurs combined with glycerol in large quantities in castor oil. The crude ricinoleic acid obtained by saponifying castor oil and decomposing the soap by means of a mineral acid is at the ordinary temperature a thick oil of specific gravity 0·9509 at 15·5° C. On cooling to − 6° to − 10° C. the acid solidifies completely, and is miscible with alcohol and ether in every proportion. *Krafft*[4] has obtained from the crude acid, by cooling to 0° and gradually pressing at temperatures not exceeding 12° C., a white, odourless, hard, crystalline mass melting at 16°-17° C., which he considers to be the pure acid. The melted acid solidifies easily when cooled considerably below the melting point. The acid cannot be distilled without undergoing decomposition,[5] even under a pressure of only 15 mm. The

[1] *Jour. Soc. Chem. Ind.* 1884, 448.
[2] *Ibid.* 1885, 585.
[3] Goldsobel, *Berichte*, 1894, 3121.
[4] *Jour. Soc. Chem. Ind.* 1888, 755.
[5] An acid of the formula $C_{18}H_{32}O_2$ being formed (Mangold, *Berichte*, 1894, Ref. 629).

pure triglyceride of ricinoleic acid is solid, whilst castor oil is fluid at the ordinary temperature (cp. Castor Oil, chap. xi. p. 421). According to Juillard,[1] however, the acid so prepared is not pure, as it still contains stearic and (natural) dihydroxystearic acids. The pure acid is best obtained from its barium salt after repeated crystallisation of the latter from alcohol. The pure acid melts at 4°-5° C.

Ricinoleic acid assimilates two atoms of bromine or iodine, but does not absorb hydrogen. Nitrous acid transforms it into its stereometrical isomeride, ricinelaïdic acid. On exposure to the atmosphere ricinoleic acid does not absorb oxygen. By reducing agents it is converted into stearic acid.

According to *H. Meyer*[2] ricinoleic acid becomes polymerised on standing, forming polyricinoleic acids, easily convertible into ricinoleic acid on boiling with alcoholic potash.

Most of the metallic salts are obtained in the crystalline state; they behave with solvents very much like the corresponding salts of oleic acid. The calcium and barium ricinoleates are soluble in alcohol; the lead ricinoleate is easily soluble in ether, and melts at 100° C.

By the action of concentrated sulphuric acid on ricinoleic acid the following products are obtained:[3] — *ricinoleo-sulphuric acid*, $OH . SO_2 . O . C_{17}H_{32} . COOH$,

dihydroxystearo-sulphuric acid, $\begin{matrix} OH . SO_2 . O \\ OH \end{matrix} > C_{17}H_{33} . COOH$

dibasic diricinoleic acid, $O < \begin{matrix} C_{17} H_{32} . COOH \\ C_{17} H_{32} . COOH \end{matrix}$

monobasic diricinoleic acid, $OH . C_{17}H_{32}COO . C_{17}H_{32} . COOH$, *dihydroxystearic acid*, $C_{18}H_{36}O_4$, *a solid acid*, $C_{36}H_{70}O_7$, and *isoricinoleic acid*, $C_{18}H_{34}O_3$ (cp. Turkey-red Oils, p. 727).

On oxidising ricinoleic acid with potassium permanganate two atoms of oxygen are assimilated. *Hazura* and *Grüssner*[4] found that two isomeric trihydroxystearic acids were formed by this process, and concluded, therefore, that the liquid fatty acid of castor oil is a mixture of two isomerides, ricinoleic and *ricinisoleic* acids. *Mangold*,[5] however, points out that this conclusion need not be necessarily adopted, as two stereochemical isomerides may be obtained from one and the same ricinoleic acid.[3]

Ricinelaïdic acid is produced from ricinoleic acid by the action of nitrous acid. It crystallises in needles, melting point 52°-53° C. The acid absorbs two atoms of bromine. Oxidised by potassium permanganate ricinelaïdic acid yields two isomeric (most likely stereometric) trihydroxylated acids (*Mangold*).

[1] *Jour. Chem. Soc.* 1895, Abstr. i. 500. [2] *Jour. Soc. Chem. Ind.* 1897, 684.

[3] *Ibid.* 1894, 820. An isoricinoleic acid has been described by Juillard; this acid appears to be a ketonic acid, and is a by-product formed by the action of sulphuric acid on ricinoleic acid; it is distinguished from ricinoleic acid by its solubility in petroleum ether.

[4] *Jour. Soc. Chem. Ind.* 1888, 681. [5] *Jour. Chem. Soc.* 1893, Abstracts, 1304.

Ricinic acid has been obtained by *Krafft* on heating barium ricinoleate in a vacuum, when the barium salt of ricinic acid remains in the retort. The acid forms glistening laminæ (from alcohol), melting point 81° C. It boils under 15 mm. pressure with very slight decomposition.

The existence of this acid points again to the possible existence of two ricinoleic acids, which, however, need not be chemical isomerides, but may represent stereometric isomerides, ricinoleic acid possessing one so-called asymmetric carbon atom, and therefore possibly forming dextro- and lævo-rotatory acids. In fact, *Walden*[1] has shown since that both ricinoleic and ricinelaïdic acids are optically active, whereas ricinic acid is inactive. The two active acids are dextro-rotatory, their lævo-rotatory isomerides being unknown yet.

VIII.—Acids of the Series $C_nH_{2n}O_4$, Dihydroxylated Acids

Dihydroxystearic Acid, $C_{18}H_{36}O_4$

This natural dihydroxylated acid occurs, according to Juillard,[2] in castor oil to the extent of about 1 per cent, and is prepared from crude ricinoleic acid by keeping the latter at a temperature below 12° C. The crystalline magma is drained, pressed, and recrystallised from alcohol, and thus yields a mixture of dihydroxystearic and stearic acids. The latter is removed by washing with hot toluene, and the remaining crude dihydroxystearic acid is recrystallised from boiling alcohol.

The pure acid melts at 140°-143° C. It is insoluble in ether, petroleum ether, and benzene, slightly soluble in cold toluene, more so in the hot solvents; it dissolves in boiling alcohol and boiling acetic acid.

By reducing agents the acid is easily converted into stearic acid; by hydrochloric acid at 180° C., and subsequent treatment with caustic potash, this dihydroxystearic acid is changed into the dibasic acid $COOH.(HO)C_{17}H_{33}.O.C_{17}H_{33}(OH)COOH$.

It is possible that this acid—being a natural product—is optically active.

Lanoceric Acid, $C_{30}H_{60}O_4$

Lanoceric acid has been isolated from the mixture of soaps obtained by saponifying wool wax with alcoholic potash.[3]

The acid crystallises from alcohol in microscopic laminæ; it softens at 102° C. and melts at 104°-105° C.; it then solidifies at 103°-101°, and melts again at the same temperature as before. It has, however, lost one molecule of water, probably from the two hydroxyl

[1] *Berichte*, 1894, 3472. [2] *Jour. Soc. Chem. Ind.* 1895, 811.

[3] Darmstaedter and Lifschütz, *Berichte*, 1896, 1474, 2893; *Jour. Soc. Chem. Ind.* 1896, 548. (The acid is described there as lanocerinic acid.)

groups, for it still has acid properties. The acid very readily forms a lactone, *e.g.* when boiled with dilute hydrochloric acid; the lactone melts at 86° C.

Lanoceric acid is almost insoluble in cold water and alcohol, but readily soluble in hot alcohol. It does not combine readily with aqueous potash; a little alcohol, however, easily induces combination; the salt is therefore best prepared in alcoholic solution. The potassium salt behaves exactly like that of lanopalmic acid (p. 63), viz. it dissociates on cooling into the acid salt, which separates, and into free alkali.

APPENDIX TO THE FATTY ACIDS

The acids already mentioned occur in natural fats and waxes. Besides these, however, several saturated hydroxylated acids or their inner anhydrides are found in various products of the fat industry. These we describe below, along with some other hydroxylated fatty acids, which are of great importance for the identification of glycerides of unsaturated acids.

As the outcome of their own and *Saytzeff's* researches, the following general law has been stated by *Hazura* and *Grüssner*.[1] All unsaturated fatty acids, when oxidised with potassium permanganate in alkaline solution, have as many hydroxyl groups added as the fatty acids contain unsaturated valencies, yielding thereby saturated hydroxylated acids which contain the same number of carbon atoms in the molecule. The following table shows the hydroxylated acids obtained hitherto by this reaction:—

Fatty Acid.	Hydroxylated Acid.
Tiglic acid	(Dihydroxytiglic) Tigliceric acid
(Unknown)	Dihydroxyasellic acid
Oleic acid	Dihydroxystearic acid
Elaïdic acid	Dihydroxystearidic acid
Isooleic acid	Para-dihydroxystearic acid
(Unknown)	Dihydroxyjecoleic acid
Ricinoleic acid	Trihydroxystearic acid α-Isotrihydroxystearic acid
Ricinelaïdic acid	β-Isotrihydroxystearic acid γ-Isotrihydroxystearic acid
Linolic acid	Tetrahydroxystearic (sativic) acid
Linolenic acid	Hexahydroxystearic (linusic) acid
Isolinolenic acid (?)	Isolinusic acid
Erucic acid	Dihydroxybehenic acid
Brassidic acid	Isodihydroxybehenic acid
Isoerucic acid	Para-dihydroxybehenic acid

[1] *Jour. Soc. Chem. Ind.* 1888, 506.

A dihydroxypalmitic acid has also been prepared starting from the dibromo-addition product of hypogæic acid. But it cannot be doubted that the dihydroxypalmitic acid could be prepared by oxidising hypogæic acid itself with potassium permanganate.

The oxidation of the unsaturated acids is carried out as follows :— 30 grms. of the acids are neutralised by 36 c.c. of caustic potash, specific gravity 1·27, and the resulting soap is dissolved in 2000 c.c. of water. Into this solution are run gradually, with shaking or stirring, 2000 c.c. of a 1·5 per cent solution of potassium permanganate. After a short time as much sulphurous acid is added as will reduce the excess of permanganate and dissolve the separated hydrated manganese peroxide. The hydroxylated fatty acids separate out almost entirely, being mostly insoluble in water (see p. 69). During the reaction, perhaps owing to the further oxidation of the hydroxylated acids, dibasic acids are also formed ; for this reason we shall briefly describe those dibasic acids that have been found amongst the products of oxidation, and are likely to be met with in similar researches.

In the case of cod liver oil fatty acids, *Heyerdahl* found that under the conditions just laid down oxidation proceeds too far, 2 grms. only of hydroxylated acids having been obtained from 50 grms. of crude acids. Good results, however, were obtained when the oxidation was carried out with half-saturated solution at the temperature of the freezing point. For the oxidation of higher unsaturated fatty acids, such as erucic and brassidic acids, a large excess of caustic potash must be used.

I.—Hydroxylated Acids

1. Monohydroxylated Acids

β-Hydroxystearic Acid, $C_{18}H_{36}O_3 = C_{18}H_{35}O_2(OH)$

This acid is formed on dissolving ordinary oleic acid in concentrated sulphuric acid, along with sulphostearic acid and stearolactone (see Turkey-red Oils). The glyceride of the same acid is obtained on subjecting triolein, the glyceride of oleic acid, to the same operation.

β-hydroxystearic acid crystallises in hexagonal plates (from alcohol), melting at 81°-81·5° (*Geitel*), 83°-85° C. (*Saytzeff*). 100 parts of absolute alcohol dissolve 8·78 parts of the acid at 20° C. ; at the same temperature 100 parts of ether dissolve 2·3 parts of the acid.

On heating the acid to 200° C. with or without zinc chloride, a viscous mass is obtained containing the anhydride $C_{18}H_{34}O_2$ and also oleic acid.[1] The hydroxystearic acid is regenerated by boiling the anhydride with caustic potash.

[1] It may be pointed out here that the anhydride $C_{18}H_{34}O_2$, being a saturated compound, does not absorb iodine ; therefore the oleic acid can be determined quantitatively in the mixture (cp. chap. vi. p. 197).

On distilling β-hydroxystearic acid in a vacuum, a portion of the acid passes over unchanged along with oleic and isooleic acids.

The sodium, zinc, and copper salts are soluble in alcohol; the barium salt is insoluble both in alcohol and ether.

α-Hydroxystearic Acid, $C_{18}H_{36}O_3 = C_{18}H_{35}O_2(OH)$

On treating isooleic acid with sulphuric acid in the manner already described for ordinary oleic acid, this isomeride of β-hydroxystearic acid is obtained, together with β-hydroxystearic acid in varying proportions, depending on the temperature during the interaction. The lower the temperature the larger is the yield of α-hydroxystearic acid. α-hydroxystearic acid is also formed on digesting with silver hydroxide the iodo-stearic acid obtained from isooleic acid and hydriodic acid.

This hydroxystearic acid distils undecomposed under a pressure of 100 mm. (difference from β-hydroxystearic acid), and crystallises (from alcohol) in plates, melting point 77°-79° C. It is more easily soluble in ether than the β isomeride, whilst less readily soluble in absolute alcohol; 100 parts of the latter dissolve at 20° C. only 0·58 parts of the acid.

(γ-Hydroxystearic Acid, $C_{18}H_{36}O_3 = C_{18}H_{35}O_2(OH)$)
Stearolactone, $C_{18}H_{34}O_2$

The free acid has not been prepared yet, its inner anhydride, or lactone, being formed whenever the free acid might be expected. This lactone is obtained when concentrated sulphuric acid acts on ordinary oleic acid [1] (see β-hydroxystearic acid). Larger quantities are obtained by heating oleic acid with 10 per cent of zinc chloride to 185° C. (*Schmidt's* process, cp. chap. xii. p. 747). Stearolactone forms fine white crystalline laminæ, having the melting point 47°-48° C.; it can be distilled almost unchanged. Insoluble in water, it dissolves easily in alcohol, ether, and petroleum ether. Boiling alkalis dissolve the stearolactone with formation of metallic salts of the γ-hydroxystearic acid. On adding a mineral acid to the solution of any of the salts, not the acid, as might be expected, but stearolactone is precipitated.

2. Dihydroxylated Acids

(Dihydroxytiglic) Tigliceric Acid,[2] $C_5H_{10}O_4 = C_5H_8O_2(OH)_2$

Tigliceric acid is obtained by oxidising tiglic acid with potassium permanganate. It crystallises in small plates (from ether), melting point 88° C. The acid is very readily soluble in water; also soluble in alcohol and acetone, but insoluble in petroleum ether, chloroform, and benzene.

[1] Cp. Lewkowitsch, *Jour. Soc. Chem. Ind.* 1897, 392.
[2] Fittig, *Liebig's Annalen*, 283. 111.

Dihydroxypalmitic Acid, $C_{16}H_{32}O_4 = C_{16}H_{30}O_2(OH)_2$

This acid has been obtained from dibromopalmitic acid (dibromo-addition product of hypogæic acid) by boiling with silver oxide (compare above). It forms small laminæ (from alcohol), melting point 115° C.; they dissolve readily in alcohol and ether.

Dihydroxyasellic Acid (Dihydroxyheptadecylic Acid), $C_{17}H_{34}O_4 = C_{17}H_{32}O_2(OH)_2$

Amongst the unsaturated acids of sardine oil *Fahrion*[1] assumes the presence of an acid $C_{17}H_{32}O_2$, inasmuch as he isolated from the oxidised oil a dihydroxylated acid of the formula $C_{17}H_{34}O_4$.

This acid forms white nacreous laminæ, of the melting point 114°-116° C. It is insoluble in cold, sparingly soluble in hot water, insoluble in petroleum ether, easily soluble in warm alcohol, and dissolves with difficulty in ether.

The barium salt dissolves in about 2000 parts of boiling water.

Dihydroxystearic Acid,[2] $C_{18}H_{36}O_4 = C_{18}H_{34}O_2(OH)_2$

Dihydroxystearic acid is best prepared by oxidising ordinary oleic acid with potash permanganate in alkaline solution.

It forms crystalline laminæ, melting at 136·5° C., and solidifying between 119° and 122° C. The acid is absolutely insoluble in water, easily soluble in hot, less so in cold alcohol, and sparingly in ether.

This dihydroxystearic acid has been split into two optically active isomerides by means of its strychnine salt.[3]

Dihydroxystearidic Acid, $C_{18}H_{36}O_4 = C_{18}H_{34}O_2(OH)_2$

Elaïdic acid yields this acid on oxidation. Melting-point 99°-100° C.

p-Dihydroxystearic Acid, $C_{18}H_{36}O_4 = C_{18}H_{34}O_2(OH)_2$

This second isomeride of the dihydroxylated stearic acid has been prepared from isooleic acid. It forms a crystalline powder, melting at 79° C., easily soluble in alcohol and ether.

Dihydroxyjecoleic Acid, $C_{19}H_{38}O_4 = C_{19}H_{36}O_2(OH)_2$

On oxidising the liquid cod liver oil fatty acids with half-saturated solution of potassium permanganate at 0° C. this acid is obtained. Melting point 114°-116° C.

[1] *Jour. Soc. Chem. Ind.* 1893, 936.
[2] Natural dihydroxystearic acid, cp. p. 66.
[3] Freundler, *Jour. Chem. Soc.* 1896, Abstr. I. 596.

Dihydroxybehenic Acid, $C_{22}H_{44}O_4 = C_{22}H_{42}O_2(OH)_2$

This acid is obtained by oxidising erucic acid with potassium permanganate; it forms granular crystals, melting at 132°-133° C., dissolving readily in warm alcohol, but insoluble in cold ether.

Isodihydroxybehenic Acid,[1] $C_{22}H_{44}O_4 = C_{22}H_{42}O_2(OH)_2$

Isodihydroxybehenic acid is prepared by oxidising brassidic acid with potassium permanganate. The acid melts at 99°-100° C., and solidifies at 88°-87° C.

Para-dihydroxybehenic Acid,[2] $C_{22}H_{44}O_4 = C_{22}H_{42}O_2(OH)_2$

This third acid of the composition $C_{22}H_{44}O_4$ is prepared from isoerucic acid; it melts at 86°-88° C., and solidifies at 82°-80° C.

3. Trihydroxystearic Acids, $C_{18}H_{33}O_2(OH)_3$

All the acids having this composition have been prepared by oxidising ricinoleic and ricinelaïdic acids. Three acids have been described hitherto by *Hazura* and *Grüssner*,[3] two having been derived from ricinoleic, and the third from ricinelaïdic acid. *Mangold* has shown that also ricinelaïdic yields two trihydroxylated acids, one of which is certainly identical with that prepared by *Hazura* and *Grüssner*. The properties of these acids are briefly described below.

Trihydroxystearic Acid, $C_{18}H_{33}O_2(OH)_3$

This acid has been obtained from ricinoleic acid together with the following acid. It crystallises from hot water in microscopic needles, melting at 140°-142° C. It is insoluble in cold, and dissolves with difficulty in hot water, and likewise in alcohol and ether in the cold. Warm alcohol and glacial acetic acid dissolve it readily. Trihydroxystearic acid is insoluble in carbon bisulphide, chloroform, benzene, and petroleum ether. It is very likely that this acid is optically active.[4]

α-Isotrihydroxystearic Acid, $C_{18}H_{33}O_2(OH)_3$

It differs from the preceding acid by its melting point 110° to 111° C., and by its ready solubility in ether and benzene; it is optically active.[4]

β-Isotrihydroxystearic Acid, $C_{18}H_{33}O_2(OH)_3$

On oxidising ricinelaïdic acid two isomerides are obtained according to *Mangold*. One acid derived from ricinelaïdic acid has been described

[1] Saytzeff, *Jour. prakt. Chem.* 1894 (50), 82.
[2] Alexandroff and Saytzeff, *Jour. prakt. Chem.* 1894 (49), 63.
[3] Cp. also Dieff, *ibid.* 1889 (39), 339. [4] Walden, *Berichte*, 1894, 3475.

by *Hazura* and *Grüssner* as having the melting point 114° to 115° C., and being sparingly soluble in hot water, ether, chloroform, and petroleum ether, and dissolving readily in alcohol. Probably *Mangold's* acid, having the melting point 113° to 116° C., is identical with β-isotrihydroxystearic acid.

The second trihydroxystearic acid from ricinelaïdic acid melts between 117° and 120° C.

It appears very likely indeed that these two acids will rotate the plane of polarised light.

4. Tetrahydroxystearic Acid, $C_{18}H_{32}O_2(OH)_4$

Tetrahydroxystearic or **Sativic** acid is the oxidation product of linolic acid. It crystallises from water in long needles or pyramidal prisms, possessing silky lustre, melting point 173° C. 2000 parts of boiling water dissolve one part of the acid. Sativic acid is insoluble in cold water, ether, chloroform, carbon, bisulphide, and benzene. Hot alcohol and glacial acetic acid dissolve it readily. Potassium permanganate oxidises it to azelaic acid.

5. Hexahydroxystearic Acids, $C_{18}H_{30}O_2(OH)_6$

Linusic Acid,[1] $C_{18}H_{30}O_2(OH)_6$

The linolenic acid contained in linseed oil yields on oxidation the hexahydroxylated acid: linusic acid. It crystallises from water in rhombic plates, occasionally also in needles, melting between 203° and 205° C. Water dissolves it more readily than sativic acid. Linusic acid is insoluble in ether, and sparingly soluble in alcohol.

Isolinusic Acid,[1] $C_{18}H_{30}O_2(OH)_6$

This acid is also formed on oxidising the linseed oil fatty acids, and from its occurrence the existence of isolinolenic acid is inferred.

Isolinusic acid crystallises in prismatic needles, melting between 173° and 175° C. It is sparingly soluble in cold water, but dissolves easily in hot water and hot alcohol; it is insoluble in ether, benzene, carbon bisulphide, and chloroform.

II.—Dibasic Acids

Acids belonging to this class may be met with in the course of the examination of fatty acids obtained by the oxidation process (p. 68). They will be found in the aqueous solution, their presence

[1] Reformatzky does not consider the existence of these acids as proved.

being due to secondary reactions. We shall only describe the two that are most likely to occur. Their solubility in water and their melting points afford the surest indications of the direction in which further investigations as to their identity necessarily lie.

Suberic Acid, $C_8H_{14}O_4 = C_6H_{12}(COOH)_2$

Suberic acid crystallises from water in long needles or irregular plates, melting at 140° C.; it boils *in vacuo* at 152·5° C., and under a pressure of 15 mm. at 230° C.

Azelaic Acid, $C_9H_{16}O_4 = C_7H_{14}(COOH)_2$

This acid crystallises from water in large laminæ or long flat needles, melting at 106° C.; it boils *in vacuo* at 158° C., and under a pressure of 15 mm. at 237° C.

B. ALCOHOLS.

I.—Alcohols of the Ethane Series, $C_nH_{2n+2}O$

The alcohols belonging to this series occur in waxes, or in the wax-like constituents of some fats, and are solid, white, crystallisable substances, melting without decomposition. They are not acted on by dilute alkalis or acids. On boiling with alcoholic potash and diluting the solution with water, they are precipitated unchanged; in other words, they are "unsaponifiable."

On heating the alcohols with organic acids, or their chlorides, or anhydrides, combination takes place with separation of water, ethers being formed; thus on heating cetyl alcohol with acetic acid in presence of sulphuric acid, cetyl acetate is formed, as explained by the following equation :—

$$C_{16}H_{33} . OH + CH_3 . CO . OH = H_2O + C_{16}H_{33} . O . CO . CH_3.$$

The alcohols dissolve in concentrated sulphuric acid in the cold, forming alkyl sulphuric acids, which are split into their components on boiling with dilute acids.

A characteristic property of the alcohols, which can be made use of for their identification, is their behaviour with soda-lime, heated with which they are converted into the corresponding fatty acids, with evolution of hydrogen. Thus cetyl alcohol yields palmitic acid, according to the equation—

$$C_{15}H_{31} . CH_2 . OH + NaOH = C_{15}H_{31} . COONa + 2H_2.$$

The last-mentioned reactions have been employed for the quantitative determination of these alcohols, as will be detailed further on (chap. vi. p. 213).

Cetyl Alcohol, $C_{16}H_{34}O$

Cetyl alcohol, or ethal, occurs, combined with palmitic acid, in spermaceti, from which it is obtained on saponification. The alcohol has also been found in the sebaceous glands of geese and ducks.

Cetyl alcohol is a white, tasteless, and odourless crystalline mass, melting at 50° C., and boiling at 344° C., without decomposition, at the ordinary pressure; under a pressure of 15 mm. it boils at 189·5° C., *in vacuo* at 119° C. The specific gravity at 49·5° C. is 0·8176 compared with water at 4° C.; at 60° C. 0·8105, and at 98·7° C. 0·7837.

Cetyl alcohol is insoluble in water, but dissolves in alcohol, and is very easily soluble in ether and benzene. It is stated in text-books that cetyl alcohol, when heated with potassium bichromate and dilute sulphuric acid, is converted into cetyl aldehyde crystallising from alcohol and ether in lustrous laminæ. This is incorrect, cetyl alcohol remaining for the most part unchanged when oxidised in aqueous solution; in acetic acid solution the oxidising mixture yields palmitic acid.

Cetyl alcohol dissolves in cold concentrated sulphuric acid to form cetyl sulphuric acid, $C_{16}H_{33}O.SO_3H$; on boiling this product with aqueous hydrochloric acid the alcohol is regenerated.[1]

Cetyl acetate crystallises in needles, melting from 22°-23° C., and boiling at 199·5°-200·5° C. under a pressure of 15 mm. It dissolves sparingly in alcohol.

Cetyl benzoate crystallises in scales, melting at 30° C.; it is readily soluble in ether, but dissolves with difficulty in alcohol.

Octodecyl Alcohol, $C_{18}H_{38}O$

This alcohol also occurs, combined with acids, in spermaceti. It crystallises in large silvery laminæ (from alcohol), melting at 59° C., and boiling at 40·5° C. under 15 mm. pressure. Distilled under a pressure of 100 mm. it undergoes decomposition. The specific gravity is 0·8124 at 59° C.; 0·8048 at 70° C., and 0·7849 at 99·1° C.

Octodecyl acetate melts at 31° C., and boils at 222°-223° C. under a pressure of 15 mm.

Carnaübyl Alcohol, $C_{25}H_{54}O$ ($C_{24}H_{50}O$)

Carnaübyl alcohol occurs in wool wax;[2] from its alcoholic solution (in 75 to 80 per cent alcohol) crystals are obtained melting at 68°-69° C., solidifying at 67°-65° C. The alcohol very tenaciously retains water, forming a tallow-like mass, consisting of 26·7 per cent of this alcohol and 73·3 per cent of water, which does not lose in weight on exposure to the air.

On oxidising this alcohol with chromic acid, carnaübic acid is obtained.

[1] Cochenhausen, *Dingl. Polyt. Jour.* 1897 (303), 284.

[2] Darmstädter and Lifschütz, *Berichte*, 1896 (29), 2890; *Jour. Soc. Chem. Ind.* 1897, 150.

An alcohol, $C_{24}H_{50}O$ or $C_{25}H_{52}O$, has been found in small quantities in beeswax.

Ceryl Alcohol, $C_{26}H_{54}O$ ($C_{27}H_{56}O$)

Ceryl alcohol occurs as ceryl cerotate in Chinese wax,[1] and as ceryl palmitate in opium wax. The alcohol occurs in wool fat in the free state,[2] and perhaps also as ceryl cerotate.[3] Ceryl alcohol has also been recognised as a constituent of the wax of flax[4] and of carnaüba wax.

It is obtained in crystals from its alcoholic solution; the crystals melt at 79° C., but cannot be distilled unchanged. On heating ceryl alcohol with soda-lime, cerotic acid is obtained.

Ceryl alcohol behaves with concentrated sulphuric acid like cetyl alcohol.

Ceryl acetate melts at 65° C.

Isoceryl Alcohol, $C_{27}H_{56}O$

This alcohol has been found in the wax of *Ficus gummiflua*. The alcohol melts at 62° C.; its acetate at 57° C.

Myricyl Alcohol (Melissyl Alcohol), $C_{30}H_{62}O$ ($C_{31}H_{64}O$)

Myricyl alcohol occurs as palmitate in beeswax, this ether forming that part of beeswax which is insoluble in alcohol (*Brodie*). In the free state and in combination with acids it has been found in carnaüba wax. It crystallises in small needles possessing silky lustre, and melting at 85° C. or 88° C. (*Gascard*). It may be partly distilled unchanged. Nearly insoluble in cold, is dissolves readily in hot alcohol. Heated with soda-lime, it is converted into melissic acid. According to *Schwalb*,[5] the myricyl alcohol from beeswax possesses the formula $C_{31}H_{64}O$. *Gascard*[6] states that the myricyl alcohols from beeswax and carnaüba wax are identical, and have the composition $C_{31}H_{64}O$.

II.—Alcohols of the Allylic Series,[7] $C_nH_{2n}O$

The alcohols belonging to this group have not yet been studied thoroughly; it is noteworthy that they, like the alcohols of the preceding and following groups, occur in waxes.

[1] Ceryl alcohol from Chinese wax has, according to Henriques, the formula $C_{25}H_{54}O$.
[2] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1892, 138.
[3] Buisine, *Bull. Soc. Chim.* 1887 (72), 201.
[4] Cross and Bevan, *Jour. Chem. Soc.* 1890, 196.
[5] *Liebig's Annalen*, 235. 126. [6] *Jour. Soc. Chem. Ind.* 1893, 955.
[7] Most likely the unsaturated alcohols occurring in sperm oil (Lewkowitsch, *Jour. Soc. Chem. Ind.* 1892, 134) belong to this series.

Lanolin Alcohol, $C_{12}H_{22}O_3$

This alcohol has been stated by *Marchetti*[1] to occur in wool wax; shortly afterwards *Darmstaedter* and *Lifschütz*[2] described two more alcohols of the formula $C_{10}H_{20}O$ and $C_{11}H_{22}O$, also isolated from wool wax. The latter chemists, believing to have discovered the next homologues, proposed the name "Lanestols" for these alcohols, but more accurate examination undertaken by them in consequence of *Lewkowitsch's* researches[3] proved that the two alcohols $C_{10}H_{20}O$ and $C_{11}H_{22}O$ do not exist in wool wax. Therefore also the existence of *Marchetti's* alcohol becomes doubtful.

An alcohol, having the composition $C_{15}H_{30}O$, has been found in the ether-soluble part of the wax of *Ficus gummiflua*. Another alcohol of the formula $C_{36}H_{72}O$ is said to occur, combined with acids, in the fat of cochineal.

Psyllostearyl Alcohol, $C_{33}H_{66}O$

This alcohol has been discovered recently in the wax secreted by the aphide *Psylla Alni*.[4] It crystallises in the shape of fine flexible microscopical needles, melting point 95°-96° C. The alcohol is easily soluble in hot chloroform and acetic anhydride, with difficulty in hot absolute alcohol, and is insoluble in cold spirits of wine and hot ether.

III.—Alcohols of the Glycolic Series, $C_nH_{2n+2}O_2$

An alcohol having the composition $C_{25}H_{52}O_2 = C_{23}H_{46}\begin{matrix}CH_2 . OH \\ CH_2 . OH\end{matrix}$ occurs, according to *Stürcke*[5] in carnaüba wax, combined with acids. This alcohol forms a crystalline powder, melting point 103·5°-103·8° C.; it dissolves sparingly in boiling petroleum ether, and somewhat more readily in ether and in benzene. On heating with soda-lime, a dibasic acid, $C_{23}H_{46}\begin{matrix}COOH \\ COOH'\end{matrix}$ is obtained.

Coceryl Alcohol, $C_{30}H_{62}O_2$

The wax of cochineal contains the coccerate of this alcohol. The alcohol is a crystalline powder (from alcohol), melting between 101° and 104° C. On oxidising it with chromic acid in acetic acid solution, pentadecylic acid, $C_{15}H_{30}O_2$ is obtained.

[1] *Gazz. Chimica*, 1895, 22.
[2] *Jour. Soc. Chem. Ind.* 1896, 206.
[3] *Ibid.* 1896, 15.
[4] *Jour. Chem. Soc.* 1893, Abstr. i. 125.
[5] *Liebig's Annalen*, 223. 283.

IV.—Alcohols of the Series $C_nH_{2n+2}O_3$

Glycerol, $C_3H_8O_3 = CH_2(OH).CH(OH).CH_2(OH)$

Glycerol occurs in combination with fatty acids in all fats and fatty oils.

Pure glycerol is a colourless, odourless, viscid liquid, having a purely sweet taste and possessing neutral reaction. Exposed for a long time to an intense cold it crystallises in rhombic crystals, melting at 20° C. With the help of a few crystals of glycerol previously solidified it can easily be transformed into crystals at the freezing point of water.

Glycerol is oily to the touch, and produces on the skin, and especially on the mucous membrane, the sensation of heat, due to its absorbing moisture from the tissues.

At ordinary temperature glycerol does not volatilise; at the boiling point of water, however, perceptible quantities are volatilised, its vapour tension at 100° C. and 760 mm. pressure being 64 mm. According to *Clausnitzer* [1] glycerol can be completely freed from water by allowing it to stand *in vacuo* over sulphuric acid.

A dilute solution of glycerol may be boiled without any loss of glycerol until the solution contains 70 per cent.[2] If the boiling be continued glycerol volatilises with the water vapours. Pure glycerol boils under 760 mm. pressure at 290° C., undergoing slight decomposition. Under a pressure of 50 mm. it boils at 210° C., and under 12·5 mm. at 179·5° C. In a vacuum it distils unchanged.

Heated slowly in a dish to 150°-160° C. pure glycerol evaporates without leaving any residue. At 150° C. it burns with a blue flame without emitting any odour. When it is heated rapidly, especially in a platinum dish, it burns with production of acrolein, yielding at the same time a residue of polyglycerols.

The specific gravity of pure glycerol has been determined by several observers, whose statements do not agree, owing no doubt to the difficulty of freeing it from the last traces of water. In the following table some of the values are recorded together with the names of the observers (cp. chap. xii. p. 795):—

Specific Gravity.		Observer.
$d\frac{15°}{0°}$ C.	1·26358	Mendelejeff.
$d\frac{15°}{15°}$ C.	1·26468	Do.
$d\frac{15°}{15°}$ C.	1·2653	Gerlach.
$d\frac{17·5°}{17·5°}$ C.	1·2620	Strohmer.
$d\frac{12°}{12°}$ C.	1·2691	Lenz.
$d\frac{20°}{20°}$ C.	1·26348	Nicol.

[1] *Zeitsch. f. analyt. Chemie*, 20. 65.

[2] Hehner, *The Analyst*, 1887, 65.

Glycerol, on exposure to the atmosphere, absorbs as much as 50 per cent of its own weight of water. It is miscible with water in all proportions, a contraction of volume and an increase of the temperature taking place at the same time. The greatest increase of temperature occurs on mixing 58 parts of glycerol (by weight) with 42 parts of water, and amounts to 5° C.; the greatest contraction equals 1·1 per cent (*Gerlach*).

Glycerol is also miscible in all proportions with alcohol; it dissolves easily in a mixture of alcohol and ether, but is sparingly soluble in the latter solvent, one part of glycerol, spec. gravity 1·23, requiring about 500 parts of ether. It is therefore impossible to extract glycerol from its aqueous solution by means of ether. Glycerol is insoluble in chloroform, petroleum ether, carbon bisulphide, and benzene; it is also insoluble in fats and oils.

In concentrated sulphuric acid glycerol dissolves to form glycerosulphuric acid, $C_3H_7O_3SO_3H$, which is dissociated into glycerol and sulphuric acid on boiling with dilute acids.

Glycerol possesses powerful solvent properties, combining in this respect the properties of water and alcohol; many substances dissolve even more easily in it than either of the two liquids. The following table of solubilities will serve to illustrate this :—

100 parts of glycerol dissolve	98	parts of crystal soda.
	60	,, ,, borax.
	50	,, ,, zinc chloride.
	40	,, ,, alum.
	40	,, ,, potassium iodide.
	30	,, ,, copper sulphate.
	25	,, ,, ferrous sulphate.
	20	,, ,, lead acetate.
	20	,, ,, ammonium carbonate.
	20	,, ,, ammonium chloride.
	10	,, ,, barium chloride.
	8	,, ,, sodium carbonate.
	7·5	,, ,, mercury bichloride.
	3·5	,, ,, potassium chlorate.

An aqueous glycerol solution, spec. gravity 1·114, dissolves 0·957 per cent of calcium sulphate.

Soaps that are insoluble in water are partly dissolved by glycerol; thus—

100 parts of glycerol, sp. gr. 1·114, dissolve	0·71	parts of iron oleate.
	0·94	,, ,, magnesium oleate.
	1·18	,, ,, calcium oleate.

Metallic Glyceroxides

Glycerol dissolves caustic alkalis, alkaline earths, and lead oxide to form compounds with them. Lime, strontia, and baryta are precipitated nearly completely from such solutions by carbonic dioxide, a small quantity only of the earths escaping precipitation. Ferric

oxide, cupric oxide, and bismuth oxide are dissolved by glycerol in presence of caustic potash.

Monosodium glyceroxide, $NaC_3H_7O_3$, is obtained on mixing a solution of metallic sodium in absolute alcohol, *i.e.* sodium ethoxide, with glycerol. A precipitate is formed consisting of very deliquescent, rhombic crystals possessing the formula $NaC_3H_7O_3 + C_2H_6O$. On heating to 100° C., the molecule of alcohol escapes, leaving the monosodium glyceroxide behind as a white, highly hygroscopic powder, which is split up by water into glycerol and caustic soda. If, in the preparation of monosodium glyceroxide, sodium methoxide be used, the crystalline compound has the following composition :— $NaC_3H_7O_3 + CH_4O$.

Disodium glyceroxide, $Na_2C_3H_6O_3$.—This compound is prepared by triturating the crystals of monosodium glyceroxide with one molecule of sodium ethoxide under absolute alcohol, and boiling the mixture for several hours.

The potassium derivatives correspond completely to those of sodium just described.

Calcium glyceroxide, $CaC_3H_6O_3$, is a crystalline powder obtained by heating 14 parts of calcium oxide with 23 parts of anhydrous glycerol to 100° C., and cooling the mixture as soon as a violent reaction sets in. Water decomposes it into calcium oxide and glycerol.

Barium glyceroxide, $BaC_3H_6O_3$, is a deliquescent powder. It is prepared by warming 67·1 parts of anhydrous glycerol with 100 parts of baryta to 70° C. Hot water decomposes it at once into glycerol and baryta ; cold water acts but slowly on it.

Monoplumbo-glyceroxide, $PbC_3H_6O_3$, is prepared by adding 500 grms. of lead hydroxide (obtained by pouring a warm solution of lead nitrate into a large excess of warm ammonia and drying the precipitate on the water bath) to 1000 grms. of boiling glycerol (85 per cent) with constant stirring. The mass is cooled down to 0° C., and finally 2500 c.c. of alcohol added at 0° C.[1] The monoplumbo-glyceroxide thus prepared contains a little nitric acid, and very likely has the composition $2Pb.C_3H_5O_3$, $Pb(NO)_3 + (OH)Pb(NO_3)$. A product free from nitric acid is obtained by *Morawski's* method of preparation :— Dissolve 22 grms. of lead acetate in 250 c.c. of water, add 20 grms. of glycerol, heat and pour into the boiling solution a concentrated solution of 15 grms. of potassium hydrate. A slight precipitate is filtered off, and the filtrate allowed to crystallise ; in the course of a couple of days a large quantity of fine white needles, the monoplumbo-glyceroxide, separate.

If basic lead acetate is used instead of sugar of lead, basic plumbo-glyceroxides are obtained of the composition $Pb_3(C_3H_5O_3)_2$ and $4PbC_3H_6O_3.PbO$.

Disodium-mangano-glyceroxide, $Na_2(C_3H_5O_3)_2Mn$.—This compound is prepared by boiling anhydrous glycerol with 1·1 parts of caustic soda (spec. gravity 1·38) to which 4 parts of freshly precipitated hydrated manganese peroxide have been added.

[1] Fischer and Tafel, *Berichte*, 1888, 2635.

Ethers of Glycerol

Glycerol, possessing the properties of a weak base, combines also with acid radicles to form ethers. The most important ethers are those resulting from the combination of glycerol with fatty acids, viz. the glycerides, or the natural fats and oils. Of the ethers formed by the combination of inorganic acid radicles and glycerol but two need be mentioned here, glycyl trinitrate and glycyl arsenite, both being used in the arts, especially the former, which is manufactured on an extensive scale, and forms the main outlet for the large quantities of glycerol that are produced commercially.

Glycyl trinitrate, *Nitroglycerin*, $C_3H_5(O.NO_2)_3$, is prepared by allowing glycerol to run into a mixture of one part of strongest nitric acid and two parts (by weight) of concentrated sulphuric acid. It is a heavy oily liquid of spec. gravity 1·600. Its most remarkable property is that of exploding violently under certain conditions. Nitroglycerin forms the chief ingredient of almost all modern "high explosives" and "smokeless powders." Thus dynamite is produced by mixing nitroglycerin with kieselguhr, whilst "blasting gelatin" is prepared by dissolving nitrocellulose in nitroglycerin.

Glycyl arsenite, $C_3H_5AsO_3$, is formed by dissolving arsenious oxide in glycerol. It is a fat-like substance, melting at 50° C. to a thick liquid. It decomposes above 250° C., but is volatile with the vapours of glycerol. This property explains why distilled and so-called chemically pure glycerins contain arsenic.[1] Glycyl arsenite is used in calico-printing works.

Reactions of Glycerol

One of the most characteristic reactions of glycerol is the penetrating smell of acrolein which is emitted when it is rapidly heated. The same smell is noted when glycerides are burnt, as, *e.g.*, when an oil-lamp or a tallow candle has been blown out. More distinctly still than by the heating of glycerol alone, the formation of acrolein is observed when the glycerol has been previously mixed with dehydrating substances, such as (twice its weight of) hydrogen potassium sulphate. The acrolein is formed according to the following equation :—

$$C_3H_8O_3 = C_3H_4O + 2H_2O.$$

Acrolein is a liquid, possessing a most penetrating odour; its vapours affect the eyes intensely, causing a copious flow of tears. It is readily soluble in water, boils at 42·4° C., and is easily converted into a resinous mass on exposure to the air. The most delicate reagents for detecting acrolein in aqueous solutions are — an ammoniacal solution of silver nitrate (reduction to metallic silver with production of a mirror) and *Schiff's* reagent, a solution of

[1] Lewkowitsch, *Year Book of Pharmacy*, 1890, 380.

rosaniline which has been decolourised by sulphur dioxide (restoration of the pink colour of decolourised rosaniline). The latter reaction, however, is less delicate than the silver test.

A borax bead moistened with glycerol or a dilute glycerol solution gives a green colouration by the flame test. This reaction, however, cannot be considered a very characteristic one, as it is a general reaction of alcohols.

Glycerol displaces boric acid in solutions of borax. On this reaction the following method for the detection of glycerol may be based. Both the liquid to be tested and a solution of borax are tinged blue by addition of a few drops of tincture of litmus, and subsequently mixed. If glycerol be present the solution turns red in consequence of borac acid having been set free. On warming, the liquid becomes blue, and on cooling the red colouration reappears.

On adding potassium permanganate to a solution of glycerol acidulated with sulphuric acid, decolouration takes place but very slowly. Also on boiling, the glycerol only undergoes complete oxidation with difficulty. Experiments made by *Lenz*[1] have shown that on boiling an acidulated solution of glycerol with an excess of a 1 per cent solution of potassium permanganate no more than 34 per cent of the quantity required for complete oxidation is reduced. It is only by a large excess of concentrated permanganate solution that glycerol is burnt to carbonic acid.

According to *Campani* and *Bizarri*, on oxidising glycerol with potassium permanganate in alkaline solution, the following products are obtained: carbonic anhydride, formic, acetic, propionic, and oxalic acids, and also small quantities of tartronic acid. If, however, the oxidation in alkaline solution is carried out according to the directions given by *Benedikt* and *Zsigmondy* (see Quantitative Estimation of Glycerol, chap. vi. p. 208), the glycerol is completely split up into oxalic and carbonic acids according to the following equation :—

$$C_3H_8O_3 + 2K_2Mn_2O_8 = K_2C_2O_4 + K_2CO_3 + 4MnO_2 + 4H_2O.$$

Glycerol is completely burnt to carbonic anhydride and water by treatment with potassium bichromate and sulphuric acid—

$$3C_3H_8O_3 + 7Cr_2O_7K_2 + 28SO_4H_2 = 7[Cr_2(SO_4)_3 + SO_4K_2] + 9CO_2 + 40H_2O$$

or in a simpler form—

$$2C_3H_8O_3 + 7O_2 = 6CO_2 + 8H_2O.$$

Copper oxide is not dissolved by glycerol; if, however, a solution of a copper salt is mixed with a sufficient quantity of glycerol, potassium hydrate causes a blue colouration, but does not give a precipitate.

Fehling's solution is slightly reduced by glycerol if it is diluted with but little water. On boiling such a solution of glycerol with

[1] *Jour. Soc. Chem. Ind.* 1885, 368.

Fehling's solution for ten minutes, and allowing to stand for 24 to 48 hours, a red or a yellow precipitate is obtained. If, however, the glycerol be diluted with ten times its bulk of water no reduction occurs.

At the temperature of boiling water a mixture of glycerol and silver nitrate solution gives on addition of a few drops of ammonia a precipitate of metallic silver. If an excess of ammonia be mixed with the glycerol in the cold, and then heat applied, according to the directions of the German Pharmacopœia (cp. chap. xii. p. 788), as a rule no reduction takes place on addition of silver nitrate, simply because the glycerol has not been heated sufficiently; the addition of caustic soda or potash, however, causes metallic silver to separate slowly. According to *Bullnheimer*[1] 1 part of metallic silver corresponds to 11·3 parts of glycerol.

On heating solutions of platinum, gold, mercury (rhodium and palladium) containing an excess of caustic soda with glycerol the metals separate just as in the case of silver. The oxides of other metals are not all reduced, or only to a lower stage of oxidation.

The following two colour tests for glycerol have been recommended by *Reichl*:[2]—

1. Put two drops of glycerol in a dry test-tube, add two drops of previously liquefied phenol, and the same quantity of sulphuric acid, and heat very cautiously to a little above 120° C. When cold, a little water is added and a few drops of ammonia, when the brownish-yellow melt dissolves with a splendid carmine-red. This reaction is not observed if substances are present that yield carbonaceous products with sulphuric acid, the brown colour of these masking the pink in the solution.

2. Add to the dilute glycerol solution a small quantity of pyrogallol and a few drops of sulphuric acid, diluted with its own volume of water, and boil. A red colouration is produced, turning violet on the addition of tin tetrachloride. As carbohydrates and some alcohols give a similar reaction, care must be taken that these substances are excluded.

On heating glycerol with hydriodic acid, allyliodide and propylen (in presence of an excess of hydriodic acid, also isopropylioide) are formed. Experiments undertaken with a view to exclude the formation of propylen (in which case it would have been possible to determine the glycerol quantitatively by means of *Benedikt* and *Grüssner's* methoxyl method[3]) have proved unsuccessful. With the same object in view, viz. to obtain one derivative of glycerol that would facilitate its quantitative determination, *Niemilowicz*[4] has studied the action of hydrobromic acid on a solution of glycerol in concentrated sulphuric acid. There are, however, two products formed: tribromopropaldehyde and tribromopropionic acid.

[1] *Forschungsb. Lebensmittel, Hyg., forens. Chemie*, 1897 (4), 12; *Chem. Ztg.* 1897, Repert. 76.

[2] *Jour. Soc. Chem. Ind.* 1882, 202; 1883, 356.

[3] *Ibid.* 1889, 925.

[4] *Jour. Chem. Soc.* 1890, Abstr. 861.

Isoglycerol (?).—*Wanklyn* and *Fox*[1] are of the opinion that the natural fats consist of glycerides and "isoglycerides." The latter are assumed to contain the hypothetical "isoglycerol," having a formula corresponding to that of orthopropionic acid, $C_2H_5 . C(OH)_3$. This acid is supposed to instantly split up into propionic acid and water, the orthopropionic acid not being able to exist in the free state. Such assumptions scarcely deserve serious refutation.

V.—Alcohols of the Aromatic Series

Cholesterol, $C_{26}H_{44}O$

Cholesterol occurs in considerable quantities in sheep's wool, from which it is recovered on a large scale, and brought into commerce under the name wool fat, a product consisting chiefly of cholesteryl and isocholesteryl ethers. It is found in human bile, the biliary calculi being almost wholly composed of cholesterol. In somewhat larger quantities it also occurs in liver oils. Cholesterol appears to be frequently met with in the animal organism, its presence having been proved in blood, in the brain, in hair, in the epidermis, in the yolk of eggs, in the testicles, and in various morbid products of the animal body—*e.g.* the hydropic liquid of the stomach, ovarian tumours, etc.

The chemical formula of cholesterol has not yet been established satisfactorily. *Reinitzer*[2] is of the opinion that three homologues of cholesterol exist, and that the formula may, therefore, vary according to the source of cholesterol. The three homologues have, in his opinion, the formulæ $C_{25}H_{42}O$, $C_{26}H_{44}O$, and $C_{27}H_{46}O$. Cholesterol prepared from biliary calculi has the composition $C_{27}H_{46}O$. *Mauthner* and *Suida* favour the formula $C_{27}H_{44}O$; *Walitzki*, again, the formula $C_{27}H_{46}O$.

Cholesterol crystallises from chloroform in anhydrous needles (cp. p. 86, under Phytosterol), having the specific gravity 1·067, and melting point 147° C. Carefully heated it volatilises undecomposed, but it is best distilled in a vacuum. From its hot alcoholic solution it crystallises in laminæ, containing one molecule of water which evaporates on standing over sulphuric acid, but more quickly on drying the crystals at a temperature of 100° C. Cholesterol is insoluble in water, and very sparingly soluble in cold dilute alcohol. It dissolves in 9 parts of boiling alcohol, specific gravity 0·87, and in 5·55 parts of boiling alcohol, specific gravity 0·83. Ether, carbon bisulphide, chloroform, and petroleum ether dissolve it easily.

Solutions of cholesterol are lævo-rotatory. *Hesse* found for the specific rotation in ethereal and chloroformic solutions, $[\alpha]_D = -31·12$ and $[\alpha]_D = -(36·61 + 0·249c)$ respectively.

[1] *Chem. News*, 48, 49. The literature on this subject, especially *Allen's* and *Hehner's* criticisms, will be found in the *Analyst*, *Chemical News*, and *Jour. Soc. Chem. Ind.*

[2] *Jour. Soc. Chem. Ind.* 1888, 585. Cp. *Jahrbuch. der Chemie*, 1896, 360.

On adding a solution of bromine in carbon bisulphide to cholesterol dissolved in the same menstruum, a bromo-addition product, cholesterol dibromide, $C_{26}H_{44}O.Br_2$, is obtained. An iodo-chloro-addition product is most likely obtained[1] by using *Hübl's* iodine absorption method; cholesterol may thus be estimated quantitatively (chap. vii. p. 232).

Cholesterol dissolves in concentrated sulphuric acid but does not form, like the aliphatic alcohols, compounds with sulphuric acid which are split up into their components on boiling with dilute acid. It appears that the cholesterol is converted into cholesterones.[2]

On heating with soda-lime[3] no fatty acids are formed, or, at any rate, very small quantities (important difference from aliphatic alcohols).

Cholesteryl acetate, $C_{26}H_{43}O.C_2H_3O$, is prepared by boiling cholesterol with one and a half times its quantity of acetic anhydride in a flask connected with an inverted condenser. This reaction also may be used for the quantitative determination of cholesterol.[4] Cholesteryl acetate crystallises in small needles, melting point 114° C., nearly insoluble in cold and sparingly soluble in boiling alcohol.

Cholesteryl benzoate, $C_{26}H_{43}O.CO.C_6H_5$, is formed by heating cholesterol with benzoic anhydride in a sealed tube to a temperature of 200° C. It is nearly insoluble in boiling alcohol, and crystallises from ether in rectangular plates, melting at 150°-151° C.

Colour Reactions of Cholesterol (cp. Lewkowitsch, *Jour. Soc. Chem. Ind.* 1892, 144).

The following two reactions have been recommended by *Schulze*:—

1. If a minute quantity of cholesterol be carefully heated with a drop of concentrated nitric acid to dryness on a crucible cover, a yellow stain is obtained; on pouring a little ammonia on it a yellowish-red tint is produced.

2. If a little cholesterol be triturated on a crucible cover, with one drop of a mixture consisting of three measures of concentrated hydrochloric acid and one measure of a 10 per cent solution of ferric chloride, on evaporating to dryness a violet-red colouration is produced, changing to blue. It must, however, be remembered that oil of turpentine, camphor, and other substances behave in the same way.

A very delicate and characteristic reaction has been described by *Hager*, and slightly modified by *Salkowski*.

A few centigrammes of cholesterol are dissolved in 2 c.c. of chloroform, an equal volume of concentrated sulphuric acid is added, and the mixture shaken. The chloroformic solution immediately becomes coloured blood-red, afterwards cherry-red and purple; this last tint remains for several days. The sulphuric acid layer under the chloroform shows a strong green fluorescence.[5] On pouring a few drops of the purple chloroform layer into a porcelain basin, the red colour changes rapidly to blue, green, and finally to yellow. On diluting

[1] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1892, 43.
[2] Cochenhausen, *Dingl. Polyt. Jour.* 1897 (303), 284.
[3] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1896, 14. [4] *Ibid.* 1892, 43.
[5] This green fluorescence is, in my opinion, due to presence of isocholesterol.

the purple chloroformic solution with more chloroform it becomes nearly colourless, or acquires an intense blue colour; if it now be shaken again with the sulphuric acid layer the former colouration reappears. These changes of colour are due to traces of water in the chloroform.[1]

If on shaking a chloroformic solution of cholesterol, prepared from fats, with concentrated sulphuric acid, the blue colouration is noticed at once, the presence of so-called "lipochromes" is indicated, which have been shown to occur in cod liver oil, the fat of the yolk of eggs, palm oil, and in small quantities in cow butter. But even in these cases the red colouration soon appears.

Liebermann's "cholestol" reaction is very characteristic, and is shown by the minutest quantities of cholesterol. A solution of cholesterol in acetic anhydride gives a violet-pink colouration[2] on adding concentrated sulphuric acid, drop by drop. Sharper still is the modified form of this test as proposed by *Burchard*:—Dissolve a little cholesterol in 2 c.c. of chloroform, add 20 drops of acetic anhydride, and one drop of concentrated sulphuric acid. Unfortunately resin acids (colophony) and other substances give the same or very similar reactions.

Nagelvoort[3] has obtained from a specimen of cod liver oil pointed acicular crystals, intermixed with rather long, narrow, and obtruncated ones. They had the appearance of phytosterol, but gave the colour reaction of cholesterol, becoming reddish-brown when mixed with sulphuric acid, and dirty green on subsequent addition of water.

Isocholesterol, $C_{26}H_{44}O$

Isocholesterol is isomeric with cholesterol, and resembles it in many respects. It occurs together with cholesterol in wool fat.

Isocholesterol crystallises from ether in fine needles, melting at 137°-138° C. It dissolves sparingly in cold, but rapidly in boiling alcohol, from which, on cooling, it separates in a jelly-like mass. It is readily soluble in ether and in petroleum ether.

Solutions of isocholesterol are also optically active; in contradistinction to those of cholesterol they are dextro-rotatory. $[\alpha]_D = +60°$ in ethereal solution.

Isocholesteryl acetate, $C_{26}H_{43}O.C_2H_3O$, has been obtained as an uncrystallisable mass.

Isocholesteryl benzoate, $C_{26}H_{43}O.C_7H_5O$, is a crystalline powder, consisting of very fine needles melting at 190°-191° C. It dissolves sparingly in alcohol, more easily in hot acetone, and very easily in ether.

Colour Reactions of Isocholesterol.—Isocholesterol gives the same

[1] According to Herbig (*Dingl. Polyt. Journ.* 1897 (303), 191) cholesteryl palmitate and cholesteryl cerotate give the same colour reaction.

[2] It appears that wool fat cholesterol does not show the violet-pink given by gallstone cholesterol, but becomes red at once. This question is under examination.

[3] *Analyst*, 1889, 217.

reaction as cholesterol with nitric acid and ammonia. Its solution in acetic anhydride, on addition of one drop of concentrated sulphuric acid, gives a yellow and afterwards a reddish-yellow colouration, showing at the same time a green fluorescence. The same reaction becomes more distinct on using *Liebermann's* "cholestol" test in *Burchard's* form (see above).

In a mixture of cholesterol and isocholesterol the colour reaction of the latter seems to prevail and to mask the violet-pink colouration due to cholesterol.

Phytosterol, $C_{26}H_{44}O$

Phytosterol, the "cholesterol of plants," occurs in the seeds of peas, beans, and almonds; it has been found further in the gluten of wheat, in maize, and in Calabar beans, and in minute quantities in most vegetable oils (chap. ix. p. 317).

Phytosterol very much resembles cholesterol; they differ, however, in their crystalline form and their melting points. The crystals of cholesterol deposited from its hot alcoholic solution appear as a magma of laminæ, which are discerned, under a microscope, as extremely thin rhombic plates, showing often re-entering angles. Phytosterol, however, crystallises in solid needles, grouped in tufts; under the microscope there are discerned long, solid needles arranged in star- or bunch-like groups. The crystals have the composition expressed by the formula $C_{26}H_{44}O + H_2O$; they melt at 132°-134° C., whilst the melting point of cholesterol is 147° C. Solutions of phytosterol are lævo-rotatory $[\alpha]_D = -34{\cdot}2$.

A chloroformic solution of phytosterol gives the same reaction with sulphuric acid as the corresponding solution of cholesterol, but there is this slight difference that the colouration obtained with phytosterol passes after a few days into a bluish-red, whereas the cholesterol solution becomes more of a cherry-red.

CHAPTER IV

DETERMINATION OF FOREIGN MATTERS OF A NON-FATTY NATURE, AND PREPARATION OF THE FATTY SUBSTANCE FOR EXAMINATION

1. Sampling

In sampling fat one must be careful to obtain a sample really representing the bulk. This can easily be done with liquid fats. In the case, however, of solid fats it is more difficult, and great care has to be exercised, or grave errors may be committed.

A. Norman Tate, *G. d'Endeville*, and *Cuthleert* have agreed upon the following reliable method of sampling tallow and other solid fats, which is practically the method used at seaports and in large works. By means of an auger a cylindrical sample of fat, at least eight inches long and one inch thick, is taken from each cask, or a convenient number of casks, and each sample is labelled with the number and marks of the cask, the gross weight and tare of each cask being also noted. The several samples are mixed by the chemist in quantities corresponding to the net weight of their respective casks, and the sample thus obtained is roughly divided into three equal parts, two of which are melted in a dish at a temperature not exceeding 60° C. with constant stirring. As soon as the fat is melted to a clear liquid, the dish is removed from the source of heat, and the third part is added. As a rule the liquefied fat retains enough heat to melt the added quantity; the whole mass is thereby cooled, and solidifies more rapidly. As soon as the fat commences to become pasty, it is necessary to stir vigorously in order to prevent water and impurities from settling down to the bottom of the dish.

The first operation in the examination of fats is the estimation of water and of those substances of a non-fatty nature which necessarily adhere to them owing to the process of manufacture, or which have been added fraudulently.

It must not, however, be forgotten that a number of fat-like substances, as resin, paraffin wax, paraffin oils, tar oils, and resin oils, may be retained by the fat in intimate intermixture with it. These

bodies are determined severally when the examination of the dry and preliminary purified fat is reached (chap. vii.)

2. Estimation of Water

About 5 grms. of the fat are accurately weighed in a small beaker or flask containing a thin glass rod, and dried at 100° C. until the weight remains constant. Whilst drying, the fat is conveniently stirred up from time to time, as the water will collect below the fat and only slowly evaporates through it. For this reason *Sonnenschein*[1] proposes to dry the fat in a flask closed by a cork perforated with two holes, through one of which passes a straight tube to the bottom of the flask, whilst the other is fitted with a bent tube ending with the cork. The flask is tared with all the fittings, the fat poured into it, and its weight determined. A calcium chloride tube is then attached to the straight tube, and the bent tube being connected with the filter pump, a current of dried air is drawn through the fat at 100° C. As, however, liquid fats and fatty acids are easily oxidised under these conditions, more accurate results will be obtained by aspirating an indifferent gas (*e.g.* dried carbonic anhydride or coal gas) through the fat. (Cp. also chap. xii. Oleaginous Seeds.)

Henzold recommends, especially for the determination of water in cow butter, the following method: weigh off 20 grms. of freshly heated pumice stone, cooled under a desiccator, in a shallow dish, add 10 to 12 grms. of the fat, and heat to 100° C. for two hours, but not longer, stirring occasionally with a glass rod which has been tared with the dish.

Sometimes solid fats, such as tallow, contain small quantities of caustic potash or of potash soap which have been fraudulently added in order to facilitate the incorporation of water with the fat. In that case the fat cannot be freed from the last traces of water by drying at 100° C., and the safest plan will be to determine the amount of fatty bodies, impurities, and of potash separately, and to find the percentage of water by difference.

3. Determination of Foreign Matters of a Non-fatty Nature in Fats

To determine solid substances, such as remnants of animal or vegetable tissue, dirt, or fraudulent admixtures, 10-20 grms. of the fat are extracted in a flask by shaking with one of the following solvents: petroleum ether, chloroform, carbon tetrachloride, ether, or benzene. The solution is then poured through a tared filter, and the residue washed on the filter with the same solvent, until a few drops of the filtrate, evaporated on paper, no longer leave a grease-spot. The filter with its contents is then dried at 100° C. and weighed. The dried residue may be incinerated and weighed again, when the difference

[1] *Jour. Soc. Chem. Ind.* 1886, 508 (Illustration).

will give the amount of organic matter. If the amount of ash is large (salt, chalk, clay, or lime from fraudulently added lime soap), a further examination is sometimes of importance.

Of the foregoing solvents, petroleum ether will be found the most convenient, inasmuch as it dissolves smaller quantities of resinous bodies than any of the other solvents mentioned. Therefore, if there be no reason against the use of petroleum ether—*e.g.* in the case of castor oil—this solvent should be employed; all the more so, as it can easily be obtained in a state of purity and free from acid, and, furthermore, it need not be dried beforehand. It should, however, be rectified carefully by means of a fractionating column, and all portions boiling above 80° C. should be discarded. If necessary, it should be purified by shaking with a little concentrated sulphuric acid; after separation from the dark acid layer the petroleum ether must be washed with water until entirely free from acid.

Nördlinger has obtained colourless extracts when using petroleum ether for palm nuts, coprah, etc., whereas ether gave coloured solutions.

If a considerable quantity of organic matter has remained on the filter, it should be tested for metallic soaps (lime soaps, aluminium soaps, etc.) and for starch. On treating with mineral acids the former will be decomposed with liberation of fatty acids, whilst the metals will pass into the aqueous solution.

Starch can be detected in the organic residue by means of the blue colouration it gives with iodine solution, and its presence may be confirmed by the microscope. *Chateau* has recommended the following method:—Heat one part of the suspected fat with two parts of acidulated water in a test-tube, or in a small beaker, and boil for a few minutes. Place the test-tube or beaker in water of 40° C., so as to allow the fat to solidify gradually and the impurities to settle out. On adding a solution of iodine the blue colour will be noticed distinctly if starch be present.

It is important to note that on dissolving a fat in petroleum ether, etc., starchy matter is liable to retain some fat. Hence the amount of starch does not correspond exactly to the weight of the dried residue. *König* recommends, therefore, especially in butter analysis, to wash the residue, after exhaustion with ether, with cold water, in order to remove any substances soluble in water. The residue is made soluble by boiling with water, and finally converted into glucose by heating with hydrochloric acid. The glucose may be estimated by means of *Fehling's* solution.

Substances **soluble in water** (some of them, *e.g.* common salt, may be found on the filter) are removed from the fat by shaking a large quantity, say 50-100 grms., with warm water, whereby solid fats are easily liquefied. The mixture is allowed to stand in a warm place until it has separated completely into two layers. Should the separation not be complete, after a short time, or if part of the fat be retained as an emulsion by the aqueous layer, addition of a little ether will be found effective in causing separation. The aqueous liquid is then removed by means of a separating funnel and examined.

Any traces of sulphuric acid left in the oil from refining operations will be found in this aqueous layer, and may be estimated by titration with standard alkali, using methylorange as indicator. Other substances present may be determined in the residue left on evaporation.

Ethereal oils contained in the fats, as in nutmeg butter, are best determined by distillation in a current of steam. On weighing the remaining dried fat the quantity of essential oils will be found by difference. The distillate may be shaken out with ether, and the ether residue further examined.

4. Determination of Fat

The determination of fat in a sample may be conveniently combined with that already described for the estimation of foreign substances, by collecting the filtrate in a tared flask, evaporating the solvent, and weighing the dried residue.

If mucilaginous or starchy substances are present in the fat the following process will be found more convenient and, at the same time, more reliable. 5-6 grms. of the sample are intimately mixed with 4-6 times its weight of pure, finely-powdered gypsum, and the mixture dried at 100° C. It is then transferred to an automatic exhausting extractor.

Gebek,[1] however, states that on using gypsum (or charcoal) for the determination of fat in fodders discordant results are obtained, and proposes, therefore, the employment of Spanish earth used for clarifying wine.

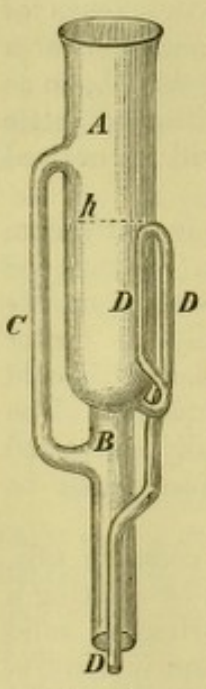


Fig. 1.

Gantter recommends, instead of gypsum, the use of cellulose as obtained by the sulphite process; of course, the cellulose has to be previously extracted with the petroleum ether. 3 grms. of the sulphite cellulose are placed in a weighing bottle, dried and weighed. 5 grms. of the fat are then added and, after drying for one and a half hours, re-weighed, when the difference found will give the proportion of water. The dried substance is finally transferred to an extractor to be exhausted.

The most convenient apparatus for extraction of fat is the one devised by *Soxhlet* (*Szombathy*) (Fig. 1). A modification of this apparatus, which is preferred by many as being less liable to break, is shown in Fig. 2.

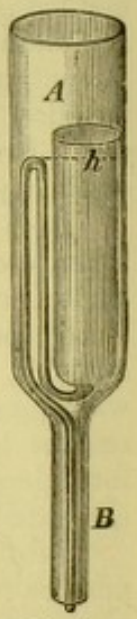


Fig. 2.

The substance to be extracted is put in a cartridge of filter paper, easily prepared by rolling it round a cylindrical piece of wood of suitable size, and folding it up at one end. The cartridge is filled with the substance and transferred to the extractor

[1] *Jour. Soc. Chem. Ind.* 1893, 713.

A. Care must be taken that the syphon tube does not become stopped by the paper case; nor should the cartridge be filled up to the top, lest some particles of the substance be washed over by the solvent and carried away. To be quite safe, it will be found convenient to place a plug of (extracted) cotton-wool on the top of the substance, or to close the top by folding the paper. The tube B is then fitted by means of a cork to a flask holding 100-150 c.c., and containing about 50 c.c. of the solvent (petroleum ether, ether, chloroform, etc.) Another portion of the solvent is carefully poured on the substance in B until it commences to run off through the syphon D. Finally an inverted condenser is adapted to A, and the whole apparatus placed on a water bath. As the solvent boils, the vapours pass through B and C into the condenser and fall condensed on the substance in the paper case. When the liquid has reached the level *h*, the solution syphons off automatically through D, and A is emptied completely. The solvent is again evaporated and recondensed, and serves again for extracting, and so on. The filling and emptying of A may easily be repeated twenty to thirty times within an hour.

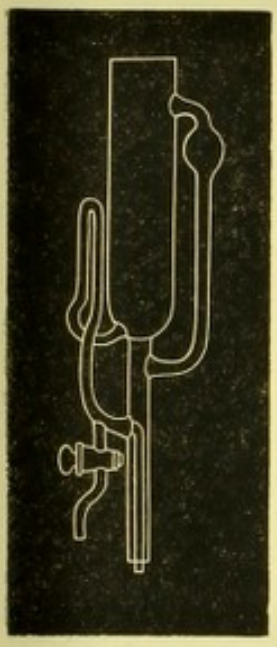


Fig. 3.

In using the form of *Soxhlet's* extractor described above, there is always some doubt as to the exact time when the exhaustion is completed, and, as a rule, the operation lasts a far longer time than necessary, involving both loss of time and of the solvent. To avoid this *Lewkowitsch*[1] has a tap fitted on to the syphon tube, allowing some of the solvent to be withdrawn at any time, with a view to ascertain when extraction is complete (Fig. 3).



Fig. 4.

If the substance to be exhausted had been collected on a filter, the simplest plan is to fold the filter up and place it at once in the extractor.

Frühling[2] has proposed a modified form of the Soxhlet extractor which admits of convenient handling on weighing before and after the extraction. The essential part of the apparatus, serving for the reception of the sample, is shown in Fig. 4. It has the shape of an ordinary filter-weighing bottle, but differs from it in that the bottom has a funnel-like shape. It is provided with a syphon, the longer limb of which passes through the bottom, where it is cut off aslant. The sides of A are continued beyond the protruding limb of the syphon, so as to allow of its standing in an upright position on the pan of a balance, and at the same time serving to protect the tube from breakage. The shorter limb of the syphon reaches to the bottom of the bottle, and is provided with a bulb in its upper part,

[1] *Jour. Chem. Soc.* 1889, 360. [2] *Jour. Soc. Chem. Ind.* 1889, 568.

which serves to sever the column of the solvent when the bottle is taken out of the tube B (Fig. 5). This tube is the ordinary form of the Soxhlet extractor without its syphon tube, and serves for the reception of A. The upper part of B may be fitted with a carefully-ground stopper, having tube C attached to it. The whole arrangement and application of the apparatus will be readily understood from a glance at the annexed figures.

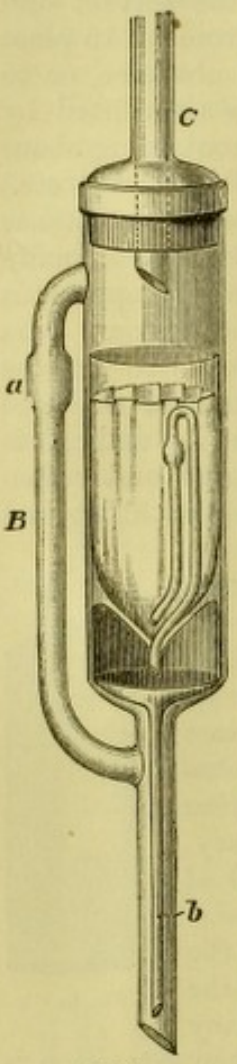


Fig. 5.

For the extraction of substances at the boiling point of the solvent, *F. K. Stock* has recommended a modified extractor.[1]

The number of modifications and improvements of *Soxhlet's* ingenious apparatus is almost legion. As the above-described forms will be found suitable for most purposes, the reader must be referred to the pages of the *Journal of the Society of Chemical Industry*, where a complete record of all proposed forms will be found.

When the extraction is completed the flask containing the solution is detached from the extractor, the solvent distilled off on the water-bath, and the fat dried in an air-bath at a temperature not exceeding 100°-110° C. until the weight remains fairly constant. Care must be taken not to dry too long, nor at too high a temperature, inasmuch as on the one hand volatile fatty acids may escape, causing loss of substance, whilst on the other hand an increase of weight may take place owing to oxidation (cp. Oleaginous Seeds and Oil-cakes, chap. xii. p. 673).

The apparatuses described will also be found useful for the estimation of fat contained in oleaginous seeds, oil-cakes, and other bodies. Previous to the extraction, these substances should be pounded or disintegrated, and, if required, dried at a suitable temperature (cp. chap. xii. p. 674).

5. Preparation of the Fat for Examination

The most important operation in the analysis of fats is the examination of the fatty substance after it has been freed from water and foreign matters. In most cases it will suffice to dry and filter the melted fat in order to obtain it sufficiently pure; washing with warm water or distillation in a current of steam will but rarely be required.

The drying and filtering of the fat is best carried out in a spacious drying oven provided with a thermostat (thermo-regulator).

[1] *Jour. Soc. Chem. Ind.* 1897, 107.

The drying oven may be one of the customary type of about the following dimensions: 10 inches high, 10 inches broad, and 6 inches deep. I use an apparatus made with slight alterations after *Sidersky's*[1] design. This is a jacketed cylindrical oven provided with a door having a thick glass plate and closing hermetically. Suitable taps allow the drying to proceed *in vacuo* or in a current of dried air (or carbonic anhydride), which can be aspirated slowly through the drying chamber. The space between the two cylinders can be filled with water or any other suitable liquid, and thus any required temperature may be kept constant without attention for any length of time.

A very efficient thermostat has been described by *Reichert*. Its improved form is represented by Fig. 6. It consists of a capillary tube enlarged at the bottom to a bulb *c*,—in short, of a thermometer, the top part of which is widened out as shown. The capillary branch tube is supplied with a screw S, by means of which the level of the mercury may be adjusted at will. The gas-supply tube A is carefully ground into the upper part of the thermometer tube, and extends down to the joint of the stem. Besides having the opening at the bottom, A is perforated with a very small hole at *a*. The gas entering A leaves the regulator at B. The thermostat is fixed along with an ordinary thermometer by means of a cork perforated with two holes into the nozzle of the drying oven; A is then connected with the gas supply, and B with the gas burner. The tube A must be adjusted in such a way that communication with B is established through *a*, whilst S has been screwed out of the tube sufficiently to allow the mercury to fall below the tapered part. The oven is then heated, and at the moment the desired temperature has been reached S is screwed into the tube until the column of mercury just reaches the tube A. The exact moment is easily observed by the flame of the burner becoming smaller. Gas is then supplied to the burner through *a* only, until in consequence of the falling of the temperature in the oven the mercury falls, thus allowing an additional supply of gas to flow through A, the lower end of which had been closed before by the mercury. With a rise of temperature the mercury expands, and again closes the lower opening of A, thus causing the temperature to fall, and so on. It is thus possible to keep the temperature constant, or nearly so, within very small limits indeed. In the case of the flame of the burner being too high for the desired temperature, even when gas passes through *a* only, the gas supply must be diminished by turning the tube A a little, thus partially closing the opening *a*.

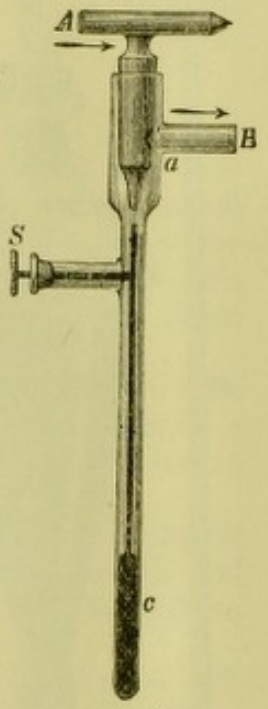


Fig. 6.
½ actual size.

[1] *Jour. Soc. Chem. Ind.* 1890, 967.

The screw S is usually cemented by the maker of the instrument with sealing-wax, which, however, easily melts, allowing mercury to ooze through the cork ; care should therefore be taken to protect the wax from becoming overheated.[1]

As another objection to *Reichert's* thermostat, it has been pointed out recently by *J. W. James*,[2] that after short use,—a few days or weeks, depending on the purity of the gas,—the upper surface of the mercury becomes coated with a black powder (mercuric sulphide) which before long impairs the delicacy of the regulator. It becomes then necessary to take the apparatus to pieces for cleaning. *James* has therefore designed a thermostat, making use of *Reichert's* principle, but avoiding the objectionable passing of the gas over the surface of the mercury. For the drawing and instructions for use the original paper should be consulted. Another new thermostat, made entirely of metal and not containing mercury, has been described by *Porges*.[3]

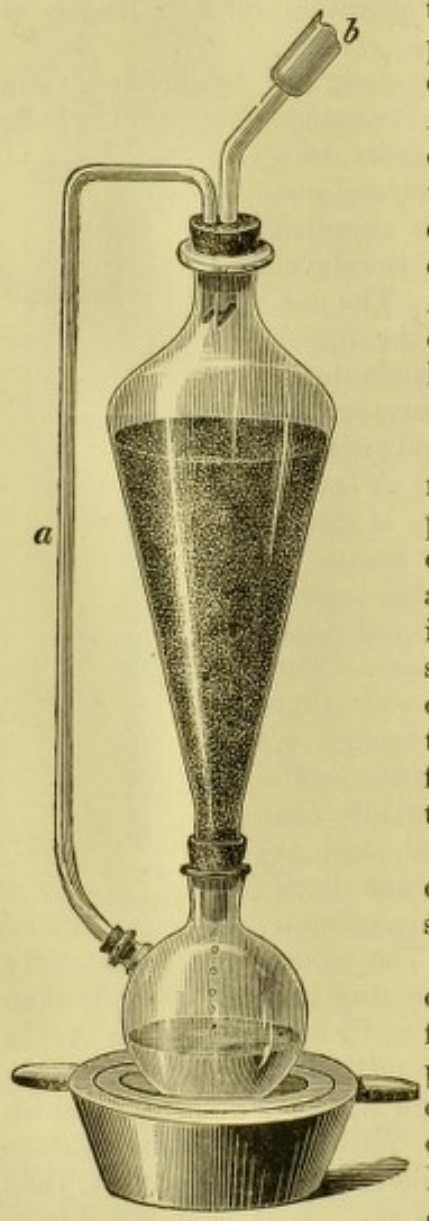


Fig. 7.

The temperature at which the fat is melted should not exceed its melting point by more than 20° C. Solid fats, containing large quantities of water, such as butter fat, are best allowed to stand in the melted state until the water has settled out. The best plan is to pour off the fat into another vessel, and then to filter through dry paper. Before filtering, the fat should have been allowed to become perfectly dry.

Dieterich dries beeswax by melting it over anhydrous sodium sulphate with subsequent filtering.

If a fat contains such a large quantity of solid substances as to make direct filtration impossible, or if it has to be prepared from oleaginous seeds or oil-cakes, a previous extraction by means of petroleum ether becomes imperative. Ether, carbon bisulphide, benzene, or chloroform, do not give such satisfactory results as pure petroleum ether.

Any of the exhausters described above may be employed. For large quantities, however, the apparatus represented in Fig. 7 will be

[1] The principle underlying Reichert's thermo-regulator, but avoiding the last mentioned drawback, has been employed by *Berlemont*, cp. *Jour. Soc. Chem. Ind.* 1895, 821.
[2] *Jour. Soc. Chem. Ind.* 1893, 225. [3] *Zeitsch. f. analyt. Chemie*, 1893, 212.

found most convenient. Its construction will be readily understood by a glance at the illustration; *a* may be a lead pipe covered with a non-conducting mass (asbestos, or simply string); *b* is adapted to a condenser.

It should be remembered that the fats prepared as described still contain small quantities of foreign organic substances (cp. chap. i.)

6. Determination of Inorganic Substances in the Fatty Matter

The fatty matter prepared as described in some cases contains sulphur or phosphorus, or chlorine or metals. Therefore the fatty substance before being examined should be tested for these impurities.

Qualitative Test for Sulphur

Until recently the presence of sulphur in a liquid fat was considered as sufficient proof of the presence of rape, or some other oil extracted from the seeds of *Cruciferæ;* but it has been shown that the cold-pressed oils are free from sulphur. On the other hand, oils which have been extracted by carbon bisulphide may retain small quantities of sulphur.

Sulphur is detected by saponifying the oil under examination with caustic soda or caustic potash, when sodium or potassium sulphide is formed. On adding an alkaline lead solution a black or brown precipitate will be obtained.

Valenta recommends boiling a somewhat large quantity of the oil with a small quantity of caustic potash with constant stirring, and then to add a little water. The soap solution is then separated from the unsaponified oil and tested with the lead solution.

A rapid method is to immerse a bright silver coin into the boiling oil. In presence of sulphur the coin will become brown or black.

Sulphuric acid or sulphonated fatty acids cannot be detected by the preceding methods. On washing the oil with water any sulphuric acid present will pass into the aqueous layer, and can be detected by barium chloride. Sulphonated fatty acids, produced by prolonged treatment of the oil with sulphuric acid (see Turkey-red Oil), must be decomposed first, either by boiling with hydrochloric acid or by fusing with caustic potash and potassium nitrate.

Quantitative Determination of Sulphur

(*a*) *Liebig's Method.*—Weigh off carefully a somewhat large quantity of the sample, and saponify it in a silver dish with aqueous or alcoholic potash; boil down until the mass becomes syrupy, allow to cool, add a few sticks of pure caustic potash and also potassium

nitrate, about one-eighth of the weight of the potash used, and finally a few drops of water. Heat the mass carefully with constant stirring—using a silver stirrer—and raise the heat gradually until the mass is fused and has become perfectly white. Then allow to cool, dissolve in water, and transfer to a large beaker, in which the sulphuric acid formed is precipitated in the usual way with barium chloride. In very accurate work it is preferable to boil out the heated barium sulphate with dilute hydrochloric acid and to weigh again.

Morpurgo[1] saponifies 25 grms. of the sample with caustic soda and adds 10 c.c. of a 10 per cent lead acetate solution and a few drops of acetic acid, when a precipitate consisting of free fatty acid, lead sulphide, and lead soap is obtained. The aqueous portion is allowed to drain off and the precipitate mixed with 50 c.c. of 90 per cent alcohol, and then with an excess of acetic acid. The mixture is warmed on a water bath, so that lead sulphide may settle out. The free fatty acids are then removed, and the lead sulphide repeatedly washed with dilute acetic acid, and finally with dilute ammonia, and collected on a filter and weighed.

(*b*) *Allen's Method.*—*Allen*[2] proposes for the determination of the sulphur in oils, *e.g.* rape oil, an apparatus similar to that used for the estimation of sulphur in coal gas (Fig. 8). 5 grms. of the oil are mixed with 45 grms. of purified methylated spirit, and burnt in the lamp A fitted by a bung into the wider end of a curved adapter. *e* contains solid ammonium carbonate. The gases pass through C into the condenser D filled with wetted glass balls. The lower end of D is furnished with a glass stop-cock *h* for drawing off the condensed liquid. A second condenser G is attached to D to condense the vapours escaping from D. The upper tubulure of G is connected with an aspirator to produce a slight draught. The flame should be a small one, and should be surrounded by wire gauze to prevent overheating. The liquid drawn from the condensers contains the sulphur as sulphite and sulphate, which may be estimated by well-known methods.

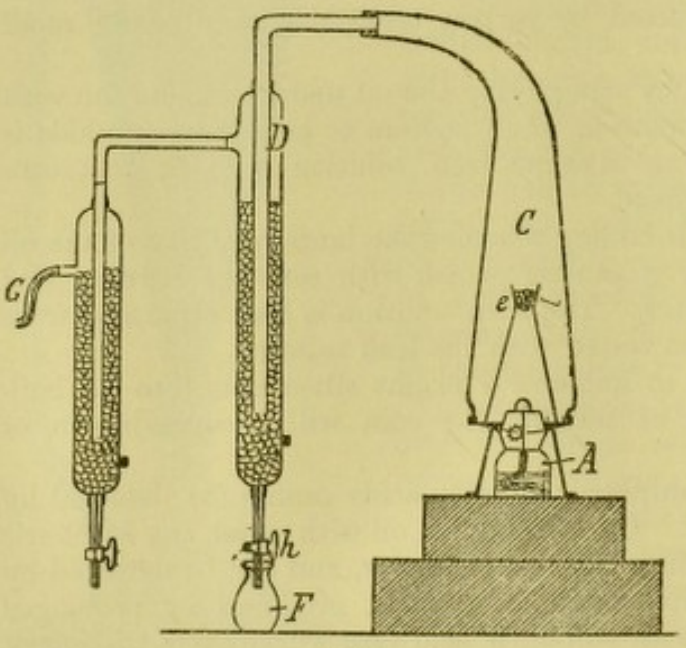


Fig. 8.

[1] *Jour. Soc. Chem. Ind.* 1897, 167.

[2] *Analyst*, 1888, 43.

Similar contrivances have been described by *Mabery*,[1] *Heusler*,[2] *Engler*,[3] and *Kissling*.[4]

Estimation of Phosphorus

In order to determine phosphorus, as in fats containing lecithin, the sample is saponified with alcoholic potash ; the alcohol is evaporated off, and the concentrated soap solution shaken out with ether in order to remove any cholesterol present. The soap solution is then decomposed by a mineral acid and the fatty acids separated from the acid liquid. The latter contains all the phosphorus as glycerol-phosphoric acid, $C_3H_5(OH)_2PO_4H_2$. It is boiled down to dryness and the residue fused with potassium hydrate and potassium nitrate. The melt is then dissolved in water, and the phosphoric acid precipitated by magnesia mixture and weighed as pyrophosphate. On multiplying the P_2O_5 found by 11·366, the amount of *lecithin*, $C_{44}H_{90}NPO_9$, will be obtained.

Although the estimation of phosphorus will but rarely be made, it may serve in some cases for the identification of some fats, especially those obtained from leguminous seeds (see p. 7).

Estimation of Chlorine

Fats that have been bleached by means of chlorine may retain small quantities of this bleaching agent.

Benedikt and *Zikes*[5] determine very small quantities of chlorine by allowing 25 grms. of the sample under examination to drop slowly from a separating funnel into a combustion tube filled with lime.

The estimation is then carried out in the well-known manner of determining chlorine in organic substances.

Detection and Determination of Metals

Since fats possess the property of dissolving small quantities of metallic soaps, traces of metals are likely to be found in them. Especially the following bases may have to be tested for : Sodium and potassium hydrates, lime, alumina, lead oxide, copper oxide, ferric oxide, and zinc oxide.

The **alkali metals** are tested for by the methods used in the analysis of soaps (see p. 776).

Lime is sometimes fraudulently added to a fat in order to facilitate the incorporation of large quantities of water. On treating such a fat with petroleum ether the lime soap will remain undissolved, and is isolated by filtration. The residue on the filter is then incinerated, and the ash treated with dilute hydrochloric acid. After filtering, the filtrate is tested for lime by ammonium oxalate and ammonia. A white precipitate will prove the presence of lime.

[1] *Jour. Soc. Chem. Ind.* 1895, 197. [2] *Ibid.* 1895, 828.
[3] *Ibid.* 1896, 383. [4] *Ibid.* 1896, 384. [5] *Ibid.* 1894, 984.

For the quantitative estimation of lime proceed as above, but allow the precipitated calcium oxalate to stand in a moderately warm place for twelve hours, filter and dry the residue, and heat over the blowpipe until the weight of the calcium oxide remains constant.

The determination of metals in a fat is best effected by warming the fat on the water bath with very dilute nitric acid in a porcelain dish; they then pass into the acid liquid; or a somewhat large quantity of the fat may be incinerated in a platinum dish, the resulting ash dissolved in a few drops of nitric acid, and the solution diluted with water. A less convenient process is to dissolve the fat under examination in ether, and to shake out with acidulated water.

Part of the acid solution obtained by any of the preceding methods is tested with sulphuretted hydrogen, when the presence of a heavy metal will be indicated by the appearance of a black or brown precipitate or colouration.

Other portions of the solution are tested (1) with potassium ferrocyanide (brown precipitate), and with ammonia (blue colouration) for *copper;* (2) with sulphuric acid (white precipitate), and with potassium chromate (yellow precipitate, soluble in potash) for *lead.* For the detection and estimation of *iron* see below. *Zinc* and *alumina* are tested for by the well-known methods of qualitative analysis.

Copper oxide is sometimes mixed with oils in order to impart to them a green colour. Rancid fats (as lard), when kept in copper or in lead-glazed vessels, may easily dissolve some **copper or lead.** The detection of these two metals in sweet oils and in culinary fats deserves, therefore, special attention.

Quantitative Determination of Copper

Weigh off accurately 10 to 20 grms. of the fat under examination in a platinum dish and incinerate. Dissolve the ash in a few drops of nitric acid, dilute with water, and filter into a beaker. Heat the solution nearly to the boiling point, add pure caustic soda or potash, and heat again for a few minutes. Filter off the black precipitate of copper oxide, dry, ignite, and weigh.

Another process is to thoroughly stir the warmed fat with hydrochloric acid, and pour the acid liquid through a filter; the fat is then washed several times with water; and the washings added to the main portion. Next the solution is heated whilst a current of sulphuretted hydrogen is passed through. The precipitated cupric sulphide is filtered off, washed with water containing sulphuretted hydrogen, dried, mixed with sulphur, and heated in a porcelain crucible in a current of hydrogen. The copper is thus transformed into cuprous sulphide, Cu_2S.

Quantitative Determination of Lead

(1) The lead is brought into solution as lead nitrate by one of the methods detailed above. Dilute sulphuric acid is then added,

and the solution warmed on the water-bath until all the nitric acid has evaporated off. The remaining liquid is mixed with a little water and twice the volume of alcohol. After allowing to stand for a few hours the precipitate is filtered off, washed with dilute alcohol, dried, and ignited. The filter, of course, must be incinerated separately. The resulting lead sulphate is calculated to *lead oxide* or *lead*.

(2) A more rapid, though less accurate method, is the following:—Burn off several grms. of the fat in a tared porcelain crucible. The residue, consisting of a mixture of metallic lead and lead oxide, is weighed first, and then treated with warm acetic acid to dissolve the lead oxide. The metallic lead is washed by decantation, and the crucible dried and weighed again, when the amount of metallic lead is found. The difference between the two last weights corresponds to the amount of lead oxide; it is calculated to lead, and the quantity added to that found for the metallic lead.

(3) Shake the ethereal solution of the fat or oil with dilute sulphuric acid, filter, ignite the precipitate, and weigh as lead sulphate.[1]

Detection and Estimation of Iron

Oils used for dyeing purposes and for currying leather should be free from iron. Alizarin oil, which contains about 15 to 20 per cent of free fatty acids, if kept in iron vessels, is especially liable to be contaminated, and the examination of Turkey-red oils for iron is therefore important.

According to *Emde*[2] the following method will be found very convenient. A quantity of the oil is shaken up in a graduated cylinder with water acidulated with sulphuric acid. A few drops of potassium ferrocyanide are added, and the whole shaken up with a little ether. The oil dissolves in the ether, and forms a sharply-defined layer on the water. In the presence of iron, a more or less dense layer of Prussian blue, containing all the iron, will appear on the border line between the two liquids. If in comparative tests the same quantities of oil, water, acid, and potassium ferrocyanide be used, the thickness of the layer of Prussian blue may admit of a rough estimation of the quantity of iron.

For accurate estimation it is of course necessary to precipitate the iron as hydrated ferric oxide and weigh it.[1]

7. Preparation of the Insoluble Fatty Acids of a Fat for Examination

The insoluble fatty acids being often required for analytical examination, the method of preparing them may be described here once for all.

[1] Fresenius and Schattenfroh, *Jour. Soc. Chem. Ind.* 1895, 895.
[2] *Jour. Soc. Chem. Ind.* 1888, 591.

A sufficient quantity of fat is saponified according to one of the methods already described, say by boiling 50 grms. with 40 c.c. of caustic potash solution, specific gravity 1·4, and 40 c.c. of alcohol in a porcelain dish on the water bath with constant stirring until the soap becomes pasty. This is then dissolved in 1000 c.c. of water, and the solution boiled for at least three-quarters of an hour, when all the alcohol will be driven off. Sufficient water is added, if necessary, and the soap decomposed by means of sulphuric acid. When by continued boiling the fatty acids have been finally obtained as a clear oily layer, free from solid particles floating on the aqueous liquid, the mass is allowed to cool. In case the fatty acids solidify the cake is perforated by means of a glass rod, the acid liquid poured off, and the cake boiled several times with fresh quantities of distilled water, and finally dried. If the fatty acids remain liquid at the ordinary temperature, their separation from the water is effected by means of a syphon or of a separating funnel.

On using a syphon it will be found most convenient, in order not to lose any fatty acid, to syphon off the aqueous layer by means of a filter-pump, interposing between the syphon and pump a strong bottle of about 2000 c.c. capacity, and fitted with a cork perforated with two holes. Both holes are provided with bent tubes, one of which

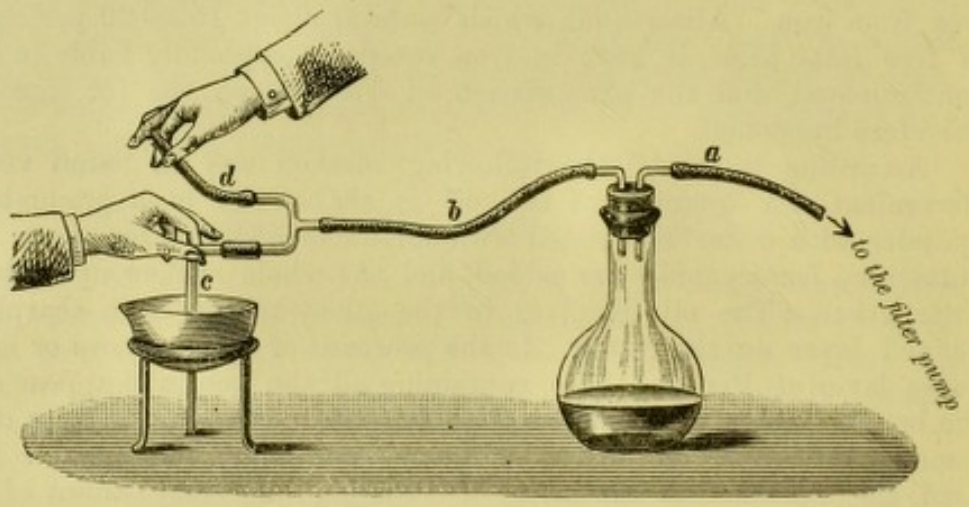


Fig. 9.

leads to the pump, whilst the other is connected by means of india-rubber tubing and a T piece with the syphon. To the other end of the T pipe is attached an india-rubber tubing, which is closed with the fingers while syphoning off. As soon as fat commences to enter the syphon the india-rubber tube is opened (Fig. 9).

Provided the fat under examination is free from unsaponifiable matter, the fatty acids may be tested for any undecomposed fat by the following method proposed by *Geitel*. This test is necessary if the solidifying point of the fatty acids has to be determined. 2 grms. of the fatty acids are dissolved in 15 c.c. of hot alcohol, and 15 c.c. of aqueous ammonia are added. The mixture will become turbid if

an appreciable quantity of neutral fat is present. If the solution has remained clear, cold methyl alcohol is allowed to run on to the top of the ammoniacal solution, forming a separate layer. Traces of neutral fat are then indicated by a turbid zone appearing between the two layers. In the case of palm oil or deeply-coloured fats the last-mentioned test is of no avail, the turbid ring not being visible.

8. Weighing the Fat for Analysis

Liquid fat is either weighed directly in the flask or vessel in which it is to be examined, or is poured out from a tared beaker or bottle, which should not be put on the pan of the balance without using a watch-glass. The quantity required is poured out (along a glass rod which may be tared with the beaker), and its weight determined by re-weighing.

Solid or butter-like fats or waxes are weighed off in the same way. As they have, however, to be filled in the melted state into the beaker, this must be allowed to cool under a desiccator before weighing. The fat is melted again, the required quantity poured off, and the beaker, after complete cooling, re-weighed. If a small quantity of a solid fat is required, as for the determination of the iodine absorption value, it may be introduced by means of a glass rod into a thin-walled weighed glass tube about 4 cm. long and 1 cm. wide, open at both ends. I use for that purpose a somewhat larger filter-weighing bottle with hollow stopper, and place inside the bottle a wide glass tube drawn out into a capillary. This affords the further advantage of allowing approximately equal quantities to be employed for a number of tests by counting the number of drops. A similar contrivance has been recently described by *Gantter*.[1]

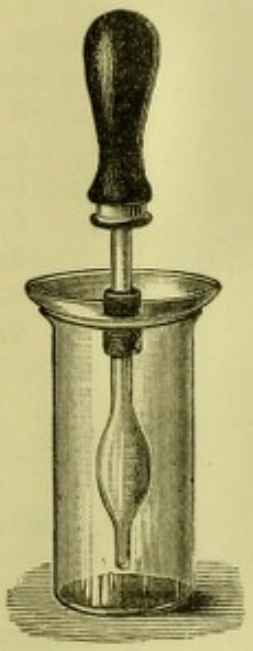


Fig. 10.

Mangold uses a small pipette fitted with an india-rubber ball. The neck of the pipette is fastened, by means of a piece of india-rubber tubing, to a perforated watch-glass, holding it thereby so tightly that it can be lifted up with it. This is placed in a beaker and weighed with it. By compressing the india-rubber ball and allowing it to expand, a small quantity of the oil can be made to rise in the pipette, and emptied by compressing it again. The apparatus is shown in Fig. 10. Essentially the same apparatus has been described by *Hefelmann*.[2]

[1] Cp. also *Jour. Soc. Chem. Ind.* 1894, 838.
[2] *Ibid.* 1891, 862.

CHAPTER V

PHYSICAL METHODS OF EXAMINING FATS AND WAXES

THE examination of the physical properties of fats and waxes is in most instances a valuable aid towards identification. These properties and the determination of the constants involved will be described under the following heads :—

1. Consistency and Viscosity.
2. Colour.
3. Optical Refraction.
4. Rotatory Power.
5. Microscopical Appearance.
6. Electrical Conductivity.
7. Critical Temperature of Dissolution.
8. Specific Gravity.
9. Melting and Solidifying Points.

1. Consistency and Viscosity

A comparative study of the **consistency** of fats and waxes is still wanting.

Some authors classify the fats according to their consistency at ordinary temperature into—

(*a*) Liquid (fluid) fats or oils ;
(*b*) Semi-solid fats, as lards and butters ;
(*c*) Solid fats.

The waxes are mostly solid and brittle at ordinary temperature.

The first attempts to employ the determination of consistency for analytical purposes were made by *Serra Carpi* and by *Legler ;* both authors proposed their method in the first instance for the examination of olive oil.

Serra Carpi[1] cools the olive oil down to − 20° C. for three hours, and places on the solidified fat, by means of a suitable arrangement, a

[1] *Zeitsch. f. analyt. Chem.* 23. 566.

cylindrical iron rod 2 mm. in diameter and 1 cm. long, and conical at the bottom. Weights are then put on the rod until it sinks completely into the fat. Thus, for pure olive oil 1700 grms. were required; a sophisticated oil required 1000 grms. only, whereas for cotton-seed oil 25 grms. were found to be sufficient.

Whilst *Serra Carpi* examines the oil itself, *Legler* treats it previously with nitrous acid so as to produce the harder elaïdin (see Elaïdin Test, chap. ix. p. 280). He recommends the apparatus shown in Fig. 11. This consists of a strong glass tube A, in which a strong glass rod is allowed to slide. The rod is widened at *a* into a disc holding down the spring, which easily responds to a weight of 20-50 grms. placed on the top B. The point to which the glass rod slides down by its own weight is marked by 0 on the rod; from there upwards, marks indicating millimeters are scratched into the rod. Substantially the same principle and the same apparatus have been recommended recently by *Brullé*[1] for the examination of butter, and by *Sohn*.[2] The latter proposes three forms of apparatus, and lays down the following rules, which must be strictly adhered to if erroneous calculations are to be avoided :—

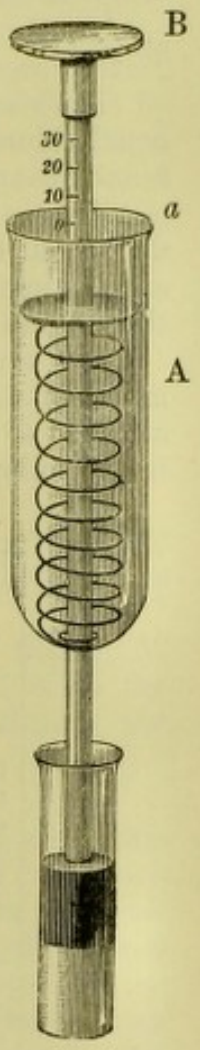


Fig. 11.

(1) The rod must descend in an absolutely perpendicular direction.
(2) It must slide in its bearing with the least possible friction.
(3) Conditions of temperature must be constant.
(4) Vessels of one diameter must be used for the material under examination.
(5) The rod must enter the centre of the vessel, or at a fixed distance from the circumference.
(6) The same depth of material must always be used.
(7) The material must be allowed to rest a certain fixed time before testing.

Much greater importance attaches to the determination of the **viscosity** of oils. This may be defined as the resistance the smallest particles offer to their separation from one another. The viscosity is therefore proportional to the internal friction of the oils, which by no means bears any relation to the density of the liquids.

The determination of viscosity is based on Poiseuille's law, which is expressed by the following formula :—

$$\mu_1 = \frac{\pi\, pr^2}{8\, vl} . t$$

[1] *Jour. Soc. Chem. Ind.* 1893, 717. [2] *Analyst*, 1893, 218.

where μ_1 is the coëfficient of the inner friction or viscosity;

p the pressure on the unit surface of the orifice of the delivery tube;

r the radius of the delivery tube;

l the length of the efflux tube;

v the volume of liquid that has passed through the apparatus in t seconds.

This law holds good only if the orifice is a capillary and as long as $\frac{l}{2r}$.

The viscosity is usually determined by ascertaining the times two equal volumes of the liquids under comparison take to flow through a narrow aperture under exactly the same conditions.

For a rough comparison, it may suffice to use a wide glass tube drawn out to a narrow aperture of about 2 mm., at the lower end, and having an upper and lower mark for the exact measurement of the volume of liquid.

The earliest experiments are those carried out by *Schübler*, by means of a glass tube of 2 cm. diameter and 10 cm. height, having attached to it a narrow tube of 1·6 mm. diameter. They are given in the following table:—

Name of Oil.	Number of Seconds required at		Viscosity at	
	+15° R.	+7·5° R.	+15° R.	+7·5° R.
Castor oil	1830	3390	203·3	377·0
Olive oil	195	284	21·6	31·5
Colza oil	162	222	18·0	22·4
Winter rape oil	159	204	17·6	22·6
Beechnut oil	158	237	17·5	26·3
White mustard oil	157	216	17·4	24·0
Almond oil	150	209	16·6	23·3
Summer rape oil	148	205	16·4	22·7
Rape oil	142	200	15·8	22·2
Mustard seed oil	141	175	15·6	19·4
Summer rubsen oil	136	198	15·1	22·0
Poppy seed oil	123	165	13·6	18·3
Camelina oil	119	160	13·2	17·7
Sunflower oil	114	148	12·6	16·4
Peach kernel oil	93	132	10·3	14·7
Walnut oil	88	106	9·7	11·8
Linseed oil	88	104	9·7	11·5
Hemp seed oil	87	107	9·6	11·9
Distilled water	9	9	1·0	1·0

On dividing the number of seconds required for an oil—*e.g.* 1830—by that required for water at the same temperature—*e.g.* 9—a number is obtained termed *specific viscosity*, or in short, *viscosity*.

Thus the viscosity of castor oil, according to *Schübler*, would be $\frac{1830}{9} = 203{\cdot}3$ at 15° C.

In practice the viscosity of oils is usually compared with that of rape oil. *Redwood*[1] has found from a number of tests carried out with refined rape oil by means of his apparatus, that 535 seconds may be considered as the average number occupied by the outflow of 50 c.c. of refined rape oil at 60° F. (15·5° C.), the viscosity of water being under similar circumstances 25·5.

Taking rape oil as a standard, and putting its viscosity = 100, the viscosity of any other oil under examination will be found by multiplying the number of seconds occupied by the outflow of 50 c.c. by 100, and dividing by 535. In case of the oil having a different specific gravity from that of rape oil—0·915 at 60° C.—a correction should be made according to *Redwood* by multiplying the result by the specific gravity of the sample, and dividing by 915. The formula is, therefore, if n be the number of seconds for an oil under examination, and s its specific gravity—

$$\text{Viscosity} = \frac{n \times 100 \times s}{535 \times 915} = \frac{n \times 100 \times s}{489525}$$

Since, however, there is no correlation between specific gravity and viscosity (see above), I consider it more useful to adopt the numbers as obtained by direct determination of the viscosity.

Engler uses water as a standard liquid, 200 c.c. taking 53 seconds at 20° C. to flow through his apparatus. If n be the number of seconds required by an oil under the same conditions, the quotient $\frac{n}{53}$ will represent the specific viscosity of the oil.

In order to obtain comparable results it is essential that complete uniformity of construction in apparatus be attended to. Passing over a number of forms of apparatus that have been proposed from time to time,[2] we shall describe only three—those of *Redwood*, *Saybolt*, and *Engler*. The first apparatus has been adopted by the War Department, the principal Railway Companies, and the Scottish Mineral Oil Association; the second is largely used in the United States; and the third occupies, in Germany, a similar position to that of *Redwood's* in this country.

Redwood's viscosimeter[3] (Fig. 12) consists of a silvered copper oil-cylinder C, about $1\frac{7}{8}$ in. in diameter, by about $3\frac{1}{2}$ in. in depth. The bottom of this cylinder is provided with an agate jet D, the cup-

[1] *Jour. Soc. Chem. Ind.* 1886, 127.

[2] Dollfus, *Dingl. Polyt. Jour.* 153. 231; Vogel, *ibid.* 168. 267; Fischer, *ibid.* 236. 487; Lamansky, *ibid.* 248. 29. Lamansky's viscosimeter has been improved in the Nobel refineries at Baku, cp. Chem. Rev. über Fett u. Harz Industrie, 1897, 90. Lepenau, *Zeitsch. f. analyt. Chemie*, 24. 465. See also Redwood, *Jour. Soc. Chem. Ind.* 1886, 121; Mills, *ibid.* 1886, 148; Hurst, *ibid.* 1892, 418; Neumann Wender, *ibid.* 1895, 596; Killing, *ibid.*; Redwood, *Petroleum*, 1896, vol. ii. pp. 602-620.

[3] *Jour. Soc. Chem. Ind.* 1886, 126.

shaped cavity of which can be stopped up by means of the plug E, consisting of a small silvered brass sphere attached to a wire. Inside the oil cup and at a short distance from the top there is fixed a small

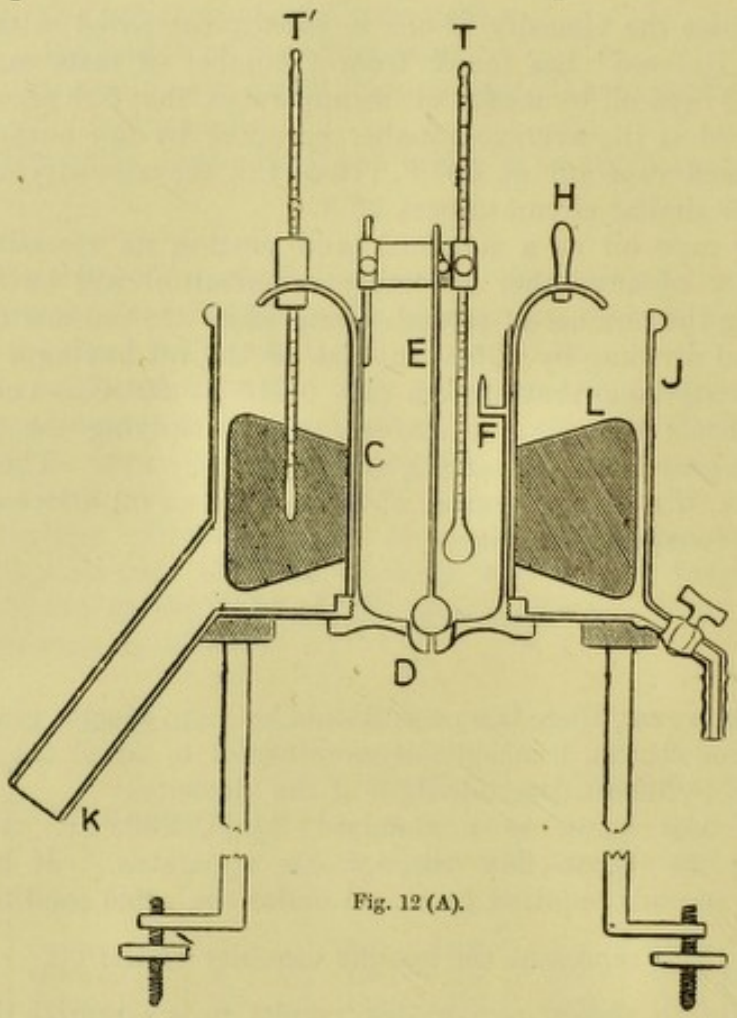


Fig. 12 (A).

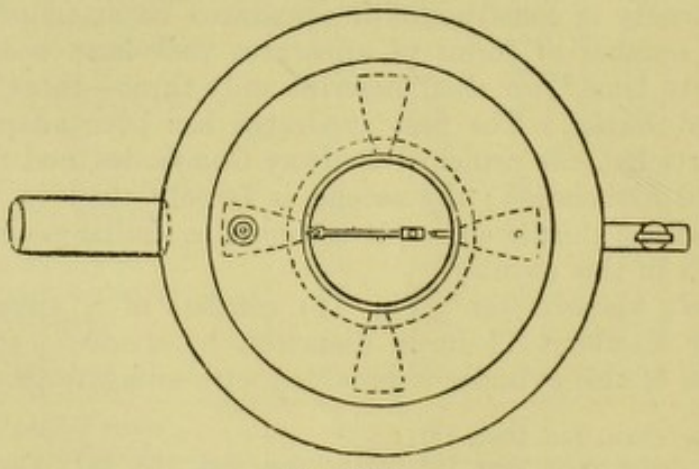


Fig. 12 (B).

bracket F, terminating in a point. This serves as a gauge of the height to which the oil must be filled. A thermometer T is usually immersed in the oil and supported by means of a clip holding the

plug E. The cylinder C is surrounded with a copper jacket J, having a closed side tube K, by means of which the liquid in the jacket can be brought to any desired temperature. The heated liquid rising from K is uniformly distributed through the bath by means of a revolving agitator worked by the handle H. The temperature of the liquid is controlled by the thermometer T'. The whole instrument is supported on a tripod stand provided with levelling screws.

It is of the greatest importance that the orifice in the agate jet should be of a standard size, as slight variations in the size of the hole in various instruments are apt to give discordant results.

The viscosimeter is employed in the following manner:—The copper jacket is filled with water for temperatures up to about 95° C., and for higher temperatures with a suitable mineral oil, up to a height corresponding roughly with the pointer F in the cylinder C. The liquid in the bath having been heated to the required temperature, the oil to be tested, previously purified and dried, and brought to the same temperature, is poured into C until its level just coincides with the point of the gauge. Great care must be taken that this level be reached exactly, and that the temperature remains constant during the observation. A narrow-necked flask, holding 50 c.c. to a point marked on the neck, is then placed beneath the jet in a vessel containing a liquid of the same temperature as the oil. The plug is then raised, and the number of seconds required for 50 c.c. of the oil to flow out is carefully observed by means of a chronometer. At least two tests of the same oil should be made at the same temperature, and the two results should be very closely concordant if due care has been exercised.

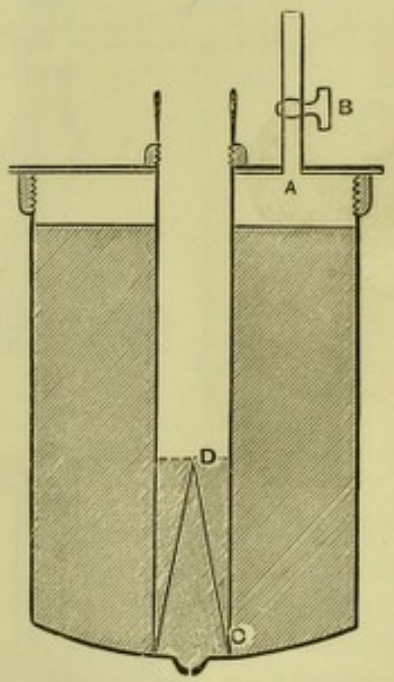


Fig. 13.

Allen[1] has modified *Redwood's* viscosimeter with a view to maintaining a given head of oil throughout the experiment. For this purpose the top of the oil-cylinder (Fig. 13) is fitted with an air-tight cap perforated by two holes, one of which is furnished with a tap B, while into the other a tube is screwed air-tight. This tube C is prolonged on two sides till it is in contact with the agate orifice, while the angles of the inverted V-shaped slits, cut on each side, terminate at a definite height D above the orifice. The cylinder is completely filled with oil before commencing an experiment, the tap B closed, and the orifice opened till the oil sinks in the inner tube to the level D. Air then bubbles in regularly at D, and rises into the closed space above the oil, and when this is

[1] *Jour. Soc. Chem. Ind.* 1886, 131.

observed to happen, the oil is collected in a graduated cylinder. When using this apparatus there is no necessity to collect exactly 50 c.c., because the oil runs through at a constant rate.

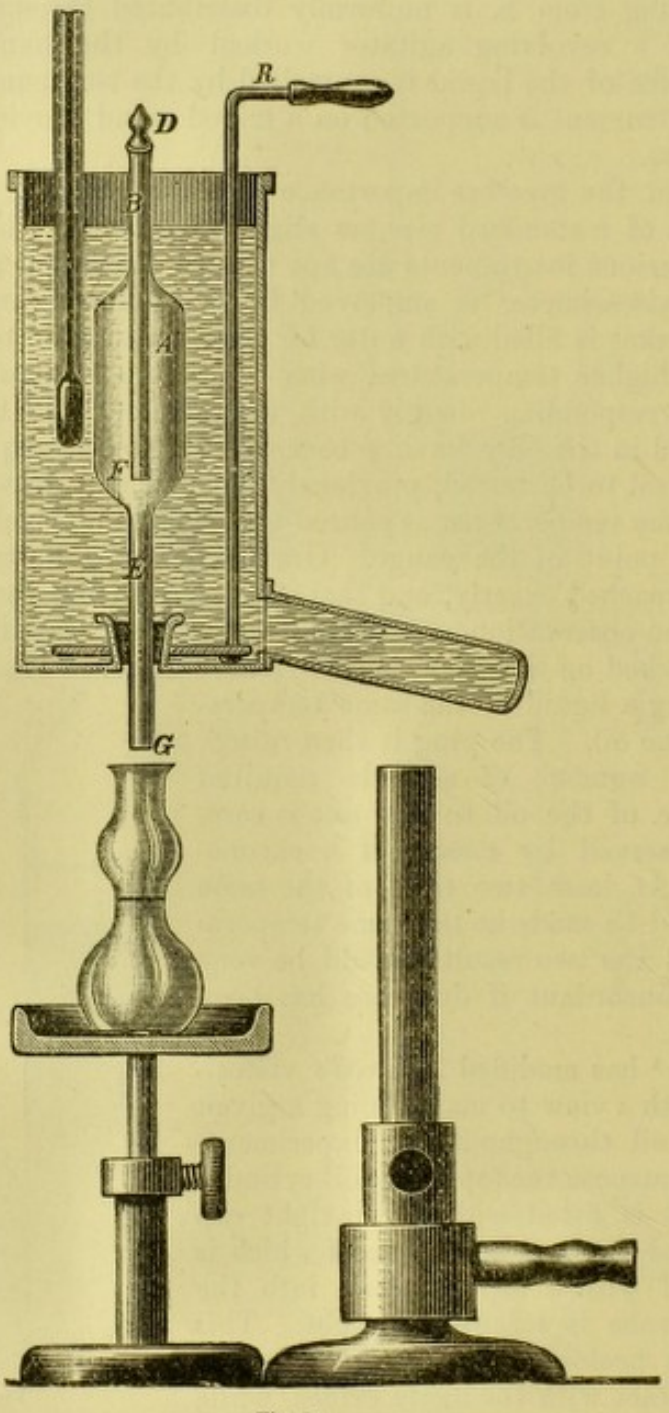


Fig. 14.

The same principle has been adopted by *E. Schmid*[1] for the improved *Reischauer* viscosimeter (see Fig. 14).

Saybolt's viscosimeter.[2] The oil vessel of this viscosimeter is placed

[1] *Chem. Ztg.* 1885, 1514.

[2] The description of this viscosimeter is taken from Redwood, *Petroleum*, vol. ii. p. 608.

in a water-bath of considerable capacity. The jet of the viscosimeter is of metal, and is enclosed in a tube extending below the orifice. The oil vessel is contracted, as shown (Fig. 15), above the jet, and is cut away longitudinally on each side, to expose a glass tube which lines it. Glass windows are provided in the water-bath. The upper edge of the oil vessel is fitted with an oil-tight gallery having a raised edge, and communicating with the oil vessel, which extends to the same level as the top of the gallery, by a number of small holes. In using the apparatus the water-bath is filled with water at the required temperature, and a cork having been inserted in the mouth of the tube enclosing the jet, the oil vessel is filled with the sample to be tested, until overflow occurs through the holes into the gallery. The oil is then stirred with a thermometer, and the temperature ad-

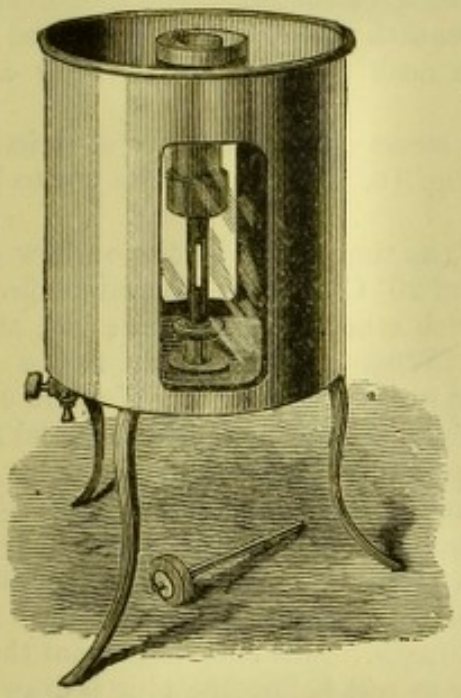


Fig. 15.

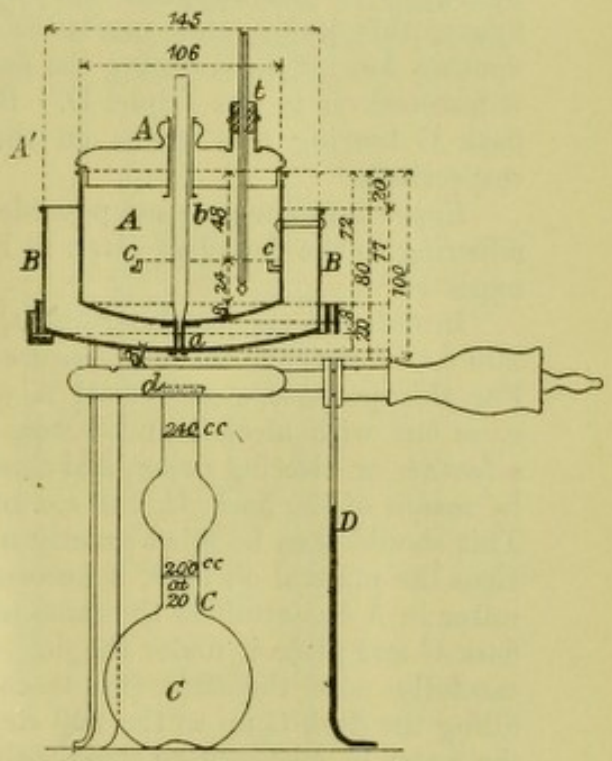


Fig. 16.

justed if necessary. On withdrawing the thermometer, the oil which it had displaced flows back from the gallery, which is then emptied by means of a pipette. The length of the oil column is, of course, determined by the position of the holes connecting the oil vessel with the gallery. The flow of oil from the jet is started by withdrawing the cork, and a stop-watch is set in motion. The watch is stopped when the operator sees the surface of the oil through the glass tube above mentioned.

Engler's viscosimeter[1] in its latest form, as designed by him in conjunction with the officials of the Charlottenburg Mechanisch-Technische Versuchsanstalt, is shown in Fig. 16. The oil vessel A

[1] *Jour. Soc. Chem. Ind.* 1893, 292.

is made of sheet brass, the inside of which should be gold-plated for very accurate determinations. This vessel is closed by a cover, A′, perforated by two holes, into one of which the thermometer *t* is fitted, whilst the other serves to receive the plug *b*. The delivery tube *a* projecting from the convex bottom of the vessel A must be exactly 20 mm. long, and 2·9 mm. in diameter at the top and 2·8 mm. at the bottom. The delivery tube should preferably be made of platinum, as in course of time even brass is attacked by neutral oils. The plug *b* should be made of hard wood. The three pointers *c* serve the double purpose of indicating the correct level of the apparatus and of marking the exact volume of 240 c.c. The vessel A is jacketed, vessel B serving as a receiver for mineral oil, which may be heated up to 150° C. by means of gas supplied through tube *d*. As shown in the figure, this jacket also surrounds the delivery tube *a*, thus preventing loss of heat during the flowing of the oil. The instrument is fastened on to the tripod D. Beneath the apparatus is placed a flask C bearing two marks on the neck for 200 c.c. and 240 c.c. respectively.

Engler lays the greatest possible stress on the necessity of strictly adhering to the measures given in Fig. 16, if correct results are to be expected.[1]

In order to test the instrument, the time taken by the outflow of 200 c.c. of water at the temperature of 20° C. must be determined first. For this purpose clean vessel A with ether or petroleum ether, and rinse out with alcohol and water. Wipe out tube *a* by means of a feather or filtering paper, and close it with the plug *b*. Measure off, by means of the flask, C, 240 c.c. of water, and pour it into vessel A. This should then be filled exactly up to the level of the pointers *c*. Heat the mineral oil in B, if necessary, to 20° C., and wait until the water in A has attained the same temperature. In the meantime dry flask C and place it under the delivery tube *a*. Draw the plug and carefully note the time (by means of a chronometer) occupied in filling the flask C up to the 200 c.c. mark. It is most important that the water in A should be completely at rest before the plug is drawn. The time required should be from 51 to 53 seconds for a correct instrument, and repeated observation should not differ by more than 0·5 of a second.

Before an oil is examined every trace of dirt and moisture must be removed from A by wiping it out carefully and rinsing it successively with alcohol and ether (or petroleum ether); finally it should be rinsed out with the filtered and dried oil. The oil is then poured into A up to the pointers *c*, and heated to the desired temperature, at which it must be kept for at least two or three minutes before allowing it to run out.

[1] "The normal apparatus" is manufactured under the joint control of the Charlottenburg Technische Anstalt and the Karlsruhe Chemisch-Technische Versuchsanstalt, and may be also had from *C. Desaga* of Heidelberg. Apparatuses from other sources are, according to *Engler*, not made with the requisite care, and give discordant results.

The following table gives a comparison of results based on a number of experiments with the three viscosimeters : [1]—

Viscosimeter.	Seconds for outflow of	
	50 c.c. at 70° F.	200 c.c. at 20° C.
Redwood's . .	100	—
Saybolt's . .	56	—
Engler's . .	—	170

As will be seen, *Engler's* viscosimeter requires much more time than either of the other two viscosimeters, and it has been proposed to shorten the observation by taking the number of seconds after 50 c.c. or 100 c.c. have run out, and multiplying the number of seconds by empirically found constants.[2] Surely, it would be simpler to use an apparatus based on the outflow of 50 c.c., like Redwood's.

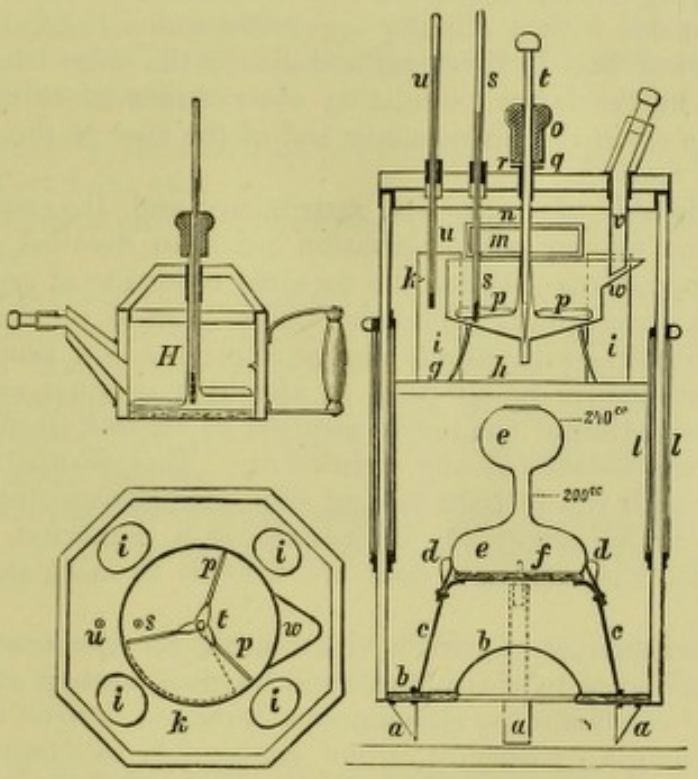


Fig. 17.

As a rule, the viscosity of an oil destined to serve as a lubricant is determined at a temperature approximating to that at which the oil is actually used. The last-described viscosimeter not having been found suitable for observations at higher temperatures, *Engler* and *Künkler*[3] have designed a "viscosimeter for examination of oils under constant temperature." This instrument is represented by Fig. 17.

[1] Redwood, *Petroleum*, vol. ii. p. 610.

[2] Singer, Chem. Rev. über die Fett u. Harz Industrie, 1897, 93, shows that the constants 5 for 50 c.c., and 2·34 for 100 c.c., give results agreeing with those found by allowing 200 c.c. to run out.

[3] *Jour. Soc. Chem. Ind.* 1890, 654.

It is an octagonal jacketed air-bath made of sheet brass, 35 cm. high and 20 cm. wide. The feet *a* stand in the ring of a tripod in such a way that the level of the air-bath can be adjusted so as to control the level of the liquid in the viscosimeter itself which is contained in the upper portion of the bath. In order to lose as little as possible of the heat supplied by a Bunsen burner, the flame is made to impinge on the arched copper plate *b*, isolated by a sheet of asbestos. Above this is placed the tripod *c* and the measuring vessel *e*, supported by *d*, and protected from direct radiation from *b* by the asbestos plate *f*. Above this is the dividing plate *g*, supporting the four oval tubes *i* and the viscosimeter *k*. Plate *g* is perforated by the large hole *h*, through which the oil flows into the measuring vessel. Circulation of hot air into the upper chamber takes place through *h*, and also through the four oval tubes *i*. Through the cover of the instrument pass the thermometers *u*, *s*, the axis of the stirring apparatus with the plug *t* for the delivery tube, and the jacketed funnel *v* for introducing the oil, previously heated to the required temperature in the can H, which is also provided with a stirring apparatus and a thermometer fixed in its hollow axis. In the cover and also in the sides windows *l* and *m* are let in, the latter permitting observations to be made of the level of the oil in the viscosimeter and of the flow of the oil into the measuring vessel *e*.

The method of using the instrument and the manipulations required for making an observation need no detailed description. That the apparatus satisfies the required condition of constant temperature is proved by the following observation of its designers. If the viscosimeter—without any charge of oil in *k*—be heated to 100° C., the temperature in all parts of the bath is equal and constant, with the exception of the lowest stratum of air in *k* itself, owing, no doubt, to the absence of any circulation. This drawback, however, disappears with the introduction of oil. At temperatures exceeding 100° C., the air above the oil vessel has a somewhat lower temperature, but the difference does not amount to more than 4° C. at 150° C.[1]

A description of *Künkler's* viscosimeter for the examination of small quantities of lubricating oils will be given in chap. xii. p. 723.

Traube[2] condemns the viscosimeters described here on the grounds that, according to theory, it is not permissible to compare directly the respective times of delivery of heavy and light oils, and still less the times of delivery of oils and water observed in one and the same apparatus. For a description of the apparatus by which *Traube* proposes to replace the viscosimeters in use the reader must consult the original paper.

[1] A similar principle is made use of in *Marten's* viscosimeter, *Mitth. Königl. Technisch. Versuchsanst.* Berlin, 1889, Ergänzungsheft, V. 6.

[2] *Jour. Soc. Chem. Ind.* 1887, 414.

2. Spectroscopical Examination

With the exception of palm oil, the more important fats and oils are whitish or yellowish; it is therefore impossible to detect any characteristic differences with the naked eye. On examining the fats, however, spectroscopically, characteristic absorption spectra are obtained. Although they are not due to the fatty substance itself, but to the presence of minute quantities of colouring matters, they serve in some instances to distinguish different oils. Thus an admixture of vegetable oils with those of animal origin may be detected by the characteristic absorption bands which chlorophyll produces. Olive oil and linseed oil give three absorption bands,—a very dark one in red, a faint one in orange, and a distinct one in green. Sesamé oil produces a weak band in red, whilst castor oil gives no bands at all.[1]

Chautard has subdivided the oils into two classes, active and inactive, according as they absorb certain prismatic colours, or allow them to pass through unabsorbed.

Doumer groups the oils, according to their spectroscopical behaviour, into four classes:—

1. Oils showing the spectrum of chlorophyll: olive oil, hemp seed oil, and nut oil.
2. Oils without any light-absorbing power: castor oil and almond oils.
3. Oils absorbing the "chemical rays" of the spectrum; the red, orange, yellow, and part of the green remaining unabsorbed. On examining such oils the spectrum from red to green appears, therefore, quite normal, whilst the other parts are invisible. To this class belong rape oil, linseed oil, and mustard seed oil.
4. Oils showing absorption bands in the different parts of the spectrum: sesamé oil, arachis oil, poppy seed oil, and cotton seed oil.[2]

Zune, who has resumed the study of the spectroscopic behaviour of oils, adopts *Chautard's* classification.[3]

3. Determination of the Refractive Power

The results obtained by the refractometric examination of fats and oils cannot be considered as affording an absolutely reliable means of detecting adulterations. This becomes evident when we consider that a fat or oil is not a definite chemical compound, but a mixture of several chemical compounds, and that different specimens of the same oil may vary according to the treatment to which it may have been subjected in the process of refining, the age of the oil, the amount of free fatty acids, the amount of oxidation it has undergone, etc.

[1] Vogel, *Practische Spectralanalyse*, 1877, 279.
[2] Cp. Kenrick, *Analyst*, 1895, 136. [3] *Analyse des Beurres*, II. 48.

Strohmer[1] thinks that the magnitude of the refractometric indices is so far influenced by the last-mentioned factors as to render them useless. This is, however, too sweeping an assertion. Recent researches carried on by *Müller*, *Skalweit*, *Amagat* and *Jean*, *Wollny*, and others (cp. chap. ix. p. 262) have shown that valuable indications as to the purity of fats, especially of butter fat, may be gained from the determination of their refractive indices.

Müller and *Skalweit* have used *Abbe's* refractometer. In this instrument the index of refraction is found by observing the total reflection which a very thin stratum of a liquid placed between prisms of a more highly refracting substance produces in trans-

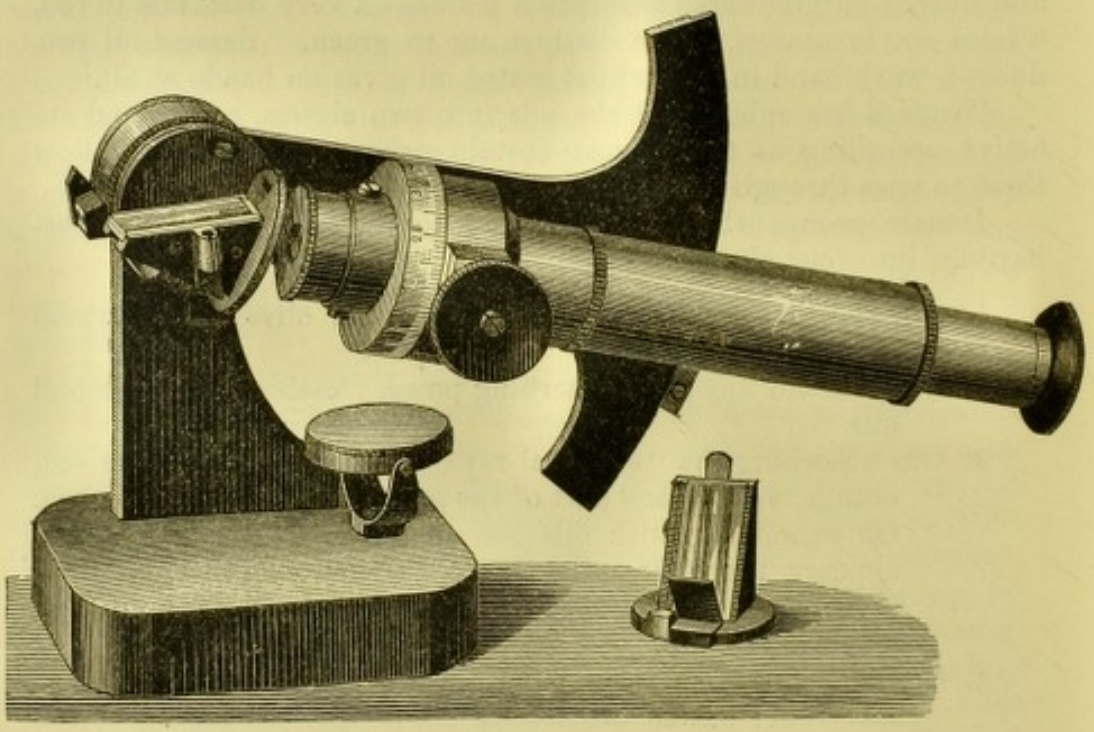


Fig. 18.

mitted light.[2] A single drop of any fluid is therefore sufficient for the examination, however opaque that fluid may be in a thick layer.

The instrument[3] is shown in Fig. 18 and Fig. 19. The former illustrates the position in which the drop of the fat under examination is applied; the latter shows that position of the instrument in which the readings are taken. The instrument consists of a double prism of a highly refracting flint glass (Fig. 18) fixed to an alhidade in such a way that both admit of being turned round the centre of a divided arc. This arc has fastened to it a telescope turning with it on a horizontal pin. The elongated part of the telescope fits in

[1] *Zeitsch. f. Zuckerindustrie*, 1889, 189.

[2] E. Abbe, *Neue Apparate zur Bestimmung des Brechungs- und Zerstreuungsvermögens fester und flüssiger Körper*. Jena, 1874.

[3] Made by Carl Zeiss, Optische Werkstätte, Jena.

a support carrying a system of two revolving *Amici* prisms. This system acts as a compensator for achromatising the critical line of total reflection, the amount of rotation being indicated by a divided drum. The drop of liquid to be examined is brought between the two prisms, one of which can be removed easily as shown. In order to make this prism easily accessible, the telescope with the arc may be turned down.

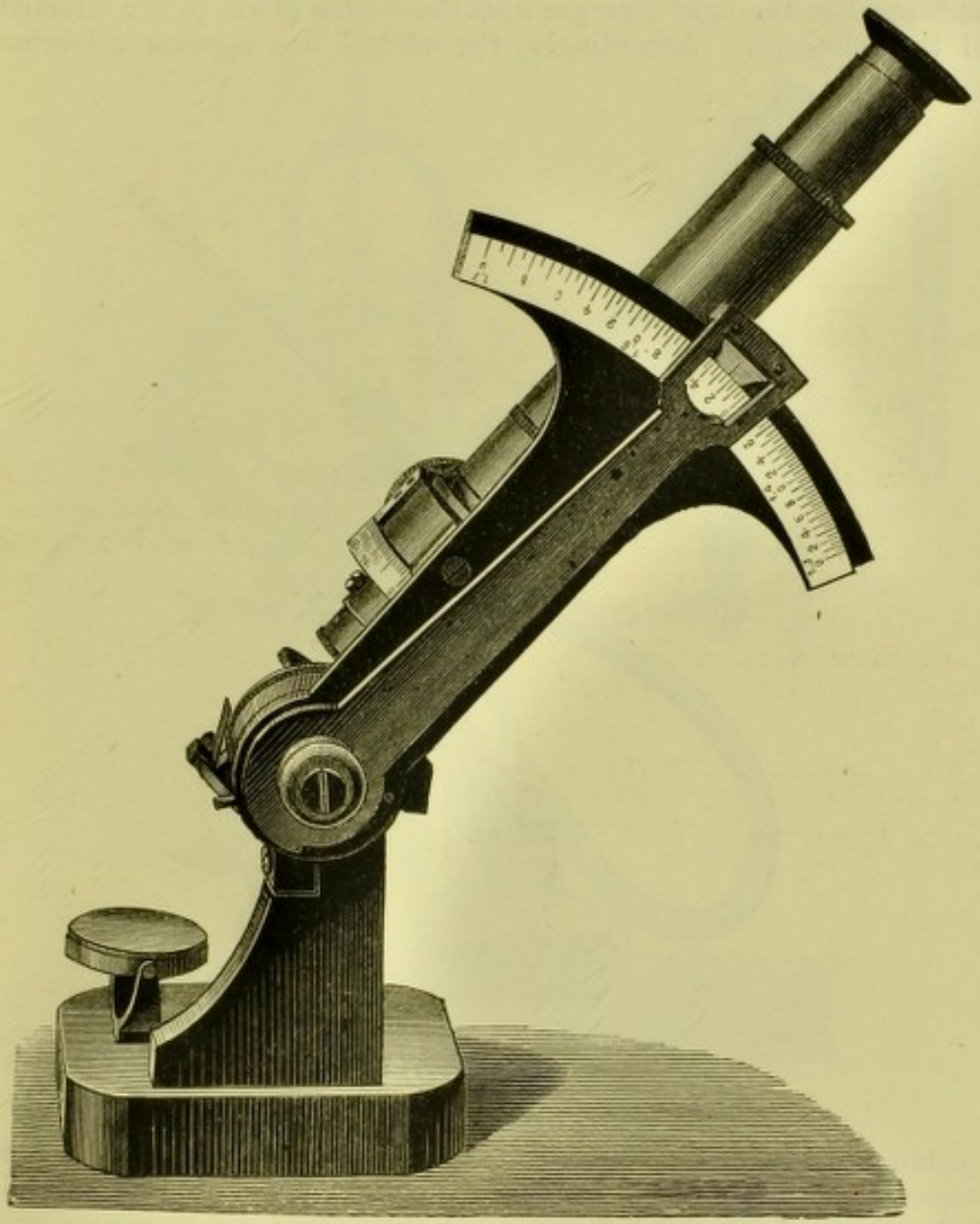


Fig. 19.

The examination may be made with diffused daylight or lamp-light, and consists in a single adjustment of the alhidade. The refractive index is read directly off the divided arc to the third decimal, no calculation being necessary. The fourth decimal may be estimated accurately within two units.

For the examination of butters *Zeiss's* butyro-refractometer (Fig. 20) has been recommended by *Wollny*. This instrument differs from those previously described, in that the critical line of total reflection for a certain substance—in this case butter—is achromatised, not by a special compensating arrangement, but by the refractometer prisms themselves, the dispersion co-existent with the total reflection between glass and substance being exactly compensated by the dispersion due to the surface when the light emerges from the double prism in the direction of the telescope. Accordingly, the critical line appears colourless

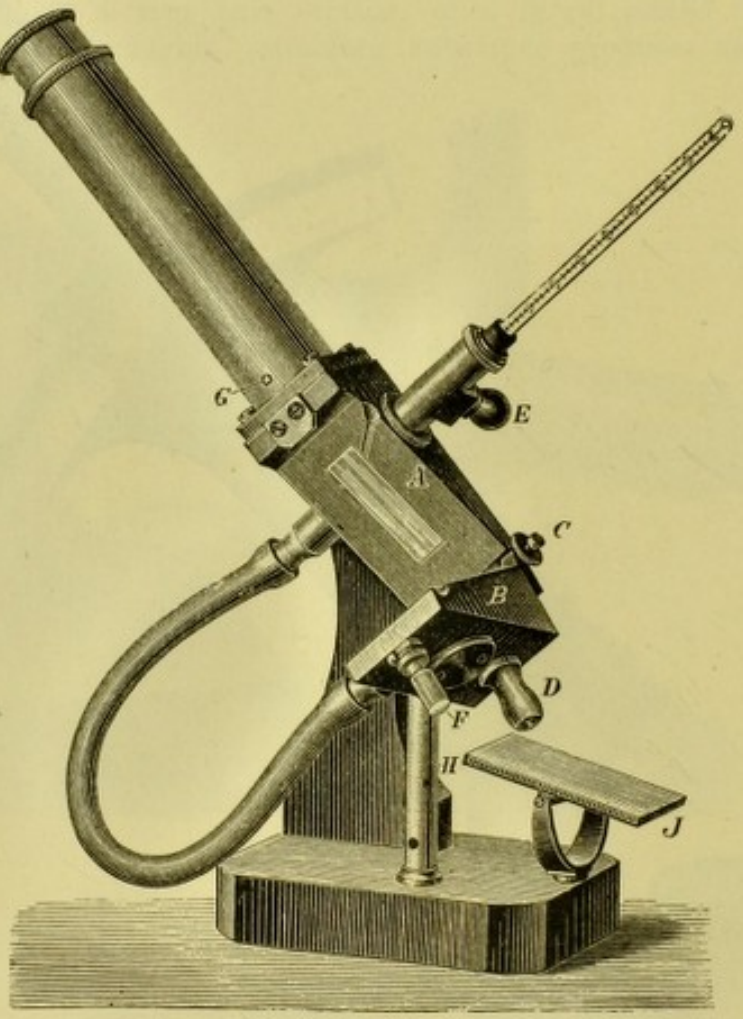


Fig. 20.

(achromatised) for the standard substance for which the prisms have been calculated, whilst all substances differing from the standard in refractive and dispersive power cause the critical line to appear more or less blue or red. This latter line, however, is in all cases sufficiently distinct to admit of its exact position being ascertained. Thus two different substances are not only distinguished by the different positions of the critical line, but also by the difference in its appearance. The prisms of the butyro-refractometer being specially calculated for pure butter, sophistications of that article of food may be easily detected by a simple examination under this instrument.

The same instrument could, of course, be adapted just as well to the refractometric examinations of other fats and oils, and also for ascertaining the proportion of water in solutions of glycerol.

The butyro-refractometer will be more fully described under "Butter Fat" (chap. xi. p. 625).

Thörner[1] recommends the use of the refractometer designed by *Pulfrich*,[2] provided with a special arrangement (which is also supplied

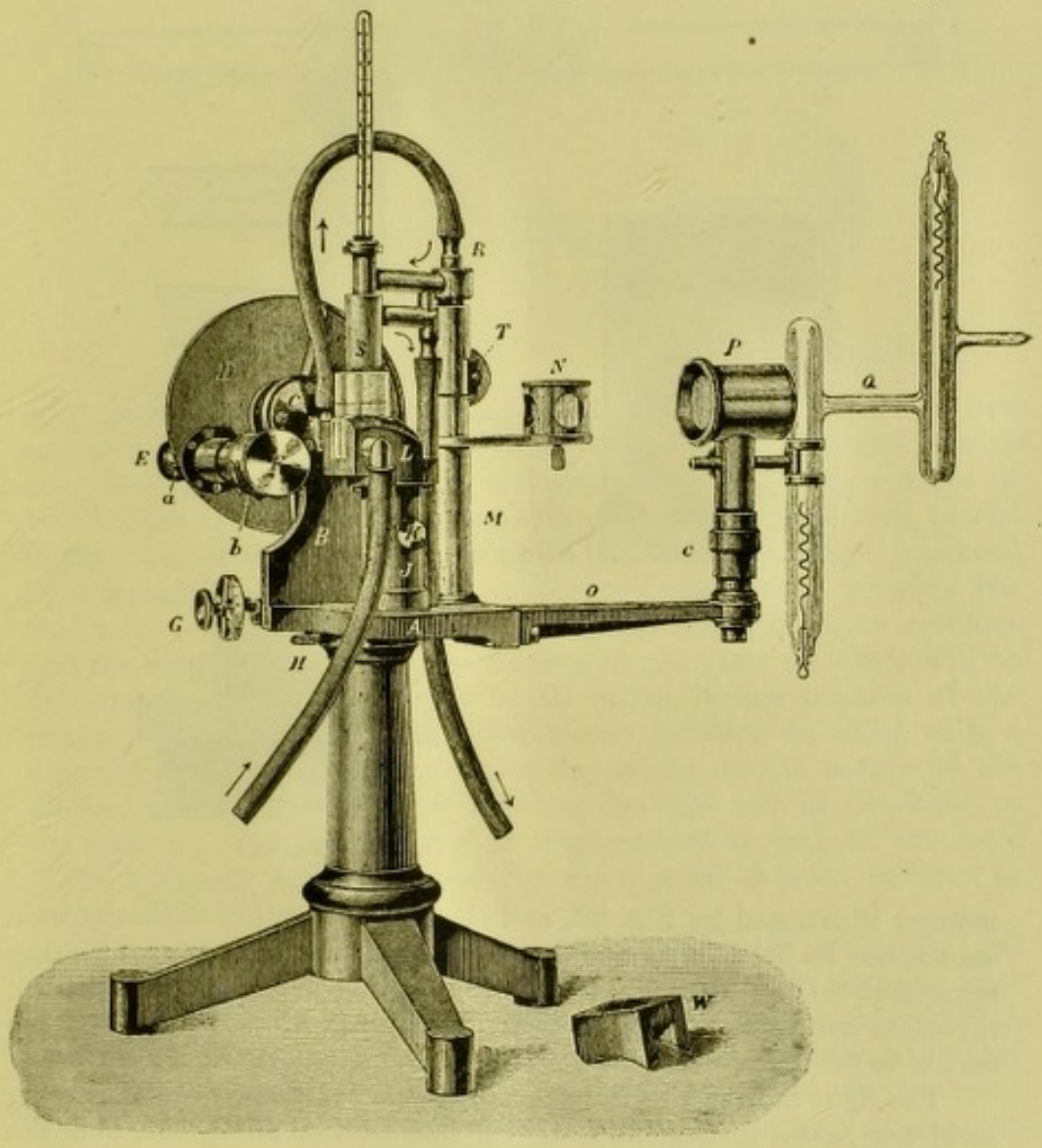


Fig. 21.

with the refractometers just described) for determinations at higher temperatures.

Pulfrich's refractometer[3] is shown in Fig. 21. The observations are made with sodium light, placed opposite the reflecting prism N, or with hydrogen light, emanating from the Geissler tube Q. The

[1] *Jour. Soc. Chem. Ind.* 1889, 308.

[2] C. Pulfrich, *Das Totalreflectometer und das Refractometer für Chemiker*, etc. Leipzig, 1890.

[3] Made by Carl Zeiss, Optische Werkstätte, Jena.

sodium light is thrown by means of the reflecting prism N, the hydrogen light by means of the condenser P, on to the substance under examination. (The illumination can be changed rapidly from one source of light to the other by displacing N.) The substance is placed direct on to the surface of the refractometer prism in the

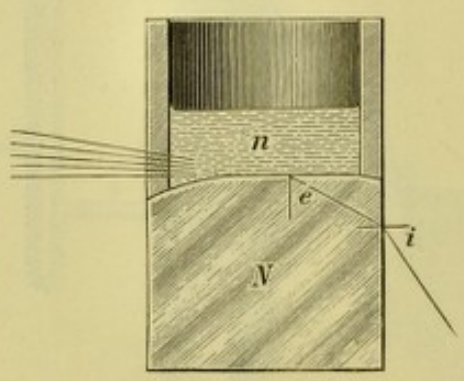


Fig. 22.

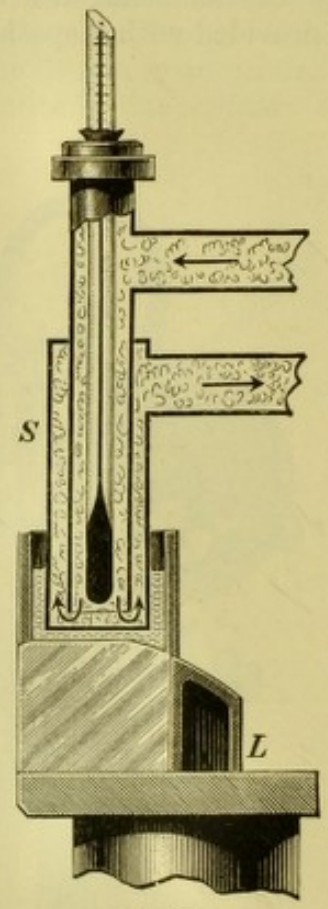


Fig. 23.

manner illustrated by Fig. 22, and the prism, together with the substance, can be brought to any desired temperature in a special heating apparatus S (Fig. 23) by allowing the heating liquid to flow in the direction indicated by the arrows. The piece of wood *W* (Fig. 21) serves to prevent loss of heat.

The light falling into the substance to be examined under grazing incidence passes through the vertical face of the 90° prism, and the angle i at which the limiting ray emerges from the vertical face is read off by means of a telescope and graduated circle. The refractive index n of the substance is calculated by means of the formula $n = \sqrt{N^2 - \sin^2 i}$ where N is the (known) refractive index of the prism.

Whilst *Abbe's* and *Pulfrich's* refractometers allow of the scientific determination of the refractive index of a substance, the apparatus recommended recently by *Amagat* and *Jean* for the examination of

fats and oils, and especially for testing butter, is an instrument based on an entirely arbitrary scale. This instrument, called by its designers oleo-refractometer (Fig. 24), consists essentially of a collimator, a telescope, and a metallic vessel. The latter is fitted with parallel plate-glass sides, and its position to the collimator and telescope is fixed in such a way that a ray of light entering through the collimator

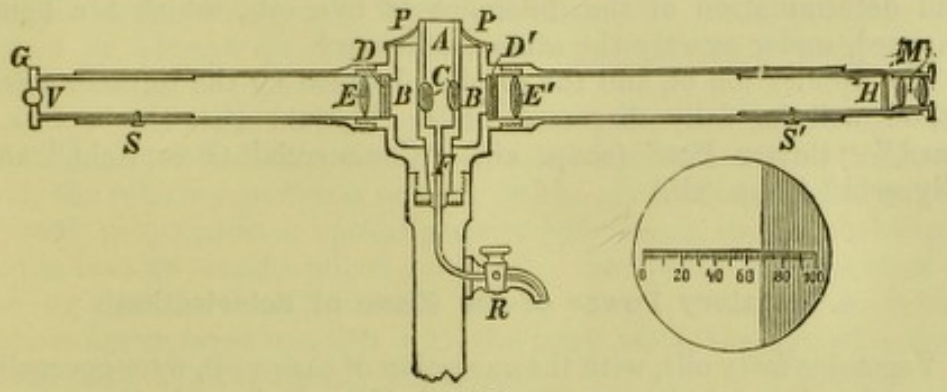


Fig. 24.

must pass through the plate-glass sides and the telescope. In the centre of the metallic vessel a small hollow silver cylinder A with two plate-glass ends is inserted, arranged so as to form an angle of 107°. The telescope is furnished with an arbitrary glass scale, placed in the focus of the eye-piece, on which is thrown the image produced by a semicircular stop inserted in the collimator, thus dividing the field into a dark and light portion. Supposing the silver cylinder and the outer circular vessel be filled with the same oil, there will be no refraction, and consequently no alteration in the position of the image. If, however, the interior silver cylinder be filled with a different oil, there will be refraction depending on the nature of the oil, and consequently the line dividing the field will be displaced to the right or left. The amount of displacement is read off the scale of the telescope, and is expressed by the number of scale divisions or "degrees."

For practical use the outer vessel is filled with a standard oil (*huile type*) [the composition of which is, curiously enough, kept secret by the inventors[1]; it must be bought with the instrument], and the semicircular stop so adjusted that the line dividing the field into a dark and light portion falls on the zero point of the scale. The interior cylinder is then filled with the oil under examination, and the displacement of the dividing line, *i.e.* the amount of refraction, read off. Instead of using the "standard oil" it is, of course, possible to compare a sample of oil with a sample of the same kind known to be pure.

For the sake of greater convenience in practical use both the cylindrical vessel and the silver cylinder can be emptied (and washed out) by means of taps, one of which only, R, is shown in Fig. 20. Besides, a water-jacket surrounding the centre part of the instrument

[1] The "huile type" is sheep's-foot oil.

(not shown) allows the temperature of the oil under examination to be regulated. The water in the jacket can be heated by means of a lamp to any desired temperature, which is indicated by a thermometer.

Amagat's and *Jean's* oleo-refractometer has that advantage over *Abbe's* refractometer that, being a differential apparatus, it allows of a rapid determination of the difference of two oils, which are being compared, under exactly the same conditions.[1]

The application of, and the results obtained by the refractometric method will be fully discussed under "Liquid Fats" (chap. ix.), "Lard," "Butter Fat" (chap. xi.), "Commercial Oleic Acid," and "Glycerol" (chap. xii.)

4. Rotatory Power of the Plane of Polarisation

Vegetable fatty oils, with the exception of castor oil, were generally supposed to be optically inactive, until *Bishop*[2] showed that several rotate the plane of polarised light slightly. The instrument used by him was a *Laurent's* saccharimeter having a 20 cm. tube. The following table gives that author's results :—

Kind of Oil.	Rotation in Saccharimeter. Degrees.
Sweet almond oil	−0·7
Arachis oil	−0·4
Colza (French) oil	−2·1
,, (Japanese)	−1·6
Linseed oil	−0·3
Walnut oil	−0.3
Poppy seed oil	−0·0
Olive oil	+0·6
Sesamé oil, cold expressed	+3·1
,, ,, warm expressed	+7·2
,, ,, 1878	+4·6
,, ,, 1882	+3·9
,, ,, 1882	+9·0
,, ,, Indian	+7·7

Peter,[3] who has also examined a number of oils by means of Laurent's saccharimeter, finds that almond, rape, hemp seed, linseed, and poppy seed oils are lævo-rotatory, whilst some samples of arachis oil were dextro-rotatory, others again lævo-rotatory. But with regard to almond, rape, linseed, arachis, and poppy seed oils *Thoerner*,[4] who examined these oils in a 20 cm. tube in *Wild's* Polaristrobometer, leaves it open to doubt whether definite rotation occurs. The same chemist gives for castor oil and sesamé oils the numbers + 6·4° and + 1·0° respectively.

[1] Allen (*Analyst*, 1895, 135) points out that the angle of the prism is not strictly the same in all instruments, he having found for a sample of lard in 3 instruments 4½°, 6°, and 11° respectively.

[2] *Jour. Soc. Chem. Ind.* 1887, 750.

[3] *Bull. Soc. Chim.* 1887, 483.

[4] *Jour. Soc. Chem. Ind.* 1895, 43.

Olive oil, more than a hundred samples of which have been examined, rotated the polarised light to the right. This is not confirmed by *Thoerner's* observations. The high angles observed for the dextro-rotatory croton and castor oils are remarkable. Walnut oil was found to be inactive, and hazelnut oil lævo-rotatory.

Fatty acids, according to *Peter*, have the same optical activity as the oils from which they have been derived. This has been confirmed by *Thoerner* for castor oil and sesamé oil fatty acids, and by *Walden* for the former oil.

It is very likely that, with the exception of castor oil, whose rotatory power is due to the asymmetric carbon-atom of the ricinoleic acid, the rotatory power is not due to the glycerides themselves, but to small proportions of optically active substances, such as cholesterol. In the case of sesamé oil, at all events, the optical activity must be due to cholesterol and sesamin (chap. xi. p. 389). As such substances are isolated together with the fatty acids, the optical activity of the fatty acids is readily explained.

5. Microscopical Appearance

The use of the microscope for the examination of fats and the recognition of adulterations has been repeatedly recommended by a number of authors, of whom we may mention *Taylor*, *Brown*, *Hehner* and *Angell*, *Mylius*, *Skalweit*, and *Wiley*. For this purpose the fat should be dissolved in ether, or chloroform, or carbon bisulphide, or petroleum ether, and a few drops of the solution allowed to evaporate on the object glass.

Butter fat, beef tallow, mutton fat, and lard show characteristic crystals.

According to *Long* the best results are obtained with chloroform as a solvent. Diagrams showing the microscopical appearance of a number of fats will be found in Zune's *Analyse des Beurres*. The appearance of the crystals in polarised light is specially characteristic. This method of examination is, at present, coming more to the fore (cp. Beef Fat in Lard, p. 582).

The application of the polarisation microscope to the examination of oils and fats is, up till now, more restricted still.

6. Electrical Conductivity

The determination of the electrical conductivity has been proposed by *Palmieri*[1] as a means of detecting the sophistication of olive oil. For this purpose he has constructed a special apparatus called a diagometer.

Recently *A. Bartoli*[2] has made an extensive examination of the electrical conductivity of oils and fats, of which the following are the main results. The conductivity of an oil increases with the rise of temperature, its amount, however, varying with the nature of the oil.

[1] *Rend. della Acc. di Napoli*, 1881. [2] *Il nuovo Cimento*, 1890, tomo 28. 25.

The drying oils, when exposed to the air, acquire a greater conductivity than the non-drying oils. An increase, though to a smaller extent, is also observed in the case of the latter, when they become rancid. A table, arranged according to the magnitude of the electrical conductivity, begins with purest olive oil, and ends with linseed oil.

The solid fats exhibit the same phenomenon, viz. increase of conductivity at elevated temperatures, with the exception of lard, at temperatures from 170° to 220° C. Nutmeg butter is characterised by a sudden increase at the temperature of its melting point. A similar table of conductivities for the solid fats opens with chicken fat, and closes with nutmeg butter.

The measurement of the electrical conductivity of the potash soaps obtained by saponifying the fat or oil under examination is proposed by *L. Herlant*.[1] It is, of course, essential to employ in each case the same amount of fat and alkali, and to dilute the solutions to exactly the same strength, and also to make all observations at one and the same temperature. For the examination 10 grms. of a fat or oil are mixed in a flask with 45 c.c. of pure normal alcoholic potash and saponified by heating for thirty minutes on the water bath, the flask being attached to a reflux condenser. The alcoholic soap solution is then made up with distilled water to 250 c.c. and electrolysed.

The resistance which a cube with a side of 1 cm. filled with the solution offers is the *specific resistance* r of this solution, and its inverse ratio $\frac{1}{r}$ expresses its *specific conductivity*. For practical purposes comparison is made with the specific conductivity of a $\frac{1}{500}$ norm. solution of potassium chloride, for which $\frac{1}{r} = 0{\cdot}002244$ at 18° C. If K be a coëfficient depending on the trough, then we have for the potassium chloride solution $\frac{1}{r}\mathrm{K} = 0{\cdot}002244$, and for the specific conductivity of any other solution in this trough $l = \frac{1}{r\,l} \times \mathrm{K}$.

7. Critical Temperature of Dissolution

The determination of the critical temperature of dissolution as a physical constant is proposed by *Crismer*.[2] This physical constant is analogous to the critical temperature of gases, and denotes the temperature above which a fat and alcohol (of a certain strength) form a homogeneous mixture.

[1] *Jour. Soc. Chem. Ind.* 1896, 562.

[2] *Bulletin de l'Assoc. Belge des Chimistes*, 1895, ix. 71, 143; 1896, ix. 359; x. 312.

Crismer places a few drops of the oil or melted fat in a glass tube 9 cm. long and 5-6 mm. wide, and adds about twice the volume of 90 per cent alcohol. The tube is then sealed and fixed by means of a platinum thread to the bulb of a thermometer, and heated in a bath of sulphuric acid or glycerin, until the meniscus separating the two layers has become flattened into a plane. After heating a little longer, so as to allow the temperature to rise, say, another 10° C., the thermometer is withdrawn from the bath and sharply turned several times. It is then replaced in the bath and the tube observed carefully, whilst the thermometer is being gently shaken. The temperature at which a marked turbidity appears is recorded as the critical temperature of dissolution.

If the critical temperature does not exceed the boiling point of alcohol, 78° C., an open tube may be used in place of a sealed one. Thus in the case of butter fat 0·5 c.c. of the filtered fat is placed in a tube 7 to 8 cm. long and about 1 cm. in diameter, with twice its volume of absolute alcohol. The tube is provided with a cork, fitted with a thermometer, the bulb of which is immersed wholly in the liquid on inserting the cork into the tube. The tube is gently heated in a larger tube, serving as an air or water bath, whilst by agitating the contents vertically a homogeneous liquid is obtained. The mixture is then allowed to cool, and the critical temperature is determined as described above.

This method has been used hitherto chiefly in the examination of butter (chap. xi. p. 628).

The critical temperatures of dissolution of mixture is, according to the same author, approximately the arithmetical mean of those of its constituents; it may be calculated from the following formula:—

$$T_m = \frac{nT_a + (100 - n)T_b}{100},$$

where

T_m = the critical temperature of the mixture.
T_a = the critical temperature of the constituent a.
T_b = the critical temperature of the constituent b.
n = the volume of constituent a in 100 volumes.
$100 - n$ = the volume of constituent b in 100 volumes.

As a further deduction from the experiments made hitherto, the rule has been derived that substances of the same nature have practically the same critical temperature of dissolution.

8. Determination of the Specific Gravity [1]

The specific gravity of the liquid fats and waxes may be ascertained at the ordinary temperature by the well-known methods adopted for any other liquid, viz. by means of a hydrometer, picnometer, or the hydrostatic balance.

[1] Instead of weighing a definite volume, Zaloziecki measures the volume of fatty acids yielded by a known weight of fat (cp. p. 623).

It is hardly necessary to emphasise the importance of making sure of the accuracy and delicacy of the hydrometer to be used. The readiest indications will be obtained by means of hydrometers referring to the density of water, whilst the use of *Twaddell's* hydrometer involves a calculation, simple though it be.

On the Continent and in America various hydrometers, based on an arbitrary scale, are used in commerce and still employed by the custom-house officials. These hydrometers, gauged for a certain temperature, express the densities in "degrees"; the real specific gravities s can be calculated by means of the subjoined table, n being the number of "degrees."

Hydrometer.	Temperature.	For Liquids heavier than Water.	For Liquids lighter than Water.
Balling . .	17·5° C.	$s=\frac{200}{200-n}$	$s=\frac{200}{200+n}$
Baumé I . .	12·5° C.	$s=\frac{144}{144-n}$	$s=\frac{144}{144+n}$
Baumé II . .	15° C.	$s=\frac{144{\cdot}3}{144{\cdot}3-n}$	$s=\frac{144{\cdot}3}{144{\cdot}3+n}$
Baumé III . .	17·5° C.	$s=\frac{146{\cdot}78}{146{\cdot}78-n}$	$s=\frac{146{\cdot}78}{146{\cdot}78+n}$
Beck . . .	12·5° C.	$s=\frac{170}{170-n}$	$s=\frac{170}{170+n}$
Brix . . .	12·5° R. 15·625° C.	$s=\frac{400}{400-n}$	$s=\frac{400}{400+n}$
Cartier . .	12·5° C.	$s=\frac{136{\cdot}8}{126{\cdot}1-n}$	$s=\frac{136{\cdot}8}{126{\cdot}1+n}$
Fischer . .	12·5° R. 15·625° C.	$s=\frac{400}{400-n}$	$s=\frac{400}{400+n}$
Gay-Lussac . .	4° C.	$s=\frac{100}{n}$	$s=\frac{100}{n}$
E. G. Greiner .	12·5° R. 15·625° C.	$s=\frac{400}{400-n}$	$s=\frac{400}{400+n}$
Stoppani . .	12·5° R. 15·625° C.	$s=\frac{166}{166-n}$	$s=\frac{166}{166+n}$
Twaddell . .	...	$s=\frac{\frac{n}{2}+100}{100}$	

Hydrometers should only be employed where rapidity is of greater importance than accuracy.

Specific gravity is usually determined by means of a picnometer of one kind or other. Of these the ordinary specific gravity bottle, consisting of a plain flask with a stopper having a capillary perforation, will be found useful for commercial work, and with care even the fourth decimal may be determined accurately. Such a picnometer is preferable to an ordinary 100 c.c. flask, as proposed by *Stohmann*, inasmuch as a smaller quantity of oil is required, and much greater accuracy in adjusting the volume is obtainable than in

the somewhat wide-mouthed 100 c.c. flask, although in the latter case it is only necessary to weigh the flask accurately to the first decimal.

The greatest degree of accuracy is obtained by means of Sprengel's picnometer (Fig. 25). This is a U-tube made of thin glass, ending in two capillary tubes *a* and *b* bent at right angles and ground at their ends, so as to fit into two glass caps (the latter are not shown in the figure). The inner diameter of tube *b*, bearing the mark *m*, is about 0·5 mm., whilst that of tube *a* is less, and should not exceed 0·25 mm.[1] The tube is filled by connecting *a* with a glass bulb, and sucking the air out of it by means of india-rubber tubing whilst *b* is immersed in the oil under examination. If the glass bulb be chosen sufficiently large, the Sprengel tube will be filled automatically on closing the india-rubber tubing with the fingers. As soon as the oil enters the bulb the Sprengel tube is detached from it, and the picnometer allowed to assume the desired temperature (see below). It will be found that the liquid expands or contracts *in the tube b only*, *i.e.* in the direction of the least resistance, whilst the capillary tube *a* will always remain full. If the meniscus of the liquid is found to be beyond the mark *m*, a little of the oil can

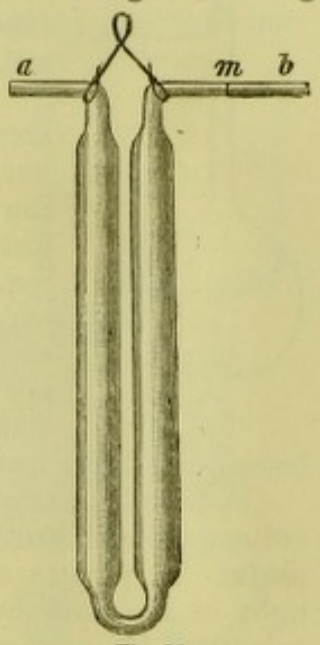


Fig. 25.

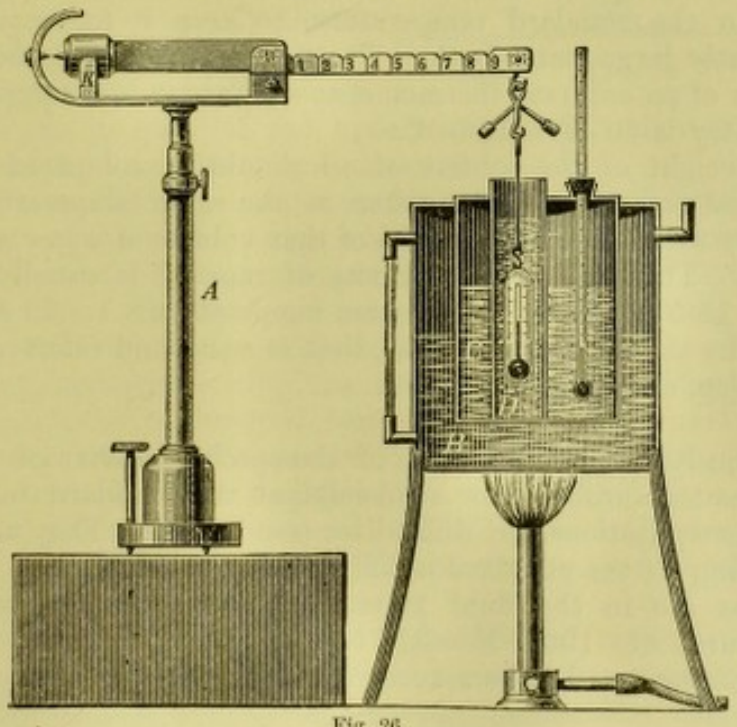


Fig. 26.

be abstracted by means of a roll of filter-paper applied to the end of *a*; if, however, the tube contains too little, *a* may be touched by

[1] This point should be noted, as this essential feature of the Sprengel tube is lost sight of by some makers.

a glass rod which has been dipped into the oil, thus allowing some to be sucked in by the capillary tube, the liquid moving forward in tube *b*. Thus the exact volume can be adjusted easily. Finally, the two glass caps are put on the tubes *a* and *b*, and the picnometer is then ready for weighing.

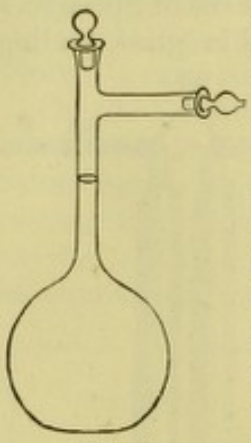


Fig. 27.

Mohr's or the hydrostatic balance is not so accurate, but still quite satisfactory for ordinary purposes, and is largely used on account of the convenience and rapidity of the operation. One form of this instrument is shown in Fig. 26, and requires no further explanation.[1] The plummet, it may be added, displaces exactly 10 c.c., and therefore the weights put on the lever to restore equilibrium are exactly the weight of 10 c.c. of the substance. Thus all calculation is avoided, the specific gravity being read direct from the weights used.

For the determination in the case of viscous oils (as boiled oil) at ordinary temperature the picnometer described by *Brühl* (Fig. 27) is useful. A pipette containing the viscous substance is inserted air-tight in the flask by means of an india-rubber tube, and the air exhausted by connecting the side tube with a filter pump.

In specific gravity determinations great care must be taken to ensure the oil having the same temperature throughout its entire mass. For this purpose it will be found best, after having brought the oil to the standard temperature, to keep it for some time in a sufficiently large water-bath. The temperature should be observed by means of an accurate thermometer. The standard temperature in this country is 60° F. = 15·5° C.

The weight of the volume of oil should be compared with that of an equal volume of water taken at the same temperature. It is customary to consider the weight of that volume of water at 15·5° C. as unity. Thus the specific gravity of rape oil is usually stated as 0·915 at 15·5° C., water at the same temperature = 1. In exact work the weight should be reduced to that *in vacuo* and referred to water at 4° C. (cp. chap. xii. p. 794).

Obviously the determination of the specific gravity of those fats and waxes that are solid or semi-solid at the standard temperature leads to complications and difficulties (see below). They are avoided by adopting as the standard a convenient temperature at which the substances are in the fluid state. *Bell* and *Muter* proposed the temperature of 100° F. = 37·75° C., whilst *Estcourt*, *Archbutt*, *Königs*, *Skalweit*, and others recommend the temperature of boiling water.

Leune and *Haburet*, *Königs*, and *Adolf Mayer* determine the specific gravity at 100° C. by means of the hydrometer.

Königs has modified the method originally proposed by *Estcourt*,

[1] Cp. Thörner, *Jour. Soc. Chem. Ind.* 1895, 44 (Illustration).

and recommends the apparatus shown in Fig. 28. This is a water-bath provided with an arrangement to keep the water at a constant level, and is closed at the top by a cover perforated with five holes. The centre hole forms an outlet for the steam ; in the other four holes there are fitted, by means of india-rubber rings, so that they protrude about half an inch above the cover, four test-tubes 8 to 9 inches long, $1\frac{1}{4}$ inches wide. The specific gravity is taken by means of a hydrometer about $5\frac{1}{2}$ inches long. This apparatus was designed, and is used in Germany, especially for the examination of butter; in order to eliminate errors due to slight variations of temperature, etc., and to ensure completely comparable conditions, one tube is filled with the sample of butter under examination, whilst the other three are charged severally with tallow, oleomargarine, and genuine butter fat.

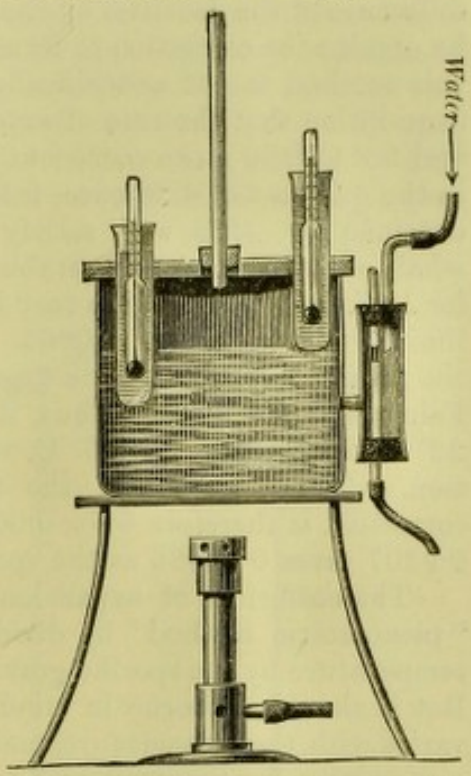


Fig. 28.

If the temperature of exactly 100° C. be required, the steam outlet tube must be partly closed. The accuracy of determinations under such conditions will largely depend on the accuracy of the hydrometers used. For this reason alone this method cannot be recommended.

Skalweit's method is more accurate. He uses a specific gravity bottle; but as there are many inherent errors in this method, for determination at the boiling point of water it will be found best to use a Sprengel tube. The Sprengel tube is immersed in boiling water in such a way that only the ends of the capillary tubes protrude. After about twenty minutes' boiling the glass caps are placed on the ends, the Sprengel tube is removed from the water-bath, wiped dry, and weighed after cooling. The weight of the oil may be referred to the weight of water at the boiling point, or, as has been done by most observers, to the weight of water at 15·5° C. The unity chosen must, of course, be distinctly stated. The correct method would be, of course, to take water at 4° C. as unity.

Whilst the hydrostatic balance may be found very convenient at the ordinary temperature, its employment at higher temperatures, as proposed by *J. Bell* and by *Wolkenhaar*, necessitates the use of a somewhat complicated arrangement. That recommended by *Bell* is shown (partly in section) in Fig. 26. It is designed for the temperature of 100° C. D is a glass tube containing the sample of fat ; C is filled with paraffin wax, and is surrounded by the water-jacket H.

In cases where, for some particular reason, neither of the two temperatures 15·5° C. nor 100° C. can be employed, a correction must be made, depending on the coëfficient of expansion of that particular oil. *Allen* [1] has determined the rate of expansion of a number of fats by taking their densities at 98° C. and 15·5° C., and dividing the difference of the densities by the difference of the temperatures. Thus he obtains the correction to be made for a variation of 1° C. Although this method is not scientifically correct, inasmuch as it rests on the assumption that the rate of expansion does not vary between 15·5° C. and 98° C. [the mean coëfficient of expansion differs from the true one as the quotient of differences from the differential quotient], the values obtained by *Allen* will satisfy practical requirements. Excepting whale oil, which possesses an abnormal rate of expansion, the correction for 1° C. has been found to vary for seventeen kinds of fats between the limits 0·000615 and 0·000665. Therefore *Allen* proposes to take as the mean correction for one degree Celsius 0·00064 (or for one degree Fahrenheit 0·00035). Thus, if the density of an oil is 0·9207 at 22° C., its density at 15·5° C. will be found by the following calculation. The difference of the temperatures is $22 - 15{\cdot}5 = 6{\cdot}5$; the correction is therefore $6{\cdot}5 \times 0{\cdot}00064 = 0{\cdot}00416$. This figure added to 0·9207 gives 0·92486 as the specific gravity at 15·5° C.

The coëfficient of expansion of an oil may also be found by this "picnometric method" by dividing the correction for one degree of temperature by the specific gravity of the oil at the lower temperature. But it should be borne in mind that the volume of the picnometer varies with the temperature, and that it is therefore necessary to make a correction for the expansion of the glass.

Several methods have been proposed for the determination of the specific gravity of solid fats and waxes at ordinary temperatures. Although it is far more convenient, as explained above, to use a higher temperature, a few of these methods may be described here.

Gintl [2] uses the picnometer shown in Fig. 29. It consists of a small cylindrical, flat-bottomed vessel, *I*, made of very thin glass and provided with a ground-glass cover. The vessel fits into the frame *a* (Fig. 30), the screw *b* serving to press the glass cover tightly on the cylinder. The vessel is weighed empty and afterwards when filled with water at the standard temperature. After emptying the water and drying carefully, *I* is filled with the melted fat until quite full, and allowed to cool to the standard temperature. The glass cover is then carefully placed on *I*, so that the surplus fat is squeezed out, and secured in its position by means of the screw. The fat outside is washed off by means of ether and the vessel weighed again.

Wynter Blyth [3] proposes to weigh the fat in a glass tube, containing besides the substance some mercury or shot, first in air and afterwards

[1] *Commercial Organic Analysis*, ii. 19. [2] *Dingl. Polyt. Jour.* 194. 42.
[3] *Analyst*, 5. 76.

under water at 15·5° C. From these data the specific gravity may be calculated.

R. Wagner, *Hager*, and other authors, favour the method proposed originally by *Fresenius* and *Schulze*, which we describe in the form given it by *Hager*.

This chemist melts the solid fat or wax at a temperature below 100° C. in a capsule, and allows several drops to fall from a height of 2-3 cm. into cold 60-90 per cent alcohol, forming a layer of 1·5-2 cm. depth in a flat-bottomed dish. Each drop should fall on a different place, so that a number of globules may be obtained. They are fished out with a spoon and placed in a beaker or a bottle 4 cm. wide and

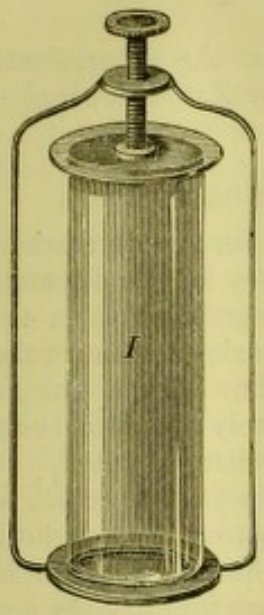


Fig. 29.

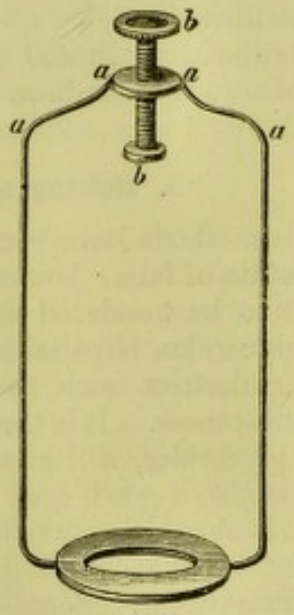


Fig. 30.

6-7 cm. high, containing dilute alcohol. To the latter either alcohol or very dilute alcohol (but not water alone, so as to avoid air-bubbles), as the case may be, is added until the fat globules will just float in the liquid. The specific gravity of the fat is then exactly the same as that of the liquid, the density of which may be determined (after filtration through glass-wool) by one of the foregoing methods.

Chattaway and *Allen*[1] take exception to the accuracy of *Hager's* method on the ground that a solid fat, and especially wax and spermaceti, suffer an abnormal contraction owing to the sudden cooling when dropped into the dilute alcohol. They found, however, that this source of error is eliminated if the wax is melted on a watch-glass placed on boiling water, and small pieces are cut from the *spontaneously* cooled mass. They are next brushed over with a wet brush in order to remove adherent air-bubbles, and carefully placed in dilute alcohol by means of a pair of forceps. *Dieterich*, however, has shown that *Hager's* method yields reliable results if the following procedure be adopted. A somewhat large piece of wax is allowed to

[1] *Commercial Organic Analysis*, ii. 184.

melt at its edge by holding it near a spirit lamp, and as close as possible to the surface of some alcohol contained in a flat-bottomed capsule, so as to avoid air being enveloped by the falling drops. The wax globules are placed on blotting paper and allowed to remain there from *eighteen to twenty-four hours*. Ten or twelve of the globules are then brought successively into eight standard mixtures of alcohol and water, having the specific gravities—at 15·5 C.—of 0·960, 0·961, 0·962, and so on up to 0·967, until that liquid has been found in which the wax globules will just float. Should any of the globules hold some air enclosed they will behave differently from the rest, and should be removed. It is hardly necessary to add that moist wax should be dried previously, say, by melting over Glauber's salt and subsequent filtration.

A somewhat complicated apparatus for the determination of the densities of soft fats has been proposed by Zawalkiewicz.[1]

9. Melting and Solidifying Points

Various methods have been proposed for the determination of the **melting points** of fats. Unfortunately they lead to discordant results. Nor is this to be wondered at if we remember (see p. 4) that even the pure glycerides, tripalmitin and tristearin, present in their melting points irregularities such as are not shown, as a rule, by definite chemical substances. It is therefore unlikely that fats, being mixtures of several glycerides, will give definite melting points.[2]

There is also a good deal of uncertainty as to which of the two temperatures should be taken as the melting point, whether that at which a fat commences to liquefy, or that at which it has become perfectly transparent. Some experimenters identify the melting point with the temperature at which the fat undergoes a certain degree of softening, either sufficient to suffer a plug of fat, contained in a glass tube open at either end, to be forced up by the hydrostatic pressure of water, or to allow the fat to form a globule.

The want of a uniform method for the determination of the melting point is therefore much felt, and one that would command general acceptance is still a desideratum.

It should be borne in mind that fats do not possess their normal melting point shortly after being melted. It is only recovered after the lapse of a day or two ; therefore if a sample has been melted it should be allowed to stand some time before the melting point is determined.

On the Continent *Pohl's* method is largely employed. This chemist ascertains the temperature at which a fat is just becoming liquid, although it may still retain solid particles. The bulb of a mercury thermometer is immersed in the melted fat and quickly removed, so that a thin coating only of fat adheres to it. After a day or two the thermometer is fixed into a long and wide test-tube by means of a cork, so that the bulb is still at a distance of about half an inch from

[1] *Jour. Soc. Chem. Ind.* 1894, 839.

[2] Cp. also Bevan, *Jour. Soc. Chem. Ind.* 1894, 70 ; and chap. i. p. 3, footnote 2.

the bottom. The test-tube is then fastened in a clamp and gently warmed by the heat radiating from a heated sheet of iron or asbestos placed below it at a distance of about one inch. The temperature is allowed to rise only very gradually. The moment a drop of liquid fat is observed to form at the bottom of the bulb the temperature is read off and recorded as the melting point.

A somewhat modified form of the same method has been introduced by *Redwood*. A very minute quantity of the melted fat, nearly cooled to its solidifying point, is placed by means of a thin glass rod on clean mercury contained in a small dish and allowed to solidify. The dish may be placed in a beaker containing water, which is heated very gradually. A thermometer is dipped in the mercury, and that temperature recorded as the melting point at which the fat spreads over the mercury.

Frequently the melting point is ascertained in a very thin capillary tube, as usually employed for organic substances. The "Society of Bavarian Analytical Chemists" have agreed upon the following *modus operandi*:—Draw up the melted fat into a thin-walled capillary tube 1 or 2 cm. high, corresponding to the length of the bulb of the thermometer to be used; seal one end of the tube, and attach the latter to the stem of the thermometer in such a way that the substance and the mercury bulb are at the same level. After an interval of about twenty-four hours immerse the thermometer in glycerin contained in a test-tube about an inch and a half wide, and heat the liquid very gently. The temperature at which the thin cylinder of fat has become perfectly clear and transparent should be considered as the melting point.

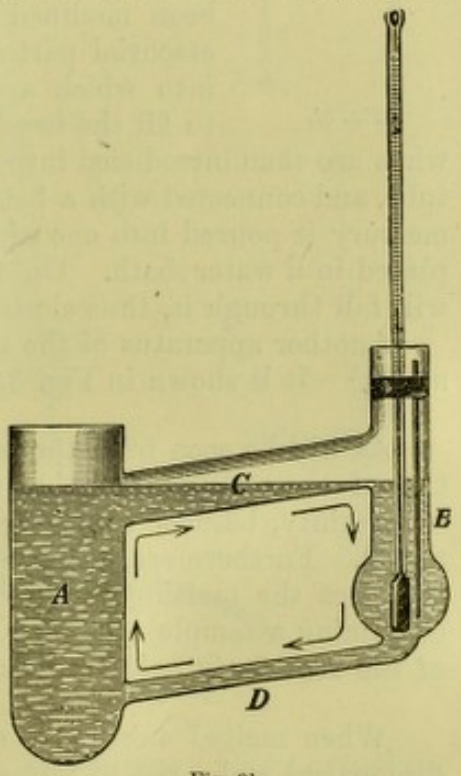


Fig. 31.

Olberg has designed an apparatus (Fig. 31) adapted for this method. The vessel is filled with oil, and on this being heated at A a natural circulation takes place without requiring any stirring.

Bensemann[1] determines two points, viz. the point of *incipient fusion* and the point of *complete fusion*. A drop of the melted fat is placed in a tube as shown in Fig. 32, *a*, and allowed to solidify in such a position that it forms a globule at A. The tube is then attached to a thermometer and immersed in water contained in a beaker. By gently warming the water over a very small flame a point is reached when the fat is just beginning to flow down the side

[1] *Jour. Soc. Chem. Ind.* 1885, 535.

of the tube. The temperature at which this takes place is recorded as the "point of incipient fusion." The drop of fat will then have taken the position shown in *b*. By further application of heat the drop becomes at last completely transparent; the corresponding temperature is the "point of complete fusion." The difference between these two points is about 3° to 4° C.

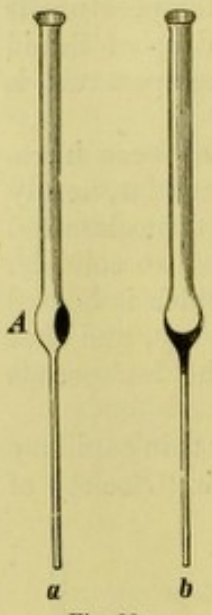


Fig. 32.

Several chemists have proposed an acoustical method for ascertaining the melting point of fats. The principle on which an apparatus of this kind is based is the following:—Two platinum wires connected to a battery and an electrical bell are immersed in the solid fat. On the latter becoming melted the circuit is closed, and this moment is indicated by the ringing of the bell. The first apparatus of this kind was designed by *Loewe*, and has been modified in some minor points by *Jean*. The essential part of *Jean's* apparatus consists in a U tube, into which a quantity of the melted fat, sufficient to fill the bend of the tube, is poured. Two platinum wires are then introduced into the solidified fat down each limb of the tube, and connected with a battery and an electric bell. Next a little mercury is poured into one of the limbs of the tube, and the latter placed in a water bath. On the fat becoming melted the mercury will fall through it, thus closing the circuit.

Another apparatus of the same type has been designed by *Christomanos*.[1] It is shown in Fig. 33.

As will be seen from the preceding remarks, the exact determination of the melting point of a fat is attended with difficulties and uncertainty, besides requiring some time before a sample can be tested. Furthermore, small amounts of free fatty acids in the fat influence the melting point to a considerable extent. Therefore, in examining a sample of fat for commercial purposes the **melting point of the free fatty acids** derived from it is usually taken (see below).

When melted substances **solidify**, the "latent heat of fusion" is disengaged and a rise of temperature takes place. Fatty acids show this rise most distinctly, whilst in the case of fats it is not so well marked, and is more characterised by the temperature remaining constant for some time before further falling. *Rüdorff* has studied the **solidifying points** of fats with a view to employing them as constants. His method was to melt a fat and to agitate it continually with a thermometer, noting the temperature from time to time. He found that in the case of some fats the temperature fell to a certain point, remaining constant thereat for a time, then falling again. During the period of constant temperature the fat solidified; this temperature was called the solidifying point.

[1] *Jour. Soc. Chem. Ind.* 1890, 894.

In the case of other fats again, on solidification setting in, a fall of temperature takes place with a subsequent rise until a maximum is reached, and then the temperature remains constant until the mass has become solid throughout.

A number of other fats, finally, as beef and mutton tallow, have no solidifying point proper, the temperature rising a few degrees, but not remaining constant. These fats behave like mixtures, part of which has become solid whilst the remainder is still liquid.

It is therefore preferable to examine the **fatty acids** instead of the fats themselves.

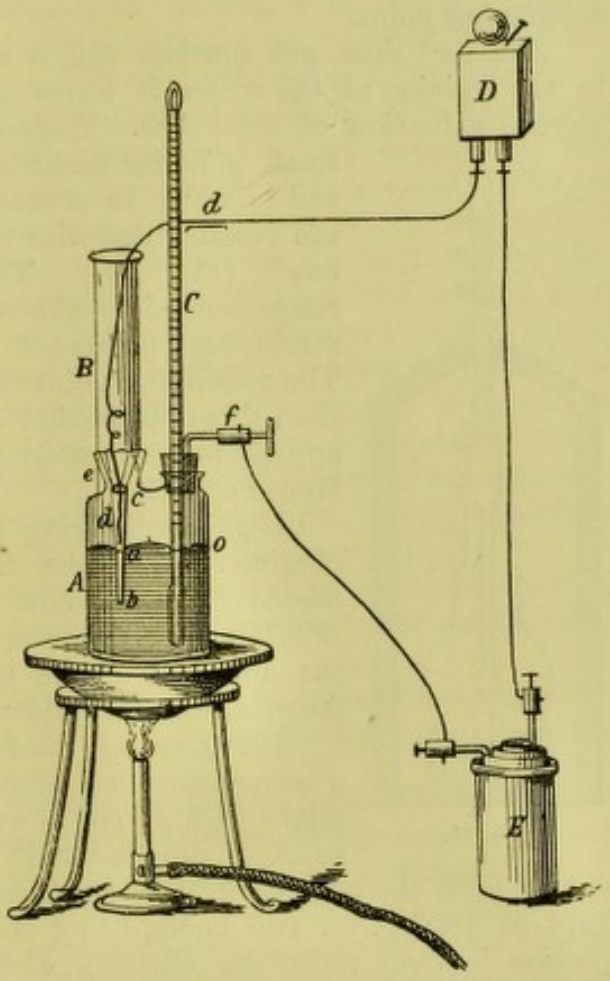


Fig. 33.

Dalican has proposed a method for the determination of the solidifying point of fatty acids, which has been adopted both in this country and in France for the commercial examination and valuation of fats. It is known under the name of "Titer Test," and gives, as the writer can testify from his own experience, fairly constant and reliable results, if the test is made under exactly the same conditions. 100 grms. of the fat under examination are saponified, and the separated fatty acids freed from water and filtered into a porcelain dish. They are allowed to solidify and to stand over night under a desiccator. The fatty substance is then carefully melted in an air-bath, and as much of it poured into a test-tube, 16 cm. long and 3·5 cm. wide, as will fill the tube more than half full. The tube is then placed in the neck of a suitable flask—say a 2-litre flask—and a delicate thermometer, indicating one-fifth of a degree, inserted, so that the bulb reaches the centre of the mass. When a few crystals appear at the bottom of the tube, the mass is stirred by giving the thermometer a rotary movement, first three times from right to left, and then three times from left to right. Next stir continually, by giving to the thermometer a quick circular movement, without allowing it to touch the sides of the vessel, but taking care that all

solidifying portions, as they form, are well stirred into the mass. The mass will gradually become cloudy throughout. The thermometer must now be observed carefully. A good plan is to write down the temperature at short intervals. At first the temperature will continue to fall, but then it will rise suddenly a few tenths of a degree and reach a maximum, remaining thereat stationary for some little time before it falls again. This point is called the **"titer" or solidifying point.**

Finkener[1] does not consider this a satisfactory method, whereas in the opinion of the writer it forms a reliable basis for the commercial valuation of solid fats. *Finkener* uses larger quantities in small globular flasks of about 50 mm. diameter, and in order to prevent a rapid cooling he places the vessels filled with the melted acids in a wooden box[2] (Fig. 34). The same apparatus is also recommended by him for the determination of the solidifying points of different kinds of tallow. The solidifying points found by *Finkener* are higher than those obtained by *Dalican's* method. *Finkener's* apparatus has been adopted by the German Custom House officials.

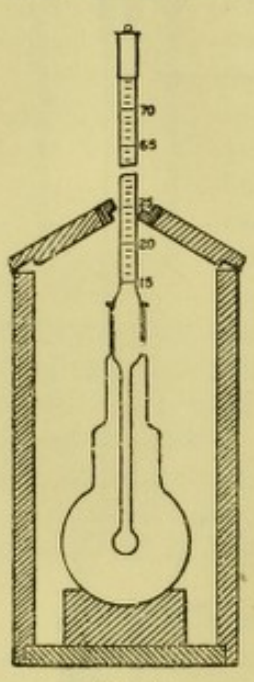


Fig. 34.

Higher solidifying points—by 0·5 C.—are also obtained when the fatty acids are previously heated for two hours at 100° C. as proposed by *Wolfbauer*.[3] The latter's method, worked out with the approval of the late *Benedikt*, is adopted in Austria, and I therefore describe it in full.

120 grms. of the fat are melted in a beaker at a temperature but slightly above its melting point, mixed with 45 c.c. of caustic potash solution (1250 grms. of caustic potash in one litre of water), and stirred until the fat is completely emulsified. It is then covered and kept at 100° C. for two hours, being occasionally stirred. A small portion is then tested by warming with alcohol (50 per cent) to ascertain whether saponification is complete, which is indicated by a clear solution; otherwise, it must be replaced in the bath and there allowed to remain until this is accomplished.

The soap is now decomposed by boiling with 165 c.c. of dilute sulphuric acid, sp. gr. 1·142, preferably in a silver dish, until the free fatty acid rises to the top as a perfectly clear oily layer. The silver dish is covered with an evaporating dish filled with cold water, to check the evaporation. The aqueous solution is then completely drawn off, and the fatty acid washed by boiling one-quarter of an hour with dilute sulphuric acid (5 c.c. of concentrated sulphuric acid and 100 c.c. of water). After settling and removing the dilute acid, it is boiled with 100 c.c. of pure water, this last operation being repeated until the washings are no longer acid. It is then dried in an open dish at 100° C. for two hours.

[1] *Jour. Soc. Chem. Ind.* 1889, 424. [2] *Ibid.* 1890, 107. [3] *Ibid.* 1894, 181. 908.

Only fatty acids obtained as above can be considered sufficiently pure and dry to be used for the determination of the solidifying point.

In the determination proper the following apparatus is employed: a thin-walled test-tube, 3·5[1] cm. by 15 cm. is fixed by means of a cork in a suitable bottle. A centigrade thermometer, extending from 1° to 60° C., and graduated in fifths of a degree, is fixed in the test-tube by a second cork, which must be sufficiently loose to permit of an easy stirring of the contents of the tube with the thermometer. As the thermometer should be as short as possible, its scale is shortened by an enlargement blown in the bore in the interval between 2° and 28° C. The amount of mercury *above* the surface of the fatty acid is thus diminished, and a very appreciable error (a lowering of the freezing point) is consequently avoided. The test-tube is then filled to within 1 cm., or 1½ cm., of the top with the melted fatty acid, the thermometer immersed in the liquor to about the 35° mark (when the instrument should clear the bottom of the tube by about 4 cm. or 5 cm.), and the liquid stirred until it becomes quite opaque, and partial solidification sets in. Care should be taken at this point that the thermometer be not more deeply immersed, and after stirring rapidly in a circle ten more times, the thermometer is allowed to stand. The mercury now begins to rise in consequence of the latent heat liberated from the solidifying fatty acid; the highest temperature noted may be taken as the freezing point.

The reading of the thermometer should be corrected for its inherent errors, previously determined. Its zero point should also be redetermined from time to time.

Each determination should be repeated, and the difference between the two should not exceed 0·1° C.; as a rule, it will not exceed 0·05.[2]

The **solidifying or freezing (congealing) point of oils** that are liquid at ordinary temperature is determined by means of freezing mixtures with which the tube containing the oil is surrounded. The thermometer is inserted in the tube by means of a cork; conveniently a thermometer is used the scale of which commences above the cork. The following table[3] gives the proportions of water and certain salts for the preparation of some freezing mixtures.

Substances used.	Parts per 100 of Water.	Freezing Point. °C.
Distilled water		0
Potassium nitrate . . .	13	−2·85
Potassium nitrate . . .	13 }	−5·0
Sodium chloride . . .	3·3 }	
Barium chloride . . .	35·8	−8·7
Ammonium chloride . . .	25·0	−15·4

[1] In a narrower tube, say 2·5 cm. diameter, the solidifying point was found to be lower by 0·20° C.

[2] For *Garrigues'* "method" cp. *Jour. Soc. Chem. Ind.* 1895, 280.

[3] *Jour. Soc. Chem. Ind.* 1889, 423.

If snow is available, lower temperatures are obtainable, as will be seen from the following table :—

Substances used per 100 parts of Snow.	Freezing Mixture. °C.
13·5 parts potassium nitrate and 26 parts ammonium chloride .	−17·8
52 parts ammonium nitrate and 55 parts sodium nitrate . .	−25·8
9 parts potassium nitrate and 67 parts ammonium rhodanate .	−28·2
13 parts ammonium chloride and 37·5 parts sodium nitrate . .	−30·7
32 parts potassium nitrate and 59 parts ammonium rhodanate .	−30·6
2 parts potassium nitrate and 112 parts potassium rhodanate .	−34·1
39·5 parts ammonium rhodanate and 54·5 parts sodium rhodanate	−37·4

The determination of the freezing point of fatty oils is not frequently made, this constant not being characteristic enough. Methods for the examination of lubricating oils in this respect (especially mineral oils) have been worked out by the officials of the Königliche Technische Versuchsanstalten, Berlin. Reference to their methods

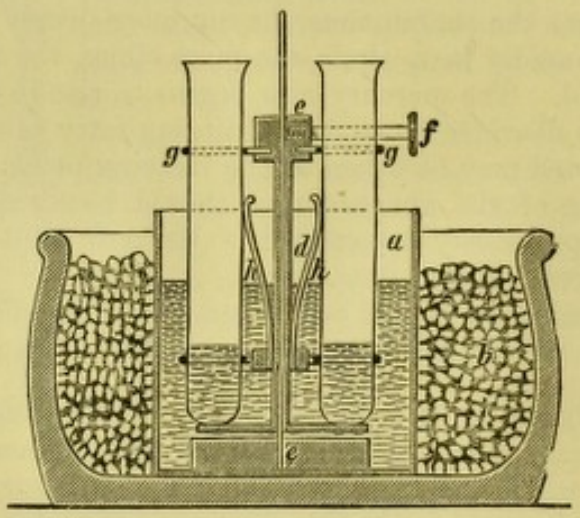


Fig. 35.

will be found in the *Journal of the Society of Chemical Industry*, 1889, 423; 1890, 772. Fig. 35 illustrates the apparatus in which the operation is carried out. (Cp. also Cold-Test, chap. xii. p. 713.)

CHAPTER VI

CHEMICAL METHODS OF EXAMINING FATS AND WAXES

1. Ultimate Analysis of Fats and Waxes

THE ultimate analysis of fats will be found of very little use for technical purposes,—the proportions of carbon, hydrogen, and oxygen of the different fats varying very little indeed. A glance at the following table, giving the percentages of the three elements contained in palmitin, stearin, olein, linolin, which may be considered as the chief constituents of most fats, will show this plainly :—

Triglyceride.	Formula.	Carbon. Per cent.	Hydrogen. Per cent.	Oxygen. Per cent.
Palmitin . . .	$C_{51}H_{98}O_6$	75·93	12·16	11·91
Stearin . . .	$C_{57}H_{110}O_6$	76·85	12·36	10·79
Olein . . .	$C_{57}H_{104}O_6$	77·38	11·76	10·86
Linolin . . .	$C_{57}H_{98}O_6$	77·90	11·16	10·94

Ricinolein only differs considerably from these glycerides in its composition :—

Formula.	Carbon. Per cent.	Hydrogen. Per cent.	Oxygen. Per cent.
$C_{57}H_{104}O_9$	73·46	15·37	11·17

The following table gives analyses of some of the more important animal and vegetable fats :—

Kind of Fat.	Carbon. Per cent.	Hydrogen. Per cent.	Oxygen. Per cent.
Mutton tallow [1]	76·61	12·03	11·36
Beef tallow [1]	76·50	11·91	11·59
Lard [1]	76·54	11·94	11·52
Horse fat [1]	77·07	11·69	11·24
Butter fat [1]	75·63	11·87	12·50
Seal oil [2]	77·10	13·50	9·40
Finback oil [2]	77·05	12·05	10·90
Train oil [2]	76·85	11·80	11·35
Cod liver oil [2]	75·91	12·22	11·87
Linseed oil [1]	76·80	11·20	12·00
,, ,,	77·80	11·20	11·80
,, ,,	78·00	11·00	11·00
Rape oil [1]	77·99	12·03	9·98
,, ,,	78·20	12·08	9·72
,, ,,	77·91	12·02	10·07

The ultimate analysis of waxes would be of less use still for identification.

Ultimate analysis may, however, prove useful for the identification of the fatty acids, or some other constituent of fats and waxes. Of course, these substances must have been brought previously by crystallisation, etc., to a sufficient state of purity.

2. Qualitative Examination of Fats of known Origin by strictly Scientific Methods

It has been pointed out repeatedly that the natural fats are more or less complicated mixtures of several triglycerides, containing varying quantities of free fatty acids, of wax-like substances, and occasionally small quantities of hydrocarbons. The object of an exhaustive scientific examination of a pure fat or a wax is to resolve it into its constituents, and to identify them, *i.e.* to find out of which fatty acids and alcohols it is composed.

It does not fall within the province of a general technical analysis of fats and waxes to institute such an exhaustive inquiry into their components. The methods used for such researches, viz. fractional distillation, fractional precipitation, and crystallisation, etc., being difficult to carry out, and absorbing a large amount of time, must naturally be reserved for an investigation of a strictly scientific character. We shall, therefore, only glance at the processes adopted in such research work.

[1] Schulze and Reinecke; *Liebig's Annalen*, 142. 198; König, *Chemische Zusammensetzung der Nahrungsmittel*, etc. i. 199; 200; 429.

[2] Schaedler, *Technologie der Fette und Oele*, 750.

A. Examination of the Acid Constituents

Examination of the volatile fatty acids—fractional saturation with alkali

The aqueous solution of the volatile fatty acids prepared by saponifying the fat, separating the fatty acids, and distilling the latter in a current of steam, is divided, according to *Liebig*, into two equal parts. One part is neutralised exactly by caustic potash; the second part is then added, and the whole subjected to distillation. The acids having lower boiling points pass into the distillate, whilst the higher boiling acids remain as potassium salts in the distilling flask. Acetic acid, however, also remains behind as potassium salt. By repeatedly treating both the distilled and the remaining acids in the same way, finally pure fractions of the several acids are obtained.

Liebig employed this method for separating butyric acid from a mixture of butyric and isovaleric acids, and further for isolating acetic acid when mixed with either of these two acids. *Veiel*, however, has arrived at the opposite result, having found that isovaleric acid distilled over, whereas butyric acid remained behind. *Lieben* partially confirmed *Veiel's* results, by stating that *Liebig's* method is not accurate, but that an approximately satisfactory separation is obtained by suitably modifying it, viz. by partially neutralising the mixture of acids, when the higher acids will distil off and the lower remain behind as salts. *Wechsler*[1] has tested *Lieben's* method by applying it to equivalent amounts of two acids; he examined the following mixtures: Formic and acetic, acetic and propionic, acetic and butyric, acetic and isobutyric, propionic and butyric, butyric and caproic acids. The mixed acids were neutralised with four-fifths of the theoretical amount of alkali, and distilled so long as the distillate was found to be acid. The remaining salts were then treated with a quantity of sulphuric acid sufficient to exactly liberate three-fifths of the fatty acids, and again distilled. The last fifth was finally obtained by acidulating the residue and distilling it. The first fraction was found to contain the higher acid, and the last fraction the lower acid, in an almost pure state. The mixture of butyric and isovaleric acids, however, could not be separated by this method, a result at variance with the statements of both *Liebig* and *Veiel*. *Crossley*,[2] however, could not obtain such good results as one is led to expect from *Wechsler's* statements, and in his opinion the latter's method cannot in any way be looked upon as satisfactory for separating mixtures of fatty acids.

Erlenmeyer and *Hell*[3] propose to separate the several volatile acids by fractional saturation with silver carbonate. The acids having a higher boiling point are precipitated first.

Fitz[4] has shown that by mere fractional distillation of the free

[1] *Jour. Soc. Chem. Ind.* 1894, 181; cp. also Sorel, *ibid.* 1896, 143.
[2] *Proc. Chem. Soc.* 1897, 21.
[3] *Liebig's Annalen*, 160. 296, footnote.
[4] *Berichte*, 11. 46.

acids, if care is taken to replace the water distilled off, a separation can be effected, the acid of higher molecular weight passing over first. This result has been corroborated by *Hecht*.[1]

EXAMINATION OF THE NON-VOLATILE FATTY ACIDS

The non-volatile acids can be separated into *solid* (saturated) and *liquid* (unsaturated) acids by exhausting their lead salts with ether (see below).

The **solid** saturated acids may be further separated by fractional precipitation of their alcoholic solutions (saturated in the cold) with alcoholic solutions of barium or magnesium acetate.[2] *Pebal*[3] uses as a precipitant an alcoholic solution of lead acetate. Every fraction is decomposed by hydrochloric acid, and the fatty acids of the same melting point are united. The several fractions are repeatedly subjected to the same process until pure substances are obtained. A fraction may only then be looked upon as a chemical individual if its melting point is not altered by further recrystallisation, and if by partial precipitation fractions having identical melting points are obtained.

It is thus evident that pure acids can only be obtained by a very frequent repetition of the fractional precipitation.

It is further evident that quantitative separation of the individual acids is altogether out of the question.

Experiments made by *Hehner* and *Mitchell*[4] on mixtures of palmitic and stearic acids with a view to determine the usefulness of such methods for analytical purposes, give an approximate idea as to how far separation may be effected. Pure stearic and palmitic acids were mixed in the proportions given in the following table, and precipitated with measured quantities of aqueous barium acetate solutions, sufficient to precipitate the stated amounts of stearic acid.

Separation effected by Precipitation of mixed Stearic and Palmitic Acids with Aqueous Barium Acetate

Stearic Acid. Grms.	Palmitic Acid. Grms.	Barium Acetate added sufficient to precipitate Stearic Acid. Grms.	Stearic Acid in Precipitate. Per cent.
1	1	1	71·7
1	2	1	62·8
1	3	1	27·9
1	3	1	30·9
0·5	0·5	0·5	62·7
1	1	0·5	46·6

[1] *Liebig's Annalen*, 209. 319.
[2] Heintz, *Jour. prakt. Chemie*, 66. 1.
[3] *Annalen*, 91. 138.
[4] *Analyst*, 1896, 318.

On precipitating the filtrates in a similar fashion, it not infrequently happened that the second fraction contained a larger proportion of stearic acid than the first proportion.

Similar experiments with aqueous solution of magnesium acetate and alcoholic solutions of lead acetate gave no better results.

The liquid fatty acids are further examined by *Hazura's*[1] method of oxidising with a dilute solution of potassium permanganate. As a rule, the oxidation products of oleic, linolic, and the linolenic acids, viz. dihydroxystearic, sativic, and linusic and isolinusic acids, will have to be looked for.

An examination of this kind was carried out in the following manner: 30 grms. of the liquid fatty acids were neutralised with 36 c.c. of caustic potash of 1·27 specific gravity. The resulting soap was then dissolved in 2000 c.c. of water, and an equal volume of a 1½ per cent solution of potassium permanganate allowed to run in in a thin stream with constant stirring. The solution was allowed to stand for ten minutes, and a quantity of sulphurous acid solution added, with continuous agitation, sufficient to dissolve all the precipitated hydrated manganese peroxide, and to impart an acid reaction to the solution. *Dihydroxystearic* and *sativic* acids were precipitated (A), whereas *linusic* and *isolinusic* acids remained dissolved (B).

The precipitated acids (A) were washed first with a little ether in order to remove some of the original liquid acids that had escaped oxidation, and then exhausted with large quantities of ether at the ordinary temperature, 2000 c.c. of ether being used for every 20 grms. of the precipitate. The *ethereal solution*, containing dihydroxystearic acid, was evaporated down to 150 c.c., when, on cooling, crystals were obtained which after recrystallisation from alcohol were identified by their habitus, their melting point, and some "quantitative reactions" (see following chapter) as *dihydroxystearic* acid. That portion which was found to be insoluble in the cold ether was boiled out repeatedly with large quantities of water. Each quantity was filtered off whilst boiling hot and allowed to deposit crystals on cooling, which were examined separately by ascertaining their melting points and crystalline forms, and identified as *sativic* acid. A small quantity of insoluble acid was recognised as dihydroxystearic acid that had not been dissolved by ether.

The acid filtrate (B) was neutralised with caustic potash, boiled down to one-twelfth or one-fourteenth of the original volume and acidulated with sulphuric acid. The precipitate, consisting of a brown flocculent mass, was dried in the air and treated with ether, which dissolves azelaic acid and other acid secondary products of oxidation. The insoluble portion was recrystallised first from alcohol and then from water. By means of the melting points and the detection of characteristic needles on the one hand, and obtruncated

[1] *Monatshefte f. Chemie*, 1887, 147; 156; 260. 1888, 180; 190; 469; 478; 944; 947. 1889, 190.

rhombic plates on the other, *isolinusic* and *linusic* acids were identified. To effect a separation of the two acids the substance was recrystallised from a moderate quantity of water, so as to separate the more soluble isolinusic acid from the less soluble linusic acid. By weighing the several acids thus obtained the quantitative composition of the liquid acids was estimated approximately.

A synopsis of the preceding operations is given in the following table :—

Hydroxy Acids

A. Precipitate.		B. Filtrate.	
a. Soluble in Ether.	*b*. Insoluble in Ether.	*a*. Easily Soluble in Water.	*b*. Sparingly soluble in Water.
Dihydroxystearic acid	Sativic acid	Isolinusic acid.	Linusic acid

The following table, summarising some of the properties of the four acids, will assist in mapping out another method of separation by means of the barium salts :—

[TABLE

Acid.	Formula.	Melting Point. °C.	Solubility of the						
			Acids in					Barium Salts in	
			Water.		Alcohol.		Ether.	Water.	
			Cold.	Hot.	Cold.	Hot.		Cold.	Hot.
Dihydroxystearic .	$C_{18}H_{34}O_2(OH)_2$	137	Insoluble	Insoluble	Sparingly soluble	Soluble	Sparingly soluble	Insoluble	Insoluble
Sativic . . .	$C_{18}H_{32}O_2(OH)_4$	173	Insoluble	Sparingly soluble	Sparingly soluble	Soluble	Insoluble	Insoluble	Insoluble
Linusic . . .	$C_{18}H_{30}O_2(OH)_6$	203–205	Sparingly soluble	Soluble	Sparingly soluble	Sparingly soluble	Insoluble	Sparingly soluble	Readily soluble
Isolinusic . .	$C_{18}H_{30}O_2(OH)_6$	173–175	Sparingly soluble	Readily soluble	Soluble	Soluble	Insoluble	Sparingly soluble	Readily soluble

Similar methods will have to be adopted to identify other liquid acids by means of their oxidation products, as the acids in, say, castor oil (cp. table, p. 67).

Fahrion[1] proposes to shorten *Hazura's* method by avoiding the preliminary preparation of the fatty acids, and the separation of the saturated solid fatty acids from the liquid unsaturated acids. He finds that the saturated fatty acids are not acted upon by potassium permanganate as long as unsaturated ones are present, oxalic acid, the oxidation product of glycerol, passing into the aqueous solution. The separation of the hydroxy acids from the saturated acids, and from the unoxidised unsaturated acids, is effected by means of petroleum ether, which does not dissolve the former acids. The operation is carried out as follows :—Saponify 10 grms. of the fat in a porcelain dish of 1500 c.c. capacity, with 10 grms. of caustic soda, adding alcohol and a little water. Evaporate to dryness on the water-bath, dissolve the soap in 1000 c.c. of water, heat to boiling, and add gradually, as a 5 per cent solution, 10-25 grms. of potassium permanganate (according to the iodine absorption value of the fat) with constant stirring. Heat finally for a short time, filter through a plaited filter, and acidulate the filtrate with hydrochloric acid. The separated acids, when quite cold, are filtered through linen, expressed as completely as possible by hand, and finally exhausted with petroleum ether. The saturated fatty acids, and that part of the unsaturated which escaped oxidation, are dissolved by the petroleum ether whilst the hydroxy acids remain behind.[2] If isolinusic acid be present, part of it may be found in the aqueous solution. The yield, however, is a very poor one. Thus 10 grms. of tallow gave only about 1 grm. of solid acids, viz. dihydroxystearic acid containing some azelaic acid. The former, after recrystallisation from alcohol, melted at 126° C. (137° C., *Hazura*).

To detect **linolic acid** in non-drying oils, the precipitated fatty acids need not be exhausted, according to *Fahrion*, with petroleum ether, but may be boiled with 1000 c.c. of water. The boiling solution is filtered, the filtrate boiled down to 100 to 150 c.c., and transferred, whilst still warm, to a separating funnel. The solution, when quite cold, is acidulated with hydrochloric acid and shaken out with ordinary ether. The presence of sativic acid, the oxidation product of linolic acid, will be indicated by white flocks floating about in the lower part of the ethereal solution. 10 grms. of cotton-seed oil examined by this method yielded 0·6 grm. of flocks, melting, after recrystallisation, at 152° C. (173° C., *Hazura*).

F. Krafft[3] has resorted to the method of **fractional distillation** *in vacuo* in order to purify and isolate some of the acids belonging to the oleic series. He has found as a very suitable pressure for practical use that of 100 mm. of mercury, slight variations of pressure exercising

[1] *Jour. Soc. Chem. Ind.* 1893, 951.
[2] Cp., however, p. 204.
[3] *Jour. Chem. Soc.* 1889, Abstr. 690.

in that case a smaller influence on the boiling point than if a lower pressure be chosen, and the troublesome frothing of the liquid being all but prevented.

Krafft's apparatus is shown in Fig. 36. Between the receiving vessel of the distilling apparatus and the filter pump *p* a thick-walled

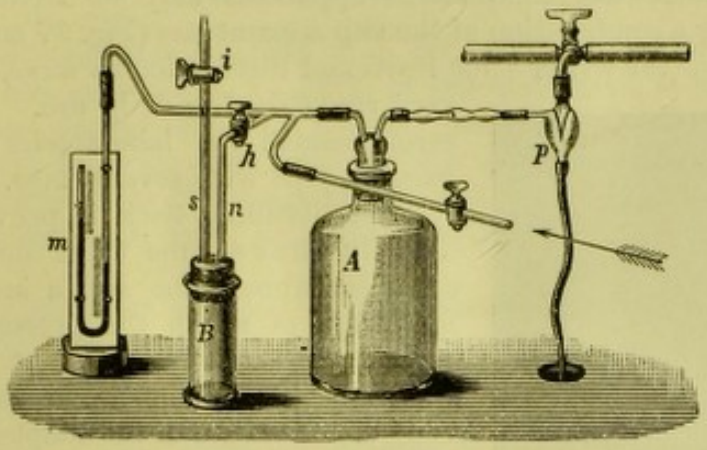


Fig. 36.

bottle A is inserted as a vacuum vessel. By means of tap *h* this vessel is connected with a cylinder B, fitted with two tubes *n* and *s*. *s* ends in a finely-drawn tube, and is provided with the regulating tap *i*.

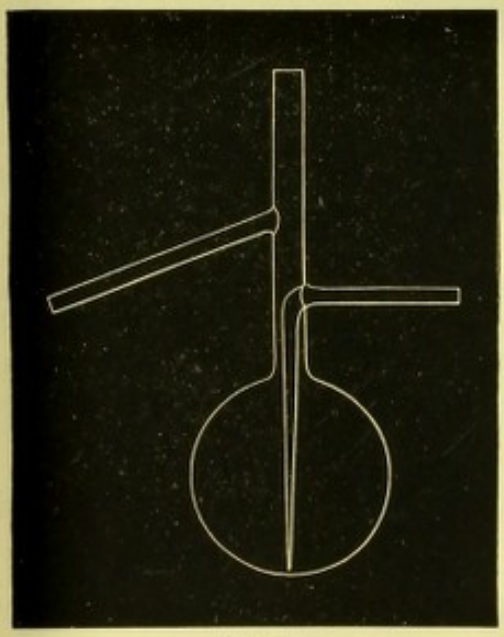


Fig. 37.

A is also connected with a mercury gauge *m*. In order to regulate the pressure the whole apparatus is first exhausted a few millimeters below the required pressure; next tap *h* is opened completely, and tap *i* so far, that the air rushing in keeps the gauge at the desired height.

More recently *Krafft*[1] uses for determining boiling points the

[1] *Berichte*, 1896, 1316.

vacuum of the cathode light; so high a vacuum, for the measurement of which the reading of a mercury gauge is useless, can be obtained without difficulty by employment of a *Babo* vacuum pump. The boiling points of fatty acids, recorded p. 30, have been determined by means of this apparatus.

This somewhat complicated apparatus may be advantageously replaced by a combination of the two apparatuses (Fig. 37 and Fig. 38), designed by the writer[1] for fractional distillation *in vacuo*, and found very convenient in daily use. It may be recommended for laboratories having a vacuum pipe with several taps.

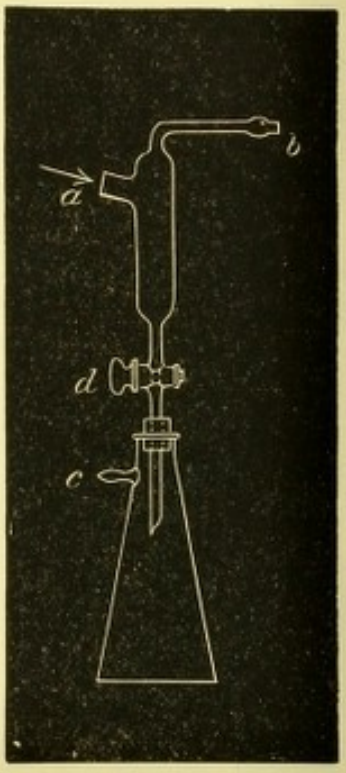


Fig. 38.

The distilling flask is provided with a finely-drawn tube fitted outside with an india-rubber tube and a screw-clamp, by means of which the pressure can be regulated accurately, and at the same time frothing of the liquid can be prevented. Nozzle *a* of the adapter (Fig. 38) is connected with a Liebig condenser, and *b* and *c* by means of strong india-rubber tubing with two taps of a vacuum pipe. On starting the distillation, the distilling flask, the adapter, and the conical receiving flask are exhausted through *b* and *c*, the stopcock *d* being open. When the first fraction has distilled over, close the tap *d* and then the vacuum tap connected with *c*. The receiving flask is thus shut off from the vacuum pipe, and is filled with air by disconnecting the india-rubber tubing from *c*. The flask can be taken off easily and emptied, or replaced by another, whilst the distillation proceeds without any interruption. When the receiving flask is fitted on again it is exhausted through *c*, as before, and connected with the system by opening tap *d*.

B. Examination of the Basic Constituents

All fats yield on saponification **Glycerol**, and it is therefore only necessary to determine its proportion. This is done by the methods detailed, p. 208.

The waxes yield as basic constituents alcohols of the aliphatic series, or cholesterols. Any hydrocarbons contained in the waxes are isolated together with the former as "*unsaponifiable matter.*"

If a mixture of alcohols has been obtained, the isolation of the individual alcohols may be effected by fractional crystallisation. It will be found useful to convert the alcohols into their benzoic or acetic

[1] *Jour. Chem. Soc.* 1889, Trans. 360.

ethers; the latter are easier to distil than the original substances, and can therefore be more effectively resolved into fractions (cp. also p. 229).

3. General Methods of Quantitative Analysis of Fats, or Mixed Fats and Waxes

In the quantitative analysis of a fat, or a mixture of different fats, or of fats and waxes, we have, in the first place, to determine its proximate components, viz. alcohols (as glycerol, cetyl alcohol, etc.) and fatty acids (as oleic acid, palmitic acid, etc.); secondly, we have to examine it for the presence of foreign bodies in admixture, such as mineral oils, resin, etc., and ascertain their proportion and character.

The determination of these latter substances will be discussed in the following two chapters. Here we consider the examination of the dried fat or wax as obtained in the manner described (p. 92), with a view to determine its proximate constituents.

Though we cannot make our examination with strictly scientific accuracy, there are a number of methods answering very satisfactorily the requirements of technical analysis, and these may conveniently be arranged under two heads as follows:—

A. Quantitative Reactions, and
B. Quantitative Determination of some Constituents of Fats and Waxes.

Besides the "quantitative reactions" we have a number of chemical reactions, which are usefully applied to the examination of fatty substances, such as the elaïdin test, oxygen absorption test, thermal tests, etc.

But hitherto they have not been worked out so fully as to admit of their being classed amongst the quantitative reactions, although in all probability at least some of them are likely to attain to that rank. Meanwhile we must look upon them as preliminary tests, that can be usefully employed as sorting tests, especially for purposes of classifying the liquid fats and waxes. For these reasons the "preliminary tests" will be described later on, where the application of the physical and chemical methods to the systematic examination of fatty substances is dealt with.

A. QUANTITATIVE REACTIONS

The methods described under this head, although generally not admitting of an absolute estimation of the constituents of a fat or wax, are of the greatest help in technical analysis, inasmuch as they afford a means for a comparative determination of the most important constituents. Thus we are enabled to ascertain—

i. The ACID VALUE—the measure of the proportion of free fatty acids in a fat or wax.

ii. The SAPONIFICATION VALUE (KÖTTSTORFER VALUE) — the measure of the amount of alkali requisite for neutralising the total fatty acids.

iii. The ETHER VALUE—the measure of the proportion of triglycerides or other compound ethers of fatty acids present in a fat or wax.

iv. The REICHERT (or REICHERT-MEISSL) VALUE—the measure of the proportion of volatile fatty acids.

v. The HEHNER VALUE—the percentage of insoluble fatty acids.

vi. The ACETYL VALUE—the measure of the proportion of hydroxy acids or free alcohols.

vii. The (BROMINE or) IODINE VALUE—the measure of the proportion of unsaturated fatty acids.

i. The Acid Value

The acid value indicates the number of milligrammes of potassium hydrate required to saturate the free fatty acids in one gramme of a fat or wax; or, in other words, *it gives the amount of potassium hydrate, expressed in tenths per cent, necessary to neutralise the free fatty acids in one gramme of a fat or wax.* This value is therefore a measure of the free fatty acids in a fat or wax.

For the determination of the acid value of a fat or wax the sample is dissolved in alcohol (purified methylated spirit), or in methyl alcohol, or a mixture of alcohol and ether, and titrated with aqueous or alcoholic standard alkali, phenolphthalein being used as indicator.

The standard alkali may be, according to the quantity of fat available for the analysis, half-, or fifth-, or tenth-normal. Some analysts prefer an alcoholic standard solution to an aqueous, although the accuracy of the analysis is hardly increased thereby. On the contrary, an alcoholic standard solution has the drawback of altering its titer more quickly, and therefore requiring occasional re-standardising. The alcoholic alkali is prepared by dissolving the requisite quantity of caustic potash or caustic soda in the smallest possible quantity of water, and making the solution up to the required standard with alcohol, purified as described above (p. 19). The end-point of titration is distinctly recognisable, saponification of the neutral fat not taking place immediately by the small excess of alkali necessary to produce the pink colouration. On standing, however, for some time, even if access of air and consequent decolouration by absorption of carbonic acid be excluded, the pink colour will disappear in some cases, owing to saponification of neutral ethers [1] taking place. This will be especially the case if the specimen under examination were dissolved in ether-alcohol. It would, obviously, be erroneous to add more alkali from time to time as the pink colouration disappears.

[1] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1890, 846.

Mineral acid in the oil should, of course, be first removed by washing with water, and the solvents employed should be tested for acidity. Before using the solvent it will be found a good plan to neutralise it exactly with decinormal alkali, phenolphthalein being the indicator.

Liquid fats are weighed off or measured off accurately in a flask, neutralised alcohol and a few drops of phenolphthalein solution are then added, and the liquid is titrated with constant shaking. Convenient quantities are 10 grms. (or 10 c.c.) of oil and 50 c.c. of alcohol, to be titrated with $\frac{1}{5}$ normal alkali.

Solid fats must be heated with the alcohol on the water-bath until the alcohol boils; they are then titrated in the same manner. Should the fat solidify during the operation, the flask must be heated again before the titration can be brought to an end. Of course, to guard against partial saponification of the neutral fat, excess of alkali must be avoided. If it should be deemed preferable to work with clear solutions, the fat may be dissolved in a mixture consisting of two parts of ether and one part of alcohol, and then titrated with alcoholic standard solution. *Archbutt* proposes to use as solvent methyl alcohol purified by distilling it twice.

One or two examples will illustrate clearly the method of calculating the acid value.

1. Weighed off 3·254 grms. of tallow. Required for neutralising the free fatty acids 3·5 c.c. decinormal caustic potash (or soda) or 3·5 × 5·61 milligrms. KOH. The amount of KOH required for one grm. of tallow, or its acid value, is therefore

$$A = \frac{3{\cdot}5 \times 5{\cdot}61}{3{\cdot}254} = 6{\cdot}03.$$

2. Measured off 25 c.c. of olive oil, spec. grav. 0·917. Required for neutralising the free fatty acids 9·4 c.c. of a solution of caustic potash, 1 c.c. of which contains 0·0257 grm., or 25·7 milligrms. KOH. The weight of the oil is 25 × 0·917 = 22·925 grms., therefore

$$A = \frac{9{\cdot}4 \times 25{\cdot}7}{22{\cdot}925} = 10{\cdot}5.$$

The proportion of free fatty acids in a fat is frequently expressed in a different manner.

In this country, especially in the case of oils, it is usual to calculate the free acid as oleic acid, molecular weight 282, and to express the amount of free fatty acids in per cents of the fat. Thus in the first example the percentage of free fatty acids would be given as

$$\frac{3{\cdot}5 \times 0{\cdot}0282}{3{\cdot}254} \times 100 = 3{\cdot}03\ \%,$$

and in the second example

$$\frac{9{\cdot}4 \times 0{\cdot}0257 \times 0{\cdot}282}{0{\cdot}0561 \times 22{\cdot}925} \times 100 = 5{\cdot}28\ \%.$$

Since the molecular weight of oleic acid, 282, is approximately five times 56·1, the molecular weight of KOH, and the acid value expresses the amount of KOH in tenths per cent, a rapid and in most cases sufficiently accurate method of converting the acid value into per cents of oleic acid is to multiply the former by 0·5.

In other cases, as for lubricating oils, the free fatty acids are sometimes expressed in terms of sulphuric anhydride, SO_3, and the result is given in per cents of the fat employed. Thus in the first example we should find

$$\frac{3{\cdot}5 \times 0{\cdot}004}{3{\cdot}254} \times 100 = 0{\cdot}43\ \%,$$

and in the second

$$\frac{9{\cdot}4 \times 0{\cdot}0257 \times 0{\cdot}04}{0{\cdot}0561 \times 22{\cdot}925} \times 100 = 0{\cdot}75\ \%,$$

Köttstorfer expresses the acidity by the number of c.c. of normal potash required by 100 grms. of the fat. In this connection the number of c.c. is termed "degrees of acidity."

In the subjoined table a comparison is made of the different methods of expressing the acidity; an easy calculation allows of transforming one term into any other.

Acid Value, being $\frac{1}{10}$ per cent of KOH.	Oleic Acid. Per cent.	Sulphuric Anhydride. Per cent.	Degrees Köttstorfer, being c.c. normal KOH per 100 grms. Fat.
1	0·5027	0·0713	1·782
1·9893	1	0·1418	3·546
14·0250	7·0500	1	25·000
0·5610	0·2820	0·0400	1

In case the nature of the free acid, and consequently its molecular weight, be known, the absolute quantity of free fatty acids may be calculated as shown above for oleic acid. In such cases the following table may be found useful:—

Acid Values of Some Fatty Acids

Acid.	Formula.	Molecular Weight.	Acid Value.
Butyric	$C_4H_8O_2$	88	636·3
Caproic	$C_6H_{12}O_2$	116	482·8
Capric	$C_{10}H_{20}O_2$	172	325·0
Lauric	$C_{12}H_{24}O_2$	200	280·0
Myristic	$C_{14}H_{28}O_2$	228	245·5
Palmitic	$C_{16}H_{32}O_2$	256	218·7
Stearic	$C_{18}H_{36}O_2$	284	197·1
Oleic	$C_{18}H_{34}O_2$	282	198·6
Linolic	$C_{18}H_{32}O_2$	280	200·0
Ricinoleic	$C_{18}H_{34}O_3$	298	188·0
Erucic	$C_{22}H_{42}O_2$	338	166·0
Cerotic	$C_{26}H_{52}O_2$	396	141·7

ii. The Saponification Value (Köttstorfer Value)

The saponification value (or Köttstorfer value) indicates the number of milligrammes of potassium hydrate required for the complete saponification of one gramme of a fat or wax; or, in other words, *it represents the amount of potassium hydrate, expressed in tenths per cent, requisite to neutralise the total fatty acids in one gramme of a fat or wax.*

For the determination of the saponification value are required—(1) An accurately standardised hydrochloric acid solution, the titer of which is expressed in terms of KOH; it is most convenient to use half-normal acid; (2) an alcoholic potash solution prepared by dissolving about 30 grms. of caustic potash, pure from alcohol, in a little water, and making it up with strong alcohol to 1000 c.c. The alcoholic solution is allowed to stand for one day, and is then filtered through a large plaited filter into a bottle, conveniently closed by an india-rubber stopper fitted with a 25 c.c. pipette, the upper end of the pipette being closed in its turn by a short piece of india-rubber tubing and a clamp, or a glass rod. The bottle should be kept in an equably warm place protected from light.

The alcohol used for preparing the potash solution should be as pure as possible. Commercial spirits of wine tested with a strong caustic potash solution should remain white; if it becomes yellow immediately, it must be rejected. Methylated spirit may be used, but it must be purified as described, p. 19. If the alcohol has been pure, the alcoholic potash will not become brown even after several months' standing; it assumes, however, in course of time a light yellow colouration, but this does not interfere with the accuracy of the titration.

The determination of the saponification value is carried out as follows: Weigh off accurately, in a flask holding 150 to 200 c.c., 1·5 to 2 grms. of the purified and filtered fat. Next run into the flask 25 c.c. of the alcoholic potash, measuring it off by means of the pipette fitted in the stopper of the bottle. It is not necessary to add exactly 25 c.c., but care must be taken that for each determination precisely the same quantity is used. A good plan is to allow the contents of the pipette to run out entirely, and to drain it until, say, three more drops have dropped off. Then attach a long cooling tube or an inverted condenser to the flask, and heat it on the boiling water-bath for half an hour so that the alcohol is simmering, frequently imparting to the contents of the flask a rotatory motion. Next add 1 c.c. of a one per cent phenolphthalein solution, and titrate back the excess of potash with the half-normal hydrochloric acid.

It is always best to make a blank test, treating the same amount of alcoholic potash in exactly the same manner[1] as the solution of fat. Every source of error, as carbonic acid, etc., has therefore, as nearly as possible, in both tests the same influence on the final result, and is thus eliminated. The difference of the numbers of c.c. of acid

[1] This should extend as well to the material of the flask. Cheap German flasks are attacked by the alkali to a considerable extent. It is best to use flasks made of Bohemian or Jena glass.

used for the blank test and the real test corresponds to the quantity of potash required; this is calculated to milligrms. of potash for one grm. of fat.

Sulphuric acid should not be substituted for the hydrochloric acid, potassium sulphate being precipitated, whereby the delicacy of the end reaction is impaired.

For *Henriques'* method cp. chap. ii. p. 20.

In the case of dark-coloured solutions M'Ilhiney[1] proposes to measure the amount of alkali used, by the amount of ammonia it will liberate from an ammonium salt. He proceeds as follows: The substance (2 grms.) is saponified with excess of alcoholic caustic soda as usual, and the alcohol evaporated off. 250 c.c. of 93 per cent alcohol are added next, the soap dissolved by warming, and carbon dioxide passed through the solution for about one hour, in order to precipitate the excess of alkali as carbonate and bicarbonate. The precipitate is then filtered off, the alcohol evaporated from the filtrate, and 100 c.c. of a 10 per cent solution of ammonium chloride added, and heated, whereby the ammonia is distilled off. It is received in hydrochloric acid and titrated. A correction must, of course, be made for the sodium bicarbonate dissolved by the 93 per cent alcohol. This process is cumbersome and certainly introduces errors; it is by far simpler to dilute the soap solution with sufficient alcohol, so as to obtain a distinct end reaction [or to employ as indicator alkali-blue (*De Negri* and *Fabris*)].

Example.—Weighed off 1·532 grms. of olive oil, and saponified with 25 c.c. of alcoholic potash solution. Required for titrating back 12·0 c.c. half-normal acid; further, required for the blank test 22·5 c.c. of the same acid. Therefore employed for saponification a quantity of caustic potash corresponding to

$$\frac{(22{\cdot}5 - 12{\cdot}0)\ 0{\cdot}0561}{2} \text{ grms.} = 294{\cdot}5 \text{ milligrms. KOH.}$$

Hence

$$\text{Used for one grm. of fat } \frac{294{\cdot}5}{1{\cdot}532} \text{ milligrms. KOH} = 192{\cdot}2 \text{ milligrms. KOH.}$$

The saponification value of the olive oil is therefore 192·2.

Allen[2] has proposed to use instead of the saponification value as defined here the *saponification equivalent*, this being the number of grammes of fat saponified by one equivalent of potassium hydrate in grammes, *i.e.* by 56·1 grms. KOH; or, what amounts to the same, by one litre of a normal solution of caustic potash or caustic soda. The saponification equivalent is found by dividing the percentage of potassium hydrate required for saponification into 5610.

There is no advantage gained by expressing this important value in the manner proposed by *Allen*, and we shall therefore adhere to the use of the saponification value as adopted above. The relation between

[1] *Jour. Soc. Chem. Ind.* 1895, 197.
[2] *Commercial Organic Analysis*, ii. 40.

the *saponification value* and *Allen's saponification equivalent* is shown by the following formulæ :—

$$\text{Sap. Val.} = \frac{\text{c.c. of normal potash} \times 56{\cdot}1}{\text{grms. of fat employed}} = \frac{\text{c.c. of normal potash} \times 56100}{\text{milligrms. of fat employed}}$$

$$\text{Sap. Equiv.} = \frac{5610}{\text{per cent KOH}} = \frac{5610}{\frac{\text{c.c. of normal potash} \times 0{\cdot}0561}{\text{grms. of fat employed}} \times 100}$$

$$= \frac{\text{grms. of fat employed} \times 5610}{\text{c.c. of normal potash} \times 5{\cdot}61} =$$

$$= \frac{\text{grms. of fat employed} \times 1000}{\text{c.c. of normal potash}} =$$

$$= \frac{\text{milligrms. of fat employed}}{\text{c.c. of normal potash}}$$

or, if a be the number of c.c. of normal potash, and b the number of milligrms. of fat employed :

$$\text{Sap. Val.} = \frac{a}{b} \times 56100 \; ; \; \text{Sap. Equiv.} = \frac{b}{a}.$$

Hence it is clear that *Allen's* saponification equivalent can be found by dividing 56100 by the saponification value ; conversely, the saponification value is obtained by dividing 56100 by the saponification equivalent :

$$\text{Sap. Val.} = \frac{56100}{\text{Sap. Equiv.}} \; ; \; \text{Sap. Equiv.} = \frac{56100}{\text{Sap. Val.}}$$

The saponification value of neutral glycerides and other ethers of fatty acids varies, of course, with the nature of the fatty acids ; the lower the molecular weight of the fatty acids (or, what amounts to the same, of the ethers) the more potash will be required to neutralise the fatty acids of one grm. of fat or wax, or, in other words, the higher will the saponification value be. To illustrate this more clearly, we give in the following tables the saponification values of some pure triglycerides and some pure ethers of mono-atomic alcohols :—

Saponification Values of Triglycerides

Triglyceride.	Formula.	Molecular Weight.	Saponific. Value.
Butyrin . .	$C_3H_5(O.C_4H_7O)_3$	302	557·3
Valerin . .	$C_3H_5(O.C_5H_9O)_3$	344	489·2
Caproin . .	$C_3H_5(O.C_6H_{11}O)_3$	384	438·3
Caprin . .	$C_3H_5(O.C_{10}H_{19}O)_3$	552	305·0
Laurin . .	$C_3H_5(O.C_{12}H_{23}O)_3$	638	263·8
Myristin . .	$C_3H_5(O.C_{14}H_{27}O)_3$	722	233·1
Palmitin . .	$C_3H_5(O.C_{16}H_{31}O)_3$	806	208·8
Stearin . .	$C_3H_5(O.C_{18}H_{35}O)_3$	890	189·1
Olein . .	$C_3H_5(O.C_{18}H_{33}O)_3$	884	190·4
Linolin . .	$C_3H_5(O.C_{18}H_{31}O)_3$	878	191·7
Ricinolein . .	$C_3H_5(O.C_{18}H_{33}O_2)_3$	932	180·6
Erucin . .	$C_3H_5(O.C_{22}H_{41}O)_3$	1052	160·0

Saponification Values of Ethers of Mono-atomic Alcohols

Ether.	Formula.	Molecular Weight.	Saponific. Value.
Cetyl palmitate	$C_{16}H_{31}O \cdot OC_{16}H_{33}$	480	116·9
Myricyl palmitate	$C_{16}H_{31}O \cdot OC_{30}H_{61}$	676	83·0
Ceryl cerotate	$C_{26}H_{51}O \cdot OC_{26}H_{53}$	760	73·1

Frequently the term "saponification number of fatty acids" is met with; the saponification value of a fatty acid is, of course, identical with its acid value (cp. table, p. 150).

In the tables given in chap. xi. I shall use the term saponification value of the fatty acids in order to avoid confusion between "acid value of the fat" and "acid value of the fatty acids." The latter value is a "constant," whereas the acid value of a fat varies.

iii. The Ether Value

The ether value indicates the number of milligrammes of potassium hydrate required for the saponification of the neutral ethers in one gramme of a fat or wax.

It is evident that the ether value will be identical with the saponification value if the fat or wax contains no free fatty acids, or, in other words, is quite neutral.

As a rule, however, fats and waxes contain small quantities of free fatty acids, and in that case the saponification value will be the sum of the acid and ether values. The ether value is therefore represented by the difference of the saponification and acid values.

The ether value can be found direct by first neutralising a weighed sample with alcoholic potash, as in the determination of the acid value (see above), and then saponifying with alcoholic potash as detailed in the preceding paragraph.

Fatty acids have, of course, no ether values, their acid and saponification values being identical (cp., however, p. 206).

iv. The Reichert (or Reichert-Meissl) Value

The Reichert (or Reichert-Meissl) value indicates the number of cubic centimetres of decinormal potash requisite for the neutralisation of that portion of the volatile fatty acids which is obtained from 2·5 *(or* 5*) grammes of a fat or wax by the Reichert distillation process.*

There is no convenient method in use to determine quantitatively the amount of volatile fatty acids in a fat. *Reichert*[1] was the first to suggest a process (in the examination of butter) for estimating a

[1] *Zeitsch. f. analyt. Chemie*, 18. 68.

definite proportion thereof; although not yielding absolute values, still it constitutes a valuable method by furnishing numbers which are comparable.

Reichert originally proposed to ascertain the number of c.c. of decinormal alkali required for the saturation of the volatile fatty acids from 2·5 grms. of a fat, but at present it is customary to work according to *Meissl's* modification, employing 5 grms. of substance.

In order to avoid errors, therefore, the quantity of fat to which the value found relates should always be stated. In the following pages the *Reichert* value always refers to 2·5 grms. of fat, and the *Reichert-Meissl* value to 5 grms. of fat.[1]

The *Reichert* value being an arbitrary one, it is absolutely essential to adhere strictly to the conditions of operating as laid down by the different authors whose processes will be described. We subdivide these into two groups :—

(*a*) *Processes in which the Volatile Fatty Acids are distilled off.*

Reichert's Process with Meissl's Modification.—Weigh off accurately 5 grms.[2] of the melted and purified fat in a flask of about 200 c.c. capacity, and add to it about 2 grms. of stick potash (conveniently kept in stock in pieces of about the same length) and 50 c.c. of 70 per cent alcohol. Saponify by heating on the water-bath with constant shaking, until the alcohol has evaporated off completely. Dissolve the remaining soap paste in 100 c.c. of water, add 40 c.c. of dilute sulphuric acid (1 : 10) and a few small pieces of pumice. Fit to the flask a T piece provided with a bulb, and connect with a Liebig condenser. Distil the liquid carefully so that 110 c.c. pass over within about one hour's time. They are received in a measuring flask, and 100 c.c. of it filtered into another measuring flask. Add to the filtered liquid tincture of litmus or phenolphthalein, and titrate with decinormal caustic potash until the acid is exactly neutralised. The number of c.c. used is multiplied by 1·1, and thus the *Reichert-Meissl* value obtained. (About half of this is the Reichert value.)

Thus, if for 5 grms. of butter fat 28 c.c. of decinormal caustic alkali were required, the *Reichert-Meissl* value of that butter fat is 28.

It is hardly necessary to emphasise the necessity of using alcohol free from acid and aldehyde. The safest plan will be to work a blank test side by side with the sample, and to take the difference found as the actual result. Even with the purest alcohol a slight acidity will be noticeable in the blank test. *Schweissinger*[3] has found for a sample of absolute alcohol a *Reichert-Meissl* value of 0·56, and for a sample of purest commercial alcohol 1·32. Impure alcohol gives rise to the formation of acetic acid and should therefore be rejected altogether.

It should be distinctly understood that by this distillation process a portion only of the volatile fatty acids is recovered. *Richard Meyer*

[1] It should be noted that the Reichert-Meissl value is not necessarily twice the Reichert value.

[2] *Dingl. Polyt. Jour.* 233. 229.

[3] *Pharmac. Centralhalle*, 8. 320.

has shown that on distilling in a current of steam a value greater by 25 per cent is obtained. Hence the necessity of always working under strictly the same conditions.

Along with the volatile acids traces of higher fatty acids will pass over; they will be found in the distillate as minute oily drops or solid particles; but they do not vitiate the result, as they are removed by the subsequent filtration.

The excellent *Reichert* process has not escaped the fate of nearly all modern methods used in fat analysis, viz. to receive at the hands of numerous analysts a number of supposed improvements, most of which are altogether insignificant and hardly offer any advantage whatever.

Thus *Munier* and others proposed to substitute phosphoric acid for sulphuric acid[1]; but *Cornwall*[2] has shown that the values obtained are too low. *Wollny*[3] has raised a number of objections to the foregoing process, pointing out the following sources of error:—(1) absorption of carbonic dioxide during the saponification, introducing an error up to 10 per cent; (2) formation of ethers during the saponification, causing a loss of 8 per cent; (3) formation of ethers during the distillation with a loss of 5 per cent; (4) coherence of the fatty acids during the distillation, which may, in some cases, involve a loss of as much as 30 per cent; (5) the form and size of the distillation apparatus and the time the distillation lasts, which may influence the result to the extent of ± 5 per cent.

These objections have been refuted by *v. Raumer* and *Sendtner*. However, as a number of determinations, carried out by various chemists according to *Wollny's* somewhat too detailed modifications, have found a place in the literature of the subject, his process may be described fully.

Wollny's Modification.—5 grms. of the clarified fat are treated in a round-bottomed flask of 300 c.c. capacity (length of neck 7-8 cm., width of neck 2 cm.) with 2 c.c. of a 50 per cent caustic soda solution, free from carbonic dioxide, and 10 c.c. of 96 per cent (by volume) alcohol on the boiling water-bath for 15 minutes, the flask being connected with an inverted condenser. Next the alcohol is distilled off by immersing the flask for at least half an hour in boiling water, and then 100 c.c. of distilled water are added. The flask is kept for another quarter of an hour, protected from carbon dioxide in the air, in the boiling water-bath to ensure complete solution of the soap. The clear solution is then cooled down to 50°-66° C., but not lower, by allowing water to run over the flask and 40 c.c. of dilute sulphuric acid (25 c.c. of D. O. V. in 1000 c.c. of water; 30-35 c.c. of this acid should neutralise 2 c.c. of the caustic soda used), and two small pieces of pumice are quickly added. The flask is immediately connected with a condenser, a T piece of 7 mm. diameter with a bulb of 20-25 mm. diameter, and having the side-tube bent twice at an

[1] Sulphuric acid might liberate from any potassium chloride present (contained in the commercial caustic potash) hydrochloric acid, which phosphoric acid does not.

[2] *Chemical News*, 53. 20.

[3] *Jour. Soc. Chem. Ind.* 1887, 831.

angle, being interposed between the two. The contents of the flask are warmed at first by a gentle heat until the insoluble acids are just melted to a clear transparent layer, when the temperature is raised, so that 110 c.c. may pass over in half an hour. The distillate is well mixed by shaking up, and 100 c.c. of it are filtered into a measuring flask. This quantity is poured out into a beaker, and titrated with decinormal baryta solution, phenolphthalein being used as indicator (0·5 grms. of phenolphthalein dissolved in 1000 c.c. of 50 per cent alcohol). When the solution has become pink, it is poured back into the flask to rinse it out, and baryta added again, until a faint pink colouration remains. The number of c.c. thus found is multiplied by 1·1. A blank experiment is conducted under exactly the same conditions, and the number of c.c. found—which, however, should not exceed 0·33 c.c.—subtracted from the result. *Sendtner*, who maintains that the *Reichert-Meissl* process yields quite as good results as *Wollny's*, adopts the titration with decinormal baryta solution, but saponifies in a flask of 300-350 c.c. capacity with 10 c.c. of an alcoholic potash, prepared by dissolving 20 grms. of potassium hydrate in 100 c.c. of alcohol of specific gravity 0·889. In order to remove the last traces of alcohol air is blown into the flask before dissolving the soap. *Sendtner's* results differ from *Wollny's* by 2·4 per cent at the most. Working after *Wollny's* modification, as a rule, less baryta water is used than in *Reichert-Meissl's* process.

The well-known fact that in the *Reichert* distillation process only part of the volatile acids is distilled off[1] has induced some analysts to modify it in the attempt to obtain the total quantity. Thus it has been proposed to repeat the distillation several times with fresh quantities of water. But not only does this take up more time than can be conveniently allowed for a technical analysis, but a cause of error is thereby introduced, as *v. Raumer* has shown that with each distillation decomposition of the non-volatile acids takes place. *Goldmann*, again, suggests for the same purpose distillation in a current of steam, which is continued until 100 c.c. of the distillate require no more than 0·05 c.c. of decinormal baryta. His most elaborately detailed process, for a description of which the reader must be referred to the *Journal of the Society of Chemical Industry* (1888, 238 and 349), is far too complicated for practical use. Besides, if we consider that in an experiment carried out with 5 grms. of butter fat, the first 100 c.c. required 24·25 c.c., and the following 100 c.c. severally, 1·40, 0·55, 0·35, 0·25, 0·20, 0·15, 0·15, 0·20, 0·10, 0·10, 0·10, until at last the thirteenth 100 c.c. took only 0·05, it looks more like the distortion of a valuable process than a quantitative analysis. At best, *Goldmann's* process may be used as a method for completely separating the volatile acids from the non-volatile.—*Beal*[2] distils in a current of steam, and is satisfied with distilling over 500 c.c.

[1] Thus *H. D. Richmond* states (*Analyst*, 1895, 218) that by the Reichert-Wollny process, in the case of butters, only about 87 per cent of the total volatile acids is found in the distillate. I found for 2·5 grms. butter by distilling 500 c.c. the number of c.c. decinormal potash required = 22.

[2] *Jour. Soc. Chem. Ind.* 1895, 197.

In order to obviate the formation of ethylic ethers of the volatile fatty acids (*Wollny's* second objection), *Mansfeld*[1] proposes saponification with strong aqueous alkali in a closed flask without addition of alcohol, whilst *Schmidt*[2] substitutes glycerin for alcohol, as has been done before him by *Leffmann* and *Beam*[3] (cp. chap. xi. p. 632).

Instead of saponifying the fat with alkali, *Kreiss* recommends, especially for butter fat, saponification with concentrated sulphuric acid. The volatile acids are then distilled off and titrated, as described above for the *Reichert* method. The details of the method and a criticism thereof will be given later on under the heading "Butter Fat" (chap. xi. p. 635).

(b) Processes by which the Volatile Fatty Acids are not distilled off.

The volatile fatty acids being likewise those soluble in water, several methods have been proposed having for their object the determination of the *soluble* acids. The values thus obtained nearly coincide with those obtained by the distillation process.

1. *Bondzyński and Rufi's*[4] *Method.*—Four or five grms. of a dry and filtered fat are saponified with 50-60 c.c. of half-normal alcoholic potash, and the excess of potash neutralised with half-normal hydrochloric acid (cp. determination of the Saponification Value). The alcohol is evaporated off, the soap decomposed with hydrochloric acid, and the liberated fatty acids washed on a filter with hot water (see p. 160). The insoluble acids are then dissolved in alcohol, and titrated with half-normal hydrochloric acid. By subtracting the number thus found from the quantity used for saponification, the number of c.c. required for the neutralisation of the soluble (volatile) fatty acids will be obtained. The amount calculated for 5 grms. is the *Reichert-Meissl* value.

Thus, if for the saponification of 4·573 grms. of butter fat 1040 milligrms. KOH, and for the neutralisation of the insoluble acids 910 milligrms. have been used, the difference of 130 milligrms. will correspond to the alkali required for the soluble acids. The soluble acids from 5 grms. of fat require, therefore, 142 milligrms. of KOH, which equals 25·3 c.c. of decinormal caustic potash (1 c.c. of decinormal caustic potash containing 5·61 milligrms. KOH). The *Reichert-Meissl* value of the butter fat under examination is, therefore, 25·3.

2. The same value can be also obtained directly (*Morse* and *Burton*,[5] *Bondzyński* and *Rufi*, *Planchon*[6]) by operating in the following manner:—Saponify 4-5 grms. of a fat with 50-60 c.c. of standardised alcoholic potash. Evaporate off the alcohol, dissolve the soap in water, and

[1] *Jour. Soc. Chem. Ind.* 1888, 526. [2] *Ibid.* 1893, 467.
[3] *Analyst*, 1891, 153; cp. also *Karsch. Chem. Ztg.* 1896, 207.
[4] Bondzyński and Rufi, *Jour. Soc. Chem. Ind.* 1890, 44.
[5] *Jour. Soc. Chem. Ind.* 1888, 697. [6] *Moniteur scient.* 1888, 1096.

add an amount of standardised sulphuric acid *exactly* corresponding to the caustic potash used. Filter off the liberated acids, wash with boiling water, and titrate the filtrate with decinormal alkali. The number of c.c. used, calculated for 5 grms. of substance, gives the *Reichert-Meissl* value. It is evident that by adopting this method the saponification value and *Hehner* value may be determined in *one* operation. The saponification value is determined first as described above, by neutralising the excess of caustic potash with standardised hydrochloric acid. The solution is then diluted with water, the alcohol driven off by boiling down, and as much decinormal hydrochloric acid added as exactly liberates the fatty acids, the quantity required for which can be easily calculated from the saponification value.

Morse and *Burton's* method will be fully described under "Butter Fat" (chap. xi. p. 631).

3. *G. Firtsch*[1] and, after him, *J. König* and *F. Hart*[2] have proposed to neutralise the soluble fatty acids by baryta, and to determine the latter quantitatively. *Firtsch* saponifies with an aqueous solution of barium hydroxide in a closed vessel, *i.e.* under pressure, whilst *König* and *Hart* boil an alcoholic solution of the fat with baryta water under ordinary pressure. It is doubtful whether by these processes complete saponification of the fat can be obtained. *König* and *Hart* operate as follows:—5 grms. of the fat are mixed in a graduated 300 c.c. flask with 60 c.c. of alcohol, the mixture is heated on the water-bath, and 40 c.c. of hot baryta water (17·5 of barium hydroxide in 100 c.c.) added. The flask is connected with an inverted condenser, and its contents are boiled for 3-3½ hours. When cold, water is added to the 300 c.c. mark, and after mixing thoroughly, 250 c.c. are filtered off, and treated with carbonic anhydride until the alkaline reaction has disappeared. The liquid is then evaporated nearly to dryness on the water-bath, allowed to cool, and water added gradually with constant stirring. After making up to 250 c.c., 200 c.c. are filtered off, and the baryta determined in the filtrate by precipitation with sulphuric acid. The barium sulphate obtained is calculated to barium oxide, and expressed in milligrms. The number found is multiplied by 1·5, and this amount of barium oxide, corresponding to 5 grms. of the fat, is termed *baryta value.*

The baryta value indicates the number of milligrammes of BaO *contained in the soluble barium salts from* 5 *grms. of a fat.* Thus a butter fat, the *Reichert-Meissl* value of which was 27·5, had a *baryta value* of 236·0. The authors of this method are of opinion that it is simpler and more reliable than *Reichert's* process. *H. Kreiss* and *W. Baldin*,[3] and *Laves*,[4] however, have shown that the baryta method by no means yields any better results than the distillation process.

It is unlikely that the "baryta value" will obtain much favour among analysts.

[1] *Dingl. Polyt. Jour.* 278. (1890), 422. [2] *Jour. Chem. Soc.* 1891 ; Abstracts, 1301.
[3] *Schweiz. Wochenschr. Chem. Pharm.* 1892, 189.
[4] *Arch. f. Pharmacie*, 1893, 356.

v. The Hehner Value

The Hehner value indicates the proportion of insoluble fatty acids in a fat or wax.

This important number may be determined by one of the following methods :

(*a*) *Hehner's Method.*[1]—Weigh accurately the purified fat contained in a small beaker furnished with a glass rod, and pour about 3-4 grms. (the exact quantity being determined by re-weighing) into a porcelain dish of about 5 inches diameter. Add 50 c.c. of alcohol and 1-2 grms. of solid caustic potash, and heat on the water-bath with constant stirring until a clear solution is obtained. After about five minutes allow one drop of distilled water to fall into the solution. If the saponification is complete the solution will remain clear; if, however, a turbidity is noticed, the heating must be continued until this test indicates that all the fat has been saponified. Then boil down the clear solution of soap to pastiness, dissolve in 100 to 150 c.c. of water, and acidify with hydrochloric or dilute sulphuric acid. Next heat the liquid until the liberated fatty acids float on the top as a clear oily layer. Filter through a paper of about 4-5 inches diameter, previously dried at 100° C. and accurately weighed. The filter-paper should be of stout material, ordinary filtering paper readily allowing the liquid to run through turbid. A good plan is to have the filter half full of hot water before any fatty matter is transferred on to it, keeping it full till all the liquid is added. Finally wash the fatty acids on the filter with boiling water until a few c.c. of the wash-water does not redden sensitive tincture of litmus. (*Fleischmann* and *Vieth*[2] recommend to wash until the extremely weak acid reaction, produced by 5 c.c. of the filtrate and one drop of tincture of litmus, does not appear to lose its intensity in successive tests.) For 3 grms. of fat sometimes 2000 to 3000 c.c. of wash-water are required in order to completely remove the last traces of the acids occupying an intermediate place between soluble and insoluble acids (as lauric acid). The washing being completed, immerse the funnel with the filter in a vessel of cold water, so that the water outside and the acids inside are at the same level. As a rule, the fatty acids will solidify. Allow the water then to drain off, transfer the filter to a tared beaker, and dry at 100° C. for two hours. Weigh accurately, dry for another two hours and a half, and weigh again. The difference between the two weights will, as a rule, be below one milligrm. Completely concordant results cannot be expected, the two chief sources of error, however, tending to compensate each other,—one causing an increase, the other a decrease in weight. For on the one hand the unsaturated acids may become oxidised, whilst on the other hand loss is incurred through a very slight volatilisation of fatty acids (cp. below B. Quant. Determ., etc., p. 180).

[1] *Zeitsch. f. analyt. Chemie*, 76. 145. [2] *Ibid.* 17. 287.

(*b*) *Dalican's Modification.*[1]—*Hehner's* process has been modified by *Dalican* in the following fashion :—Melt 10 grms. of fat in a flask of 250 to 300 c.c. capacity, and saponify with 80 c.c. of 85 per cent alcohol and a solution of 6 grms. of caustic soda in 6 to 8 c.c. of water on the water-bath. The saponification will, as a rule, be complete after thirty to forty minutes. Leave the flask on the water-bath until all the alcohol has evaporated off, dissolve the soap in 150 c.c. of water, and add gradually, in small quantities, 25 c.c. of hydrochloric acid (1 volume of concentrated acid diluted with 4 volumes of water), agitating the contents of the flask after each addition of acid. Heat the flask for another thirty minutes on the water-bath, until the fatty acids have separated on the top as a transparent oily layer, then remove the flask from the bath and cool thoroughly. After about two hours break the cake of fatty acids with a glass rod, and pour off the liquid through a plain filter. Then melt the fatty acids over 100 c.c. of boiling water and add 150 c.c. more boiling water. Allow to stand forty minutes, cool thoroughly, and proceed as before. Repeat this process of washing until litmus paper dipped in the wash-water does not turn red after twenty minutes' standing. As a rule, eight to ten washings will be found sufficient for the complete removal of the soluble fatty acids. Next transfer the insoluble fatty acids to a porcelain dish, and wash the flask thoroughly with boiling water, passing all the wash-waters through the filter, which must be kept moist, so as to allow the small quantity of fatty acids adhering to it to be easily united with the bulk. Finally heat the dish from 100° to 110° C. for one hour at first, and then, after weighing, again for twenty minutes until the weight remains fairly constant.

(*c*) *Hager* modifies *Hehner's* method by melting together with the fatty acids a weighed quantity of paraffin wax or bleached beeswax, as is usually done in soap analysis (chap. xii. p. 774), and washing four times with water containing 20 per cent of alcohol. This modification does not give such exact results as the preceding methods.

(*d*) *Knight's Process.*[2]—*J. West Knight* rejects *Hehner's* process on account of the difficulty of avoiding losses during the various operations, and proposes another method based on the insolubility of the barium salts of the higher fatty acids in water on the one hand, and on the ready solubility of the barium salts of the volatile acids on the other.

The following is a description of *Knight's* process :—1-3 grms. of the dried and filtered fat is saponified by heating on the water-bath with twice its volume of alcoholic potash for about half an hour. The solution is then brought up to 300 c.c. with cold distilled water, and an aqueous solution of barium chloride added until no further precipitation takes place. The precipitate is collected on a filter, washed with warm water, and then transferred to a Muter tube. Next the barium salts are decomposed with hydrochloric acid, and the liberated fatty acids shaken up with ether, in which they dissolve easily. The ethereal solution is made up to 100 c.c., and an accurately measured

[1] *Moniteur scient.* 12. 989. [2] *Analyst*, 1881.

quantity—say 50 c.c.—run off into a weighed flask. The ether is then distilled off and the dried residue weighed.

A priori, it is open to doubt whether *Hehner's* and *Knight's* methods will yield concordant results, inasmuch as the solubility of the acids may not correspond to the solubility of their barium salts. However, as *Knight's* results agree closely with those obtained by *Hehner's* process, it must be considered a correct method, although the use of an ethereal solution and the measuring off of an aliquot part may possibly introduce errors.[1]

vi. The Acetyl Value

The acetyl value furnishes a measure of the proportion of hydroxy acids or free alcohols, or of both together, in a fat or wax (provided mono- or diglycerides are absent).

The method of determining the acetyl value, as proposed by *Benedikt*, is based on the principle that hydroxy acids and alcohols, on being heated with acetic anhydride, exchange the hydrogen atom of their alcoholic hydroxyl group or groups for the radicle of acetic acid according to the following equations :—

1. $C_{17}H_{32}(OH) . COOH + (C_2H_3O_2)O = C_{17}H_{32}(O . C_2H_3O)COOH + C_2H_4O_2$.
   Ricinoleic acid. — Acetic anhydride. — Acetyl-ricinoleic acid. — Acetic Acid.

2. $C_{16}H_{33} . OH + (C_2H_3O)_2O = C_{16}H_{33}O . C_2H_3O + C_2H_4O_2$.
   Cetyl alcohol. — Acetic anhydride. — Cetyl acetate. — Acetic acid.

The acetyl value of **fatty acids** is determined, according to *Benedikt* and *Ulzer*,[2] in the following manner :—20 to 50 grms. of the insoluble fatty acids prepared in the usual manner (p. 99) are boiled with an equal volume of acetic anhydride for two hours in a round-bottomed flask attached to an inverted condenser. The mixture is then transferred to a beaker of 1 litre capacity, mixed with 500 to 600 c.c. of water and boiled for half an hour, a slow current of carbonic dioxide being at the same time passed into the liquid through a finely-drawn-out tube reaching nearly to the bottom of the beaker ; this is done to prevent bumping. The mixture is then allowed to separate into two layers, the water is syphoned off, and the oily layer again boiled out in the same manner three successive times. The last trace of acetic acid is thus removed, as may be ascertained by testing with litmus paper. The acetylated acids are filtered through a dry filter-paper in a drying oven to remove water, and a portion of the product, say 3 to 5 grms., is weighed off accurately in a flask and dissolved in pure alcohol. Then proceed exactly as for the determination of the acid value (p. 148) and saponification value

[1] Asbóth states that also the lead salts of the volatile acids are soluble in water. But as his paper does not give any proof for this assertion, his statement must be accepted with reserve.

[2] *Monatshefte für Chemie*, 8. 40.

(p. 151). Add a little phenolphthalein, and titrate with half-normal potash until pink, whereby the free acid is neutralised. The acid value thus obtained is termed "*acetyl acid value.*" Then run into the flask an accurately measured quantity of alcoholic potash, standardised by half-normal hydrochloric acid, heat to boiling, and titrate back the excess of alkali. The amount of alkali now used gives the "*acetyl value.*" The sum of the *acetyl acid value* and of the *acetyl value* is termed "*acetyl saponification value.*" The acetyl value is therefore equal to the difference of the saponification and acid values of the *acetylated* fatty acids.

The acetyl value of the *fatty acids* indicates the number of milligrammes of KOH required for the neutralisation of the acetic acid obtained on saponifying one gramme of the acetylated insoluble fatty acids.

Example.—3·379 grms. of the acetylated fatty acids from castor oil were neutralised by 17·2 c.c. of half-normal potash, *i.e.* 17·2 × 0·02805 grm. = 0·4825 grm. KOH; hence the acetyl acid value is 142·8. Then 32·8 c.c. more potash were added, and, after boiling, the excess titrated back with 14·3 c.c. half-normal hydrochloric acid. The acetic acid obtained on saponification therefore required for neutralisation 32·8 – 14·3 c.c. = 18·5 c.c. half-normal potash, or 18·5 × 0·02805 = 0·5189 grm. KOH. Hence the acetyl value $\frac{5189}{3379} = 153{\cdot}6$.

Therefore,

Acetyl acid value	142·8
Acetyl value	153·6
Acetyl saponification value	296·4

The neutralisation and the saponification of the acetylated acids were therefore supposed to take place in two stages according to the following equations :—

1. $C_{17}H_{32}(O \cdot C_2H_3O) \cdot COOH + KOH = C_{17}H_{32}(O \cdot C_2H_3O)COOK + H_2O.$
   Acetyl-ricinoleic acid. Potassium salt.

2. $C_{17}H_{32}(O \cdot C_2H_3O)COOK + KOH = C_{17}H_{32}(OH)COOK + C_2H_3O_2K.$
   Potassium acetyl-ricinoleate. Potassium ricinoleate.

The hydroxyl in the carboxyl group of the fatty acids should therefore not have been affected by the acetic anhydride during the acetylating process. Hence fatty acids containing no alcoholic hydroxyl, such as stearic, oleic, etc., should not yield an acetyl value, the acid and saponification values in that case being identical.

Lewkowitsch,[1] however, has shown that pure capric, lauric, palmitic, stearic, cerotic, and oleic acids gave very considerable acetyl values when treated according to *Benedikt* and *Ulzer's* process. This result could only be explained by the fact that the fatty acids had been con-

[1] *Proceed. Chem. Soc.* 1890, 72; 91; *Jour. Soc. Chem. Ind.* 1890, 660.

verted into their anhydrides, the acetic anhydride acting in the manner explained by the following equation :—

$$2C_{15}H_{31}.COOH + \begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\!\!>\!O = \begin{matrix} C_{15}H_{31}CO \\ C_{15}H_{31}CO \end{matrix}\!\!>\!O + 2C_2H_3O.OH.$$

Palmitic acid. — Acetic anhydride. — Palmitic anhydride. — Acetic acid.

The anhydrides were thus actually obtained and their great stability in presence of even boiling water proved.

When these anhydrides were dissolved in *cold alcohol* for the purpose of titrating, on adding the potash hydrolysis (saponification) of the anhydrides took place at once to a certain extent, and as the acid combined with a certain quantity of potash, an (apparent) acid value of the substance was obtained. When, however, the anhydrides were shaken up with *water*, the first drop of potash gave a pink colouration (in the presence of phenolphthalein), which disappeared but slowly. Thus in the *alcoholic* solution a partial hydrolysis of the anhydrides took place, hydrolysis ceasing when an equilibrium was established in the solution. Under these conditions apparent acetyl values were obtained for the fatty acids above mentioned, being, in truth, nothing but fictitious values.

Hydroxylated fatty acids are certainly acetylated when boiled with acetic anhydride, but simultaneously the acetylated acids are converted into their anhydrides in consequence of the large excess of acetic anhydride used. During the subsequent boiling with water a portion of the anhydrides may or may not become hydrolysed, thus yielding possibly a mixture of free acetylated acids and acetylated anhydrides.

When this is dissolved in alcohol and titrated with caustic potash, after neutralisation of the free acids, if any, partial hydrolysis will set in, as explained above in the case of capric acid, etc., and an acid value will thus be obtained (*Benedikt's* "acetyl acid value"). But such acid value will be lower than the true acid value of the acetylated fatty acids, the anhydrides remaining unacted on to a certain extent. Consequently the saponification value of the acetylated product (*Benedikt's* "acetyl saponification value") will be found too high, the not-hydrolysed anhydrides becoming then saponified by the boiling alcoholic potash. The difference between saponification and acid values, supposed to be the acetyl value of the acids, will therefore be devoid of any quantitative meaning.

The same conclusion, of course, holds good in the case of a mixture of hydroxy and ordinary fatty acids.

The **true** acetyl value of the **fatty acids**, however, is found, according to *Lewkowitsch*,[1] by actually titrating the amount of acetic acid assimilated by the hydroxy acids in the form of acetyl (C_2H_3O) and given up, on saponification, as acetic acid to the alkali. This is done by boiling the acetylated product with alcoholic potash and estimating

[1] *Jour. Soc. Chem. Ind.* 1890, 846.

the acetic acid formed in a similar fashion to that adopted in the determination of volatile fatty acids by *Reichert's* distillation process. There is, however, this important difference that the *total* amount of volatile acids, in the present case acetic acid, is driven off. The distillation is therefore carried on until practically no acidity is shown by the distillates. This occurs as a rule when about 500 to 700 c.c. have been distilled over. The distilled liquors are then titrated with decinormal alkali, phenolphthalein being the indicator. The number of c.c. of decinormal potash used per gramme of the acetylated substance multiplied by 5·61 represents the acetyl value of the fatty acids.

Example.—3·364 grms. of the acetylated fatty acids from Sawarri fat yielded a distillate requiring 8·4 c.c. of decinormal potash for neutralisation. Hence for 1 grm. 2·5 c.c. decinormal potash were used. Therefore the acetyl value is $2{\cdot}5 \times 5{\cdot}61 = 14{\cdot}03$.

It is therefore evident that the "acetyl values" found by various observers working according to *Benedikt* and *Ulzer's* method cannot be accepted as correct.

The determination of the acetyl value by *Lewkowitsch's* method, though giving correct results, has the important drawback that this constant refers to the insoluble fatty acids rather than to the oils and fats themselves. This naturally tends to obliterate at the outset important differences existing between the various glycerides, for in the process of preparing the fatty acids volatile acids are washed away, and the characteristic differences of such fats as, *e.g.*, butter and tallow, may entirely disappear. There is the further drawback that during the operations entailed by washing and drying the fatty acids they may become oxidised with formation of hydroxy acids.

In order to bring this important constant into line with the other constants, *Lewkowitsch*[1] determines the **acetyl value of the glycerides** themselves. He proceeds as follows:—10 grms., or any other convenient number of grammes, are boiled with an equal volume of acetic anhydride in the manner described above. The acetylated product when washed free from acetic acid is separated from water and filtered through filtered paper in a drying oven.

This operation may be carried out quantitatively, and in that case the fatty matter is treated in a similar fashion to the *modus operandi* described for the determination of the *Hehner value* (p. 160). It may be useful to work quantitatively if it is desired to ascertain preliminarily whether a notable amount of hydroxy acids is present in an unknown fat (cp. chap. vi. p. 204, and chap. vii. p. 232).

2 to 4 grms. of the acetylated product are then saponified by boiling with alcoholic potash, as in the determination of the saponification value. If the "distillation process" be adopted, it is not necessary to work with an accurately measured quantity of standardised alcoholic potash. In case the "filtration process" be used, the alcoholic potash must be measured exactly. (It is advisable to use in either case a known volume of standard alkali, as one is then

[1] *Jour. Soc. Chem. Ind.* 1897, 503.

enabled to determine the saponification value of the acetylated oil or fat). Next the alcohol is evaporated off and the soap dissolved in water. From this stage the determination is carried out either by (*a*) the distillation process, or (*b*) filtration process.

(*a*) *Distillation process.*—Add dilute sulphuric acid (1:10), more than to saturate the potash used, and distil the liquid as is usual in *Reichert's* distillation process. Since several hundred c.c. of water must be distilled off, either a current of steam is blown through the suspended fatty acids, or water is run into the distilling flask from time to time through a stoppered funnel fixed in the cork, or any other convenient device may be adopted. It will be found that it is sufficient to distil off 500 to 700 c.c. of water, as the last 100 c.c. require no more than 0·1 c.c. of decinormal alkali. Then titrate the distillates with decinormal potash, phenolphthalein being the indicator, multiply the number of c.c. by 5·61, and divide by the weight of substance taken. This gives the acetyl value.

(*b*) *Filtration process.*—Add to the soap solution a quantity of standardised sulphuric acid *exactly* corresponding to the amount of alcoholic potash employed and warm gently, whereupon the fatty acids will readily collect on the top as an oily layer. (If the saponification value has been determined, it is of course necessary to take into account the volume of acid used for titrating back the excess of potash.) Filter off the liberated acids, wash with boiling water until the washings are no longer acid, and titrate the filtrate with decinormal alkali. The acetyl value is calculated in the manner shown above (*a*).

Both methods give identical results; the latter will be found shorter and therefore more convenient. We now arrive at the definition:—

The acetyl value indicates the number of milligrammes of KOH required for the neutralisation of the acetic acid obtained on saponifying one gramme of the acetylated fat or wax.

In the case of those oils and fats which have a high *Reichert* value (cp. Croton Oil, chap. ix. p. 313) the *apparent* acetyl value would be too high, owing to the presence of the volatile acids. Their influence will make itself felt to a greater extent in the distillation process than in the filtration process. To eliminate this error determine the volatile acids of the original oil or fat in *precisely* the same manner, and deduct the value thus obtained from the apparent acetyl value.

It should be noted that in the case of a fat containing **free alcohols**[1] (phytosterol, cholesterol), or in the case of **waxes,** the acetyl value will be a measure of both the hydroxy acids *and* the free alcohols. If the *free* alcohol is isolated its acetyl value (see below) may be determined as well. The difference between the acetyl value of the fat or wax and the acetyl number proportionate to the amount of free alcohol present will be the true measure of the hydroxy acids.

If a **free alcohol** is acetylated no complication through formation of anhydrides can arise, and in that case simply the saponification

[1] If mono- or diglycerides (see p. 190) be present, acetic acid radicles are also absorbed by them.

value of the acetylated product—the acetate of the alcohol—is determined. This value is also the acetyl value of the alcohol (the saponification value of the original alcohol being, of course, *nil*).

vii. The (Bromine or) Iodine Value

The (bromine or) iodine value indicates the percentage of (bromine or) iodine absorbed by a fat or wax.

This value is, therefore, a measure of the proportion of unsaturated fatty acids in a fat,—these acids, both in their free state and in combination with glycerol, having the property of assimilating the halogens with formation of additive compounds.

Theoretically, the acids (or their glycerides) belonging to the oleic and ricinoleic series should absorb two atoms of chlorine, bromine, or iodine; similarly the acids of the linolic series should assimilate four atoms, the members of the linolenic series six atoms of the halogens, etc.

Obviously the determination of absorbed chlorine is attended with more difficulty than that of bromine or iodine, and the latter reagents only have been found useful in technical analysis.

(*a*) *Bromine Value*

If dry bromine is allowed to act on an oil, the former is absorbed, a more or less violent reaction taking place and hydrobromic acid being evolved. The reaction must therefore be moderated by previously dissolving both the bromine and the oil in a suitable solvent.

The determination of **bromine absorption** values was proposed by *Cailletet* (1857), but the application of this method for the analysis of fats is due to *Mills*[1] and his collaborators *Snodgrass* and *Akitt*.

Mills proceeds as follows:—0·1 grm. of a fat, dried thoroughly and filtered, is dissolved in 50 c.c. of carbon tetrachloride contained in a narrow-mouthed stoppered bottle of 100 c.c. capacity. To this solution is added standard bromine solution in carbon tetrachloride (about 0·006 - 0·008 grm. per c.c.) until there is at the end of fifteen minutes a permanent colouration. The excess of bromine can be measured either by comparing the colouration with that similarly produced in a blank experiment, or, more accurately, by titrating back with a standard solution of β-naphthol in carbon tetrachloride, when monobromnaphthol is formed. The bromine absorbed is calculated for 100 grms. of fat. The average probable error is stated to be 0·46 per cent.

Mills laid the greatest stress on the necessity of rigidly excluding moisture, since he observed that the bromine absorption increased in presence of water; therefore aqueous solutions of bromine must not be used. Carbon tetrachloride was substituted for carbon bisulphide as a solvent for bromine, for the reason that the solution of bromine

[1] *Jour. Soc. Chem. Ind.* 1883, 435; 1884, 366.

in the former possesses much greater stability at the ordinary temperature than in the latter.[1] Instead of β-naphthol, potassium iodide may be added, and the liberated iodine titrated with sodium thiosulphate, calculating to bromine.—Other chemists determine the bromine absorption by methods deviating from *Mills'* directions in essential points.

Levallois[2] saponifies 5 grms. of fat with alcoholic potash, and makes the solution up to 50 c.c. To 5 c.c. of it he adds hydrochloric acid, and then standardised aqueous bromine solution, until a permanent yellow colouration is noticed. The bromine solution used by *Levallois* is as concentrated as possible. No wonder, therefore, that the bromine absorptions obtained by this method differ very materially from those obtained by *Mills*, whose figures undoubtedly deserve more confidence (see p. 308).

Halphen[3] operates in the following way:—1 grm. of the fatty acids, weighed off accurately, is placed in a bottle of 250 c.c. capacity, dissolved in 20 c.c. of carbon bisulphide, and an accurately measured quantity of a standardised aqueous solution of bromine allowed to run in. There should be an excess of at least 0·5 grm. of bromine. The solution is thoroughly mixed by shaking, and allowed to stand for fifteen hours, when the excess of bromine is titrated back by a standard caustic soda solution prepared by dissolving 2 grms. of eosin in 20 c.c. of caustic soda of 36° Bé., and making up to 1000 c.c. The alkali solution is standardised by running it gradually from a burette into a bottle containing 20 c.c. of carbon bisulphide and exactly 10 c.c. of a bromine solution of known strength, shaking well after each addition of the caustic soda. At first the liquid acquires a brownish colouration, and becomes successively yellowish-brown, then nearly colourless, and at last rose-coloured. The titer of the caustic soda is expressed in terms of bromine. This standardation need only be carried out once for all; the bromine value of any fresh caustic soda solution in reference to any fresh bromine solution being ascertained by comparison with the once standardised caustic soda. Of course the titer of the bromine solution must be ascertained before each determination of the bromine absorption.

Schlagdenhauffen and *Braun*[4] reject *Levallois'* method as inaccurate, and substitute for it the following process:—Dissolve 2·5 grms. of a fat in 50 c.c. of chloroform (or carbon bisulphide), and add to an aliquot part of the solution—say 10 c.c.—a measured volume of a solution of 1 grm. of bromine in 100 c.c. of chloroform, until the yellow colouration does not disappear on shaking. Then add 10 c.c. of a dilute solution of potassium iodide and a few drops of starch solution, and titrate with sodium thiosulphate.

Mills' process should be preferred to the others mentioned. *Mills*, however, overlooked the fact that the formation of hydrobromic acid is

[1] The following reaction going on in a solution of bromine in carbon bisulphide should be noted as involving loss of bromine. After several days' standing CS_2Br_4 is formed; this is decomposed by water (moisture) with separation of crystals of $(CBr_3)_2S_3$.

[2] *Compt. rend.* 104. 371.

[3] *Jour. Pharm. Chem.* 1889 (5), 20. 247.

[4] *Ibid.* 1891 (5), 23. 97.

not due to moisture but to the substitution of hydrogen in the molecule of the fatty substance. (The hydrobromic acid thus formed can be detected by shaking the product with water and testing the aqueous solution with silver nitrate.)

Thus concurrently with the **addition**, *i.e.* the absorption of bromine due to two atoms of bromine being assimilated by one molecule of an oil to form a saturated compound, there takes place further absorption of bromine with formation of substitution products and consequently of hydrobromic acid; therefore the **total absorption** of bromine as measured by the methods just described is due to both **addition** and **substitution.**

The more concentrated the bromine solution employed the greater will be the amount of substitution products; it is therefore evident that bromine values obtained by allowing dry bromine to act on an oil must be too high.

The quantity of hydrobromic acid formed furnishes, therefore, a measure of the amount of substitution that has taken place. Hence the **true bromine value** is expressed by the difference between the total bromine assimilated and the bromine absorbed in the substitution process.

McIlhiney[1] determines the "bromine addition" and the "bromine substitution" value of an oil in the following manner[2]:—

From 0·25 to 1·00 grm. of the oil is dissolved in 10 c.c. of carbon tetrachloride in a 500 c.c. stoppered bottle, an excess of a solution of bromine in carbon tetrachloride is added, and the mixture kept in a dark place for 18 hours. The bottle is then placed in ice so as to obtain a partial vacuum by the condensation of the vapours. A piece of india-rubber tubing is now slipped over the neck so as to form a well around the stopper. The well is filled with water, which is sucked into the bottle when the stopper is carefully lifted. 25 c.c. of water are thus introduced into the bottle, its contents are well shaken, to effect absorption of the hydrobromic acid, and 10-20 c.c. of a 20 per cent solution of potassium iodide, and about 75 c.c. more water added. The iodine liberated by the excess of bromine is measured by titration with standard thiosulphate solution and calculated to bromine. The total amount of bromine added having been ascertained similarly in a blank test, the difference between the two amounts corresponds to the **total bromine absorption,** and it is calculated to units per cent of the oil taken.

The contents of the bottle are transferred to a separating funnel, and the aqueous solution is separated and filtered. If it be blue it is decolourised by a few drops of thiosulphate solution, and the free acid determined as hydrobromic acid by titration with decinormal alkali, methylorange being used as an indicator. The bromine calculated from the hydrobromic acid and expressed in per cents of the oil gives the **bromine substitution value.** Twice this number subtracted from the total bromine absorption gives the **bromine addition number.**

[1] *Jour. Soc. Chem. Ind.* 1894, 668. [2] Cp. *Allen. Com. Org. Analys.* ii. 384.

It is evident that the substitution number must be doubled, since for each bromine atom that has been converted into hydrobromic acid there have been removed from the original bromine solution 1 molecule, or 2 atoms of bromine, as explained by the following equation :—

$$C_nH_mO_2 + Br_2 = C_nH_{m-1}O_2Br + HBr.$$

Fatty Acid. Bromosubstitution product.

The following *gravimetric* process for the determination of the bromine value has been proposed recently by *Hehner*[1] :—Weigh off accurately 1 to 3 grms. of the oil in a wide-mouthed flask, and dissolve the oil in a few cubic centimetres of chloroform. Then add pure bromine, drop by drop, until there is an excess of bromine. Heat the flask on the water-bath until the bulk of the bromine is driven off, add a little more chloroform, and heat again so as to promote the evaporation of the bromine by the vapours of the chloroform. This operation may be repeated so as to ensure complete volatilisation of the bromine in excess. The contents of the flask are finally heated at 125° C. until the weight remains constant. This takes several hours, a little acrolein and hydrobromic acid escaping during the drying. The gain in weight expressed in per cents gives the bromine value.

Essentially the same method has been described, independently, by *Waller*.[2]

Lewkowitsch,[3] however, has shown that whilst in a number of cases (*e.g.* olive oil) this method leads to results agreeing with those obtained by Hübl's standard method (see below), in other cases such enormous discrepancies are observed that this gravimetric method cannot find a place amongst the quantitative processes.

(*b*) *Iodine Value*

The determination of the bromine value has been wholly superseded by *Hübl's* method of ascertaining the **iodine absorption** value, which yields by far more constant and reliable results.[4] In fact, the reliability of the recently proposed bromine absorption processes is ascertained by their agreement with Hübl's process, bromine values being calculated into iodine values by multiplication with $\frac{127}{80} = 1{\cdot}5875$.

But it should be distinctly understood that the bromine values are not directly convertible into iodine values, as a varying amount of substitution takes place which is decidedly smaller in the case of the iodine, if any takes place at all, as one may conclude from the action of iodine on saturated fatty acids (p. 176).

[1] *Analyst*, 1895, 50.
[2] *Ibid.* 1895, 280. It should be noted that *Waller* examined olive oil only.
[3] *Jour. Soc. Chem. Ind.* 1896, 859.
[4] Hydroxybrassidic acid does not absorb bromine at ordinary temperature (*Berichte*, 26. 839). Cp. p. 308.

Hübl[1] found that iodine is only slowly assimilated by fats at ordinary temperature, whilst at higher temperatures[2] the action of iodine becomes very irregular, complicated reactions taking place. He has ascertained, however, that from an alcoholic solution of iodine, in presence of an alcoholic solution of mercury bichloride, the unsaturated fatty acids or their glycerides absorb iodine in a very regular, well-defined manner, so that a quantitative method may be based on this reaction. The following solutions are required for *Hübl's* process :—

1. *Solution of Iodine and Mercury Bichloride*, called hereafter *Iodine Solution* for brevity's sake.—This is prepared by dissolving on the one hand 25 grms. of iodine, and on the other hand 30 grms. of mercury bichloride, in 500 c.c. of pure 95 per cent alcohol, filtering the latter solution if necessary, and then mixing both solutions. The iodine solution undergoes considerable reduction in strength (*i.e.* free iodine) during the first hours after mixing, and should, therefore, be allowed to stand for twelve to twenty-four hours before use. But even after that time the iodine solution gradually loses strength in consequence of formation of hydriodic acid,[3] and must, therefore, be always standardised immediately before use. The writer finds it very convenient to keep both the iodine and the bichloride solution in stock separately, and prepare only so much *iodine solution* as is required for a test.

2. *Solution of Sodium Thiosulphate* (hyposulphite).—This is prepared by dissolving about 24 grms. of the crystallised salt in 1000 c.c. of water, and is standardised by means of iodine in the following way :—Two short glass tubes, sealed at one end, and of such dimensions that one fits with slight friction into the other, are heated and allowed to cool in the desiccator. Now transfer to the inner tube about 0·2 grm. of pure resublimed iodine, lay the tube obliquely in a sand-bath, heat till the iodine melts, then remove the tube, and allow it to cool a little in an oblique position, until it can be held with the hand. Place the larger tube over it, allow to cool in the dessicator, and weigh accurately. Then take the wider tube off, and place both tubes in a stoppered bottle containing 1 grm. of potassium iodide dissolved in 10 c.c. of water. As soon as the iodine is dissolved, add water, and allow the thiosulphate to run into it from a burette until the colour is nearly all gone. Now add a little starch solution, and then carefully, with constant agitation, drop by drop of the thiosulphate until the blue colour is just being discharged.

[1] *Jour. Soc. Chem. Ind.* 1884, 641. [2] Cp. also footnote, p. 173.

[3] Schweitzer and Lungwitz (*Jour. Soc. Chem. Ind.* 1895, 133) examined an iodine solution containing 0·6201 grm. total iodine in stated intervals, with the following result :—

After hours	Free Iodine.	Iodine as Hydriodic Acid.
12	0·6181	0·0020
36	0·6136	0·00653
84	0·5930	0·02713
132	0·5849	0·03517

Another very convenient method for standardising the thiosulphate, due to *Volhard*, is the following:—Weigh off accurately 3·8747 grms. of pure potassium bichromate,[1] and dissolve in 1000 c.c. of water. Place in a stoppered bottle 10 c.c. of a 10 per cent potassium iodide solution, and 5 c.c. of hydrochloric acid, and run in exactly 20 c.c. of the bichromate solution from a burette. Since each c.c. of this solution liberates precisely 0·01 grm. of iodine, altogether 0·2 grm. of iodine will be set free. It is titrated by means of the thiosulphate solution as described above. The advantage of this method lies in its rapidity, saving the somewhat laborious and circumstantial preparation and weighing off of the pure iodine; besides, the bichromate solution, keeping for an indefinitely long time without alteration, is always ready for ascertaining the strength of the thiosulphate solution.[2]

3. *Chloroform.*—The chloroform should be pure. It is tested by mixing 10 c.c. with 10 c.c. of the iodine solution, and titrating the free iodine after two to three hours' standing. The amount found should be exactly the same as that contained in 10 c.c. of the iodine solution. (Ether cannot be used in place of chloroform, as it very frequently contains hydrogen peroxide, which acts on potassium iodide, liberating iodine.)

4. *Solution of Potassium Iodide.*—This is prepared by dissolving 100 grms. of potassium iodide in 1000 c.c. of water.[3]

5. *Starch Solution.*—This should be prepared afresh for each analysis by stirring 0·5 grm. of pure starch in cold water, and heating to the boiling point with constant stirring.

The determination of the iodine value is carried out as follows:—From 0·15 to 0·18 grm. of a drying, or a fish oil, 0·3 to 0·4 grm. of a non-drying oil, or 0·8 to 1·0 grm. of a solid fat, are weighed off accurately, and placed in a bottle of 500 to 800 c.c. capacity provided with a well-ground stopper. The fat is dissolved in 10 c.c. of chloroform, and 25 c.c. of the iodine solution run in by means of a pipette inserted in the reagent bottle. The pipette is always emptied in exactly the same manner; this is best done by allowing it to drain until say three drops have run out. For larger quantities of fats, say 0·30 to 0·36 grm., etc., 50 c.c. must be used. In order to prevent loss of iodine by volatilisation it will be found useful to moisten the stopper with potassium iodide solution. The chloroform and iodine solution should give a clear solution on shaking, otherwise more chloroform must be added. Should the deep brown colour of the solution become discharged after a short time, another 25 c.c. of the iodine solution must be run in, an excess of iodine being required for the reaction. The solution must, after two hours, still possess

[1] It is necessary to ascertain its purity and absence of sodium bichromate by determining its oxidising value.

[2] For a method of standardising by means of BaS_2O_3, cp. Plumpton and Chorley, *Proc. Chem. Soc.* 1895, p. 38.

[3] Commercial potassium iodide frequently contains iodate, which gives free iodine with hydrochloric acid. Such impure iodide may, however, be employed if accurately measured volumes be used and the liberated iodine be taken into account.

a deep brown colour. After that time the reaction should be complete, but in order to be quite safe it is best to allow the solution to stand another two hours at ordinary temperature protected from light. From 15 to 20 c.c. of the potassium iodide solution are then run in, and the liquid shaken and diluted with from 300 to 500 c.c. of water. A red precipitate of mercury iodide would indicate that an insufficient quantity of potassium iodide had been employed, and therefore more must be added. The excess of free iodine, part of which will be in the aqueous solution, whereas the remainder is dissolved in the chloroform, is titrated with the thiosulphate solution, by running it into the bottle until after repeated agitation both the aqueous and the chloroformic layers are but faintly coloured. A few drops of the starch solution are next added and the titration brought to an end. Immediately before or after this tritration the amount of iodine contained in 25 c.c. of the original iodine solution is estimated. The difference between the two results corresponds to the iodine assimilated, and this is calculated to units per cent of the fat. The figure thus found is termed the **iodine value.**

The values as obtained by *Hübl's* method are quite constant, provided an excess of iodine of not less than 30 per cent[1] be employed, and the operations be carried out under exactly the same conditions. The result does not depend on the concentration, nor on an excess of the mercury bichloride solution, but it is necessary that for every two atoms of iodine at least one molecule of mercury bichloride should be present. *Hübl* remarks that it is indifferent whether the titrations are made after two or after forty-eight hours' standing—which is not quite borne out by the experience of other analysts, including the writer. To ensure concordant results it is preferable not to titrate before four to six hours' standing, but it is not advisable to wait any longer.[2]

When the titrated solution is allowed to stand for some time the solution becomes blue again; this is no doubt due to the splitting off of iodine, thus proving that the action of iodine on unsaturated compounds is to some extent a reversible reaction. However, this action does not in the least interfere with the accuracy of the titration.

Hübl's process has been examined by many chemists, and proved itself to be one of the most valuable methods employed in the technical analysis of fats and waxes. The chemical literature of the last few years contains numerous papers by various authors purporting to give improvements or modifications of the original method. Most of them refer simply to minor or unimportant points. Some of them even reproduce methods which *Hübl*, in his classic paper, has rejected.

[1] Benedikt, *Zeit. f. Chem. Ind.* 1887, 213.

[2] With a view to shorten the time of treatment Schweitzer and Lungwitz (*Jour. Soc. Chem. Ind.* 1894, 616) heat the liquid in the tightly-closed bottle for twenty-five minutes at 45° C., and titrate when the liquid has cooled down. This method cannot be recommended.

Thus, it has been proposed to employ mercury bibromide instead of the bichloride (*Saytzeff*); further, to use methyl alcohol instead of alcohol as a solvent (*Fahrion*), or a mixture of acetic acid and ethyl acetate or ether (see p. 172) (*Welmans*).—The exact excess of iodine to be employed is still a matter of controversy between some continental chemists (*Holde*, *Fahrion*, *Dieterich*); the same obtains as to the length of time required for the iodine to act on the fat (*Thomson* and *Ballantyne*, *Dieterich*).—Several chemists recommend a blank test, using the same amount of chloroform and iodine solution; but there again they seem to leave it open to doubt as to which titer of the blank test should be used for calculation, whether that found before the actual test is started, or that at the end of the titration, or the mean of both.—*Gantter*,[1] evidently having neglected *Hübl's* direction that for 2 atoms of iodine at least 1 molecule of $HgCl_2$ should be used, recently proposed what he calls a "new method for estimating the iodine absorption." He omits the mercury bichloride, and allows only the iodine, dissolved in carbon tetrachloride, to act on a solution of fat in the same menstruum. *Hübl* himself had abandoned the employment of iodine alone as being too slow of action, and it has been shown since (*Schlagdenhauffen* and *Braun*, *Fahrion*) that the mercury bichloride is indispensable for the attainment of *constant results*. *Gantter* employs for 1 part of fat 4-5 parts of iodine, and allows to stand for fifty hours. The iodine values thus obtained are considerably lower than *Hübl's* iodine absorptions, and are entirely devoid of that quantitative meaning which *Hübl's* values possess, the latter indicating approximately figures which are postulated by theory for additive compounds (see table below). *Gantter's* values, even if they should be constant, which has yet to be proved by a larger number of experiments, will at best only cause confusion, a great number of iodine absorption values by *Hübl's* process having been recorded in the literature as constants for certain fats. *McIlhiney*[2] has since shown that *Gantter's* method does not even yield constant results. Therefore the latter's suggestion must be considered valueless.

Waller,[3] with a view to render the iodine solution more stable, proposes to add some hydrochloric acid. He prepares the solution in the following manner:—25 grms. of iodine are dissolved in 250 c.c. of strong alcohol; 25 grms. of mercury chloride are then dissolved in 200 c.c. of strong alcohol, 25 grms. of hydrochloric acid, spec. grav. 1·19, are added, and both solutions mixed and made up to 500 c.c. with alcohol. It will be noticed that *Waller's* solution does not conform to *Hübl's* direction that there should be at least one molecule of mercury bichloride (27·5 grms.) to one molecule of iodine (25·4 grms.), as also that this solution is twice as strong as the usual iodine solution. Nevertheless the values obtained with this solution are stated by *Waller* to practically agree with those by the *Hübl* process, and this statement has been confirmed by *Dieterich*,

[1] *Jour. Soc. Chem. Ind.* 1893, 717. [2] *Ibid.* 1895, 197.
[3] *Analyst*, 1895, 280.

Pelgry, and *Henriques*. But this alleged slight advantage does not offer, in the writer's opinion, sufficient inducement to deviate from a standard method.—The same would apply to *Ephraim's* suggestion to replace the iodine solution by iodine chloride (see below).

The chemical reaction taking place when *Hübl's* iodine solution is made to act on a fat is not known yet. *Hübl* assumes that chloro-iodo-additive compounds result, having obtained from oleic acid a greasy substance, to which he ascribes the formula $C_{18}H_{34}ClIO_2$ (see p. 14). *Liebermann*[1] thinks it possible that addition of chlorine only may take place. However this may be, from a practical point of view it is unimportant whether only iodine or chlorine enter into union with the fats, or if both, in what proportions, since the amount of halogen absorbed is estimated volumetrically and calculated in terms of iodine.

In the subjoined table the theoretical iodine values for some unsaturated fatty acids are given, together with some experimental data obtained hitherto.

Fatty Acid.	Formula.	Atoms of Iodine required to form a saturated compound.	100 Grms. of Acid absorb Iodine.		Observer.
			Theory.	Experiment.	
			Grms.	Grms.	
Hypogæic . .	$C_{16}H_{30}O_2$	2	100·0	...	...
Oleic, isooleic .	$C_{18}H_{34}O_2$	2	90·07	89·8-90·5	Hübl
Elaïdic . . .	$C_{18}H_{34}O_2$	2	90·07	90·54	Saytzeff[2]
Erucic . . .	$C_{22}H_{42}O_2$	2	75·15	...	...
Brassidic . .	$C_{22}H_{42}O_2$	2	75·15	75·34	Saytzeff[3]
Isoerucic . .	$C_{22}H_{42}O_2$	2	75·15	... 74·42	Alexandroff and Saytzeff[4]
Ricinoleic . .	$C_{18}H_{34}O_3$	2	85·24	...	...
Linolic . . .	$C_{18}H_{32}O_2$	4	181·43	...	...
Linolenic . .	$C_{18}H_{30}O_2$	6	274·10	...	...

The specimen of oleic acid yielding the number 89·8-90·5 was prepared from almond oil (private communication). This oil containing, according to *Hazura's* later researches, less saturated fatty acids than oleic acid, the excellent agreement of theory and experiment is a fortuitous one, the less saturated fatty acid having been compensated, as it were, by saturated acids not completely eliminated from the specimen (cp. p. 196). It must, however, be pointed out that a specimen of oleic acid, prepared by *Geitel* (*Jour. f. prakt. Chemie*, 1888 [37], 59) from tallow by repeated crystallisation, gave the iodine value 89. The more recent determinations carried out by *Saytzeff*, and by *Alexandroff* and *Saytzeff*, on pure specimens of elaïdic, brassidic, and isocrucic acids would also appear to speak in favour of an agreement

[1] *Berichte*, 24. 4117.
[2] *Jour. f. prakt. Chemie*, 1894 [50], 75.
[3] *Ibid.* 1894 [50], 79.
[4] *Ibid.* 1894 [49], 61.

between theory and experiment. It is very desirable that this very important fact should be corroborated by further experiments.

With a view to examine the basis on which *Hübl's* principle rests, the writer[1] has experimented with the following unsaturated substances :—

Substance.	Iodine Value.	
	Theory.	Experiment.
Allyl alcohol	436·2	349–376
Undecylenic acid	137·5	121–125
Crotonic acid	300	25–25·9
Fumaric acid	219	nil
Maleïc acid	219	nil
Cinnamic acid	170·9	15·3–16·4
Styracin	191·7	81·9–82·9
Cholesterol	68·3	67·3–68·09

With the exception of cholesterol, none of the substances examined absorbed the amount of iodine required by theory.

The saturated fatty acids, as has been shown by *Hübl*, are not affected by his reagent. *Gantter*, however, having stated that lauric and stearic acids gave the iodine values of 4·3 and 6·8 respectively, the writer[1] has examined a number of pure saturated fatty acids with the following negative result :—

Acid.	Iodine Value (100 grms. absorb grms. Iodine).
Propionic	0·66
Butyric	0·36
Isobutyric	0·00
Valeric	1·32[2]
Caproic	0·30
Œnanthic	0·00
Caprylic	0·55
Pelargonic	1·83[2]
Capric	0·31
Lauric	1·12[2]
Palmitic	0·13
Stearic	0·20
Cerotic	1·34[2]

The capricious results obtained by different observers can be explained by the assumption that simultaneously with the **addition** of iodine **substitution** of iodine takes place in varying quantity according to the special conditions each worker adopted. The fact that some experimenters found very high iodine numbers when working

[1] Unpublished observations. [2] The somewhat high values may be due to impurities.

with a very large excess of iodine, and allowing it to act for some considerable time [1] on an oil, would go far to prove this assumption, although the numbers given in the last table and on p. 175 would show that in those cases substitution is almost *nil*. Thus, in a similar fashion as shown above for bromine absorption (p. 169), concurrently with addition of iodine, substitution of hydrogen by iodine may be assumed to take place, so that the total iodine absorption would be due to *both* addition and substitution.

Recently several attempts have been made to elucidate the chemistry of the Hübl iodine process.[2]

Schweitzer and *Lungwitz*,[3] following the lines adopted by McIlhiney in the determination of the bromine absorption, differentiate between iodine addition and iodine substitution. The determination of the hydriodic acid, however, cannot be done by alkalimetric methods, and must therefore be carried out in a somewhat roundabout fashion, viz. by ascertaining the amount of iodine set free from a solution of potassium iodate, according to a reaction illustrated by the following equation :—

$$5HI + IO_3H = 6I + 3H_2O.$$

Schweitzer and *Lungwitz* ascertain the iodine absorption exactly as in *Hübl's* process, by titration with sodium thiosulphate. The titration finished, they add 5 c.c. of a 2 per cent potassium iodate solution, and the iodine liberated thereby is measured by again titrating with sodium thiosulphate. The Hübl solution used for the blank test is then treated in precisely the same manner, and thus the total iodine absorbed and the amount of iodine present as hydriodic acid are found. By multiplying the latter number by two the iodine substitution number is obtained. On subtracting this number from the total iodine absorption number the iodine addition number is found.

Schweitzer and *Lungwitz* term the last value the "correct" iodine number, and in a later publication the "true" iodine number. Their experiments are, in the writer's opinion, open to some objections; at any rate they do not solve the problem in a satisfactory manner, and would only appear to increase the confusion already existing. For in a further series of experiments the same observers [4] found that, whereas in both methyl alcoholic and ethyl alcoholic solutions, in presence of mercury bichloride, the total iodine absorptions were practically identical for a number of oils, the substitution numbers varied in a very capricious manner, thus leading to a double set of *true iodine numbers* (addition numbers). The so-called true iodine numbers were considerably higher in the case of the ethyl alcoholic solutions, or in other words, the substitution was considerably less than in methyl alcoholic solutions. When in a corresponding series of experiments the mercury bichloride was left out, it was found that in methyl alcoholic solutions substitution only of iodine (*i.e.*

[1] Cp. *e.g.* Williams, *Analyst*, 1895, 276.
[2] Cp. Lewkowitsch, *Jahrbuch der Chemie*, 1896, 392.
[3] *Jour. Soc. Chem. Ind.* 1895, 131.
[4] *Ibid.* 1895, 1030.

no addition) took place, whereas in ethyl alcoholic solutions chiefly substitution occurred, but simultaneously also addition to a very small extent. In chloroformic solutions iodine absorption took place in two directions, viz. by addition and substitution. True addition of iodine without concomitant substitution was only observed in the case of iodine solutions prepared with either carbon bisulphide or carbon tetrachloride to the exclusion of mercury bichloride. But as these experiments are identical with those made by *Gantter*, and condemned for the reason stated above, the true iodine values thus obtained have no practical value. The object *Schweitzer* and *Lungwitz* had in view was to find a method by which there would be obtained solely iodine addition values (without concomitant substitution) corresponding to those indicated by theory. This was actually reached by employing a carbon bisulphide solution of iodine, and allowing this solution to act at temperatures varying from 50° to 80° C. under pressure, mercury bichloride having been added in solid form. But unfortunately crucial experiments with "chemically pure" oleic acid furnished higher numbers than theory would indicate, although no substitution was noticeable. The nature of the reactions taking place is therefore not explained by the foregoing experiments.

A more successful solution of the problem has been reached by *Ephraim's*[1] experiments. He observed that the Hübl solution required a much larger amount of sodium thiosulphate after addition of potassium iodide than without it, and concluded therefrom that on mixing the components of the Hübl solution there is formed *at once* a substance capable of liberating iodine from potassium iodide.

The chemical change is assumed to take place according to the following equation[2]:—

$$HgCl_2 + I_2 = HgClI + ICl$$

with formation of iodine monochloride. This equation would correspond to Hübl's directions, that for 2 atoms of iodine at least 1 molecule of mercury bichloride must be used. A solution of iodine monochloride of the same strength as the Hübl solution must contain 16·25 grms. in 1000 c.c. A number of experiments carried out with iodine monochloride solution of the strength named on oleic acid, linseed oil, olive oil, poppy seed oil, sesamé oil, arachis oil, castor oil, and almond oil in the same fashion as in Hübl's iodine test, furnished results identical with those obtained by Hübl's method. *Ephraim* concludes, therefore, that alcoholic solutions of iodine monochloride may be substituted for the Hübl solution.

In practice it would appear preferable to adhere to Hübl's direction, since commercial iodine monochloride is rarely pure, this fact rendering it imperative to examine each sample of iodine monochloride, in order to ascertain the amount of ICl it contains, by

[1] *Analyst*, 1895, 254.

[2] Ephraim states distinctly that this equation must not necessarily be considered as quantitatively expressing the chemical change.

titration with sodium thiosulphate, both without and with addition of potassium iodide, so as to determine the amount of iodine which the impurities in the commercial article are capable of liberating.

Additional proof for the assumption that iodine *mono*chloride is present in the Hübl solution is afforded by the fact that similar experiments with iodine trichloride on oleic acid gave altogether discordant results.[1]

A study of Hübl's process with a view to following up quantitatively its chemical changes has been carried out by *Waller*.[2]

It was found that the whole of the oil was in the chloroform solution, that the chloroform contained both iodine and chlorine, both halogens having been absorbed by the oil in fairly constant proportions, and that the whole of the mercury was in the upper alcoholic layer. During the standing of the solution free hydrochloric acid was formed (an observation also recorded by *Schweitzer* and *Lungwitz*), such hydrochloric acid increasing in proportion to the excess of mercury bichloride.

The following explanation of the course of reactions is given :— Part of the iodine is absorbed in the first instance, and the mercury bichloride is converted into mercury iodide and free chlorine. The latter forms with the water, contained in the alcohol, hydrochloric acid and free oxygen. The oxygen then combines with that portion of the oil which has not yet absorbed halogen. According to *Waller's* view, the Hübl iodine number would thus be the amount of iodine, chlorine, and oxygen absorbed, expressed in terms of iodine, and the *true* iodine number of an oil would be found by subtracting from the Hübl number the amount of hydrochloric acid formed and calculated to iodine.

Unfortunately *Waller's* true iodine number differs very considerably from *Schweitzer* and *Lungwitz's* true iodine number ; for a sample of oleic acid, of the Hübl number 93, had, according to *Waller*, the "true" iodine number 84, whereas *Schweitzer* and *Lungwitz's* "chemically pure" oleic acid led to as high a number as 93-105.

It will appear from the foregoing that a comprehensive explanation of the Hübl process is still wanting. But this much is clearly established, that by following closely the directions laid down above for carrying out the iodine test practically constant results are obtained. The writer has proved this abundantly by a very large number of experiments on various fats and oils. If it were permissible to draw conclusions from the last column of the table given above, it would appear that the results so obtained are in excellent agreement with theory.

It is therefore most desirable that analysts (especially those who use the iodine test for the first time) should strictly adhere to the directions given above, at any rate until such time when the chemical reactions underlying Hübl's process will be fully understood.

[1] This is confirmed by Seeliger (*Pharm. Centralhalle*, 1894, 89) and Waller, *Chemiker Zeitung*, 1895, 1787).

[2] *Chemiker Zeitung*, 1895, 1787, 1831.

In order to eliminate slight errors due to the presence of free acids in fats, *Morawski* and *Demski*[1] determine the iodine value of the **free fatty acids** liberated from the fats by the method described above (p. 100). It should, however, be borne in mind that in this case the influence due to the presence of any soluble fatty acids is obliterated, and differences, caused by the varying proportions of soluble fatty acids in two fats, may thus be overlooked. Besides, during the operations entailed in liberating and drying the free acids, especially in the case of drying oils, oxidation may set in, resulting in a diminution of the iodine value. Therefore it is evident that the iodine values of the fats may not be proportional to those of their fatty acids. It is, however, customary to estimate the absorption of both the fat and its fatty acids.

In the determination of the absorption values of the free fatty acids the iodine solution is allowed to act directly on the fatty acids, solution in chloroform being unnecessary.

It is evident that from the iodine value of a fat alone the percentage of glycerides of the unsaturated fatty acids cannot be calculated. In the case, however, of a fat containing the glyceride of *one* unsaturated fatty acid only, the absolute amount of that glyceride can be determined.

B. QUANTITATIVE DETERMINATION OF SOME CONSTITUENTS OF FATS AND WAXES

When estimating fatty substances by gravimetric methods, due consideration should be given to the fact that on drying fats and fatty acids constant weights must not be expected. This is due to either a slight loss caused by volatilisation of volatile acids [either contained originally in the substance or formed at the higher temperature], or to an increase of weight owing to absorption of oxygen. It is quite possible, of course, that both volatilisation and consequent decrease of weight on the one hand, and oxidation and consequent increase of weight on the other hand, may occur simultaneously, these two sources of error to some extent counterbalancing one another (cp. also p. 160).

Hence the drying should be done at the lowest possible temperature, at any rate not above 110° C., and should not be pushed beyond a point when fairly approximate results have been obtained, which, as a rule, will be reached within a few hours. Drying oils or their fatty acids are best dried in a current of hydrogen, carbon dioxide, or coal gas. A convenient form of apparatus for such purposes has been described above (p. 88, cp. also p. 674).

The following table, due to *Tatlock*,[2] will give some indications as to the amount of error caused by drying fatty acids at 90° C. :—

[1] *Jour. Soc. Chem. Ind.* 1886, 179. [2] *Ibid.* 1890, 374.

Table showing Loss (or Gain) in Weight of Dry Fatty Acids, during different Periods, at 90° C.

Time heated at 90° C.	Fatty Acids from								Stearic Acid.	Olive Oil containing 9·42 per cent Free Oleic Acid.	Olive Oil from which Free Fatty Acid was removed.
	Olive Oil (1).	Olive Oil (2).	Olive Oil (3).	Olive Oil (4).	Castor Oil.	Rape Oil.	Cotton Seed Oil.	Linseed Oil.			
Dry.	100·00.	100·00.	100·00.	100·00.	100·00.	100·00.	100·00.	100·00.	100·00.	100·00.	100·00.
24 hours . .	99·22	99·33	99·18	99·50	99·18	100·50	99·26	101·25	100·08	100·24	100·88
48 ,, . .	98·88	98·92	98·85	99·06	98·51	100·30	99·04	101·23	100·06	100·52	101·42
72 ,, . .	...	...	...	98·70	97·85	99·89	...	...	99·72	100·52	101·32
96 ,, . .	98·18	98·20	98·17	...	...	...	98·12	100·42	...	...	...
120 ,, . .	...	...	...	98·09	96·82	99·46	97·87	100·19	98·22	100·10	100·36
192 ,, . .	96·96	97·08	96·97								
360 ,, . .	95·45	95·50	95·42								
528 ,, . .	94·14	94·17	94·10								
720 ,, . .	92·62	92·67	92·57								

The quantitative analysis of fats or waxes or of mixtures of several fats, provided foreign matters (as resin, paraffin wax, mineral oils, etc.), are absent, generally embraces the determination of one or more of the following constituents :—

i. Free fatty acids and neutral fat ; mean combining weight of the fatty acids.
ii. Diglycerides.
iii. Soluble (volatile) and insoluble (non-volatile) fatty acids.
iv. Saturated and non-saturated fatty acids.
v. Mixed palmitic, stearic, and oleic acids, other non-volatile fatty acids being absent.
vi. Approximate determination of liquid fatty acids—oleic and linolic.
vii. Hydroxy acids.
viii. Lactones (inner anhydrides).
ix. Glycerol.
x. Higher aliphatic alcohols.

i. Free Fatty Acids and Neutral Fat ; Mean Molecular Weight of the Fatty Acids

(*a*) *Gravimetric Determination of the Proportion of Free Fatty Acids*

Weigh off accurately in a flask several grms. of the sample, add hot alcohol and phenolphthalein, and neutralise carefully the free fatty acids by allowing dilute alkali to run in until the solution just acquires a permanent pink colour. If the strength of the alkali solution be known, the acid value of the fat will be found simultaneously. Allow the liquid to cool, dilute with an equal volume of water, and shake out in a separating funnel with petroleum ether. Draw off the aqueous layer, and wash the ether layer repeatedly with water, separating the wash-water as completely as possible from the petroleum ether.[1] (Remove the little water remaining by running the petroleum ether first into a dry flask, and next into the tared flask, or by filtering the petroleum layer through paper into the tared flask.) Extract the aqueous layer a second time with petroleum ether in the same way, and transfer the ether to the tared flask. Next distil off the petroleum ether, dry the residue, and weigh it. This will give the **neutral fat.**

The amount of free fatty acids may be found either by difference, or direct by transferring the aqueous layer and the wash-water to a separating funnel, acidifying with dilute sulphuric acid, and extracting with petroleum ether as directed above. The weight of substance found corresponds to the amount of fatty acids.

Laugier[2] and *Hager*[3] propose the following process for the determination of free fatty acids in oils :—

[1] Morawski and Demski, *Jour. Soc. Chem. Ind.* 1886, 179.
[2] *Zeitsch. f. analyt. Chemie*, 20. 133.
[3] *Ibid.* 17. 392 ; 19. 116 ; 20. 134.

Triturate 10 grms. of the oil under examination in a mortar with 5 grms. of sodium carbonate, add 5 grms. of water, and warm on the water-bath for one hour, occasionally stirring the mass. Then admix with it a sufficient quantity of coarsely-powdered pumice-stone so as to obtain a crumbling mass, dry on the water-bath, powder, and extract with ether free from alcohol. Evaporate the ether, and weigh the remaining *neutral fat*.

In the case of a crude oil the proportion of fatty acids cannot be found by difference, such oils containing, as a rule, several per cents of foreign substances (colouring matters, mucilaginous or resinous bodies) which are not extracted by ether. The mass left after exhaustion with ether must, therefore, be extracted with alcohol. The alcoholic solution is then evaporated to dryness, the remaining soap decomposed by sulphuric acid, and the liberated fatty acids mixed with a known quantity of paraffin wax, and weighed.

Any difference from 100 will correspond to the proportion of non-fatty substances in the sample.

Considering the slight solubility of soap in ether and the possibility of foreign substances passing into the alcoholic solution, it is evident that this method cannot claim great accuracy.

Sear[1] recommends the following method :—

Dissolve 5 grms. of the fat in 100-150 c.c. of carbon bisulphide in the cold in a flask provided with a well-fitting cork, add 2·5 grms. of finely divided zinc oxide, and allow to stand for three or four hours with occasional agitation. At the expiration of this time the contents of the flask are thrown upon a filter, the filtrate being collected in a tared flask, thoroughly washed with carbon bisulphide, and the filtrate distilled as low as possible on the water-bath, dried, and weighed. The residue, which consists of neutral fat and zinc oleate, is saponified with alcoholic potash, the soap decomposed with a mineral acid, the aqueous portion separated from the fatty acids, and the zinc precipitated from a hot solution by means of potassium carbonate. The zinc carbonate is then collected on a filter, weighed as zinc oxide, and calculated to the corresponding quantity of zinc oleate. Subtracting this from the weight of the mixture of neutral fat and zinc oleate, the weight of the former is obtained. The amount of oleic acid is calculated from the zinc oleate. The quantity of free solid fatty acids is obtained by adding together the weights of the neutral fat and oleic acid, and subtracting from the weight of the oil taken.

(*b*) *Volumetric Determination of the Proportion of Free Fatty Acids*[2]

The percentage F of free fatty acids in a fat or wax can be calculated from its *acid value* A (determined as described above, p. 148) if the mean molecular weight of the free fatty acids, M, be known. M grms. require, of course, 56100 milligrms. KOH, whilst

[1] *Chem. News*, 44. 299.

[2] Hausamann, *Dingler's Polyt. Jour.* 240. 62 ; Gröger, *ibid.* 244. 303 ; Yssel de Schepper and Geitel, *ibid.* 245. 295.

F grms. corresponding to 100 grms. of fat are saturated by 100 × A milligrms. KOH. We have therefore

$$M : 56100 = F : 100\ A,$$

hence

$$F = \frac{100\ A\ M}{56100} = \frac{A\ M}{561} \quad . \quad . \quad . \quad . \quad . \quad (1).$$

This method, however, is only applicable in the case of the fat containing no soluble fatty acids, or, at any rate, only an insignificant amount. In order to determine the mean molecular weight M, the fatty acids must be first separated from the neutral fat by the method given in the beginning of the preceding paragraph (p. 182), or *Gröger's* process may be adopted. The latter is carried out as follows :—

4 to 8 grms. of the sample are placed in a flask of about 300 c.c. capacity, and dissolved in 50 c.c. of neutralised alcohol by raising it to the boiling point. A few drops of phenolphthalein having been added, the solution is titrated with standard alkali until, after thorough agitation, the pink colouration is permanent. The solution is then diluted with 150 c.c. of water, when the neutral fat will separate out nearly completely, whilst the potash soap remains dissolved. Next 60-100 c.c. of ether are added and the contents of the flask shaken thoroughly. After settling out, the greatest part of the clear soap solution is drawn off by means of a pipette, care being taken that none of the ethereal layer is withdrawn at the same time, then diluted strongly with water, and boiled until the dissolved ether and alcohol are driven off completely. By adding dilute sulphuric acid the fatty acids are liberated ; they are washed with boiling water, which is removed by means of a syphon, until the wash-water shows no longer acid reaction. The acids are then allowed to cool. If they solidify the cake is removed regardless of the small quantity adhering to the sides of the vessel ; if, however, they remain fluid at the ordinary temperature a pipette must be used. The acids are then weighed accurately, dissolved in alcohol, and titrated with standard potash ; from the quantity of the alkali used their saponification value K is calculated, *i.e.* the number of milligrms. KOH required for 1 grm. of fatty acid. Since M grms. of fatty acids require 56100 milligrms. of KOH, we have the proportion

$$1 : K = M : 56100,$$

hence

$$M = \frac{56100}{K} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

By substituting this value for M in equation (1) we obtain

$$F = \frac{A \,.\, 56100}{561 \,.\, K} = \frac{A \,.\, 100}{K} \quad . \quad . \quad . \quad . \quad . \quad (3).$$

It is evident that it is not necessary to calculate the acid value A of the fat and the saponification value K of the free fatty acids, the ratio $\frac{A}{K}$ only being required. It will suffice, therefore, to substitute

for A and K the numbers of c.c. required for 1 grm. of fat and 1 grm. of fatty acids respectively. In that case the titer of the alkali need not even be known.

Thus if a and b represent the numbers of c.c. used for the two determinations, we find—

$$F = \frac{100 \times a}{b} \quad . \quad . \quad . \quad . \quad . \quad (4).$$

If the sample of fat may be considered as completely free from foreign substances, the proportion of neutral fat N may be found by difference; we have thus

$$N = 100 - F = 100 - \frac{100 \times a}{b} \quad . \quad . \quad . \quad . \quad (5).$$

Compared with the gravimetric process described above this volumetric method hardly offers any advantage, requiring, as it does, the isolation of the free fatty acids. Although the latter need not be recovered quantitatively in this case, still, the drying and weighing of part thereof is requisite.

The determination of F, however, is much simplified by assuming that the free acids possess the same mean molecular weight as those combined with glycerol to form the neutral fat. Such an assumption may be permissible for most rancid fats; indeed, *Thum*[1] has proved by experiment that it holds good for palm and olive oils.

This assumption granted, the percentage of free fatty acids and neutral fat in a fat may be found by one of the following three methods. At the same time the probable yield of fatty acids and glycerol from a fat may be readily calculated.

1. Determine the acid value A. Next separate the total fatty acids from 50 grms. of the sample (see p. 100), and titrate 2 to 5 grms. in alcoholic solution with standard alkali, thus finding the saponification value K of the total fatty acids.

The mean molecular weight of the total fatty acids M, the percentage of free fatty acids F, and the proportion of neutral fat N, are then calculated according to equations (2) (3) (4) and (5).

Let Γ be the quantity of glycerol, and Φ the quantity of fatty acids obtainable from 1 part of neutral fat, then Φ is evidently one-hundredth part of H, the *Hehner* value of the neutral fat, or $\Phi = \frac{H}{100}$.

The general equation expressing the saponification of fats is—

$$\underset{\text{Neutral fat.}}{C_3H_5O_3 . R_3} + 3H_2O = \underset{\text{Fatty acids.}}{3R . OH} + \underset{\text{Glycerol.}}{C_3H_8O_3},$$

R standing for the radicle of any fatty acid. Writing for a moment the formula of the neutral fat, $C_3H_2(R . OH)_3$, the last equation will read thus—

$$C_3H_2 . (R . OH)_3 + 3H_2O = 3R . OH + C_3H_8O_3.$$

[1] *Jour. Soc. Chem. Ind.* 1891, 70.

If M be, as before, the molecular weight of the fatty acids, the molecular weight of the neutral fat will be $3M + 38$; $(C_3H_2 = 38)$. Therefore, $(3M + 38)$ parts of fat yield $3M$ parts of fatty acids and 92 parts of glycerol $(C_3H_8O_3 = 92)$; or 1 part of neutral fat yields

$$\Phi = \frac{H}{100} = \frac{3M}{3M+38}; \quad \Gamma = \frac{92}{3M+38} \quad . \quad . \quad . \quad (6).$$

N per cent of neutral fat yields therefore, on saponification, the following quantities of fatty acids F_1 and glycerol G in per cents—

$$F_1 = N\Phi = N \cdot \frac{3M}{3M+38} \cdot \quad . \quad . \quad . \quad . \quad . \quad (7).$$

$$G = N\Gamma = N \cdot \frac{92}{3M+38} \cdot \quad . \quad . \quad . \quad . \quad . \quad (8).$$

Equation 8 expresses at the same time the *total yield of glycerol* obtainable from a fat.

The *total yield of fatty acids*, however, is made up from two components, viz. F, the percentage of free fatty acids, and F_1, the percentage of fatty acids obtainable from the neutral fat. If the total yield of fatty acids be Q, we have

$$Q = F + F_1 \quad . \quad . \quad . \quad . \quad . \quad (9).$$

It is evident that Q is identical with the *Hehner* value of the sample which can, of course, be found in a direct way. G will be more accurately determined by means of the ether value of the fat (see below, p. 154).

The subjoined table, due to *De Schepper* and *Geitel*, contains the molecular weights of a few fatty acids and of their triglycerides, and the quantities of fatty acids and glycerol obtainable from 100 parts of these glycerides. The last column contains the number of one-tenth c.c. of a standard solution of KOH, 10 c.c. of which correspond to 1 grm. $C_{17}H_{34}O_2$[2], required to saturate 1 grm. of fatty acid.

Fatty Acid.	Formula.	Molecular Weight of		Triglyceride yields		$\frac{1}{10}$ c.c. of KOH (10 c.c. = 1 grm. $C_{17}H_{34}O_2$).
		Fatty Acid.	Triglyceride.	Fatty Acids.	Glycerol.	
Stearic acid . .	$C_{18}H_{36}O_2$	284	890	95·73	10·337	95·07
Oleic acid . .	$C_{18}H_{34}O_2$	282	884	95·70	10·408	95·74
(Margaric acid[1] . .	$C_{17}H_{34}O_2$	270	848	95·52	10·850	100·00)
Palmitic acid . .	$C_{16}H_{32}O_2$	256	806	95·28	11·415	105·47
Myristic acid . .	$C_{14}H_{28}O_2$	228	722	94·47	12·742	114·03
Lauric acid . .	$C_{12}H_{24}O_2$	200	638	94·04	14·420	135·00
Capric acid . .	$C_{10}H_{20}O_2$	172	594	93·14	15·480	156·99
Caproic acid . .	$C_6H_{12}O_2$	116	386	90·16	23·830	232·7
Butyric acid . .	$C_4H_8O_2$	88	302	87·41	30·464	306·8

[1] Chap. iii. p. 47.

2. Determine A, the acid value, and K, the saponification value, of the fat. The percentage of free fatty acids, neutral fat, and the yield of glycerol G and total fatty acids Q, can be calculated in the following way :—

The amount of glycerol is proportional to the quantity of KOH found in determining the ether value E, E being = K – A (see p. 154), or G corresponds to $\frac{100\ E}{1000}$ grms. $= \frac{E}{10}$ grms. According to the equation

$$\underset{\text{Neutral fat.}}{C_3H_5(OR)_3} + 3KOH = \underset{\text{Glycerol.}}{C_3H_8O_3} + \underset{\text{Soap.}}{3R\,.\,OK},$$

92 parts of glycerol correspond to $3 \times 56{\cdot}1$ parts of KOH. Hence the proportion

$$G : \frac{E}{10} = 92 : 3 \times 56{\cdot}1,$$

and

$$G = \frac{92\ E}{10 \times 3 \times 56{\cdot}1} = 0{\cdot}05466\ E \quad . \quad . \quad . \quad . \quad (10).$$

The yield of total fatty acids Q in per cent is therefore

$$Q = 100 - \frac{38}{92} G$$

(92 parts of glycerol being proportional to 38 parts of C_3H_2); or substituting the value for G found in (10)—

$$Q = 100 - \frac{38E}{10 \times 3 \times 56{\cdot}1} = 100 - 0{\cdot}02258\ E \quad . \quad . \quad . \quad (11).$$

1000 milligrms. of fat contain, therefore, $1000 - \frac{38E}{3 \times 561}$ milligrms. of total fatty acids, requiring for their neutralisation K milligrms. of KOH. We have, therefore, for the calculation of their mean molecular weight the proportion—

$$1000 - \frac{38E}{3 \times 56{\cdot}1} : K = M : 56{\cdot}1,$$

wherefrom

$$M = \frac{56100 - \frac{38E}{3}}{K} = \frac{168300 - 38E}{3K} \quad . \quad . \quad . \quad . \quad (12).$$

According to equation (1) we have $F = \frac{A\,.\,M}{561}$; substituting for M the value found in (12), we obtain for the percentage of free fatty acids—

$$F = \frac{A(168300 - 38E)}{561 \times 3K} = \frac{(168300 - 38E)\,A}{1683K} \quad . \quad . \quad . \quad (13).$$

3. If the composition of a neutral fat in a mixture of the neutral fat with its free fatty acids be known, the weighing off of the substance may be dispensed with by adopting *Gröger's* method.

Supposing it be required to know how far the resolution of tallow into fatty acids and glycerol has proceeded in a technical process for the saponification of fat. Let us assume that the yield of total fatty acids from neutral tallow has been found to be 95·6 per cent (by *Hehner's* method, or by the method described under 1).

A quantity of the sample about 6 to 10 grms., which need not be weighed off accurately, is titrated with alkali, the titer of which need not be known. If a and b be the numbers of c.c. required for the neutralisation of the free fatty acids on the one hand, and for the complete saponification on the other, it is evident that

$$N : F = \frac{100}{95{\cdot}6} b : a.$$

According to a well-known rule we have

$$N : N + F = \frac{100}{95{\cdot}6} b : \frac{100}{95{\cdot}6} b + a.$$

Since

$$N + F = 100 \text{ ; and } \frac{100}{95{\cdot}6} = 1{\cdot}046,$$

we have after substitution

$$N : 100 = 1{\cdot}046\, b : 1{\cdot}046\, b + a,$$

hence

$$N = \frac{104{\cdot}6\, b}{1{\cdot}046\, b + a} \quad . \quad . \quad . \quad . \quad . \quad (14).$$

(c) *Mean Molecular Weight of the Fatty Acids*

In the preceding paragraph two methods for the determination of the mean molecular weight have been described; in order to put them more clearly before the reader they may be repeated here briefly.

1. Saponify 50 grms. of the fat, dry the fatty acids, as directed (p. 182), and determine the *saponification value* K_1 *of the fatty acids.* The mean molecular weight is then found by the following equation (2):

$$M = \frac{56100}{K_1}.$$

It should be understood that M represents the mean molecular weight of the insoluble, non-volatile fatty acids only, the soluble acids having been washed away in the course of preparation.

2. Determine the *saponification value* K and *the ether value* E of the *fat.* According to equation (12) we have then

$$M = \frac{168300 - 380\, E}{3K}.$$

Provided a fat contains no foreign substances, nor any glycerides of the soluble acids, the mean molecular weight of the fatty acids can be calculated from the *Hehner* value, if the fat does not contain a considerable amount of free fatty acids. That assumption, however, rarely obtains in practice.

The mean molecular weight may then be calculated from equation (6) :—

$$\frac{H}{100}=\frac{3M}{3M+38},$$

hence

$$M=\frac{38H}{300-3H}=\frac{38H}{3(100-H)} \quad . \quad . \quad . \quad . \quad (15).$$

Thus from H = 95·6 for neutral tallow we should find the mean molecular weight of the tallow acids M = 275, which is in close agreement with their molecular weight as determined by titration.

If M be the mean molecular weight of the total fatty acids, and M_1 the mean molecular weight of the insoluble acids; further, if H, the percentage of insoluble fatty acids, and S, the percentage of the soluble fatty acids (see p. 191), be known, the *mean molecular weight of the soluble fatty acids*, M_2, can be calculated from the following equation, in which Q represents, as before, the percentage of the total fatty acids, as expressed by equation (11) :—

$$\frac{Q}{M}=\frac{S}{M_2}+\frac{H}{M_1},$$

hence

$$M_2=\frac{SMM_1}{QM_1-HM} \quad . \quad . \quad . \quad . \quad (16).$$

Another method of finding the mean molecular weight of the volatile or soluble acids is given by the *Reichert-Meissl* value of a fat, as determined by *Morse* and *Burton's* process (see p. 631). Let k be the number of milligrms. KOH required for neutralisation of the volatile acids from one grm. of fat, or of $\frac{S}{100}$ grms. of volatile acids (S being the percentage of soluble fatty acids), then we have

$$M_2:56100=\frac{S}{100}:k,$$

hence

$$M_2=\frac{561\,S}{k} \quad . \quad . \quad . \quad . \quad . \quad (17).$$

Thus, if for a butter fat the *Reichert-Meissl* value be 32 (*i.e.* for 5 grms.), and S = 7·44 per cent, k will equal $\frac{32\times 5\cdot 61}{5}$; and therefore

$$M_2=\frac{561S\times 5}{32\times 5\cdot 61}=\frac{S\times 500}{32}=\frac{7\cdot 44\times 500}{32}=\frac{3720}{32}=116\cdot 2.$$

ii. Diglycerides

The occurrence of diglycerides in a fat has hitherto been proved in the solitary case of "rape oil stearine" in which dierucin has been found (see p. 2).

A fat may be tested for diglycerides by boiling an accurately weighed quantity with acetic anhydride, and washing the resulting product with boiling water until it is free from acid. If diglycerides be present an increase of weight will be found.[1] This is due to one acetyl group having been taken up by one molecule of the diglyceride with the formation of a triglyceride, as shown by the equation

$$C_3H_5{}^{OH}_{(OR)_2} + C_2H_3O.OH = C_3H_5{}^{O.C_2H_3O}_{(OR)_2}.$$

If the quantitative estimation be carried out with due care, in the case of a *pure* diglyceride its molecular weight may be calculated from the increase in weight. Thus if a grms. of a pure diglyceride have been weighed off, and an increase of weight, i, has been found, it is evident that we have the proportion

$$a : a+i = M : M+42,$$

where M is the molecular weight of the diglyceride, and consequently M + 42 the molecular weight of the triglyceride obtained on assimilation of the group C_2H_2O(= 42). The above proportion is expressed by the equation $a(M + 42) = M(a + i)$, hence

$$M = \frac{42a}{i} \quad . \quad . \quad . \quad . \quad . \quad (18).$$

As a rule, however, the diglyceride will only form a small proportion of the fat under examination. If the chemical composition of the diglyceride be known, the absolute quantity of the diglyceride a in the fat may be calculated with the help of the same equation (18)

$$a = \frac{Mi}{42}.$$

Thus if a grms. of a fat, containing a diglyceride of the known molecular weight M, have been weighed off, and the increase i obtained on acetylating, the percentage of the diglyceride in the fat will be found from the proportion

$$a : \frac{Mi}{42} = 100 : x,$$

hence

$$x = \frac{100Mi}{42a} \quad . \quad . \quad . \quad . \quad . \quad (19).$$

The proportion of diglycerides can also be found volumetrically if the molecular weight of the diglyceride be known.[2] If M be the molecular weight of the diglyceride, K the saponification value of the sample under examination, and C the saponification value of the

[1] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1892, 138.
[2] Benedikt, *Jour. Soc. Chem. Ind.* 1888, 696.

acetylated product, then the percentage D of the diglyceride may be calculated from the following formula (56·1 being the molecular weight of KOH and 42 that of C_2H_2O):

$$D = \frac{100M(C - K)}{5610 - 42C} \quad . \quad . \quad . \quad . \quad (20).$$

I prefer to use the formula

$$D = \frac{100(C - K)M.(M + 42)}{56{\cdot}1(M - 84)} \quad . \quad . \quad . \quad . \quad (21).$$

which is arrived at as follows: M grms. of a diglyceride require $2 \times 56{\cdot}1$ grms. of KOH for saponification; $M + 42$ grms. of the triglyceride, obtained from it on digestion with acetic anhydride, require $3 \times 56{\cdot}1$ grms. KOH. Therefore 1 grm. of the diglyceride requires $\frac{2 \times 561}{M}$, and 1 grm. of the triglyceride $\frac{3 \times 56{\cdot}1}{M + 42}$.

The difference

$$\frac{3 \times 56{\cdot}1}{M+42} - \frac{2 \times 56{\cdot}1}{M} = \frac{56(M - 2 \times 42)}{M(M+42)}$$

must, for a sample consisting of a pure diglyceride, be equal to C – K, hence

$$D = \frac{100(C - K)M.(M + 42)}{56{\cdot}1(M - 2 \times 42)}.$$

Thus if the proportion of di-erucin – $C_3H_5\begin{matrix}(O_2C_{22}H_{41})_2\\OH\end{matrix}$ $(M = 732)$ in rape oil stearine has to be determined, and K be found = 46·0 for this rape oil stearine, and for the acetylated rape oil stearine C = 67·8, we have, since C – K = 21·8,

$$D = \frac{100 \times 21{\cdot}8 \times 732 \times 774}{56{\cdot}1 \times (732 - 84)} = 34.$$

The correctness of this calculation may be proved as follows:—

The saponification value of pure di-erucin $C_3H_5(OC_{22}H_{41}O)_2(OH)$ is 153·3, that of acetylated di-erucin $C_3H_5(OC_2H_3O)(OC_{22}H_{41}O)_2$ is 217·4. The difference 217·4 – 153·3 = 64·1; found C – K = 21·8; therefore

$$D = \frac{21{\cdot}8 \times 100}{64{\cdot}1} = 34.$$

If a fat contains, besides diglycerides, glycerides of hydroxylated fatty acids, the calculation becomes more complicated, since the latter, on digesting with acetic anhydride, also assimilate the acetyl group. In such cases it is necessary to prepare the free fatty acids from 50 grms. of the fat, and to determine their acetyl value.

iii. Soluble (Volatile) and Insoluble (Non-Volatile) Acids

The proportion of the *insoluble* or *non-volatile* fatty acids is indicated by the *Hehner* value H.

The proportion of the total fatty acids, as found by the ether value E, is according to equation (11)—

$$Q = 100 - 0{\cdot}02258\ E,$$

consequently the percentage of soluble (volatile) acids S is

$$S = Q - H = 100 - 0{\cdot}02258\ E - H \quad . \quad . \quad . \quad (22).$$

Thus, if for a butter fat the *Hehner* value has been found = 87·5, the saponification value = 227, and the acid value = 3, we have, since E = 224

$$S = 100 - (0{\cdot}02258 \times 224)87{\cdot}5 = 7{\cdot}44 \text{ per cent.}$$

iv. Saturated and Non-Saturated Fatty Acids—Proportion of Liquid and Solid Acids in the Insoluble Fatty Acids

Before attacking the quantitative estimation of the proportion of liquid and solid acids in the mixed insoluble fatty acids, it will be found useful to examine the mixture qualitatively for presence of any liquid or solid acids. The former are best discovered by applying *Hübl's* test, *i.e.* by determining the iodine value of all the insoluble acids. If no iodine absorption be found, it is safe to conclude that unsaturated acids are absent. If, on the contrary, a definite value has been obtained, separation of the acids by means of their lead salts (see below) must be resorted to, since some fats may contain *solid* unsaturated fatty acids, as isooleic acid and erucic acid, the lead salts of which are either insoluble or sparingly soluble in cold ether.

For the qualitative detection of solid fatty acids (stearic, palmitic) in a liquid fat, *Allen* saponifies with alcoholic potash, and neutralises accurately the excess of alkali with acetic acid, using phenolphthalein as indicator. After filtering off, the filtrate is mixed with two volumes of ether, and alcoholic solution of lead acetate is added. A white precipitate will indicate presence of solid fatty acids.

A method for the separation of the solid from the liquid acids was proposed first by *Varrentrapp*. It is based on the solubility of the lead salts of the liquid fatty acids (oleic, linolic, and their homologues) in ether, the lead salts of the solid fatty acids (stearic, palmitic, etc.) being insoluble in that menstruum. This process does not yield very accurate results, inasmuch as small quantities of the solid acids pass into the ethereal solution, as was shown first by *Mulder*,[1] whilst lead salts of the drying fatty acid remain partly undissolved. *Lewkowitsch*[2] has also shown that in the absence of drying fatty acids a complete separation of the liquid from the solid acids is impossible. Therefore the separation by means of the lead salts is not a quantitative method, but can only be looked upon as a fractional separation. A

[1] Mulder, *Chemie der austrocknenden Oele*, 1867, p. 44 (German translation).
[2] *Jour. Soc. Chem. Ind.* 1890, 845.

glance at the solubilities of the lead salts of the saturated acids in ether given in the following table will corroborate this conclusion :—

Lead Salt of	100 c.c. of Ether dissolve	Observer.
Palmitic Acid	0·0184	Lidoff [1]
Stearic Acid	0·0148	,,
Mixed Stearic and Palmitic Acids (Iodine value = 0)	0·0150 (at 25° C.)	Twitchell [2]

Varrentrapp's reaction has been used in several forms, the more important of which are detailed below.

1. *Oudemans' Process.*[3]—Prepare from the sample of fat under examination the fatty acids in the usual manner, add an excess of sodium carbonate, and evaporate on the water-bath to complete dryness. Digest the dry residue with absolute alcohol, and filter the solution through a jacketed funnel. Exhaust the insoluble part by repeated boiling out and washing with absolute alcohol until the sodium soap has been brought completely into solution, dilute the latter with a little water, and add an excess of lead acetate solution. Then thoroughly wash the precipitated lead salts, and dry them first by exposure to air and then by allowing to stand under a desiccator. Next digest an accurately weighed quantity of the lead salts with dry ether in a well-stoppered flask, filter the ethereal solution, and exhaust repeatedly the undissolved mass with fresh quantities of ether ; then distil off the ether. Dry the residue at a gentle heat and weigh. If there is reason to suppose that oleic acid only is present, the dried residue may be considered as lead oleate. If, however, the nature of the liquid acids be unknown, a determination of lead must be made as in the following process.

2. *Kremel's Modification.*[4]—By this process the object of *Oudemans*, viz. to obtain the acids in the form of completely neutral soaps, is attained in the following more expeditious way :—

Weigh off accurately 2 to 3 grms. of the sample of fat in a wide-mouthed flask of about 100 to 150 c.c. capacity, and saponify on the water-bath with about the same quantity of caustic potash and 10 c.c. of 95 per cent alcohol. Then add a little water and a few drops of a phenolphthalein solution, and neutralise accurately with acetic acid. Evaporate off the alcohol on the water-bath, dissolve the soap in 80 c.c. of hot water, and precipitate with lead acetate. The lead soaps will be found, on gentle agitation, to adhere completely to the sides of the flask. Cool completely, pour the liquid through a filter, and wash several times with boiling water. Then melt the lead salts by warming on the water-bath, allow to cool, drain any liquid through the filter, and dry the contents of the flask, as also the filter, at a gentle heat. Next digest the lead salts with ether, and filter the

[1] *Berichte*, 26, *Ref.* 97.
[2] *Jour. Soc. Chem. Ind.* 1895, 515.
[3] *Jour. f. prakt. Chem.* 99. 407.
[4] *Pharm. Centralhalle*, 5. 337.

ethereal solution through the same filter into a tared porcelain basin, keeping the filter well covered. After thorough exhaustion with ether, evaporate the filtrate, dry the residue first at a gentle heat on the water-bath, then in a desiccator over sulphuric acid, and weigh. Determine the quantity of lead oxide in an aliquot part of the residue, and subtract the total amount of lead oxide from the weight of the lead salts. The difference thus obtained will indicate the amount of anhydrides of the liquid fatty acids. By adding to this amount the quantity of water corresponding to the weight B of lead oxide found —multiplying B by $\frac{18}{223} = 0{\cdot}0807$ — the weight of the liquid acids themselves will be obtained. The lead salts of the solid fatty acids, dried on the filter by allowing the ether to evaporate, are put back into the flask and decomposed by boiling with dilute hydrochloric acid. The separated fatty acids are then dissolved in ether, and their weight determined after evaporating off the ether.

3. *Röse's Modification.*[1]—*Röse* rejects the two preceding processes on account of their tediousness and liability to error caused by oxidation, especially of the fatty acids of the linolic series, and the formation of basic lead salts during treatment with boiling ether, the basic lead salts of the liquid fatty acids being insoluble in ether. He recommends the following modification :—

Prepare the fatty acids from the sample of fat, and place 1 grm. in a 100 c.c. flask, with 0·5 grm. of lead oxide and about 80 c.c. of dry ether. Allow to stand in a cool place for twenty-four to forty-eight hours, with occasional shaking. Then make up to exactly 100 c.c. with dry ether, shake thoroughly, and allow to settle. Take out 50 c.c. and filter through a small filter into a tared flask, keeping the filter as full as possible. Evaporate the ether, dry the residue in a current of carbonic dioxide, and weigh. After weighing, determine the lead by digesting on the water-bath with 5 c.c. of dilute sulphuric acid (1 : 5), diluting with 80 c.c. of 95 per cent alcohol, and weighing the precipitated lead sulphate on a tared filter after drying at 100° C. Test experiments carried out by the author of this method with pure oleic acid gave very accurate results.

According to *Twitchell*[2] petroleum ether completely volatile at 80° C. should be substituted for ether, the former dissolving less of the stearates and palmitates than ether; but even then *Röse's* method would only be applicable when the original fat is perfectly fresh and precautions are taken to avoid oxidation during all the manipulations.

4. *Muter and de Koningh's Modification.*[3]—In this process the weighing of the lead salts and the determination of the lead is dispensed with. They proceed as follows :—

3 grms. of the sample of fat are saponified with 50 c.c. of alcohol and a few lumps of stick potash. Phenolphthalein is then added, and

[1] *Jour. Soc. Chem. Ind.* 1887, 306.

[2] *Ibid.* 1895, 515.

[3] *The Analyst*, 1889, 61. Cp. also Lane, *Jour. American Chemical Soc.* Feb. 1893; Wallenstein and Finck, *Jour. Soc. Chem. Ind.* 1895, 79.

the solution slightly acidified with acetic acid, and finally titrated with alcoholic potash until neutral. Next 30 c.c. of a 10 per cent lead acetate solution are boiled in a beaker with 200 c.c. of water, and the neutralised solution gradually run into it[1] with constant stirring. After rapidly cooling, the clear supernatant liquid is drawn off and the precipitate washed thoroughly with boiling water. The lead salts are then transferred to a flask containing 80 c.c. of ether, the beaker being washed out with small quantities of ether until the united ethereal liquids make up a volume of 120 c.c. The flask is then stoppered and shaken repeatedly during the next twelve hours, when all the lead salts of the liquid acids will have dissolved. The solution is then filtered into a Muter tube (Fig. 39) of 250 c.c. capacity, and the precipitate washed with ether until the filtrate is free from lead; 120 c.c. of ether will be found quite sufficient for the complete washing. The ethereal solution is made up with a mixture of one part of hydrochloric acid and four parts of water to 250 c.c., and shaken until the lead soaps are decomposed completely, which is indicated by the ethereal layer becoming clear. The acid liquid is then drawn off, and the ether layer washed with fresh quantities of water until the wash-water is free from acid. The volume of the ether layer is made up to 200 c.c., and 50 c.c. of it run into a small Erlenmeyer flask, and the ether partly evaporated. It is not advisable to evaporate the ether completely, since oxidation of the fatty acids may take place.[2] The residue is mixed with 50 c.c. of alcohol, and titrated with decinormal alkali. The alkali used is calculated to oleic acid, 1 c.c. of decinormal alkali equalling 0·0282 grm. $C_{18}H_{34}O_2$. The error caused by presence of linolic and linolenic acids (mol. weight 280 and 278) is so slight that it may be neglected.

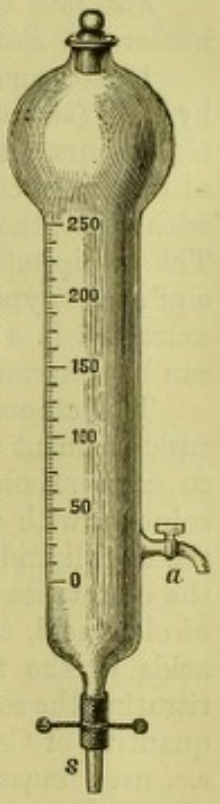


Fig. 39.

If the ether be driven off in a current of dry carbonic dioxide or hydrogen, the absolute quantity of liquid fatty acids can be determined.

Another quantity of the ethereal solution contained in the Muter tube may be used for the determination of the iodine value in the usual way, after the ether has been evaporated off in a current of carbonic acid. For this iodine value *Wallenstein* and *Finck* propose the term "inner" or "absolute" iodine number of the fat (cp. chap. ix. p. 312).

For fats, or fatty acids containing but small quantities of solid acids, *Allen's* method, as above described (p. 192), may be used, viz.

[1] The writer finds it more convenient to run the lead solution into the soap solution contained in a flask, in which the extraction with ether takes place forthwith.

[2] Although *Muter* in his experiments on the liquid fatty acids of lard—yielding 94 as their iodine number—did not use the precaution of entirely excluding access of air, *Twitchell's* objection to *Muter's* method is not conclusive, as the difference between American and European lards (see p. 573) must not be lost sight of.

collect the precipitate, decompose with hydrochloric acid, and weigh the liberated fatty acids.

If a separation of the free fatty acids from the neutral fat has been effected by one of the processes described above, the proportion of solid and liquid fatty acid in both the free acids and the neutral fat may be determined as detailed in this paragraph.

For fats containing but small quantities of free fatty acids, as butter fat, *Bondzynski* and *Rufi*[1] use the following process :—

10-20 grms. of fat are dissolved in ether, mixed with dry calcium hydrate (slaked lime), and allowed to stand for twenty-four to forty-eight hours with occasional shaking. The precipitate containing excess of lime, and calcium stearate and palmitate is filtered off and washed with ether, the neutral fat and calcium oleate passing into the filtrate. The precipitate is then decomposed by sulphuric acid, and the precipitated gypsum, together with the liberated solid fatty acids, extracted in a Soxhlet tube with ether, when the amount of the latter can be determined in the usual way.

The ethereal filtrate is evaporated in a platinum dish and the residue burnt; the ash remaining is weighed as CaO, and calculated to calcium oleate (a better plan would be to shake the ethereal solution with dilute hydrochloric acid, and determine the calcium in the acid liquid by precipitation with ammonium oxalate). On adding the quantities of solid fatty acids found by direct weighing and that of oleic acid, calculated from the CaO, the total amount of free fatty acids in the fat will be obtained. This figure can be checked by titrating the solid fatty acids with decinormal alkali, and expressing the quantity of CaO found in terms of decinormal alkali. The sum of the c.c. used must correspond to the number of c.c. of decinormal alkali obtained on titrating the original fat after washing it with water.

v. Mixed Palmitic, Stearic, and Oleic Acids, other Non-Volatile Fatty Acids being absent

The methods described under this head[2] have been proposed in the first instance for the practical requirements of the candle-maker. It should, however, be borne in mind that "distilled stearine" (distilled stearic acid) contains considerable quantities of the solid isooleic acid, which absorbs, of course, the same quantity of iodine as ordinary oleic acid. Therefore, in the formulæ given below, O represents the sum of the two isomeric oleic acids.

In order to determine the proportion of ordinary oleic acid alone, the lead-salt-ether method has to be resorted to, lead isooleate being but sparingly soluble in cold ether.

It has been pointed out above (p. 192) that the lead-salt-ether method does not yield absolutely reliable results. *Hehner*,[3] judging from a series of experiments on almond oil, cotton seed oil, cocoa nut

[1] *Zeitsch. f. analyt. Chemie*, 1890, 1.
[2] Chevreul's method referred to (p. 34) is only of historical interest.
[3] *Analyst*, 17. 181.

oil, and margarine, condemns this method as utterly untrustworthy, the solid acids having been found to give definite iodine values (cp. Lewkowitsch, *Jour. Soc. Chem. Ind.* 1890, 845).

De Koningh,[1] on the other hand, tries to vindicate this process by proposing to decompose the insoluble lead salts with hydrochloric acid, and to re-crystallise the fatty acids so obtained from hot alcohol. *Lewkowitsch* (*l.c.*) has employed this method before.

Lidoff[2] recommends the lead-salt-ether method (employing absolute ether), but makes a correction for the dissolved lead palmitate and stearate in accordance with the numbers given in the table (p. 193). This correction may meet the first of *Twitchell's*[3] objections to the lead-salt-ether method; whilst his second objection, viz. that the lead soaps of the unsaturated acids are oxidised even more rapidly than the free acids on exposure to air, does not apply with full force to oleic acid, especially if due precautions (see p. 195) are observed.

(*a*) *Determination of Oleic Acid*

If a fat contains no insoluble fatty acids other than stearic, palmitic, and oleic acids, the proportion of oleic acid can be determined from the iodine value of the fat, according to *Hübl*, or from that of its fatty acids, as proposed by *L. Mayer*.

Theory requires for oleic acid the iodine value 90·07, with which experiments agree (p. 175). The theoretical iodine value for olein is therefore 86·20.

Now, if the iodine value of a fat be found = J, the proportion of olein, O, in per cents, will be

$$O = \frac{100}{86{\cdot}2} J \text{ ; or } O = 1{\cdot}1601\ J$$

and the percentage of oleic acid, E, obtainable from the fat

$$E = \frac{100}{90{\cdot}70} J \text{ ; or } E = 1{\cdot}1102\ J.$$

If J′ be the iodine value of the fatty acids, the proportion of oleic acid, E′, thereof will be

$$E' = 1{\cdot}1102\ J'.$$

David[4] has proposed for the determination of oleic acid a method based on the fact that the solid acids (stearic and palmitic) are less soluble in a mixture of alcohol and acetic acid than oleic acid. It is very unlikely that such a process will give accurate results.

The mixture employed for the separation is prepared in the following way :—Dissolve in a measuring cylinder, indicating tenths of c.c., 1 c.c. of pure oleic acid in 3 c.c. of 95 per cent alcohol, and add drop by drop a mixture consisting of equal parts of glacial acetic acid and water as long as no turbidity appears. It will be found that at 15° C., 2·2 c.c. of the acetic acid having been added, the further addition of 0·1 c.c. will render this liquid turbid, and all the oleic acid—1 c.c.—will

[1] *Chem. News*, 65. 259.
[2] *Berichte*, 26, Ref. 97.
[3] *Jour. Soc. Chem. Ind.* 1895, 515.
[4] *Jour. Chem. Soc.* 34. 1011.

eventually float on the top. Should this reaction (the proportions stated being used) not take place, the proportions must be varied until the separation is obtained as described. An alcoholic solution of stearic acid behaves totally different, turbidity setting in immediately after the addition of the first drop of acetic acid.

Now prepare a mixture of alcohol and acetic acid in the proportions ascertained (say, 300 c.c. of alcohol and 220 c.c. of acetic acid), introduce 1 or 2 grms. of finely divided stearic acid, and keep the solution in a washing bottle, the delivery tube of which is closed at the bottom by a small sponge in order to retain any undissolved stearic acid.

For actual analysis introduce the weighed and finely divided fatty acids (free from neutral fat) into a well-stoppered bottle, add 16 c.c. of the alcohol-acetic-acid mixture per grm. of substance, and allow to stand for twenty-four hours at a temperature of 15° C. with occasional agitation. Then filter, keeping the funnel well covered, and wash the residue on the filter first with the mixture, and afterwards with cold water. Wash the solid acid on the filter into a tared porcelain dish, and heat on the water-bath until the melted acid floats on the top. Allow to cool, pour off the water, dry at 100° C., and weigh. The fatty acid in the filtrate may be separated by neutralising with alkali, evaporating the alcohol, and liberating the oleic acid with hydrochloric acid.

Tallow contains, as a rule, 95 per cent of fatty acids. If, therefore, 0·95 grm. of the fatty acids of a sample of tallow be weighed off, the quantity of solid acids obtained on weighing the residue, multiplied by 100, will give the yield of solid acids from the tallow in per cents.

This method cannot be used for liquid mixtures of fatty acids rich in oleic acid, experiments by *J. Schuster* having shown that in such cases considerable quantities of stearic acid pass into the solution.

(*b*) *Determination of Stearic Acid*[1]

On triturating the mixed fatty acid from a solid fat with dilute alcohol of specific gravity 0·911 in a mortar, the unsaturated fatty acids are almost completely dissolved, the palmitic acid is partially dissolved, whereas the stearic acid remains almost completely undissolved. In a practical experiment the mixed solid acids had an iodine value of 2-3 only.—If the admixture of oleic acid be neglected, the proportion of stearic acid may be ascertained as described below under (*c*) *Determination of Palmitic Acid*, provided no other solid acid be present; lower fatty acids than palmitic acid would be dissolved by the alcohol, but if higher fatty acids, *e.g.* arachidic acid be suspected, the method would become entirely unreliable.

Far better results, however, are obtained by treating the mixed fatty acids with an alcoholic solution of pure stearic acid saturated at 0° C. *Hehner* and *Mitchell* have shown by a series of experiments, carried out on pure stearic acid and on mixtures of stearic acid with

[1] Hehner and Mitchell, *Analyst*, 1896, 321.

(*a*) saturated acids lower than palmitic; (*b*) palmitic acid; (*c*) crude oleic acid; (*d*) mixed saturated and unsaturated fatty acids (as *e.g.* mixed lard fatty acids), that stearic acid is left undissolved and can be determined quantitatively with great accuracy.

The analysis is carried out as follows: Prepare a solution of stearic acid by dissolving about 3 grms. of pure stearic acid in 1000 c.c. of warm (methylated) alcohol of specific gravity 0·8183 (containing 94·4 per cent of alcohol by volume) in a stoppered bottle. Immerse the flask up to the neck in ice-water (kept in an ice-chest well protected against radiation of heat), and allow to stand in the ice-water overnight. After twelve hours, syphon off the mother liquor—without removing the flask from the ice-water—by means of a small thistle funnel immersed in the alcoholic solution and covered over with a piece of fine calico (so as to retain the separated stearic acid crystals in the flask). The funnel is twice bent at right angles, and is best fitted into a suction bottle, so that the clear liquor can be drawn off by means of a filter pump.

0·5 grm. to 1 grm. of the mixed fatty acids under examination, if solid, or 5 grms. if liquid, are weighed off in a flask and dissolved in 100 c.c. of the above alcoholic stearic acid solution. The flask is placed in ice-water overnight, the mixture is agitated next morning while the flask is kept in the ice-water, and then allowed to stand for at least half-an-hour in the ice-water in order to promote crystallisation. The alcohol is then filtered off as described above, care being taken to draw off the solution as completely as possible. The residue in the flask is then washed three times in succession with 10 c.c. of the alcoholic stearic acid solution, and cooled down to 0° C. The crystals adhering to the calico of the thistle funnel are then washed off with hot alcohol into the flask, the alcohol is evaporated off, and the residue dried at 100° C. and weighed. This residue is considered as pure stearic acid. It is advisable to take the melting point of the acid; it should not be much below 68·5° C.

As the walls of the flask and also the undissolved crystals retain a small quantity of the alcoholic stearic acid solution a correction must be applied. *Hehner* and *Mitchell* found that in their case the correction was 0·005 grm., which was deducted from the total weight of the residue found.

This method unfortunately breaks down in the case of Japan wax fatty acids. In a number of experiments carried out upon mixtures of these acids with pure stearic acid, the latter could only be recovered partially in some cases, whereas in other cases none at all was obtained.

(*c*) *Determination of Palmitic Acid*

In a mixture of palmitic and stearic acids the proportions of the several acids may be calculated from the mean molecular weight of the mixed fatty acids (determined as directed, p. 184), provided that this constant has been determined with the greatest accuracy.

The same method, of course, will hold good for any other mixture of two fatty acids, the molecular weights of which differ sufficiently.

The mean molecular weight of the mixed fatty acids should be determined with not less than 5 grms. of substance. Then, letting M be the mean molecular weight of the mixed acids, M_1 and M_2 the molecular weights of the single fatty acids, and x and y their percentages in the mixture, x and y can be calculated from the following equations :—

$$x+y=100$$

$$\frac{x}{M_1}+\frac{y}{M_2}=\frac{100}{M}$$

hence

$$x=100\frac{M_1(M-M_2)}{M(M_1-M_2)} \text{ and } y=100\frac{M_2(M_1-M)}{M(M_1-M_2)}.$$

Thus, if for 5 grms. of a mixture of palmitic and stearic acids 37·75 c.c. half-normal caustic soda be used, M equals 264·9, and we have, since $M_1=284$, and $M_2=256$—

$$x=100\frac{284(264\cdot9-256)}{264\cdot9(284-256)}=34\cdot08.$$

100 parts of the mixed fatty acids contain therefore

34·08 parts of stearic acid, and
65·92 parts of palmitic acid.

For other values the following table, due to *Mangold*,[1] will be found useful :—

Mixed Stearic and Palmitic Acids

Acid Value. Mgrms. of KOH per 1 grm.	Mean Molecular Weight.	100 parts of the mixture contain	
		Stearic Acid.	Palmitic Acid.
197·5	284	100	—
198·5	282·6	95	5
199·5	281·2	90	10
200·5	279·8	85	15
201·5	278·4	80	20
202·5	277·0	75	25
203·5	275·6	70	30
204·6	274·2	65	35
205·6	272·8	60	40
206·7	271·4	55	45
207·77	270·0	50	50
208·86	268·6	45	55
209·95	267·2	40	60
211·06	265·8	35	65
212·18	264·4	30	70
213·30	263·0	25	75
214·45	261·6	20	80
215·60	260·2	15	85
216·77	258·8	10	90
217·95	257·4	5	95
219·13	256·0	—	100

[1] Mangold-Marazza, *Die Stearinindustrie*, p. 167.

This method, proposed by *Hausamann* and afterwards by *Zulkowsky*, although simple in principle, does not yield very accurate results, a small quantity of foreign substance—say of a hydrocarbon—causing considerable differences, as a simple calculation will show. Besides, an error of only 0·1 c.c. normal caustic in the titration may, for 5 grms. of substance, lead to an error of nearly 3 per cent.

If, however, small quantities of oleic acid be present, the method is still applicable for the determination of palmitic acid, the difference between the molecular weights of stearic (284) and oleic (282) acids being too small to influence the result.

An approximate estimation of the proportions of palmitic and stearic acids, when quite free from oleic acid, may be obtained from the *melting* and *solidifying* points by referring to the subjoined table given by *Heintz*,[1] supplemented by more recent figures of *Hehner* and *Mitchell*.

Mixtures of Palmitic with Stearic Acid

Stearic Acid per cent.	Palmitic Acid per cent.	Melting Point ° C.		Solidifying Point ° C.
		Heintz.	H. & M.[2]	
100	0	69·2	68·5	...
90	10	67·2	66·5	62·5
80	20	65·3	64·2	60·3
70	30	62·9	61·5	59·3
60	40	60·3	59·4	56·5
50	50	56·6	55·6	55
40	60	56·3	55·5	54·5
32·5	67·5	55·2	54·5	54
30	70	55·1	54·2	54
20	80	57·5	56·5	53·8
10	90	60·1	59·0	54·5
0	100	62·0	61·8	...

(*d*) *Determination of Oleic, Palmitic, and Stearic Acids*

The proportions of these three acids in a mixture can be determined from the iodine value and the mean molecular weight of the mixed acids. Let M be the mean molecular weight of the mixed acids, E the percentage of oleic acid as calculated from the iodine value [see (*a*)], x and y the percentages of stearic and palmitic acid, then we have the two equations—

$$x+y=100-\mathrm{E}$$

$$\frac{x}{284}+\frac{y}{256}+\frac{\mathrm{E}}{282}=\frac{100}{\mathrm{M}}$$

hence

$$x=\mathrm{M}\frac{(1001100-923\mathrm{E})-2562816}{987\mathrm{M}}.$$

[1] *Liebig's Annalen*, 92. 205.

[2] The difference in the melting points of the stearic acid used by these observers will satisfactorily explain the discrepancies; purest stearic acid melts, however, at 71°-71·5° C.

In candle-works it is important to know the proportion of the solid fatty acids ("stearine") to the liquid acids ("oleine"). For the rapid—although rough—estimation, the melting and solidifying points of the mixed acids are determined and compared with empirical tables worked out for all proportions of the mixed solid and liquid fatty acids. It is, however, not permissible to employ tables worked out say, for tallow, or any other fat. For not only the proportion of solid and liquid fatty acids varies in different fats, but also that of palmitic and stearic acids; besides, small quantities of foreign substances, the influence of which almost disappears in other methods, cause considerable alterations of the melting and solidifying points (comp. "Tallow, and Palm Oil," chap. xii. p. 750).

A better and more reliable method would be to calculate the proportion of oleic acid from the iodine value (*a*), and to determine the stearic acid direct (*b*). Palmitic acid is then found by difference.

vi. Approximate Determination of Liquid Fatty Acids—Oleic and Linolic

The determination of the acids belonging to less saturated series than the oleic series is at the present state of our knowledge not yet possible, and we must have recourse to the qualitative methods detailed in chap. vi. p. 141.

An attempt to arrive at approximately quantitative results has been made by *Twitchell*[1] by combining the lead salt method for the separation of solid acids from the liquid acids with the determination of the iodine number of the several fractions into which the liquid fatty acids were broken up.

Twitchell's method will be best illustrated by giving his process as applied to the examination of the fatty acids of lard in full, with such additional explanations as to render his method and his calculations more readily intelligible than the perusal of the original paper does.

4 grms. of lard fatty acids were dissolved in 95 per cent alcohol, and precipitated with 2·5 grms. of lead acetate dissolved in 20 c.c. of the same alcohol, both solutions being hot. The mixture was allowed to stand for one hour at 15° C. and filtered. 10 c.c. of the filtrate were drawn off, treated with ether and hydrochloric acid, the isolated fatty acids dried in a current of carbon dioxide, and their iodine number determined. The remainder of the filtrate was kept at 0° C. for an hour, when a precipitate was obtained. This precipitate was filtered off and washed with 90 per cent alcohol. The fatty acids were isolated from the filtrate, and their iodine value also determined.

The examination of the original fatty acids and of these fractions gave the following results :—

[1] *Jour. Soc. Chem. Ind.* 1895, 515.

	Weight in Grms.	Iodine Value.
Original lard fatty acids . . .	...	62·57
Fatty acids from filtrate at 15° C. .	0·2675 (46·81 per cent)	109·35
Fatty acids from precipitate at 0° C.	0·1020	
Fatty acids from filtrate at 0° C. .	0·1915	118·02

The fatty acids obtained from the precipitate at 0° C. solidified at 0° C. and melted at 7° C. [According to the table given, p. 753, it would contain 0·8 per cent of solid acids.] Its iodine number was not determined, and it is only inferred by calculation that its iodine value would be nearly 90—the theoretical value of oleic acid—to make the iodine number of the mixture 109·35.

The percentage of the liquid acids can now be calculated as follows :—

The percentage of the liquid fatty acids in the alcoholic filtrate at 15° C. is calculated from the portion drawn off, and was found to be 46·81 per cent. This, multiplied by the iodine number 109·35, gives $46{\cdot}81 \times 109{\cdot}35 = 51{\cdot}19$ as the iodine required for the total liquid acids in the filtrate. The iodine number of the original fatty acids being 62·57, the difference $62{\cdot}57 - 51{\cdot}19 = 11{\cdot}38$ would correspond to the liquid acid left in the precipitate, which is most likely oleic acid. 11·38 of iodine represents $11{\cdot}38 \times 1{\cdot}11$ oleic acid (see p. 197) $= 12{\cdot}64$ per cent of oleic acid. The total liquid acids in the original fatty acids are therefore $46{\cdot}81 + 12{\cdot}64 = 59{\cdot}45$. The mean iodine number of the total liquid acids must therefore be $\frac{62{\cdot}57}{59{\cdot}45} = 105{\cdot}2$.

The linolic acid—if such be assumed to be present conjointly with oleic acid—can now be calculated from the theoretical iodine numbers of oleic and linolic acids, viz. 90 and 181, and the iodine number of the fatty acids from filtrate at 15° C., viz. 109·35, in the following manner :—

Let x be the percentage of oleic acid, and y the percentage of linolic acid in the fatty acids from filtrate ; we then have

$$x + y = 100$$

$$\frac{90x}{100} + \frac{181y}{100} = 109{\cdot}35$$

hence

$x = 78{\cdot}5$ per cent oleic acid
$y = 21{\cdot}5$,, ,, linolic acid

and the percentage of linolic acids in the original fatty acids is $21{\cdot}5 \times 46{\cdot}81 = 10{\cdot}06$.

The oleic acid in the original fatty acids would then be $78{\cdot}5 \times 46{\cdot}81 + 12{\cdot}64 = 49{\cdot}39$ per cent.

Of course, this calculation holds good only for the several assumptions made.

By working the lead-salt-ether method in the cold the normal lead salts are formed exclusively (*Röse*); it is, therefore, possible to calculate from the proportion of lead the mean molecular weight of the liquid fatty acids. Supposing three different unsaturated acids of known molecular weights are present, then the proportion of each of them can be calculated if the iodine value of the total fatty acids present has been determined. Thus, if the total fatty acids contain p per cent of unsaturated fatty acids, and their iodine value be J_t, then the mean iodine value J of the mixed unsaturated acids will be

$$J = \frac{100\ J_t}{p}.$$

Let M_1, M_2, M_3 be the known molecular weights of the three unsaturated acids, M the mean molecular weight of the mixed acids as calculated from their lead salts, and J_1, J_2, J_3 the corresponding iodine values, then the percentages x, y, z of the three acids may be calculated from the following three equations :—

$$x+y+z=p$$

$$\frac{x}{M_1}+\frac{y}{M_2}+\frac{z}{M_3}=\frac{100}{M}$$

$$\frac{J_1 x}{100}+\frac{J_2 y}{100}+\frac{J_3 z}{100}=J_t.$$

vii. Hydroxy Acids

A direct determination of the amount of hydroxylated acids in fats has been suggested by *Fahrion*,[1] in the first instance for boiled linseed oil. The method is based on the insolubility of the hydroxy acids in petroleum ether, the other fatty acids being easily soluble in that menstruum. The operation is carried out in the following way :—3-5 grms. of the sample of fat are saponified with alcoholic potash, the alcohol evaporated off, the soap dissolved in 50 to 70 c.c. of hot water, and decomposed by hydrochloric acid in a separating funnel. After cooling, the liquid is shaken thoroughly with 100 c.c. of petroleum ether (boiling below 80° C.), and allowed to stand until both the aqueous liquid and the petroleum layer have become clear. The hydroxy acids will then be found adhering to the sides of the funnel. The aqueous liquid is run off, the petroleum ether layer poured out, and the remaining hydroxy acids washed several times with petroleum ether. The hydroxy acids are then dissolved in warm alcohol, the alcoholic solution transferred to a tared basin, the alcohol evaporated off, and the residue dried for one hour at 100° to 105° C. and weighed.

But experiments (unpublished) made by the writer have proved that this method is not generally applicable, and can, at best,

[1] *Jour. Soc. Chem. Ind.* 1891, 1015.

only refer to *oxidised* acids of a similar nature to those found in boiled linseed oil. Pure hydroxystearic acid and dihydroxystearic acid are sparingly soluble in cold petroleum ether; the mixed fatty acids from castor oil behave very much like castor oil (chap. xi. p. 425), that is, they dissolve in an *equal* volume of petroleum ether. A mixture of castor oil fatty acids with oleic acid, however, could not be separated by means of petroleum ether.

In the case of the nature of the hydroxy fatty acid in a fat being known, the proportion of it in the mixed fatty acids may easily be calculated, if the increase of weight of the mixed fatty acids attained on boiling with acetic anhydride be determined, by *Lewkowitsch's* method (p. 190). Let M be the molecular weight of the monohydroxy acid, and i the increase of weight of A grms. of the mixed fatty acids, then the percentage of hydroxy acids y will be (cp. equation (19), p. 190)

$$y = \frac{100Mi}{A.42}.$$

In the case of the hydroxy acid containing n hydroxy groups, and consequently being able to assimilate n C_2H_2O groups, we shall find

$$y = \frac{100Mi}{A.n.42}.$$

The percentage of hydroxy acids, provided their molecular weight be known, may also be calculated from the acetyl value c of the fatty acids. Let M be the molecular weight of the monohydroxy acid, requiring 56100 mgrms. KOH for neutralisation, then the molecular weight of the acetylated acid will be M + 42, requiring 2 × 56100 mgrms. KOH for saponification. One grm. of the hydroxy acid will therefore require $\frac{56100}{M}$, and one grm. of the acetylated product $\frac{2 \times 56100}{M+42}$; the difference

$$\frac{2 \times 56100}{M+42} - \frac{56100}{M} = \frac{56100(M-42)}{M(M+42)}$$

would represent the acetyl value of the pure hydroxy acid, or 100 per cent; having found c as the acetyl value of the sample, the percentage of the hydroxy acid x will be obtained from the proportion

$$\frac{56100(M-42)}{M(M+42)} : 100 = c : x,$$

hence

$$x = \frac{100.c.M.(M+42)}{56100\,(M-42)}.$$

It has been assumed for this calculation that the anhydrides of the acetylated acids have been hydrolysed completely.

viii. Lactones—Inner Anhydrides

Some products of the fat industry, notably Turkey-red oils and "stearine" prepared from oleic acid by *v. Schmidt's* process (see chap. xii. p. 747), contain considerable quantities of *stearolactone*, the inner anhydride of γ-hydroxystearic acid. This lactone may be determined either volumetrically or gravimetrically.[1]

(*a*) *Volumetric Determination of Stearolactone*

Fatty acids separated from a fat by the usual method (p. 100) require for neutralisation the same amount of potash, whether aqueous caustic potash be used, or whether they be boiled with an excess of alcoholic caustic potash, or, in other words, the acid and saponification values of fatty acids are identical; consequently fatty acids have no ether value.

If, however, lactones or inner anhyrides are in admixture with the fatty acids, the mixed fatty acids will show an ether value, since on titrating with aqueous caustic potash, especially in the cold, neutrality to phenolphthalein will be reached when all the free acids are neutralised, whilst the lactones, being neutral substances, are not saponified. On boiling with alcoholic potash, however, the lactones are converted completely into soaps, but on treating these soaps with a mineral acid, the lactones (but not the free fatty acids) separate out again. Consequently, fatty acids containing a lactone possess a definite ether value, from which the proportion of the lactone may be calculated if its molecular weight be known.

Since this ether value does not disappear, the lactone being formed again on acidifying the saponified mass, this ether value has been termed "*constant ether value*," and the corresponding *acid* and *saponification values*—"*constant acid value*" and "*constant saponification value.*"

Thus, if for a mixture of fatty acids and stearolactone the constant saponification value has been found 190, and the constant acid value 140, its constant ether value will be 50. The ether value of stearolactone being 198·9, the mixture contains $\frac{100 \times 50}{198{\cdot}9} = 25{\cdot}13$ per cent of stearolactone.

(*b*) *Gravimetric Determination of Stearolactone*

10 to 100 grms. of the sample are saponified with an excess of boiling alcoholic potash. The resulting soap is then diluted with a little water, and, if there be any unsaponifiable matter present, extracted with petroleum ether after cooling. Next the strongly alkaline solution is diluted with hot water, acidified with hydrochloric acid, and evaporated on the water-bath until all the alcohol has been driven off. The fatty layer, floating on the top, is then separated from the

[1] Benedikt, *Monatshefte f. Chemie*, 11. 71; *Jour. Soc. Chem. Ind.* 1890, 658.

aqueous liquid, washed with water, and most carefully neutralised with aqueous caustic soda, the slightest excess of alkali being capable of saponifying part of the stearolactone, thus vitiating the result. One operates best in the following manner:—The whole substance is dissolved in 500 c.c. of alcohol, and 50 c.c. of it are titrated carefully with a dilute caustic soda solution (the titer of which need not be known), phenolphthalein being used as an indicator, until the solution becomes pink. The amount of caustic soda required for the remaining 450 c.c. having been calculated from this preliminary experiment, the greatest part of this quantity is added at once, and then again caustic soda carefully run in, drop by drop, until the solution becomes pink. The stearolactone is then separated from the soap solution by shaking the latter with petroleum ether, evaporating the petroleum ether solution, and weighing the residue. As a check, the saponification value of the stearolactone may be determined; its acid value and iodine absorption must, of course, be found = 0.

Lewkowitsch [1] has discovered fatty acids in wool fat which are easily converted on heating to 100° C. into inner anhydrides. Some of these have been isolated by *Darmstädter* and *Lifschütz*, and have been described above as lanoceric acid and lanopalmic acid.

Hydroxy acids especially will be likely to suffer dehydration with formation of inner anhydrides. On boiling mixtures containing inner anhydrides with acetic anhydride acetyl groups will be assimilated. This can readily be ascertained by weighing the acetylated product after thorough washing with boiling water to decompose anhydrides of fatty acids formed. An increase of weight will point unmistakably to the presence of hydroxy acid (see p. 190).

ix. Glycerol

For the determination of the proportion of glycerol which a fat yields on saponification, several methods have been proposed. (It would be incorrect to speak of the proportion of glycerol in a fat since glycerol is formed only on saponification.) The yield of glycerin obtainable by saponifying triglycerides has been given above; see table, p. 186.

The older processes having for their object the isolation of glycerol in substance, such as *Chevreul's* original method, are only suitable as qualitative methods, and the glycerol thus prepared may be tested by any of the reactions given above (p. 80). For quantitative purposes, however, they are not to be relied upon, yielding, as they do, results below the truth owing to volatilisation of small quantities of glycerol at 100° C. (p. 77). This source of error is avoided in *David's* process,[2] in which the concentration of the glycerol solution is not carried too far, but it introduces another error through the necessity of saponifying with barium hydrate (cp. p. 18).

[1] *Jour. Soc. Chem. Ind.* 1892, 139; 1896, 14. [2] *Compt. rend.* 94 (1882), 1477.

1. Determination of Glycerol by Titration with Caustic Potash

This method is an application of *Köttstorfer's* process for examining fats (p. 151).

According to the fundamental equation, in which R stands for the radicle of any fatty acid,

$$C_3H_5(RO)_3 + 3KOH = C_3H_8O_3 + 3R.OK$$

3 molecules of caustic potash are required for the saponification of 1 molecule of neutral fat, yielding 1 molecule of glycerol. Therefore, for every 168·3 grms. of KOH used, 92 grms. of glycerol will be obtained, consequently 1 grm. of KOH is equivalent to 0·54664 grm. of glycerol.[1]

If, therefore, the ether value E has been determined (p. 154), the theoretical yield of glycerol G will be

$$G = \frac{E \times 0{\cdot}54664 \times 100}{1000} = 0{\cdot}054664\ E$$

(cp. equation (10), p. 187).

This method being an indirect method, has naturally all the faults inherent in that class of analysis, and must be used with caution. Its rapidity, however, makes it suitable for determinations in works. If diglycerides or wax-like substances be present in the fat the method obviously becomes useless.

2. Determination of Glycerol by Oxidation Processes

(1) *Oxidation by Means of Potassium Permanganate in Alkaline Solution*

On being oxidised in a strongly alkaline solution at the ordinary temperature with potassium permanganate, glycerol is converted quantitatively into oxalic acid, carbonic dioxide, and water, according to the following equation :—

$$C_3H_8O_3 + 3O_2 = C_2H_2O_4 + CO_2 + 3H_2O.$$

This reaction, which was originally suggested by *Fox* and *Wanklyn*[2] as a basis for a quantitative method, has been worked out by *Benedikt* and *Zsigmondy*[3] in the following manner :—Saponify 2 to 3 grms. of the sample of fat with caustic potash and pure methyl alcohol, evaporate the latter, dissolve the soap in hot water, and decompose it with dilute hydrochloric acid. Then warm until the liberated fatty acids have separated out as a clear oily layer. In the case of a liquid fat some paraffin wax is best added so as to obtain a solid cake on cooling. Next filter from the fatty acids into a spacious flask, wash well, and neutralise with caustic potash, using methylorange as an indicator. Then add 10 grms. of caustic potash in sticks, and run in a 5 per cent solution of potassium permanganate until the liquid no

[1] Zulkowsky, *Berichte*, 16. 1140 ; 1315.

[2] *Chem. News*, 53. 15.

[3] *Jour. Soc. Chem. Ind.* 1885, 610.

longer appears green, but blue or blackish. Instead of a solution, finely powdered potassium permanganate crystals may also be used. Heat to boiling, when hydrated manganese dioxide separates and the solution becomes red; discharge the colour by adding carefully the quantity of sulphurous acid solution required (but not more) for the reduction of the excess of the permanganate, taking care that the solution still remains strongly alkaline. Filter through a plain filter of sufficiently large size to hold at least one-half of the liquid, and wash the precipitate well with boiling water. It may happen that with the last wash-waters small quantities of hydrated manganese dioxide pass through the filter, but this does not interfere at all with the accuracy of the process.

Acidify the filtrate with acetic acid, whereby sufficient sulphurous acid is set free to reduce the manganese dioxide, and heat the solution, being about 600 to 1000 c.c., almost to the boiling point, and precipitate with 10 c.c. of a 10 to 12 per cent solution of calcium chloride or calcium acetate. (If more of the precipitant be used, considerable quantities of calcium sulphate are thrown down, vitiating the quantitative determination.) The precipitate contains silicic acid in addition to calcium oxalate, hence the amount of oxalic acid cannot be calculated from the weight of the calcium carbonate (or calcium oxide) after ignition. Therefore the amount of oxalic acid must be either determined volumetrically, or inferred from the alkalinity of the ignited residue. In the latter case dissolve the ignited precipitate in an accurately measured excess of half-normal hydrochloric acid, and titrate with half-normal caustic soda, using methylorange as indicator. If the titer of the acid be expressed in terms of sodium carbonate, 106 parts of CO_3Na_2 are equivalent to 92 parts of glycerol.

Allen[1] has somewhat modified this process, and proceeds in the following manner:—The fat is saponified with aqueous caustic potash in a closed flask. The oxidation is effected as described above, but sodium sulphite is used for reducing the excess of permanganate. The liquid containing the precipitated hydrated peroxide of manganese is then poured into a 500 c.c. flask, made up to 500 c.c., and 15 c.c. of hot water are added above the mark, this being an allowance for the volume of the precipitate and for the expansion of the hot liquid. The solution is next poured through a dry filter, and 400 c.c. of the filtrate, when cold, are measured off accurately, acidulated with acetic acid, and precipitated with calcium chloride. The precipitate is filtered off, washed well, and rinsed into a porcelain dish after piercing the filter. The neck of the funnel is then plugged and the filter filled with dilute sulphuric acid; after standing for a few minutes it is allowed to run into the dish. Sufficient sulphuric acid is then added to bring the total amount of acid up to a quantity equal to 10 c.c. of concentrated sulphuric acid, when the solution is warmed to 60° C. and titrated with potassium permanganate. If decinormal permanganate be used, each c.c. used corresponds to 0·0045 grm. of $C_2H_2O_4$, or to 0·0046 grm. of glycerol.

[1] *Commercial Organic Analysis*, ii. 290.

In connection with this process the following notes may be useful:—Methyl alcohol is used in the saponification of the fat instead of ethyl alcohol, as the latter may, under certain conditions of concentration, and for a definite percentage of alkali, give rise to the formation of oxalic acid. The errors resulting from this cause will be found to increase with the amount of alcohol retained by the soap on evaporation. Again, if a complete elimination of the alcohol be attempted by repeated evaporation of the dissolved soap, loss of glycerol may result.

The liquid that is oxidised contains besides glycerol all the soluble fatty acids originally combined with it in the fat. On working strictly according to the directions as given above, neither oxalic acid nor any other organic acid yielding a calcium salt insoluble in acetic acid will be formed. Therefore, it may be safely inferred that the presence of the soluble fatty acids in no way interferes with the correctness of the determination of the glycerol. *Johnstone*,[1] it is true, maintains that in presence of butyric acid the process is useless, this acid being nearly wholly converted into oxalic acid, but both *Hehner*[2] and *Mangold*[3] have shown that in the process as given by *Benedikt* and *Zsigmondy* no oxalic acid is formed. An explanation of *Johnstone's* error may be found in *Mangold's* observation, that butyric acid yields oxalic acid when boiled for a considerable time with an excess of potassium permanganate.

An excess of sulphurous acid must be carefully avoided, since in presence of hydrated peroxide of manganese sulphurous acid oxidises the oxalic acid formed. This error is obviated by *Allen's* proposal to use sodium sulphite instead of sulphurous acid. If the hydrated peroxide be removed by filtration, and the solution be acidified with acetic acid, no action on the oxalic acid can take place. But as towards the end of the washing small quantities of the peroxide pass through the filter, and are reduced by the sulphurous acid set free by the acetic acid, and, moreover, since small quantities of calcium sulphite may be admixed with the precipitated calcium oxalate, it will be best to avoid the use of sulphurous acid or of a sulphite altogether.

Herbig[4] substitutes, therefore, for the sulphite, hydrogen peroxide; he further recommends the use of a smaller quantity of potassium permanganate. *Herbig's* method has been examined by *Mangold*,[5] and the following modification of the *Benedikt-Zsigmondy* process has been recommended by him as yielding reliable results:—The filtrate from the fatty acids, containing from 0·2 to 0·4 grm. of glycerol, conveniently made up to 300 c.c., is placed in a litre flask, and 10 grms. of potassium hydrate, and as much of a 5 per cent permanganate solution as will correspond to *one and a half* times the theoretical quantity required for the oxidation of the glycerol (6·87 parts of MnO_4K being the amount required by theory for *one* part of $C_3H_8O_3$) are added. This operation is conducted in the cold and with constant shaking. Allow to stand for half an hour at the ordinary tempera-

[1] *Jour. Soc. Chem. Ind.* 1891, 204. [2] *Ibid.* [3] *Ibid.* 1891, 803.
[4] *Inaugural Dissertation.* Leipzig, 1890. [5] *Jour. Soc. Chem. Ind.* 1891, 803.

ture, and add sufficient hydrogen peroxide, avoiding, however, a large excess, to completely decolourise the liquid. Then make up to 1000 c.c., shake well, and filter 500 c.c. through a dry filter. Boil the filtrate for half an hour to decompose all hydrogen peroxide, allow to cool to 60° C., acidify with sulphuric acid, and titrate with standard permanganate solution.

The following table contains the saponification values of several fats, and the theoretical quantities of glycerol obtainable from them, contrasted with the actual results obtained by *Benedikt-Zsigmondy's* method. The agreement will be found satisfactory, if we consider that the saponification values and yields of glycerol have been determined with *different* samples of fats. In order to prove the utter unreliability of the older methods, *von der Becke's* results are given in the last column as obtained by isolating the glycerol in substance :—

Kind of Oil.	Saponification Value.	Glycerol.		
		Calculated from Saponification Value.	Found by Benedikt-Zsigmondy.	Found by von der Becke.
Olive oil . .	191·8-203	10·49-11·10	10·15, 10·38	6·41
Linseed oil .	188·4-195·2	10·24-10·66	9·45, 9·97	6·20
Cocoa nut oil .	270-275	14·76-14·83	13·3, 14·5	
Tallow . .	196·5	10·72	9·94, 9·98, 10·21	7·84
Butter fat .	227	12·51	11·59	10·59

If the glycerol solution prepared from the fat contains any other substance yielding oxalic acid on oxidation, as notably in the case of highly oxidised linseed oil, the *Benedikt-Zsigmondy* process is, of course, useless (cp. also below **3**).

(2) *Oxidation with Potassium Permanganate in Acid Solution*

Planchon[1] oxidises glycerol completely to carbonic dioxide and water by potassium permanganate and sulphuric acid according to the following equation—

$$C_3H_8O_3 + 7O = 3CO_2 + 4H_2O.$$

This method has been examined and recommended as yielding correct results by *Herbig*,[2] *Grünwald*,[3] and *Suhr*,[4] when "chemically pure glycerin" was used in test experiments.

The carbonic acid evolved from the glycerol is determined in exactly the same way as in the ultimate analysis of carbon compounds. The filtrate from 3 grms. of saponified fat, containing about 0·3 grm. of glycerol, is concentrated in a flask of 300 c.c. capacity to about 100 c.c. The flask is attached to an inverted condenser, and the latter is

[1] *Jour. Soc. Chem. Ind.* 1888, 779.
[2] *Inaugural Dissertation*, 1890.
[3] *Jour. Soc. Chem. Ind.* 1889, 308.
[4] *Inaugural Dissertation.* München, 1892.

connected with a calcium chloride tube and the caustic potash bulbs used for the absorption of carbonic dioxide. 4 grms. of permanganate dissolved to a 5 per cent solution and 15 grms. of concentrated sulphuric acid, previously diluted with 50 c.c. of water, are quickly introduced into the flask, and the solution heated to boiling point. A current of air drawn through the apparatus will drive over the last traces of carbonic dioxide.

It must, however, be noted that commercial potassium permanganate contains quantities of carbonates appreciable enough to seriously affect the correctness of the result.

If, therefore, determination of glycerol by complete oxidation be wished, it will be preferable to employ the following method proposed by *Hehner*, *sub* (3).

A serious objection to this method, as well as to the following, with which it is identical in principle, is that any organic substance other than the glycerol will also yield carbonic acid, and render these determinations practically useless. In the *Benedikt-Zsigmondy* method erroneous results will only be obtained in the presence of organic substances yielding *oxalic acid* on oxidation, and in consequence of this limitation of the possible errors it will be found to give more reliable results than any other oxidation process.

(3) *Oxidation with Bichromate of Potash and Sulphuric Acid*

This method has been recommended by *Legler*, *Burghardt*, *Cross* and *Bevan*, and *Hehner*.[1] *Cross* and *Bevan*[2] measure the carbonic acid evolved, *Legler* proposes to weigh it, whilst *Hehner* recommends to determine the glycerol volumetrically by measuring the volume of standard bichromate solution required for the oxidation.

Hehner has exhaustively examined his method, and obtained satisfactory results.

The standard solutions required are :—

1. Solution of potassium bichromate containing 74·86 grms. of $Cr_2O_7K_2$, and 150 c.c. of strong sulphuric acid per litre.[3] The exact oxidising value of the solution must be ascertained by titration with a standardised solution of ferrous sulphate or of pure ferrous ammonium sulphate or of pure iron wire.

2. Solution of ferrous ammonium sulphate containing about 240 grms. per litre.

3. Bichromate solution, ten times more dilute than solution 1.

The ferrous solution is exactly standardised upon the stronger bichromate solution, 1 c.c. of which should correspond exactly to 0·01 grm. of glycerol.

For the determination of the yield of glycerol from a fat, saponify

[1] *Jour. Soc. Chem. Ind.* 1889, 4.

[2] *Chem. News*, 55. 2, and *Analyst*, 1887, 44. The same method has been proposed again by Gantter, *Jour. Soc. Chem. Ind.* 1895, 895.

[3] It is safer to keep the not-acidified bichromate solution in stock, and to add the sulphuric acid when testing.

about 3 grms. of the sample, weighed off accurately, with alcoholic potash. Take care not to drive off all the alcohol lest any glycerol be volatilised. Dilute to about 200 c.c. and decompose the soap with dilute sulphuric acid. Filter off the liberated fatty acids, and boil the filtrate vigorously in a covered beaker to about half its volume, when all the alcohol will have been evaporated off. Then add 25 c.c. of concentrated sulphuric acid, suitably diluted, and 50 c.c. of the stronger bichromate solution, and heat to near boiling for about two hours. Titrate back the excess of bichromate with an excess of the ferrous ammonium sulphate solution, and ultimately the latter with the dilute bichromate solution, using potassium ferricyanide as an indicator.

3. Determination of Glycerol by the Acetin Process

Since in the saponification of fat a more or less impure glycerol is necessarily obtained, those processes based on the complete oxidation of glycerol will undoubtedly yield too high results; even the *Benedikt-Zsigmondy* process may give too high values, when some of the saponification products are converted into oxalic acid. Therefore *Lewkowitsch*[1] recommends the acetin process (see chap. xii. p. 806) for the determination of the yield of glycerol from a fat.

The fat is saponified in the usual way, the resulting soap decomposed with sulphuric acid, and the liberated fatty acids filtered off. The filtrate is neutralised with an excess of barium carbonate, and boiled down on the water-bath until most of the water is driven off. The residue is next exhausted with a mixture of ether and alcohol, the ether-alcohol driven off for the most part at a gentle heat, and the residue dried in the desiccator. It is not necessary to await constant weight, since the glycerol can be determined at once in this hydrous crude glycerin.

x. Higher Aliphatic Alcohols

On saponifying a fat or wax, any higher alcohols of the aliphatic series present, as cetyl alcohol, ceryl alcohol, etc., are isolated together with the other unsaponifiable substances, and the alcohols may be detected in this mixture as detailed in the following chapter.

The following methods furnish a means of obtaining a measure of the proportion of alcohols in a fat or a wax without resorting to their isolation :—

1. Saponify 10-20 grms. of the fat with alcoholic potash, or in case of a wax with aqueous potash (cp. *Benedikt* and *Mangold's* method under "Beeswax," p. 661), dilute the soap with water, acidify and boil until the fatty substance has separated as a clear layer. Syphon off the aqueous solution, wash the fatty layer until free from mineral acid, filter and dry. The fatty substance thus obtained consists of a mixture of free fatty acids, aliphatic alcohols, and possibly of hydro-

[1] *Chemiker Zeitung*, 1889, 659.

carbons. Weigh off accurately part of the mixed substances and determine their acetyl value. Provided hydroxy acids are absent and anhydrides formed (cp. 164) are hydrolysed, we may calculate from the acetyl value the proportion of *hydroxyl* combined with the radicle of the alcohols (alcoholic hydroxyl), or of *hydrogen* contained in the alcoholic hydroxyl group. If only one alcohol of known molecular weight be present, it is, of course, possible to determine its quantity.

Instead of determining the acetyl value, the increase of weight after boiling with acetic anhydride may be determined (cp. p. 190). Also in this case the proportion of alcohol can be found, if only one alcohol of known molecular weight be present and hydroxy acids are absent.[1]

2. The following method proposed first by *C. Hell*[2] has been employed later by *Buisine* for the examination of beeswax. It is based on the fact that, on heating an aliphatic alcohol with soda-lime, one molecule of the corresponding fatty acid is formed, with evolution of two molecules of hydrogen, as expressed by the equation—

$$\underset{\text{Cetyl alcohol.}}{C_{16}H_{33}.OH} + NaOH = \underset{\text{Sodium palmitate.}}{C_{16}H_{31}O_2Na} + 2H_2.$$

It is therefore possible to infer from the quantity of gas liberated the amount of alcohol originally present. According to *Hell*, the substance, intimately mixed with soda-lime, is introduced into the tube *i* (Fig. 40), and the mixture covered with soda-lime. In order to reduce the volume of air to the smallest possible amount, the sealed tube *k* is placed inside tube *i*. The latter is closed by a perforated india-rubber stopper *p* provided with tube *r*, which connects *i* with a *Hofmann* gas burette, filled completely with mercury, and closed at the top by means of the three-way tap *h*. The tube *i* is then immersed in an air-bath provided with a thermometer. Tube *i* is at first brought into communication with the air by tap *h*, then the height of the barometer and temperature of the air is taken, and *i* connected with the burette by suitably turning the three-way tap. Part of the mercury is then withdrawn by tap *q*, and the air-bath heated to 300°-310° C., until the level of the mercury remains constant. The apparatus is then allowed to cool down to the temperature of the room, when the original

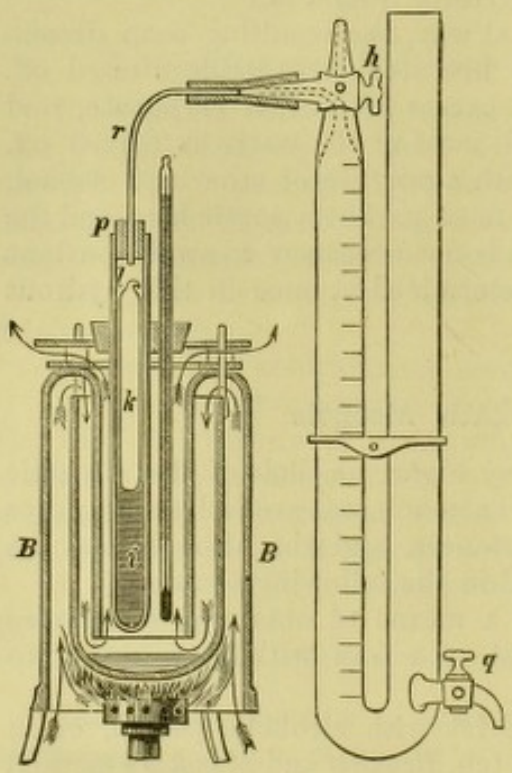


Fig. 40.

[1] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1896, 14. [2] *Liebig's Annalen*, 223. 269.

pressure is re-established by adding mercury. The volume of gas is then read off and calculated for 760 mm. pressure and 0° C. The hydrogen may either be measured saturated with moisture, when a correction for the tension of the water vapour must be made, or by previously drying the gas. This is best done by taking a longer tube *i*, and placing over *k* a layer of strongly heated soda-lime.

A. and *P. Buisine*[1] have proved that the reaction does not proceed quantitatively if a wax be heated directly with *potash-lime* (1 part of potash and 2 parts of lime). They proceed, therefore, in the following way:—2-10 grms. of a wax, weighed accurately, are melted in a porcelain crucible, and an equal weight of finely powdered

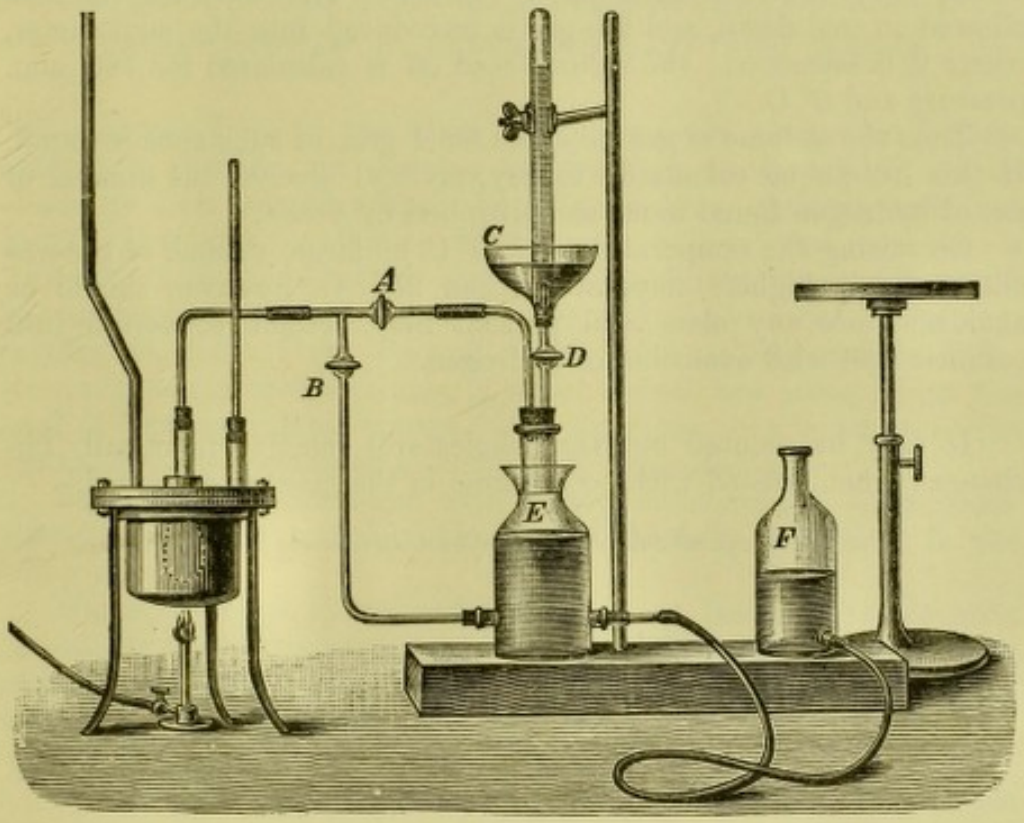


Fig. 41.

caustic potash stirred into the melted mass. The hard mass obtained on cooling is carefully powdered and intimately mixed with three parts of potash-lime for every part of wax weighed off. The mixture is filled into a test-tube or a pear-shaped flask, taking care that the vessel is nearly filled completely, and placed in an iron still, filled with mercury, and closed by a cover having three nozzles. Through the one passes the outlet tube from the glass vessel containing the substance, whilst into the second is fixed a thermometer; the third nozzle is provided with a long iron tube to condense and lead away the vapours of mercury.

Instead of collecting the gas in a *Hofmann* burette, *A.* and *P. Buisine* prefer to use the apparatus designed by *Dupré*, and shown in Fig. 41.

[1] *Monit. scientif.* 1890, 1127.

The gas evolved can be made to enter the vessel E either from the top —by opening tap A—or from the bottom—by opening tap B. The glass tubes provided with the taps A and B are of very small inner diameter without, however, being capillary tubes. When all the connections have been made, bottle E is filled with water by raising bottle F until water enters C. Tap D is then closed, bottle F lowered, tap A opened, and the mercury heated. At 180° C. the reaction will commence; the temperature is, however, raised to 250° C. and kept thereat for two hours. If gas is liberated copiously the tap A is closed and B opened; thus it is easier to control and watch the progress of the reaction. When bubbles of gas no longer rise through the water, tap B is closed again and A opened. The apparatus is then allowed to cool down, and the gas is introduced into the eudiometer, where it is measured; the volume read off is calculated for 760 mm. pressure and 0° C.

Thus the volume of gas obtained for 1 grm. of substance is found. If this has to be calculated to, say, myricyl alcohol, the number of c.c. of hydrogen found must be multiplied by 0·984.

On raising the temperature to 310° C. no larger volume of gas was obtained. A higher temperature than 250° C., however, should be avoided, since any oleic acid present may become converted into palmitic acid with evolution of hydrogen.

It may be pointed out that cholesterol remains practically unchanged when treated with potash-lime in the manner described.[1]

[1] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1896, 14.

CHAPTER VII

DETECTION AND QUANTITATIVE DETERMINATION OF UNSAPONIFIABLE MATTER IN FATS AND WAXES

We comprise here in the term "unsaponifiable matter" all those substances that do not dissolve in water or combine with caustic alkalis to form soluble soaps. Strictly speaking, glycerol itself, not being saponifiable by alkalis—in the same way as wax alcohols—is "unsaponifiable," and in this strict sense only the fatty acids would be completely saponifiable, but not so the neutral glycerides, containing, as they do, about 5 per cent of the glycerol-yielding radicle C_3H_2. However, as glycerol is soluble in water it does not come under the head of "unsaponifiable matter," and, therefore, in a wider sense the neutral fats are considered as completely saponifiable.

Resin, which is often met with in fatty substances, is almost completely saponifiable. This substance will be fully considered in the following chapter.

Waxes, although hydrolysed completely on boiling with alcoholic potash, are usually termed partially saponifiable, on account of their yielding considerable quantities of "unsaponifiable" alcohols insoluble in water.

We have, therefore, to consider here, besides waxes, the possible presence in any given fatty substance of paraffin wax, cerasin, mineral oils, neutral tar oils, and resin oils. Resin oils contain but small quantities of saponifiable substances, whilst paraffin wax, cerasin, mineral oils, and neutral tar oils are entirely unsaponifiable.

Some fats contain in their natural state small quantities of unsaponifiable matter in the shape of hydrocarbons, or, more frequently, of cholesterols.

1. Detection of Unsaponifiable Matter

A rapid method for the detection of unsaponifiable matter, if present in considerable quantities, consists in boiling the sample of fat with alcoholic potash, and adding to the soap solution aqueous ammonia, when a turbidity will appear (cp. p. 100). *Holde*[1] draws

[1] *Jour. Soc. Chem. Ind.* 1889, 735.

attention to the necessity of employing strong alcohol and of avoiding excess of ammonia. He recommends to test in the following manner :— Heat in a test-tube a piece of caustic potash about the size of a pea with 5 c.c. of absolute alcohol until dissolved; add 3 or 4 drops of the sample of fat, heat again and pour 3-4 c.c. of distilled water into the test-tube. The presence of even one per cent of unsaponifiable matter will cause distinct turbidity.

2. Quantitative Determination of Unsaponifiable Matter

i. Gravimetric Methods

Preparatory to the determination of unsaponifiable matter the sample of fat must be saponified. To accelerate the process, in the case of fats that are not readily saponifiable, it has been proposed to add some easily saponifiable fat. It will, however, be preferable in such cases to have recourse to the method given in chap. ii. p. 23, for the hydrolysis of not readily saponifiable fats.

On saponifying a fat containing hydrocarbons in the usual manner, and evaporating off the alcohol by boiling the strongly diluted aqueous soap solution, the unsaponifiable matter will, for the most part, separate as an oily layer on the top of the soap solution. A small quantity, however, will always remain dissolved in the aqueous solution, and therefore such methods as *Geissler's* and *Dalican's*, proposing to separate the oil and to weigh it, must naturally give too low results.

The following two methods, however, can be recommended as reliable :—

(*a*) *Extraction of the Soap Solution with Ether or Petroleum Ether*

The extraction of the unsaponifiable matter is effected by repeatedly shaking the saponified mass with ether or petroleum ether and separating the two layers by means of a separating funnel. The small quantities of soap that pass into the extract are removed by washing the ethereal solution with water. *H. Schwarz*[1] and *Neumann*[2] have designed special apparatus for this purpose, but their employment for the purposes of fat analysis cannot be recommended.

Regarding the choice of the solvent, it is always *safer* to use common ether in preference to petroleum ether, although the former extracts in most cases larger quantities of soap than the latter. For *Lewkowitsch*[3] found in the case of shark liver oil and some kinds of whale oil that petroleum ether gave very capricious results, all of which were far too low, owing, no doubt, to the "unsaponifiable matter" from these oils being very sparingly soluble in petroleum ether, whereas constant results were obtained on using common ether. Due attention must be paid to the fact that the solubility of soaps in

[1] *Jour. Soc. Chem. Ind.* 1884, 649.
[2] *Berichte*, 18 (1885), 3061.
[3] *Jour. Soc. Chem. Ind.* 1896, 14.

ether and petroleum ether is increased by the presence of hydrocarbon oils and wax alcohols; in accurate analysis it is necessary, therefore, after evaporating off the solvent, to shake the extracted unsaponifiable mass with a little warm water, and to extract again with ether or petroleum ether. *Lewkowitsch*[1] recommends to incinerate the extract; any residue giving an alkaline reaction on treatment with a little water would point to the presence of soap in the unsaponifiable matter. By titration with an acid the amount of alkali can be found and the amount of soap approximately calculated.

Very often a distinct separation into two well-defined layers does not take place readily, emulsions being formed on shaking that require a very long time to separate, if, indeed, they separate at all, as notably in the case of wool fat. In such cases it will be found most convenient to add a little alcohol or glycerin after shaking, if ether has been used for extraction, and to impart a slight rotatory movement to the separating funnel without, however, agitating. If petroleum ether has been employed, the formation of emulsions is best avoided by adding to the alcoholic soap solution left after saponification not more than an equal volume of water.

Sometimes a flocculent layer will appear between the aqueous solution and the solvent. In the case of wool fat *Lewkowitsch*[2] has shown that these flocks consist of a soap formed from fatty acids of high molecular weight, which is insoluble in cold water. The appearance of this flocculent stratum, however, does not interfere with the correct estimation of the unsaponifiable matter.

The petroleum ether should not contain any hydrocarbons boiling above 80° C.; otherwise it will be found almost impossible to remove the last portions of the solvent without seriously vitiating the results. The commercial article sold as boiling below 170° F. should not be taken on trust. It is, therefore, imperative to fractionate the petroleum ether, using a good dephlegmating column, say *Hempel's*, and to discard any fractions boiling above 80° C. (cp. p. 89).

Considering the importance of the subject, I think it best to describe fully several methods proposed for the estimation of the unsaponifiable matter. On the whole, preference should be given to the method recommended by *Allen* and *Thomson*.

Allen and *Thomson*[3] recommend to saponify 5 grms. of the sample with 25 c.c. of alcoholic caustic soda, containing 80 grms. of NaOH in 1000 c.c., in a porcelain basin in a water-bath, and to boil down to dryness. The resulting soap is dissolved in 50 c.c. of hot water, and transferred to a separating funnel of about 200 c.c. capacity, using about 20 to 30 c.c. of water for rinsing the dish. After cooling, 30 to 50 c.c. of ether are added and the solution thoroughly shaken. Addition of a little alcohol will accelerate the separation. The soap solution is then run off and may be exhausted again with fresh ether. The ethereal solutions are united, washed with a small quantity of water to free them from any dissolved soap, and transferred to a tared

[1] *Jour. Soc. Chem. Ind.* 1892, 139; 1896, 14.
[2] *Ibid.* 1892, 136. [3] *Chem. News*, 43. 267.

flask. The ether is distilled off on the water-bath, and the residue dried and weighed.

Nitsche[1] saponifies 10 grms. of fat with 7 grms. of caustic soda solution of specific gravity 1·35, and 30 grms. of 90-96 per cent alcohol, afterwards adding 40 grms. of glycerin, specific gravity 1·250, and exhausting the solution with 100 c.c. of petroleum ether.

Morawski and *Demski*[2] treat 10 grms. of the fat with 50 c.c. of alcohol and 5 grms. of caustic potash previously dissolved in the smallest quantity of water. The flask in which the fat is saponified is connected with an inverted condenser, and after half an hour's boiling 50 c.c. of water are added and the mass allowed to cool. It is then transferred to a separating funnel and shaken out with petroleum ether. When the two layers have separated, the aqueous layer is drawn off as completely as possible, and the petroleum ether repeatedly washed with water without, however, uniting the washings with the main soap solution. Instead of running the ethereal solution directly into the tared flask, it is first drawn off into a dry flask, and from this poured into the tared flask, when any drops of water will remain behind. The main soap solution is again extracted in the same way, and the petroleum ether added to the first portion. On distilling off the petroleum ether the unsaponifiable matter will be left behind.

Spitz and *Hönig*[3] recommend washing the petroleum ether layer with 50 per cent alcohol instead of water, thus shortening the time required for the separation of the two layers.

Gawalowski[4] states that only alkaline soaps are soluble in petroleum ether, whereas neutral soaps are absolutely insoluble. He recommends the following procedure for obtaining the petroleum ether solutions free from soap :—Saponify 10 parts of the sample of fat with alcohol and 2·5 parts of solid caustic potash, dissolve the soap in water, evaporate off the bulk of alcohol, and add, first, calcium chloride solution and then powdered sodium bicarbonate until the solution has nearly ceased to be alkaline. On boiling, owing to the formation of sodium carbonate, the solution acquires an alkaline reaction, but the carbonate, being insoluble in petroleum ether, does not interfere with the accuracy of the analysis.

(*b*) *Extraction of the Dry Soap with Solvents*

For the extraction of the dry soap ether cannot be recommended, as larger quantities of soap would be dissolved than in the foregoing processes. Therefore petroleum ether or chloroform or acetone are, as a rule, preferable.

Allen and *Thomson* have thus determined accurately the unsaponifiable matter in various fats (cp. p. 6). Their *modus operandi* is the following :—10 grms. of the sample of fat are saponified in a porcelain dish of 5 inches diameter with 50 c.c. of 8 per cent alcoholic caustic

[1] *Jour. Soc. Chem. Ind.* 1884, 322.
[2] *Ibid.* 1886, 179.
[3] *Ibid.* 1891, 1039.
[4] *Zeit. analyt. Chemie*, 26. 330.

soda, by gently boiling on the water-bath with constant stirring until the soap commences to froth ; 15 c.c. of methyl alcohol are then added, and the boiling continued until the soap is dissolved. Next 5 grms. of sodium bicarbonate are stirred into the mass, and 50-70 grms. of recently ignited pure sand mixed with it. After drying for twenty minutes in a water-oven, the mass is transferred to a Soxhlet apparatus, and extracted with petroleum ether, completely volatile below 80° C. The petroleum ether is then distilled off and the residue weighed.

For the determination of mineral oil in fatty oils, *Finkener*[1] uses the following process, which is but a slight modification of that proposed by *Allen* and *Thomson*:—Heat 10 grms. of the sample for fifteen minutes on a water-bath with 50 c.c. of nearly normal alcoholic solution of caustic soda, add 5 grms. of dry sodium bicarbonate to convert the excess of caustic soda into carbonate, and heat on the water-bath until the alcohol has been driven off. Transfer the hot mass to a stoppered cylinder, allow to cool, and shake with 300 c.c. of petroleum ether for some time. Filter into a dry flask, distil off the bulk of the petroleum ether, pour the solution on to a watch glass, and weigh after evaporating off the remainder of the petroleum ether.

According to *Allen* the methods described under (*a*) cannot be used for the determination of the unsaponifiable portion of beeswax, carnaüba wax, and other substances containing myricyl alcohol, the latter being but sparingly soluble in the cold solvent. In such cases it is best to neutralise the soap exactly with acetic acid, using phenolphthalein as an indicator, and to precipitate with lead acetate. The precipitate is washed, dried, mixed with sand, and boiled out repeatedly with petroleum ether.

In the case of shark liver oil and some kinds of whale oil, examined by *Lewkowitsch*,[2] very considerable quantities of soap were dissolved together with the alcohol, so that petroleum ether was useless in these cases.

On incineration the extract should yield but traces of ash, thus proving that only traces of soap have been dissolved. The above method, generally yielding good results, becomes, however, less accurate in the case of fats mixed with both mineral and resin oils, perceptible quantities of soap passing into the petroleum ether under these conditions.

Horn[3] proposes to extract the saponified mass with *chloroform*, which is stated not to dissolve soap even in presence of free alkali, so that addition of bicarbonate becomes unnecessary. *Grittner*[4] also recommends this solvent, but advises to mix the soap with sand if the fat contains considerable quantities of mineral oil. The sand must have been washed previously with hydrochloric acid, as any lime

[1] *Jour. Soc. Chem. Ind*, 1886, 457.
[2] *Ibid.* 1896, 14.
[3] *Ibid.* 1888, 696.
[4] *Ibid.* 1890, 772.

present would cause the formation of a lime soap, which is soluble in chloroform.

The copper, zinc, cadmium, aluminium, barium, strontium, magnesium, and calcium soaps are soluble in both common ether and petroleum ether to some extent. The least soluble are the calcium salts. Several chemists recommend, therefore, to operate on the lime salts.

Thus *Donath*[1] proposes for the determination of paraffin wax in candles to convert the alkali soaps into lime soaps previous to the extraction. He proceeds in the following way: 6 grms. of the sample are saponified with alcoholic potash, and the alcohol driven off. The soap is then dissolved in hot water and calcium chloride solution added. If considerable quantities of paraffin wax are present, a good plan is to add a little sodium carbonate before precipitating, so as to obtain calcium carbonate, which will render the precipitate more powdery. The lime soap containing all the paraffin is washed on to the filter, dried at 100° C., reduced to a fine powder, and extracted in a Soxhlet tube with petroleum ether. The error of the method is stated not to exceed 0·3 per cent.

Herbig[2] uses for the determination of the unsaponifiable matter in wool fat *acetone*, after having converted the potash soaps into lime soaps in the manner just described. (His process is not described here in full, as he does not completely saponify the wool fat, so that his "unsaponifiable" consists of the actual unsaponifiable matter *plus* that portion of wool wax which is not saponified by the ordinary method of saponification.)

ii. Volumetric Methods

Lacombe's Process.[3]—If a mixture of a fat, of *known* composition, and of unsaponifiable substances has to be examined, the saponification value of the former supplies a ready means of determining volumetrically the amount of unsaponifiable matter.

Let S_1 be the saponification value of the sample, and S the saponification value of the pure fat, S of course being greater than S_1, then evidently the percentage of unsaponifiable matter U will be

$$U = 100 - \frac{100\,S_1}{S}.$$

In the presence of waxes, of course, this method cannot be used.

Instead of determining the saponification value of the fat, *Lacombe* prefers to titrate its fatty acids. The sample is saponified in the usual manner, and an accurately weighed quantity of the mixed fatty acids is dissolved in alcohol and titrated with alkali, phenolphthalein

[1] *Dingl. Polyt. Jour.* 208. 305. [2] *Jour. Soc. Chem. Ind.* 1896, 138.
[3] Jacobsen's *Repertorium*, 1884, i. 243.

being used as an indicator. Simultaneously the corresponding pure fat is treated in the same way. The number of cubic centimetres of alkali used being proportional to the amount of triglycerides, it is not necessary to know the titer of the alkali solution.

A similar method had been proposed by *Nitsche*[1] before *Lacombe*. Although not so simple in practice it admits of a more extended use, not requiring, like the former, the composition of the neutral fat in the sample to be previously known.

Nitsche proceeds as follows:—10 grms. of the sample are saponified, the soap acidulated, and the acid value of the mixture of fatty acids and unsaponifiable matter ascertained. Another 10 grms. of the sample are then saponified and exhausted with petroleum ether, as described p. 220, when the fatty acids of the neutral fat remain in the soap solution. On acidifying the latter the free fatty acids are recovered and their acid value is determined. The calculation is identical with that given above. Instead of calculating the acid values, the numbers of cubic centimetres of alkali used may be introduced in the formula given above. In that case the alkali need not be standardised.

3. Detection of Small Quantities of Fat in Mineral Oils

Small quantities of neutral fatty oils in mineral oils may be determined by any of the gravimetric processes described above. It will, however, be found necessary, in order to check the results, to liberate the fatty acids from the soap solution, collect them on a filter, and ascertain their weight. If the quantity obtained suffices for the determination of their molecular weight, it is easy to calculate the amount of neutral fat (triglycerides) corresponding to the fatty acids.

The safest method for detecting and estimating quantitatively small amounts of neutral fat is to boil 10-20 grms. (or more if necessary) of the sample with alcoholic potash, and to determine the amount of glycerol after separating the unsaponifiable oil and the fatty acids by one of the methods described above. The yield of glycerol multiplied by 10 will approximately furnish the percentage of fatty oil present. This is a more reliable method than to treat the saponified mass with mineral acid, wash until free from mineral acid, and determine the acid value of the resulting mass, the acid value of the original sample having been previously ascertained.

Klimont[2] proposes the following test, by which it is claimed even 1 per cent of fatty oil may be detected:—Heat 15 grms. of the sample for one or two hours in a flask of 400 c.c. capacity with 100 c.c. of a 10 per cent alcoholic potash (not soda) solution; allow to cool, treat with about an equal volume of water, and filter through a wet filter. Then add to the filtrate a solution of calcium chloride, when the appearance of a flocculent precipitate of lime soap will

[1] *Dingl. Polyt. Jour.* 251. 335. [2] *Chem. Zeit.* 1893, 546.

point to the presence of fatty oil. The method described may also be used for quantitative determinations. In that case the flask and the filter are well washed with hot water, the filtrate is exactly neutralised with hydrochloric acid, and, after complete cooling, extracted in a separating funnel with a small amount of petroleum ether. The aqueous layer is then concentrated to about 100 c.c. and precipitated with calcium chloride. The precipitate is filtered through a filter previously dried at 100° C., and washed, until disappearance of the reaction for chlorides, with the smallest possible amount of cold water, dried at 110° C. and weighed. If the amount of fat is required, the filter paper is incinerated in a crucible, and the weight of calcium oxide ascertained. This weight is multiplied by 0·774 — $3CaO : (C_3H_5)_2O_3 = 168 : 130$—and the resulting number added to the amount of fatty anhydrides given by the difference between the weight of the lime soap (dried at 110° C.) and that of the lime left on ignition.

This method is not suitable for the determination of larger amounts of fat, the lime soap easily forming lumps from which it is difficult to completely wash out the excess of calcium or potassium chloride.

4. Examination of the Unsaponifiable Matter

The unsaponifiable substances isolated by one of the foregoing processes will be either liquid or solid at the ordinary temperature. Liquid substances may consist of mineral oils or tar oils, or resin oils, or of a mixture thereof. Solid unsaponifiable matter will mostly be composed of paraffin wax or cerasin (rarely of other hydrocarbons, as in waxes), and, notably in the case of waxes, of aliphatic alcohols and cholesterols.

In manufactured products, as in "commercial stearine" or "Turkey-red oil," lactones or anhydrides occur which are not readily saponified, and therefore easily mistaken for unsaponifiable matter. Due care must therefore be taken in such cases to guard against error (chap. vi. "Lactones," p. 206).

i. Liquid Unsaponifiable Substances

Unsaponifiable oils frequently occur admixed with fatty oils in burning and lubricating oils.

Mineral Oils.—Of mineral oils one may expect to find those obtained by the distillation of crude petroleum, shale, etc., viz. the fractions boiling from 250° to 300° C., specific gravity 0·855 to 0·900 (vulcan oils, mineral lubricating oils), and also the higher distillates, boiling from 300° to 350° C., specific gravity 0·900 to 0·930. Considered chemically, they consist nearly exclusively of aliphatic hydrocarbons belonging to the ethane and ethylene series.

Tar Oils.—The dead tar oils, boiling between 240° and 350° C., freed for the most part from naphthalene and anthracene by cooling, and from phenols by washing with caustic soda, are sometimes used for admixture with lubricating oils.

The specific gravity of these tar oils is higher than that of water, and therefore they will sink in water. They consist of liquid hydrocarbons of the aromatic series, holding in solution small quantities of naphthalene, anthracene, and also of paraffinoid aliphatic hydrocarbons.

Resin Oils.—These oils are obtained by subjecting colophony to dry (destructive) distillation. The distillate is fractioned by repeated distillation into a lighter—more volatile—portion, "resin spirit," and into a heavier—less volatile—portion, the fluorescent "resin oil."

The specific gravity of resin oils ranges as a rule from 0·96 to 0·99; but resin oils having the specific gravity 1·001 are also met with in commerce; they are therefore heavier than mineral oils and lighter than tar oils. Their chemical composition is not yet fully understood; they consist mostly of hydrocarbons related to the terpenes, but contain also, according to the care exercised in distilling, larger or smaller quantities of resin acids and other oxygenated substances. Thus a sample examined by *Allen* and *Thompson* yielded 1·28 per cent of saponifiable matter. For the isolation of the latter proceed as in the examination of fats. Saponify the sample with alcoholic potash, boil down until the alcohol is driven off completely, dilute with water, and boil for half an hour, when the unsaponifiable constituents will float on the top as an oily layer. Draw off the aqueous layer, filter, and acidify with hydrochloric acid; the resin acids will then separate in the shape of brown, viscid drops of characteristic smell.

If the unsaponifiable portion of an oil has been found to contain resin oil (by one of the methods described below) it is necessary to determine the amount of resin acids in the soap solution if the quantity of resin oil in the sample be required. This is best done by *Twitchell's* method (see p. 244).

Discrimination between Mineral, Resin, and Tar Oils

In the case of only one of these being present, the specific gravity may be used as a means of identifying it, as is shown by the following table:—

Class of Oil.	Specific Gravity.
Heavy mineral oils	0·850-0·920
Resin oils	0·960-1·001
Tar oils	Higher than 1·01

But in the case of a mixture of the oils the specific gravity will be of but little value.

According to *Allen*[1] a characteristic means of detecting the

[1] *Commercial Organic Analysis*, ii. 81.

presence of hydrocarbons of the first two classes is furnished by their *fluorescence*. If the oil is distinctly fluorescent an admixture with hydrocarbon oils has undoubtedly taken place. If not, the sample should be shaken up with an equal volume of concentrated sulphuric acid, when fluorescence may appear; sometimes dilution with ether may be found equally useful. It should, however, be borne in mind that fluorescence is not characteristic of hydrocarbon oils exclusively; it is also exhibited by some fatty oils and commercial oleine (as palm oil oleine). On the other hand, absence of fluorescence is not always indicative of the absence of mineral oils, for the "bloom" shown by a mixture of fatty and mineral oils is frequently masked by the addition of small quantities of nitrobenzene or nitronaphthalene (see chap. xii. "Lubricating Oils"). Besides, there are many specimens of mineral oil in commerce that have been freed from the fluorescent constituents by suitable treatment.

The fluorescence may be observed by dipping a glass rod in the sample of oil, and laying it on a table in front of a window, so that the oiled end of the rod shall project over the edge, and be seen against the dark background of the floor. Turbid oils must be filtered first. The fluorescence is not perceptible by gaslight.

If this test, although not yielding decisive results for the reasons stated above, be resorted to, it will be best to examine the isolated unsaponifiable matter.

For the detection of resin oils the following reactions and tests will be found useful:—

1. *The Liebermann-Storch*[1] *Reaction.—Liebermann's* colour reaction for resin acids has been utilised by *Storch* for the detection of resin oils. 1 to 2 c.c. of the sample under examination are shaken with acetic anhydride at a gentle heat; after cooling, the acetic anhydride is drawn off by means of a pipette, and tested by adding one drop of concentrated sulphuric acid. If resin oil is present, a fine violet (fugitive) colour is immediately produced.

This test is thoroughly reliable for the detection of resin oils in mineral oil as the writer can testify from his own experience.

On applying this colour test to a number of oils and fats *Morawski* has obtained the following results:—

Kind of Oil or Fat.	Colour produced by Acetic Anhydride and concentrated Sulphuric Acid.
Olive oil	Light green
Sesamé oil	Gradually becoming greenish-blue
Hemp seed oil	Green
Linseed oil	Green
Cotton seed oil	Green
Arachis oil	Reddish-brown
Rape oil	Greenish-yellow
Castor oil	Yellowish
Cocoa nut oil	Yellowish

[1] *Jour. Soc. Chem. Ind.* 1888, 136.

Kind of Oil or Fat.	Colour produced by Acetic Anhydride and concentrated Sulphuric Acid.
Palm nut oil	Yellowish
Beef tallow	Yellowish
Bleached palm oil	Brownish-yellow
Bone fat acids	Brownish-yellow
Whale stearine	Brownish-yellow
Olein	Brownish-yellow
Crude olive oil acids	Light brown, afterwards dark green
Herring oil	Cherry-red turning brownish-black
Sunflower oil	Blue violet to blue

These colourations, however, do not prevent the detection of resin oil.

Morawski recommends the use of sulphuric acid of specific gravity 1·53 instead of concentrated acid; the same chemist has also shown that *Holde's*[1] proposal to omit the addition of acetic anhydride is inadmissible.

It should be borne in mind that cholesterol, which occurs in animal oils, also gives a very similar colour reaction, and its presence may lead to serious error if the isolated unsaponifiable matter be examined. In case, therefore, cholesterol[2] be suspected, a rapid method to prove the presence of resin oil would be to examine the mixed fatty acids, liberated from the soap solution, for resin acids (see below), which always accompany resin oils. A more complicated method would be to separate the cholesterol as benzoate.

2. *Renard's Test.*—Resin oil (10 to 12 drops) treated with anhydrous stannic chloride (1 drop) develops a characteristic beautiful violet colouration. *Allen*[3] prefers to use for this test stannic bromide, the reaction being much more delicate and more under control. The stannic bromide is prepared by allowing bromine, previously dried by shaking with concentrated sulphuric acid, to fall drop by drop on granulated tin contained in a dry flask immersed in cold water, until a colouration of the product indicates excess of bromine. The stannic bromide is then dissolved in carbon bisulphide, and a few drops of this reagent added to about 1 c.c. of the sample to be tested, previously dissolved in carbon bisulphide. If resin oil be present in the sample the beautiful violet colouration already mentioned will appear.

3. The iodine absorption value has been proposed by *Valenta*[4] as a means of detecting the presence of resin oil, provided tar oils are absent. He finds that mineral oils absorb only 14 per cent of iodine, whilst resin oils gave iodine values of 43 to 48. The conclusions drawn from the iodine absorption should, however, be accepted with caution, since *Demski* and *Morawski* have found the iodine number 21·4, and *Lewkowitsch*[5] 26·3 for samples of mineral oil. Older determinations of *Mills*[6] have even led to values as high as 35·3 (calculated

[1] *Jour. Soc. Chem. Ind.* 1888, 526.

[2] Green fluorescence of the liquid, after the violet colour has disappeared, points to presence of isocholesterol.

[3] *Commercial Organic Analysis*, ii. 463.

[4] *Jour. Soc. Chem. Ind.* 1884, 644.

[5] *Ibid.* 1892, 144.

[6] *Ibid.* 1883, 436.

from the bromine absorption). Instead of the iodine number *Klimont* takes the bromine number, which he terms somewhat unnecessarily in the case of resin oils "terebenthene number."

4. *Valenta*[1] bases a process for detecting resin oils in presence of mineral oils on the difference of solubilities in glacial acetic acid at 50° C., a number of experiments on various mineral oils having shown that 100 grms. of glacial acetic acid dissolve 2·6 to 6·5 grms. of mineral oil, whilst of resin oil 16·9 grms. are dissolved under the same conditions. The same relation is also expressed by stating that 10 c.c. of glacial acetic acid dissolve 0·2833 to 0·6849 grm. of mineral oil and 1·7788 grms. of resin oil respectively. To perform *Valenta's* test 2 c.c. of the unsaponifiable matter are mixed in a test-tube with 10 c.c. of glacial acetic acid, and the tube, loosely closed by a cork, is immersed in a water-bath for five minutes, the contents being repeatedly shaken during that time. The mixture is then filtered through a damp filter, and the middle portion of the filtrate collected. A portion of this is weighed off accurately, and the amount of acetic acid determined by titration with normal caustic soda. The difference between the weight of the acid taken and the weight thus found is the amount of oil dissolved. *Allen*[2] points out that any resin acids present in the resin oil would alter the solubility, besides rendering inaccurate the alkalimetric determination of the acetic acid. He proposes, therefore, to neutralise the greater part of the acetic acid, dilute with water, and extract the resin oil by agitation with ether.

5. According to *Demski* and *Morawski*,[3] resin oils are miscible with *acetone* in all proportions, whereas mineral oils require several times their volume of that solvent to effect complete solution. If, therefore, the unsaponifiable oil mix completely with an equal volume of acetone, it is resin oil, or a resin oil containing but a small quantity of mineral oil; if, however, part of the oil remains undissolved, it is mineral oil, or a mixture of mineral oil with a small quantity of resin oil. Essentially the same test has been proposed by *Wiederhold*.[4]

6. Similarly *Finkener*[5] recommends the employment of a mixture of one volume of chloroform and of ten volumes of alcohol of specific gravity 0·8182 at 15·5° C. Resin oils are soluble in ten volumes of this mixture, whereas mineral oil is insoluble in even 100 volumes.

7. Resin oils are dextro-rotatory, and therefore by a polariscopic examination of the unsaponifiable matter resin oil will readily be detected when present in large quantity. *Valenta* has examined a number of samples of resin oils in a Mitscherlich polarimeter, and found, for a length of 100 mm., rotations varying from 30° to 40° (dark specimens were previously clarified by means of charcoal). *Demski* and *Morawski* likewise found the rotation about 50°. Mineral oils are, as a rule, without action on the plane of polarised light, only one sample having been found to be dextro-rotatory, causing a deviation of 1·2°. As several vegetable oils have been found to be

[1] *Jour. Soc. Chem. Ind.* 1884, 643.
[2] *Commercial Organic Analysis*, ii. 465.
[3] *Jour. Soc. Chem. Ind.* 1886, 179.
[4] *Jour. Pract. Chem.* 1893 (47), 394.
[5] *Zeitsch. analyt. Chemie*, 1887, 652.

slightly optically active, it will be safest to examine the unsaponifiable oil after isolation. It should, however, be remembered that the hydrocarbons resulting from the destructive distillation of wool fat also exhibit optical activity (*Lewkowitsch*).

The determination of the specific gravity of the unsaponifiable oil enables us to differentiate between mineral and tar oils. If a mixture of both oils be suspected, the presence of tar oils may be detected by the aid of nitric acid, specific gravity 1·45.[1] Tar oils give a decided rise of temperature on mixing with the acid, whereas pure mineral oils will become but very slightly warmer. It is best to ascertain by a preliminary test whether a violent reaction takes place or not, the size of apparatus to be chosen depending on that. In the latter case 7·5 c.c. of the sample are placed in a graduated tube, cooled to 15° C., and 7·5 c.c. of nitric acid, spec. grav. 1·45, of the same temperature, added. The tube is then closed by a cork, provided with a thermometer, and the contents shaken thoroughly. The rise of temperature is then read off. If a strong reaction has been found to take place a larger strong-walled bottle must be employed, and the cork, besides holding the thermometer, must be fitted with an open glass tube, which may be closed by the finger whilst shaking. It will, however, be best in the latter case to employ small quantities, and to proceed as in *Maumené's* temperature reaction test (see p. 291). The same reaction has been proposed by *M^c^Ilhiney*[2] for the detection of resin oil in a mixture of this oil with mineral oils.

The methods employed for the quantitative determination of mixtures of mineral and resin oils will be detailed further on under the heading "Lubricating Oils," chap. xii. p. 721.

ii. Solid Unsaponifiable Substances

The solid unsaponifiable constituents obtained in the course of analysis of fats and waxes may consist of aliphatic alcohols (cetyl alcohol, ceryl alcohol, myricyl alcohol, etc.) and cholesterols, and also, as in the case of waxes, small quantities of hydrocarbons may be found (see "Beeswax," chap. xi. p. 657). Other unsaponifiable substances, not being constituents of the fats and waxes, falling under this head are paraffin and cerasin.

The properties of *paraffin* and *cerasin* will be considered in chap. xii. under "Candle Materials."

If the isolated solid unsaponifiable matter appears to be homogeneous, *i.e.* consists of *one* chemical individual only, ultimate analysis will in the readiest way indicate its composition and nature. If, however, it consists of a mixture of several substances, separation may be effected by repeated recrystallisation from alcohol and ether, until chemically pure substances are obtained. Ultimate analysis may then be resorted to.

[1] Brenken, *Zeitsch. analyt. Chem.* 1879, 546. [2] *Jour. Soc. Chem. Ind.* 1895, 198.

The determination of the melting point of the unsaponifiable matter will not lead to decisive conclusions, as a glance at the following table, giving the melting points of some substances most likely to be met with, will show :—

Unsaponifiable Substance.	Melting Point. °C.
Cetyl alcohol	50
Ceryl alcohol	79
Myricyl alcohol	85
Paraffin	from 38 to 82
Cerasin	from 61 to 78

If a mixture of several substances is under examination the indication of the melting point becomes valueless, all the more so, as small quantities of impurities depress the melting point of the substance considerably. Only in the case of a very high melting point having been obtained conclusions may be drawn as to the presence of cholesterols, which possess characteristic melting points.

Alcohol.	Melting Point. °C.
Cholesterol	145-146
Isocholesterol	137-138
Phytosterol	132-134

But it should be remembered that a mixture of the first two cholesterols melts below 100° C.

The "alcohols" may be separated roughly from hydrocarbons by warm ethyl alcohol, in which the former are readily soluble, whilst the hydrocarbons are nearly insoluble.

A better method, however, is afforded by boiling the unsaponifiable matter with an equal weight of acetic anhydride for about two hours in a flask connected with an inverted condenser. One of the three following will happen :—

1. The unsaponifiable substance dissolves completely, and remains dissolved on cooling. This points to the presence of *aliphatic alcohols.*

2. The unsaponifiable substance dissolves completely on boiling; on cooling a magma of crystals separates from the solution—presence of *cholesterols* or *aliphatic alcohols*, or of both.

3. The unsaponifiable matter does not intermix with the reagent, floating as an oily layer on the top of the hot acetic anhydride. On cooling, the undissolved portion solidifies again, and can be taken off easily. The undissolved part consists of *paraffin* or *cerasin.*

In any case the acetic anhydride solution—in the last-mentioned case after separation from any undissolved oil whilst hot—is poured into water, when the acetates of cholesterols and aliphatic alcohols separate. They are boiled out with water until the wash-waters are no longer acid. The product thus obtained is dissolved in alcohol. The acetates of the cholesterols require large quantities of boiling alcohol for complete solution, whereas aliphatic alcohols dissolve

easily. If the former be present they will crystallise out on cooling, and may be further identified by their melting points, and iodine and saponification values. A complete separation, however, cannot be effected in this manner, as has been shown by *Lewkowitsch*.[1] In a mixture prepared from weighed quantities of cholesterol and cetyl alcohol he obtained in two experiments 60 and 69 per cent of the theoretical quantities of pure cholesterol acetate in the first crop of crystals, whilst the second crop of crystals—9 per cent—contained notable quantities of cetyl acetate. Again, on boiling the wool fat alcohols [consisting of cholesterol, isocholesterol, ceryl alcohol, and other unknown alcohols] with acetic anhydride, and trying to separate the acetates by crystallisation from alcohol, *Lewkowitsch*[2] isolated ceryl acetate in a crystalline state, whilst the acetates of the cholesterols formed with the acetates of the unknown alcohols oily substances from which no crystals could be obtained.

The alcoholic solution of the aliphatic alcohols, respectively the alcoholic filtrate from the crystallised acetates, is treated with warm water, when the dissolved acetates separate as an oily layer. This may be solidified by cooling, separated from the water, and examined further, as indicated below.

If solid hydrocarbons only have been found, their melting point will be found approximately the same as before treatment with acetic anhydride. On the other hand, the melting points of any acetates will materially differ from those of the original substances.

Cholesterol, isocholesterol, and **phytosterol** can be detected easily in the unsaponifiable substance by the reactions given above (p. 83). For the detection of phytosterol in oils compare chap. ix. p. 317.

Cholesterol and **isocholesterol** may be partially separated from the aliphatic alcohols either by boiling with acetic anhydride, and proceeding as described above, or by heating with 4 parts of benzoic anhydride[3] in a sealed tube to 200° C. for thirty hours (p. 84). In the latter case the product is boiled out repeatedly with alcohol, when cholesterol and isocholesterol benzoates remain behind.

If the benzoates have been prepared, separation of cholesterol from isocholesterol may be effected by crystallising the mixed benzoates from ether. The cholesterol benzoate crystallises in hard rectangular plates, whereas the corresponding salt of isocholesterol is obtained as a light crystalline powder, which can be separated from the former by decantation and elutriation. Cholesterol benzoate melts at 150°-151° C., isocholesterol benzoate at 190°-191° C. By saponifying the benzoates with alcoholic potash and diluting with water, cholesterol and isocholesterol are precipitated. They may be further identified by their qualitative reactions, melting points, and also by their iodine values.[4]

[1] *Jour. Soc. Chem. Ind.* 1892, 143.

[2] *Ibid.* 192, 140, where line 22 from the bottom, left column, "acetates" should be read for "alcohols."

[3] Schulze, *Berichte*, 5. 1076 ; 6. 251 ; 7. 571 ; *Jour. prakt. Chemie*, 115. 163.

[4] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1892, 142.

In order to gain a further insight into the nature of the alcohols in the unsaponifiable matter, the *increase in weight on boiling with acetic anhydride*, the *saponification values of their acetates*, and the *iodine absorptions of the alcohols themselves* may be determined. Experiments made by the writer with mixtures prepared from pure specimens of cetyl alcohol and cholesterol have proved that theoretical values are obtained.

The acetates are prepared, as described above, by boiling the alcohols with acetic anhydride. By operating with weighed quantities the increase in weight may be determined simultaneously; by comparing the values thus obtained with those given in the following table, some conclusions may be drawn as to the composition of the alcohols. The isolated acetates may then be approximately resolved into their constituents by crystallisation from alcohol, and further, by fractional distillation, into several fractions, the saponification value of which may be determined by boiling with alcoholic potash, as in *Köttstorfer's* process (p. 151). The acetates of the aliphatic alcohols are easily saponified; the cholesteryl acetates require prolonged boiling. On titrating back the excess of potash with standard acid the alcohols separate out again. They are precipitated completely by addition of water, collected on a filter, and their melting point and iodine value may then be ascertained. After separating the bulk of the cholesterols as far as possible, a definite iodine value will reveal the presence of aliphatic alcohols belonging to the allylic series.

Some numbers are given in the following table which may serve as a guide in the examination of solid unsaponifiable matter:—

Unsaponifiable Substances.	Formula.	Melting Point. °C.	Iodine Absorption.	Acetates.		Increase in Weight on boiling with Acetic Anhydride.[4] Per cent.
				Saponific. Value.	Melting Point.	
Paraffin wax . .	C_nH_{2n+2}	38-82	3·9-4·0[1]			0
Cetyl alcohol . .	$C_{16}H_{34}O$	50	0	197·5	22°-23°	17·2
Octodecyl alcohol .	$C_{18}H_{38}O$	59	0	180·0	31°	15·5
Ceryl alcohol . .	$C_{27}H_{56}O$	79	0	128·1	65°	10·6
Myricyl alcohol . .	$C_{30}H_{62}O$	85	0	116·7	70°	9·6
Cholesterol . .	$C_{26}H_{44}O$	147	68·3	135·5	92°	11·3
Isocholesterol . .	$C_{26}H_{44}O$	137-138	68·3	135·5	below 100°	11·3
Phytosterol . .	$C_{26}H_{44}O$	132-134	68·3	135·5		11·3
Mixed alcohols from sperm oil . .	?	25·5-27·5	64·6-65·8[2]	161-190		
Mixed alcohols from neutral wool fat .	?	...	36	160·9		
Mixed alcohols from crude wool fat. .	?	...	...	150·6[3]		

[1] Determined in the writer's laboratory.

[2] The iodine values of the 5 fractions into which the mixed alcohols were resolved (*Jour. Soc. Chem. Ind.* 1892, 135) were the following:—1, 46·48; 2, 63·3; 3, 69·8; 4, 81·8; 5, 84·9.

[3] Iodine absorption = 44·03 per cent.

[4] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1896, 14.

Reliable methods of separating aliphatic alcohols from cholesterols are not yet available. Two methods have, however, been proposed which may lead to satisfactory results when fully worked out.

Lewkowitsch[1] bases a method on the conversion of aliphatic alcohols into fatty acids when heated with soda-lime or potash-lime, whereas cholesterols remain practically unchanged when so treated. Crucial experiments carried out with sperm oil alcohols and with cholesterol showed that on heating the former with soda-lime the bulk of the alcohols were converted into fatty acids, only 4 to 6 per cent of unsaponifiable matter (unchanged alcohol) being recovered; whereas on treating cholesterol in the same manner 93 per cent of unchanged alcohol were recovered, only traces of fatty acids having been formed.

Cochenhausen[2] proposes heating the mixture of aliphatic alcohols and cholesterols with conc. sulphuric acid, when the aliphatic alcohols yield alkyl sulphates, whereas the cholesterols are converted into hydrocarbons—"cholesterones." The alkyl sulphates can be isolated by means of their sodium salts, from which the original alcohol may be recovered by decomposition with boiling hydrochloric acid.

If the unsaponifiable matter be heated with potash-lime, as in *Hell's* or in *A.* and *P. Buisine's* process, the volume of hydrogen gas may serve as a measure of the quantity of aliphatic alcohols present. Any solid hydrocarbons, as also cholesterols, that may be admixed with the alcohols are then obtained by extracting the powdered residue with ether in a Soxhlet extractor. The extracts are filtered, the ether distilled off, and the residue, if necessary, dissolved again in ether and filtered. The ether is then evaporated from the filtrate, and the hydrocarbons, etc., remaining are weighed (cp. "Beeswax," chap. xi. p. 664).

In the examination of waxes a good deal of information is obtained by heating the wax directly with potash-lime, measuring the volume of hydrogen gas, and determining the hydrocarbons in the residue. The preliminary isolation of the unsaponifiable matter may thus be dispensed with.

[1] *Jour. Soc. Chem. Ind.* 1892, 13; 1896, 14. [2] *Ibid.* 1897, 447.

CHAPTER VIII

DETECTION AND QUANTITATIVE DETERMINATION OF RESIN IN FATS OR FATTY ACIDS

i. Properties of Resin

Common resin or *colophony* is the residue obtained from pine resin by heating in a still until all the moisture and the oil of turpentine is distilled off. Colophony forms a light yellow to dark brown transparent mass, the colour being modified by the manner in which the distillation has been conducted and by the temperature employed. It possesses vitreous lustre, and is very brittle, breaking with shallow conchoidal fracture. The specific gravity of colophony or common resin—or shortly "resin"[1]—varies from 1·045 to 1·108 at 15° C.; it is, therefore, considerably higher than that of fats. The melting point of resin also exceeds that of fats, some varieties possessing as high a melting point as 135° C.

Resin softens at 70° C., and becomes semi-fluid in boiling water; it does not melt, however, to a clear liquid like fats or fatty acids. On warming, resin emits a pleasant terebinthinate odour; at a higher temperature, in contact with air, it burns with a dense yellow and sooty flame, sending forth a very characteristic smell.

Subjected to destructive distillation resin spirit and resin oils are obtained as distillates,[2] and coke is left behind. Distilled *in vacuo* it yields a hydrocarbon (colophene?) and an acid $C_{30}H_{32}O_2$ (isosylvic acid).[3] Insoluble in water, resin dissolves easily in alcohol, 1 part of resin requiring only 10 parts of 70 per cent alcohol for complete solution. The alcoholic solution has acid reaction, and its acidity can be ascertained by titration with alkali, using phenolphthalein as indicator. Resin is also soluble in methyl alcohol, amyl alcohol, ether, benzene, acetone, chloroform, carbon bisulphide, and oil of turpentine; most of its constituents also dissolve in petroleum spirit. Solutions of resin do not leave a grease-spot on paper.

[1] The spelling *resin* is here adopted throughout instead of "rosin" often met with; although the latter spelling would single out rosin or colophony as a special kind of resin, the salts of colophony are nevertheless spelt resinates. This inconsequence is avoided here.

[2] The aqueous distillate contains acetic acid, etc.

[3] Bischoff and Nastvogel, *Berichte*, 1890, 1919; *Jour. Soc. Chem. Ind.* 1890, 927.

The following constants have been obtained by several chemists:—

Kind of Resin.	Acid Value.	Saponific. Value.	Ether Value.	Total Bromine Absorption Value.	Bromine Substitution Value.	Bromine Addition Value.	Iodine Value.[1]	Observer.
Austrian . .	146·0	167·1	21·1	...	...	...	116·8	v. Schmidt and Erban[2]
Austrian . .	130·4	146·8	16·4	...	...	...	109·6	,,
Austrian, pale .	163·0	...	...	...	...	...	...	Kremel[3]
Austrian, dark .	151·0	...	...	...	...	...	...	,,
American . .	173·0	...	...	...	...	...	...	,,
English . .	169·0	...	...	...	...	...	...	,,
Refined . .	181·0	...	...	...	...	...	178·9[4]	Mills[5]
American . .	154·1	183·6	29·5	...	...	...	92·4-93·5	Lewkowitsch[6]
American . .	159·0	174·7	15·7	...	...	...	111-113	,,
American . .	161·4	178·9	17·5	...	...	...	113-114	,,
American . .	163·3	184·3	21·0	...	...	...	104-107	,,
American . .	164·3	194·3	30·0	...	...	...	62-64	,,
American . .	164·6	194·0	30·0	...	...	...	55-58	,,
Galipot . .	138·65	174·76	36·11	...	...	...	121·5-123·5	,,
American (W.G.)	...	...	...	212·7	106·35	0	...	McIlhiney[1]
American (E.) .	...	...	...	206·5	103·25	0	...	,,

The high acid values, and especially the definite values (cp. column "Ether Value"), prove conclusively that colophony is not, as *Maly* maintains, an anhydride, viz. abietic anhydride, but consists chiefly of free acids and small quantities of an anhydride.

The same conclusion has been arrived at by *Perrenoud*.[7] According to this author colophony does not contain any abietic anhydride, but consists of a resin in which crystals of an acid are embedded. In the case of American colophony (the resin from the trunks of *Pinus Strobus* and *Pinus Picea*, and the resin from the root of *Pinus sylvestris*) the crystals are said to be *abietic* acid, whereas in the resin from "galipot" and from the trunk of *Pinus sylvestris* they are stated to consist of the isomeric *pimaric* acid. Both acids possess the same formula $n(C_{10}H_{14}O)$; that of pimaric acid, as determined by the analysis of a crystalline ammonium salt, is most likely $C_{40}H_{56}O_4$. Both abietic and pimaric acid are optically active, and rotate the plane of polarised light to the left. The specific rotatory powers of abietic and pimaric acids are stated by *Perrenoud* to be 48° and 56° respectively.

[1] McIlhiney (*Jour. Soc. Chem. Ind.* 1894, 668), working with different samples of resin, found an average iodine value of 155·5. The iodine number varied with the time allowed for absorption and with the excess of iodine used—just as in the case of oils (cp. 173). Therefore McIlhiney's conclusion that the Hübl process is useless in the examination of resins is not justified.

[2] *Jour. Soc. Chem. Ind.* 1889, 308. [3] Wagner's *Jahresbericht*, 1886, 443.

[4] Calculated from the bromine value 112·7 by multiplying by $\frac{127}{80}$.

[5] *Jour. Soc. Chem. Ind.* 1886, 222.

[6] *Ibid.* 1893, 505, and unpublished experiments. [7] *Chem. Zeit.* 1885, 1590.

The *sylvic* acid of some authors is in *Liebermann's*[1] opinion identical with abietic acid. His researches, continued by *Haller*,[2] led to the result that pimaric acid is optically inactive. *Vesterberg*,[3] again, is of the opinion that three distinct acids are coexistent in "galipot."

Looking at these partly contradictory views on the ultimate composition of colophony, it is not surprising to find that *Mach*[4] rejects the formulæ given for abietic, sylvic, and pimaric acids by the authors mentioned. He states that these acids are identical, and proposes for *abietic acid*, the name he retains, the formula $C_{19}H_{28}O_2$, as found by numerous ultimate organic analyses and determinations of the molecular weight of specimens of the acid prepared by different methods from various samples of colophony.

Colophony also contains varying quantities of unsaponifiable matter, viz. hydrocarbons due to the partial breaking up of the acid on distilling pine resin. The following amounts of unsaponifiable matter have been found in commercial resins :—

Origin.	Unsaponifiable.	Observer.
	Per Cent.	
French . . .	15·2	Jean
American W.W. .	7·34	Evans and Black
,, W.G. .	5·00	,,
,, N. . .	9·00	,,
,, N. . .	8·21	,,
,, M. . .	7·61	,,

Abietic acid, $C_{44}H_{64}O_5$ [*Maly*], or $n(C_{10}H_{14}O)$ [*Perrenoud*], or $C_{19}H_{28}O_2$ [*Mach*], is obtained in a pure state in the form of crystals by digesting 1 part of coarsely powdered colophony with 2 parts of 70 per cent alcohol at a temperature of 50°-60° C. It separates as a crystalline powder, which is purified by recrystallisation from 3 parts of boiling alcohol of the same concentration. Another method is to pass hydrochloric acid gas through an alcoholic solution of colophony, when abietic acid separates (Flückiger, *Jahresberichte der Chemie*, 1867, 727). According to *Mach*, abietic acid occurs in colophony in varying amounts; some specimens contain 90 per cent of the crude acid, from others no acid could be isolated. On treating an alcoholic solution of colophony with water, a precipitate of impure abietic acid is obtained, which remains suspended in the liquid, forming with it an emulsion. On adding a dilute mineral acid and on warming, the resin separates in the form of globules on the side of the containing vessel, so that the clear liquid may be poured off. The resin thus obtained is at first very viscid, but it regains its former consistency by being boiled repeatedly with water, or by being heated to incipient fusion. In its pure state abietic acid crystallises in laminæ or small

[1] *Berichte*, 17. 1885. [2] *Ibid.* 18. 2167.
[3] *Ibid.* 18. 3334. [4] *Jour. Soc. Chem. Ind.* 1893, 1044.

crystals, melting at 165° C.; they are soluble in alcohol, ether, benzene, and glacial acetic acid. Abietic acid is not converted into an anhydride on heating.

Abietic acid is a dibasic acid. On warming colophony with dilute caustic alkalis, it is readily dissolved with formation of salts—resinates or pinates—that resemble in many respects the ordinary soaps. For that reason they are termed "resin soaps." Thus the solutions of the alkali salts lather on being agitated, and the "resin soaps" are thrown up from their aqueous solutions by addition of concentrated alkali or of common salt. This separation, however, does not take place so readily and completely as in the case of the soaps made from fatty acids. Dilute mineral acids liberate the free resin acids from the resinates.

Sodium resinate dissolves readily in alcohol, and also in ether containing alcohol; in pure ether, however, it is but sparingly soluble. According to experiments by *Barfoed*, 29 c.c. of ether dissolved within twenty-four hours 0·0239 grm., and 19 c.c. after eight days 0·041 grm. of sodium resinate.

The solutions of the resinates of the alkali metals are precipitated by salts of the alkaline earths and heavy metals. On the solubility of some of these salts in alcohol and ether, methods of separation of the resin acids from the fatty acids are based. The zinc, copper, silver, and manganese resinates are soluble in ether, whereas calcium resinate is insoluble in this menstruum. As to manganese and lead and copper resinates cp. chap. xii. p. 785.

In the quantitative analysis of a resin soap the acid is separated as free resin acid (abietic acid), and it is, therefore, necessary (as will be shown later on under "Analysis of Soaps") for the proper calculation of the composition of soap to convert the weight of the resin acids into the weight of the anhydrides. From the formulæ for abietic acid, $C_{44}H_{64}O_5$, and for the anhydride, $C_{44}H_{62}O_4$, it is easy to see that 100 parts of the free resin acid are equivalent to 97·32 [1] parts of anhydride.

Further information as to the composition of resin may be gained from a paper published by *Jean*,[2] in which he shows that colophony contains besides its chief constituent, viz. abietic acid, two more resinoid substances (cp. above, *Vesterberg's* opinion). The following observations are given in support of this view. On boiling colophony with twice the quantity of caustic soda of 15° Bé. (1·116 specific gravity), a soap of gelatinous consistency separates from the alkaline solution on cooling. When the latter is poured off, and the gelatinous soap washed with caustic soda of 15° Bé., the first resin acid, A, most likely abietic acid, is obtained by decomposing with a mineral acid. The alkaline solution contains the two other acids, B and C. Acid B

[1] Pending a confirmation of *Mach's* observations, these figures are still retained.
[2] *Chem. News*, 26. 207.

is thrown out by acidulating with a mineral acid, acid C remaining dissolved.

The three acids are differentiated by their solubilities in water and oil of turpentine. Acid C is soluble in water, whereas acids A and B are insoluble. Acids A and C are soluble in oil of turpentine, whereas B is insoluble in that solvent. All three acids dissolve easily in alcohol.

The sodium resinate formed from acid A is sparingly soluble in cold water, but is easily dissolved by hot water, alcohol, and oil of turpentine. Lead acetate, magnesium, sulphate, and barium chloride precipitate the resinates of the corresponding metals. Barium resinate is soluble in ether. The sodium resinate formed from acid B is insoluble in oil of turpentine; the barium resinate is incompletely precipitated by barium chloride solution.

Acid C is prepared from the acid liquid, after acid B has been precipitated and separated by filtration. The filtrate is neutralised with caustic soda, evaporated to dryness, and the residue extracted with alcohol, when a shellac-like substance is obtained possessing a faint acid reaction. Copper and silver salts precipitate the aqueous solution of the acid.

ii. Detection of Resin when admixed with Fats, Fatty Acids, and Waxes

In mixtures of resin *and neutral fats or oils* the former, if present in considerable quantity, may be recognised by its peculiar smell and characteristic taste. The determination of the specific gravity may also be usefully employed; presence of resin will be indicated by a higher specific gravity than the normal one.

The rapid detection of resin *in neutral fats or waxes* may be based on the solubility of resin in alcohol and solutions of sodium carbonate. On warming the suspected sample with 70 per cent alcohol the resin only will be dissolved. The alcoholic solution is then diluted with water, when in presence of resin a precipitate is obtained which is collected after warming, and, if necessary, after addition of a mineral acid. The substance thus obtained may be then identified as resin by its appearance, consistency, odour, etc.

Barfoed warms the sample with a dilute alcoholic solution of sodium carbonate, prepared by dissolving 1 part of soda crystals (or 0·37 parts of soda ash) in 3 parts of water, and then adding 7 parts of 30 per cent alcohol (2 measures of 93 per cent alcohol and 5 measures of water), when the resin only is stated to be dissolved. Its separation is effected as described already.

Rödiger[1] boils 100 grms. of the sample with 7 to 8 grms. of potassium carbonate and 80 to 100 grms. of water in a flask for a quarter of an hour, cools to 50° C., and then shakes vigorously with

[1] *Chem. Zeit.* 5. 498.

petroleum ether. The aqueous layer, holding in solution any resin soap present, is then drawn off and diluted with hot water. Excess of common salt is next added, the solution slightly acidulated and boiled, when an oily layer of resin acid mixed with a little fat and petroleum ether will be obtained. The latter may be driven off by heating the separated resin acid to 100° C.

The methods described here can only be used for the qualitative detection; for, on the one hand, the fats, although insoluble in water and in dilute alcohol, are dissolved, to a slight extent, by the resin soaps formed; and, on the other hand, a petroleum ether solution of fat is apt to dissolve appreciable quantities of resin soap.

The most reliable process is the following: Saponify the sample under examination with alcoholic potash and liberate the fatty acids together with the resin acids by acidulating. Then examine the mixed acids by the *Liebermann-Storch* reaction (p. 226).

According to *Morawski* the *Liebermann-Storch* reaction is in *many* cases suitable for the detection of resin acids. The writer recommends this method as thoroughly trustworthy in every case. To perform this test, the fatty acids are dissolved in acetic anhydride at a gentle heat and the solution cooled. Sulphuric acid of 1·53 sp. gr.[1] is then carefully allowed to flow into the solution, when the presence of the minutest quantity of resin acid will be indicated by the appearance of a reddish-violet colouration; if the solution be too warm, this colour will disappear almost immediately, changing into a brownish-yellow. In any case, the colour disappears quickly. Fatty acids do not produce the violet colour, but it should be remembered that cholesterol, which gives a similar reaction with acetic anhydride and sulphuric acid, might be present amongst the mixed acids. In the latter case the cholesterol must be removed previous to the liberation of the mixed fatty acids by shaking out the soap solution with ether or petroleum ether. This reaction may be also used for the detection of resin in beeswax.

Numerous other methods have been proposed, and are still being proposed, for the same purpose (by *Sutherland*, *Vohl*, *Gottlieb*, *Barfoed*, *Jean*, *Renard*, *Cornette*), but as they are not reliable they are omitted here.

For the isolation of the resin it will be found best to use the method described under vi.

iii. Quantitative Determination of Resin in Neutral Fats

In mixtures of neutral fats with resin—as linseed oil and resin—the writer determines approximately the resin by titrating an accurately weighed quantity of the sample dissolved in ether-alcohol

[1] Sulphuric acid of 1·53 sp. gr. contains 62·53 per cent of SO_4H_2; it is prepared by mixing 34·7 c.c. of conc. sulphuric acid with 37·5 c.c. of water.

with standard alkali, using phenolphthalein as an indicator. The combining weight adopted for resin is 346, and the amount of free fatty acids in the oil is, of course, neglected, being, as a rule, very small compared with the acid value corresponding to the resin. Experiments carried out on mixtures of linseed and cotton seed oils with resin gave very accurate results.

If greater accuracy be desired, the resin acids are isolated together with the mixed fatty acids, and examined as described under the following head :—

iv. Quantitative Determination of Resin Acids in Admixture with Fatty Acids

1. Barfoed's Method.—The mixed fatty acids—say 10 grms.—are neutralised with warm dilute caustic soda (one measure of caustic soda, specific gravity 1·1, in six measures of water), avoiding an excess of caustic soda [preferably by titrating with the caustic soda solution, phenolphthalein being used as an indicator]. The solution is then evaporated on the water-bath to complete dryness, the residue finely powdered and dried in a stoppered weighing-bottle at 100° C., until the weight remains constant; the drying sometimes takes several days. The dry powder is then divided into two parts; one part (*a*) is used for the determination of both resin and fatty acids; in the second part (*b*) the resin acids only are estimated.

(*a*) This part is dissolved in hot water and acidulated by addition of hydrochloric acid. After standing for twenty-four hours the separated acids are transferred to a weighed filter, washed until all traces of the mineral acid have been removed, dried at 100° C. and weighed.

(*b*) The second portion of the dried residue is placed in a stoppered graduated cylinder (preferably a Muter tube), and 5 to 10 c.c. of absolute alcohol for every grm. of substance added. The volume having been read off carefully, the stopper is tied on to the neck of the cylinder, and the cylinder immersed in a water-bath and heated for some time to 80° C., when all the resin soap and part of the fatty acid soap will pass into solution. On cooling, however, part of the dissolved fatty acid soap will separate and a contraction may take place; this is made up to the former volume with alcohol, and then five times the volume of ether, thoroughly freed from alcohol and water, is added. The contents of the cylinder are agitated at intervals for several hours, and then allowed to stand for twenty-four to forty-eight hours at the ordinary temperature. The resin soap is then dissolved completely, the fatty acid soap having been precipitated and settled out so that an accurately measured portion of the solution may be withdrawn. The resin acids dissolved in the latter may be determined by first evaporating the ether, dissolving the residue in water, and estimating the resin as

described in (*a*). The quantity found is calculated to the total volume of the ether-alcohol solution, and thus the percentage of resin acids obtained. By subtracting (*b*) from (*a*) the amount of fatty acids in the mixture is found. The undissolved fatty acid soap, as obtained in (*b*), may be collected on a filter and further examined.

This method yields reliable results only when oleic acid is almost wholly absent (which is very rarely the case); great care must also be taken to employ absolutely anhydrous alcohol and anhydrous ether, or else the results will be seriously vitiated by the presence of fatty acid in the isolated resin acid.

Experiments made by *Barfoed* on the solubilities of sodium resinate and sodium oleate in the alcohol ether mixture as described above, are recorded in the following short table:—

One part of	Soluble in parts of Alcohol-Ether Solution.
Sodium resinate	7·9
Sodium oleate	935·0

Ether alone cannot be used, sodium resinate being but sparingly soluble in it. *Barfoed's* method cannot be recommended; it has been fully described here, as process 2 (*d*) (see below) is based on it.

2. **Gladding's Method.**—This method is based on the solubility of silver resinate in ether, and the almost complete insolubility of the silver salts of the fatty acids in this solvent. It was proposed originally by *Gladding;* later on several modifications have been suggested by various authors.

(*a*) *Gladding's Original Method.*[1]—About 0·5 grm. of the mixed resin and fatty acids are dissolved in 40 c.c. of 90 per cent alcohol in a stoppered graduated cylinder, by warming on the water-bath. A drop of phenolphthalein is then added, and a concentrated solution of alcoholic caustic potash dropped in carefully until the solution has just acquired a permanent pink colour. A gentle heat may be applied in order to keep the soap dissolved. The solution is then allowed to cool, and made up with ether to exactly 200 c.c. 1 grm. of finely powdered silver nitrate is next added, and the contents of the cylinder shaken vigorously for about twenty minutes, when the precipitate, consisting of the silver salts of fatty acids, will coagulate and settle out, leaving the supernatant liquid clear. An accurately measured quantity—conveniently 100 c.c., being half of the quantity employed—is then run off into a separating funnel, and agitated again with a small quantity of powdered silver nitrate in order to ensure the complete precipitation of the fatty acids. Should there be any precipitate it will be best to reject the assay altogether and to start afresh. The ethereal solution is then shaken vigorously with 40 c.c. of dilute hydrochloric acid (1 volume of hydrochloric acid, specific gravity 1·12, and two volumes of water), and the precipitated silver chloride removed together with the acid liquid. The ethereal layer,

[1] *Chem. News*, 14. 159.

holding the liberated resin acid in solution, is washed free from mineral acid, transferred to a weighed flask, the ether evaporated, and the residue weighed. The quantity found multiplied by 2 gives the amount of resin acid in the sample.

Gladding, supported by two experiments only, makes a correction for the small quantity of silver oleate dissolved, by subtracting from the weight obtained 0·002359 grm. for each 10 c.c. of the ethereal liquid.

In order to eliminate the uncertainty of the correction, *Alder Wright* and *Thomson*[1] have determined the solubilities of the silver salts of different fatty acids. They are given in the following table, to which a few figures, found by the writer,[2] have been added :—

Kind of Acid.	Solubility of Fatty Acids (as Silver Salts) in 10 c.c. of Alcoholic Ether.			Author.
	Minimum.	Maximum.	Mean.	
	Grm.	Grm.	Grm.	
Pure stearic . .	0·0016	0·0008	0·00116	Wright and Thompson
,, ,, .	0·00058	0·00054	0·00056	Lewkowitsch
Pure oleic . .	0·0015	0·0009	0·0012	Wright and Thompson
,, ,, . .	0·01094	0·01090	0·01092	Lewkowitsch
Nearly pure palmitic	0·0030	0·0028	0·00291	Wright and Thompson
Cotton seed oil .	0·0034	0·0020	0·00269	,,
Castor oil . .	0·0062	0·0049	0·00539	,,
Cocoa nut oil (acids dried on water-bath) . . .	0·00175	0·0012	0·00148	,,
Cocoa nut oil (acids dried over vitriol)	0·0023	0·0019	0·00211	,,
Stearic and oleic, in nearly equal proportions . .	0·0022	0·0018	0·00191	,,
Stearic and cotton seed oil acid, in nearly equal proportions . .	...	...	0·00255	,,
Oleic and cotton seed oil acid, in nearly equal proportions . .	...	...	0·00245	,,
Stearic and cocoa nut oil acid (water-bath) in nearly equal proportions	...	...	0·00234	,,
Oleic and cocoa nut oil acid (water-bath) in nearly equal proportions	...	...	0·00256	,,

No account is taken in *Gladding's* original method of the volume of the precipitated silver salts, and with regard to the solubility of the silver salts of the fatty acids in ether, even granting the accuracy

[1] *Chem. News*, 53. 165. [2] *Jour. Soc. Chem. Ind.* 1893, 503.

of the corrections given in the preceding table, the proof is still wanting that these figures hold good for a mixture of those silver salts with varying proportions of silver resinates. *Lewkowitsch* has examined a number of resin soaps by this method, and although the solubility of the silver salts of the fatty acids was determined separately, altogether unreliable results were obtained. The method must therefore be rejected.

(*b*) *Hübl and Stadler's Modification of Gladding's Process.*—These chemists dissolve about 1 grm. of the mixed resin and fatty acids in about 20 c.c. of alcohol by warming in a stoppered bottle on the water-bath, and exactly neutralise the acids with caustic potash, using phenolphthalein as an indicator. The soap solution is then transferred to a beaker, made up with water to about 200 c.c., and precipitated with silver nitrate solution. The silver salts are filtered off, *protected from sunlight*, dried at 100° C. in an oven, and exhausted in a Soxhlet extractor by means of dry ether. The ethereal solution should be yellow or light brown, but not dark brown; it is filtered, if necessary, into a separating funnel, the dissolved resin acids are isolated by hydrochloric acid, as already described, and weighed. A correction for any dissolved aliphatic silver salts is not recommended.

This modification obviates the errors attaching to Gladding's original method by avoiding the measuring of an ethereal solution, so extremely liable to losses by evaporation. *Lewkowitsch*,[1] however, who has tried this method, could not get satisfactory results, the values obtained being mostly too low. It appeared that reduction of the silver salts (especially when the percentage of resin in the soap was high) took place in almost all cases, in some going so far as to yield an ethereal solution free from silver. Besides, the solubility of the silver salts of the aliphatic acids seemed to be greater than in the preceding method.

(*c*) *Grittner and Szilazi's Modification of Gladding's Process.*—These chemists dissolve the sodium salts of the mixed fatty acids in 80 per cent alcohol, neutralise, if necessary, with ammonia, and precipitate with a 10 per cent alcoholic solution of calcium nitrate. Calcium palmitate and stearate are precipitated completely, calcium oleate for the most part, whilst calcium resinate remains in solution. On adding silver nitrate to the filtrate and diluting it strongly, the silver salts are precipitated; these are filtered off and treated with ether according to Gladding's directions. The correction to be made, according to *Grittner* and *Szilazi*, is 0·016 grm. for every 10 c.c. of ether used. The figures which the authors give in their original paper[2] speak certainly in favour of the exactness of the method, but a series of experiments carried out by the writer[3] gave unsatisfactory results.

(*d*) *Allen's Modification of Gladding's Process.*—*Allen*[4] proposes to combine *Gladding's* original method with *Barfoed's*. This is done by

[1] *Jour. Soc. Chem. Ind.* 1893, 503. [2] *Chem. Zeit.* 10. 325.
[3] *Jour. Soc. Chem. Ind.* 1893, 503. [4] Thorpe, *Dict. of Applied Chem.* iii. 55.

exhausting the dried sodium salts of the mixed fatty and resin acids with ether-alcohol (whereby the resinates are dissolved easily along with part of the oleate, whereas palmitate and stearate remain behind), converting the dissolved salts into their corresponding silver salts, and treating the latter with ether. *Allen* states that the combination of the two methods yields very satisfactory results, without, however, supporting this statement by figures. Since, however, this combined process is based on the same principle as *Grittner* and *Szilazi's*, and since *Allen*[1] himself declares that this process has been wholly superseded by *Twitchell's* (see below), it need not be discussed further.

3. **Twitchell's Method.**[2]—This method is based on the property of aliphatic acids of being converted into their ethylic ethers when acted upon by hydrochloric acid gas in their alcoholic solution, whereas colophony is said to undergo practically no change under the same treatment, abietic acid separating from the solution (see p. 236). The analysis is carried out as follows :—

2 to 3 grms. of the mixed fatty and resin acids are weighed off accurately, dissolved in a flask in ten times their volume of *absolute* alcohol (90 per cent alcohol must not be used, as the conversion of fatty acids into ethers is not complete in that case), and a current of dry hydrochloric acid gas passed through, the flask being cooled by immersion in cold water. The gas is rapidly absorbed at first, and after about forty-five minutes, when gas is noticed to escape unabsorbed, the operation is finished. To ensure complete etherification the flask is allowed to stand for an hour, during which time the ethylic ethers and the resin acids separate on the top as an oily layer. The contents of the flask are then diluted with five times their volume of water, and boiled until the aqueous solution has become clear. From this stage the analysis may be carried out either (*a*) volumetrically or (*b*) gravimetrically.

(*a*) *The Volumetric Analysis.*—The contents of the flask are transferred to a separating funnel, and the flask rinsed out several times with ether. After vigorous shaking the acid layer is run off, and the remaining ethereal solution, containing the ethylic ethers and the resin acids, washed with water until the last trace of hydrochloric acid is removed. 50 c.c. of alcohol are then added, and the solution titrated with standard caustic potash or soda, using phenolphthalein as an indicator. The resin acids combine at once with the alkali, whereas the ethylic ethers remain practically unaltered. Adopting as the combining equivalent for resin 346, the number of c.c. of normal alkali used multiplied by 0·346 will give the amount of resin in the sample.[3]

[1] *Jour. Soc. Chem. Ind.* 1893, 508 ; *Analyst*, 1895, 7.

[2] *Jour. Soc. Chem. Ind.* 1891, 804.

[3] Wilson (*Jour. Soc. Chem. Ind.* 1891, 952) shortens the volumetric process by dissolving the contents of the flask in alcohol direct, thus omitting the washing with water. The solution is then titrated with alkali until neutral to methylorange, this amount of alkali being of course neglected. Phenolphthalein is then added, and again titrated until pink ; the second amount of standard alkali is calculated to resin.

(*b*) *The Gravimetric Method.*—The contents of the flask are mixed with a little petroleum ether, boiling below 80° C., and transferred to a separating funnel, the flask being washed out with the same solvent. The petroleum ether layer should measure about 50 c.c. After shaking, the acid solution is run off, and the petroleum ether layer washed once with water, and then treated in the funnel with 50 c.c. of a solution containing 0·5 grm. of KOH and 5 c.c. of alcohol. The ethylic ethers dissolved in the petroleum ether will then be found to float on the top, the resin acids being dissolved by the slightly alkaline solution. The soap solution is then run off, decomposed with hydrochloric acid, and the separated resin acids collected as such, or preferably dissolved in ether and isolated after evaporating the ether. The residue, dried and weighed, gives the amount of resin in the sample.

Of all the methods proposed hitherto for the estimation of resin acids in mixtures with fatty acids, that recommended by *Twitchell* yields the best results, and should therefore be used to the exclusion of the methods described before. The results, however, must not be considered as absolutely correct; they are only approximate, as *Lewkowitsch*[1] has shown by an exhaustive examination of both the volumetric and gravimetric processes.

The mean combining weight of different brands of commercial resin varying within considerable limits (cp. p. 235), an uncertainty adheres to the volumetric analysis, of which the gravimetric analysis is free. Under the action of the hydrochloric acid the resin appears to undergo some destruction[2] with the formation of acids of lower molecular weight, since the volumetric analysis gave, as a rule, too high results. In the gravimetric process, again, some of these secondary products pass into the aqueous solution without being dissolved by the petroleum ether. By a subsequent extraction with ether, part of the dissolved substances may be recovered, but even then the results of the gravimetric analysis were found too low. Of course, the unsaponifiable oils occurring in resin (p. 236) remain in the petroleum ether solution and thus escape being weighed. But even this cannot wholly account for the great deficiency.

The subjoined tables, giving the analysis of mixtures of oleic

[1] *Jour. Soc. Chem. Ind.* 1893, 504.

[2] The results given in table p. 247 are confirmed by several experiments made since by *Evans* and *Black*, as shewn by the following table:—

Weight of Resin.	Resin calculated from Titration.	Loss.
Grms.	Grms.	Per cent.
2·0968	2·054	2·00
2·4723	2·45	0·90
2·035	..	0·93
2·03	..	0·69
2·115	..	1·14

acid and resin acids of ascertained combining weight, will confirm the writer's critical remarks :—

Volumetric Analysis

Oleic Acid.	Resin.	Equal to Resin Acids.[1]	1/1 KOH used.	Mixture contains Resin Acids. Combining Weight 346.		Calculated for the yield of Resin Acids only.	
				Theory.	Experiment.	Theory.	Experiment.
Grms.	Grms.	Grms.	c.c.	Per cent.	Per cent.	Per cent.	Per cent.
2·5096	0·8027	0·8248	2·4	24·736	24·90	100·0	100·60
2·3988	0·8167	0·8391	2·56	25·92	27·35	100·0	105·50
1·5638	1·5532	1·5960	4·41	50·51	48·40	100·0	95·60
1·4606	1·5202	1·5620	4·19	52·72	48·93	100·0	92·81
0·8918	2·5198	2·5892	6·68	74·38	66·397	100·0	89·47
0·8296	2·5298	2·5995	6·72	75·81	67·81	100·0	89·45

[1] Weight of resin divided by ·9732 ; the resin being assumed to consist of abietic anhydride.

Gravimetric Analysis

No.	Oleic Acid.	Resin.	Equal to Resin Acids.	Found Resin Acids.	Mixture contains Resin Acids.		Calculated for yield of Resin Acids.	
					Theory.	Experiment.	Theory.	Experiment.
	Grms.	Grms.	Grms.	Grms.	Per cent.	Per cent.	Per cent.	Per cent.
1	2·4666	0·8199	0·8425	0·7385	25·46	22·32	100	87·65
2	2·8058	0·8577	0·8812	0·7736	23·90	20·98	100	87·80
3	1·6465	1·5342	1·5765	1·3200	48·91	40·96	100	83·73
4	1·4090	1·5092	1·5508	1·3128	52·39	44·35	100	84·65
5	0·8600	2·5252	2·5948	2·0930	75·11	60·58	100	80·66
6	0·8430	2·5322	2·6019	2·1744	75·53	63·12	100	83·56
7	...	4·2524	4·2701	3·5631	...	...	100	83·44
8	...	4·6864	4·7058	3·8334	...	...	100	81·46
9	...	4·6700	4·6894	3·8979	...	...	100	83·12

The following tables will give an indication as to how far, in practical cases, the results obtained by either process approach the theoretical ones.

The "mixed fatty and resin acids" were obtained from soaps specially prepared on a large scale from carefully weighed quantities of fats and resins. Average samples of the fats and the resin were examined separately for the yield of fatty acids from the former and for the combining weight of the latter, these determinations being indispensable for a correct calculation of the theoretical amount of resin acids.

Volumetric Analysis

Mixed Fatty and Resin Acids.	Resin Acids.	
	Theory.	Experiment.
No.	Per cent.	Per cent.
1	9·79	9·98, 9·34, 9·795, 9·91.
2	19·69	23·97, 24·55, 22·93, 23·28, 23·98, 24·08.
3	21·45	24·96, 24·78, 23·63.
4	24·66	24·89, 25·15, 25·06, 24·23.
5	30·31	29·69, 30·12, 28·18, 29·78.
6	39·81	40·24, 40·37, 41·44, 42·13, 41·8, 40·37, 42·18, 40·55, 40·07, 40·05, 43·69, 41·12, 41·81, 40·77, 44·82.
7	45·05	45·76, 46·50, 49·61, 47·66, 46·45, 47·84, 45·34, 44·24, 44·48, 44·39.

Gravimetric Analysis

Mixed Fatty and Resin Acids.	Resin Acids.	
	Theory.	Experiment.
No.	Per cent.	Per cent.
1	9·79	9·38, 9·97.
2	19·69	20·46, 20·55, 19·96, 19·99, 19·44, 19·33.
3	21·45	19·25, 18·27, 19·37, 17·83, 19·54, 18·61, 18·57, 19·16.
4	24·66	20·97, 16·65, 21·76.
5	30·31	25·76, 25·06, 23·66, 26·10.
6	39·81	35·97, 38·86, 36·44, 36·14, 35·42, 35·86, 32·51, 36·29.
7	45·05	37·58, 37·23, 37·29, 36·97, 35·32, 40·06, 36·8.

By washing the petroleum ether solution with alkali a second time, and extracting the acid layer with common ether, the following results were obtained :—

Mixed Fatty and Resin Acids.	Resin Acids.				
	Theory.	Experiments.			
		Extracted by First Alkali Wash.	Extracted by Second Alkali Wash.	Extracted by Ether.	Total.
No.		Per cent.	Per cent.	Per cent.	Per cent.
2	19·69	19·46	0·115	1·045	20·62
2	19·69	18·44	0·074	0·822	19·34
3	21·45	19·14	0·105	0·3615	19·607
3	21·45	19·19	0·061	0·2839	19·54
4	24·66	21·72	0·179	1·203	23·102
4	24·66	22·29	0·239	1·01	23·54
5	30·31	25·75	0·019	2·41	28·18
5	30·31	26·93	0·085	0·72	27·73
6	39·81	34·96	1·296	1·567	37·80
6	39·81	34·596	0·190	1·12	35·91

Evans and *Black*[1] try to vindicate Twitchell's method as correct. But as they, like *Twitchell* himself, experimented only with mixtures containing about 40 per cent of resin acid, for which percentage, curiously enough, the best results are obtained, their experiments cannot refute the writer's results.

In case the resin admixed originally with the fat contained notable quantities of (unsaponifiable) resin oils, the latter are determined as described under the following heading :—

v. Quantitative Determination of Resin Acids in Admixture with Fats (or Fatty Acids) and Unsaponifiable Matter

If a mixture of resin acids, fat, and unsaponifiable matter be under examination, the sample is saponified by boiling with alcoholic potash, and the alcohol driven off by prolonged boiling after diluting with water. The aqueous solution of soap is then transferred to a separating funnel—regardless of any undissolved unsaponifiable matter—and shaken out with petroleum ether, whereby the unsaponifiable matter is separated from the fat and resin (cp. p. 219). The soap solution gives, on treatment with a mineral acid, a mixture of fatty and resin acids, which are separated by *Twitchell's* process.

By using *Twitchell's* volumetric method the separation of the unsaponifiable matter may be avoided by the following procedure:[2]—The

[1] *Amer. Chem. Jour.* 1895, 59. [2] *Jour. Soc. Chem. Ind.* 1891, 804.

mixture is saponified with alcoholic potash, and the resin acids, fatty acids, and unsaponifiable matter isolated by acidulating. If a mixture of the acids and unsaponifiable matter be given at the outset, the saponification, of course, is unnecessary.

2 grms. of the mixed acids and unsaponifiable matter are weighed off accurately, titrated with normal caustic soda or potash, and the number of c.c., used until neutrality to phenolphthalein is reached, noted. Another 2 grms. are treated with hydrochloric acid gas, as described above, and titrated with normal alkali. If a be the number of c.c. used in the first experiment, and b the number found in the second experiment, then we shall find, adopting as the combining weight for resin 346, and for fatty acids (palmitic, stearic, oleic) 275—

1. Weight of resin acids = $a \times 0{\cdot}346$
2. Weight of fatty acids = $(a - b) \times 0{\cdot}275$
3. Weight of unsaponifiable = $100 - [a \times 0{\cdot}346 + (a - b) \times 0{\cdot}275]$.

The accuracy of the result will, of course, largely depend on the correctness of the assumed combining weights 346 and 275.

vi. Separation of Resin from Fatty Matter

Separation of resin acids from fatty acids is effected by passing the mixture of resin and fatty acids through the etherification process described under *Twitchell's* method. We then have a mixture of free acids and ethers, and after titration, as *e.g.* in the volumetric process, there results a mixture of resin soap and ethyl ethers of the fatty acids. Now if the alcohol is distilled off and the remaining mixture is treated with water, the soap is dissolved, leaving the ethers floating on the surface of the soap solution. The two layers are separated, and the soap solution, after washing with common ether to remove the last traces of dissolved ethylic ethers, yields on acidulating the resin acid. The ethylic ethers are saponified by means of caustic alkalis, and the fatty acids separated in the usual manner. Both the resin and the fatty acids may then be examined separately.

CHAPTER IX

APPLICATION OF PHYSICAL AND CHEMICAL METHODS TO THE SYSTEMATIC EXAMINATION OF FATTY OILS AND LIQUID WAXES

A SUBDIVISION of the liquid fats into several classes may be conveniently based on their chemical properties, as will be shown further on. But it should be borne in mind that the distinctions between the members of the different classes are not always very clearly marked, and much less so the differences between the members of one and the same class. For this reason the detection of every individual oil, when in admixture with the others, nay, even the detection of two oils when mixed, is often a very difficult task.

As most liquid fats consist chiefly of nearly the same glycerides, a quantitative separation of the individual oils contained in a mixture is altogether out of the question. But though we have no definite quantitative methods as in inorganic analysis, yet, by adopting a systematic plan of examination, we can in the majority of cases decide—

(1) Of what kind of oil a sample consists, and
(2) Whether it is a pure or an adulterated specimen.

If a mixture of but two oils be under examination, it is, as a rule, possible to detect the presence of either oil qualitatively. Frequently it will even be feasible to determine quantitatively the proportions of the mixed oils.

A mixture of three or more fatty oils is often met with. In such cases commercial analysis will not always lead to a satisfactory result; still, in most cases it will be possible to identify at least one or two of the individual oils in the mixture.

The most important prŏblem required to be solved by commercial analysis is, whether a sample is pure or sophisticated. Adulteration of fatty oils with the unsaponifiable oils (tar oils, resin oils, mineral oils) will be the easiest to detect.

Of the fatty oils themselves only those will be used as adulterants that are lower in price than the oil to be adulterated, the object of sophistication being evidently to sell a cheaper article at a higher

price. Hence a price list of the different kinds of oils will materially assist the analyst in fixing his attention on the oils lower in the scale of prices than the sample under examination.

The following list, arranged in the order of their commercial value, may be found useful. It should, however, be remembered that these prices are subject to wide fluctuations from year to year, causing, *e.g.* cotton seed oil and linseed oil to change places :—

1. Almond oil
2. Sperm oil
3. Olive oil
4. Neat's foot oil
5. Lard oil
6. Castor oil
7. Cod liver oil
8. Arctic sperm oil
9. Arachis oil
10. Poppy seed oil
11. Sesamé oil
12. Seal oil
13. Rape oil
14. Linseed oil
15. Cotton seed oil—maize oil
16. Whale oil
17. Cod oil
18. Japan fish oil
19. Mineral oil
20. Resin oil

It will also greatly facilitate the examination of a totally unknown mixture of oils to learn its price, as this alone will tend to exclude a number of the more costly oils from the scope of the analysis.

In the following pages a systematic plan for the commercial analysis of oils will be adopted, based principally on the application of the general methods described in the preceding chapters. It must, however, be left to the analyst to select the methods and tests best adapted to each special case.[1] If a known oil be under examination, it will be best to consult first the description of that oil and the tables of constants given in chap. xi.

Before entering on the general methods applicable to the systematic examination, we may cursorily glance at the so-called

Organoleptic Methods

These comprise the odour and taste of the oil. Some adulterants, such as resin and mineral oil, will frequently be detected by the odour. The odour becomes more distinct on heating the oil or, as proposed by *Clarke*, on mixing it with sulphuric acid. Olive oil, lard oil, rape oil, cameline oil, and especially the oils from marine animals, possess a characteristic smell. To be able to discriminate by smell, however, requires a good deal of practical experience, more frequently possessed in a high degree by dealers in oils than by analytical chemists. The recognition of certain oils by taste is more difficult still, and yet the taste alone is in many cases the only criterion to determine the value of particular brands of oils that are pure in the sense of being wholly

[1] Cp. "Olive Oil," chap. xi. p. 451 ; "Lard," chap. xi. p. 563 ; "Butter fat," chap. xi. p. 601.

free from adulteration. Thus taste alone can discriminate between the fine Tuscan olive oils and the more inferior oils of South-Eastern Italy.

Physical Methods

The physical methods applied to the examination of oils have been detailed in chap. v.; they may be referred to as affording valuable information. A comparison of the results supplied by the examination of the sample with the numbers registered in the following tables will be found useful. The specific gravity, solidifying point, and the melting and solidifying points of the fatty acids furnish, as a rule, the most valuable and useful criteria, but the optical methods also, wherever the necessary apparatus is at hand, should be employed, combining, as they do in many cases, rapidity of observation with certainty of result. In special cases the determination of the viscosity will prove of some assistance.

The behaviour of oils with solvents will in many cases serve as a valuable confirmation of indications furnished by other tests. Several attempts at a systematic classification of oils, based on the solubility in some solvents, have been made, but hitherto no general rule has been established. Other physical properties will be referred to for the sake of completeness, although their usefulness is either doubtful or has not yet been fully established.

Chemical Methods

Most of the chemical methods adopted in testing have been exhaustively described in chap. vi. The so-called quantitative reactions enumerated there, and further the chemical tests described below, in short, those tests that are practised on the fatty substance itself will naturally be of the greatest importance.

Those reactions that are caused by foreign matters admixed with the oils, as small quantities of resins, colouring matters, etc., give, as a rule, less decisive results, the quantity and sometimes also the nature of those impurities varying considerably in different specimens of the same oil owing to the different processes adopted for their preparation and purification. All the so-called colour reactions fall under this category. In some special cases, however, the colour reactions give definite indications.

The following tests and methods will be considered under this head :—

(1) Elaïdin Test.
(2) Sulphur Chloride Test.
(3) Oxygen Absorption Test.
(4) Thermal Reactions.
(5) Quantitative Reactions.
(6) Qualitative Tests.

A. Application of Physical Methods in the Identification of Individual Oils and Recognition of their Purity

i. Specific Gravities of Fatty Oils and Liquid Waxes

If it be simply a question of identifying two oils by comparison of their specific gravities, *Donny*[1] proposes to colour the one sample —say by alcanna—and allow a drop of the other sample to slowly fall into it. If the two oils are identical the drop will float in the oil; if it falls down or floats on the surface, its specific gravity will be greater or smaller.

We subjoin the following two tables, due to *Allen*, and a table containing a number of values found in the Paris Municipal Laboratory; the latter has been supplemented by some determinations of other observers. *Allen's* first table (in which one or two corrections have been made as suggested by more recent determinations) contains the principal oils arranged according to their specific gravity; there are added, for the sake of comparison, the specific gravities of some fatty acids and hydrocarbons. It has not been thought necessary to give a complete list of specific gravities, as they will be found in chap. xi. under each individual oil.

[1] *Dingl. Polyt. Jour.* 174. 78.

Table of Specific Gravities of Fatty Oils and Liquid Waxes at 15°-16° *C.*

Class of Oil.	0·875 to 0·884	0·884 to 0·912	0·912 to 0·920	0·920 to 0·937	0·937 to 0·970
Liquid waxes from Marine Animals	Sperm oil Bottlenose oil				
Vegetable non-drying Oils			Olive oil Almond oil Arachis oil Ben oil Rape oil Mustard oil		
Terrestrial Animal Oils			Neat's foot oil Bone oil *Manufactured* Lard oil Tallow oil		
Marine Animal Oils				Whale oil Dolphin oil Porpoise oil Seal oil Menhaden oil Cod liver oil Shark liver oil	
Vegetable more or less drying Oils			Hazelnut oil	Cotton seed oil Sesamé oil Sunflower oil Poppy seed oil Hemp seed oil Linseed (raw) oil Walnut oil *Manufactured* Cocoa nut oleine	Japanese wood oil Croton oil Castor oil *Manufactured* Boiled Linseed oil Blown oils
Free Fatty Acids		Oleic acid		Linolic acid	Ricinoleic acid
Hydrocarbons	Shale products Petroleum products	Shale products Petroleum products	Heavy Petroleum products	Heavy Mineral oils	

Table of Specific Gravities of some Fatty Oils and Liquid Waxes at 15·5° C., and at 98°-99° C.

Kind of Oil.	Specific Gravity of Oil. Water at 15·5° C. (60° F.) = 1.	
	At 15·5° C. = 60° F.	At 98° – 99° C.
Arachis oil	0·9220	0·8673
Rape oil	0·9150	0·8632
Neat's foot oil	0·9140	0·8619
Cotton seed oil	0·9250	0·8725
Sesamé oil	0·9210	0·8679
Cocoa nut oleine	0·9262	0·8710
Niger seed oil	0·9270	0·8738
Linseed oil	0·9350	0·8809
Castor oil	0·9655	0·9096
Whale oil	0·9307	0·8725
Porpoise oil	0·9260	0·8714
Seal oil	0·9240	0·8733
Cod liver oil	0·9275	0·8742
Menhaden oil	0·9320	0·8774
Sperm oil	0·8837	0·8303
Bottlenose (Doegling) oil	0·8808	0·8274

Table of Specific Gravities of some Fatty Oils at 15° C., determined by means of the Hydrostatic Balance

Kind of Oil.	Specific Gravity at 15° C.
Almond oil	0·9177, 0·9180, 0·9198
Arachis oil	0·9167, 0·9176, 0·9187
Colza oil	0·9142, 0·9154, 0·9155, 0·9156
Cotton seed oil, white	0·9249, 0·9254
Cotton seed oil, brownish	0·930, 0·950
Beechnut oil	0·9200, 0·9206, 0·9220
Linseed oil	0·9315, 0·9325, 0·9335
Cameline oil	0·9240, 0·9252
Rape oil (winter seed)	0·9152
Rape oil (summer seed)	0·9164
Walnut oil	0·9260, 0·9266, 0·9277
Poppy seed oil	0·9249, 0·9250, 0·9254, 0·9265
Olive oil (sweet oil)	0·9160, 0·9163
Olive oil (commercial)	0·9163, 0·9170
Sesamé oil	0·9210, 0·9226, 0·9237
Whale oil, Norwegian	0·9240, 0·9257
Whale oil (Southern)	0·9270, 0·9230
Whale oil (American)	0·9250
Cod liver oil, pale	0·9280
Cod liver oil, brown	0·9254
Neat's foot oil	0·9142, 0·9160
Sheep's foot oil	0·9184, 0·9187
Tallow oil	0·9029
Hemp seed oil	0·9258
Lard oil	0·9120
Maize oil	0·9215, 0·9232, 0·9327
Madia oil	0·9350
Seal oil (pale)	0·9168
Seal oil (brown)	0·9170

If the specific gravity has been taken at a temperature other than the standard temperature, the value for the latter may be obtained by making a correction as shown p. 128.

The specific gravity of *rancid* oils differs from that of neutral (sweet) oils. A definite relation, however, does not exist between the amount of free fatty acids and the lowering of the specific gravity, though *Allen* has thought that such a relation could be established from *Archbutt's* determinations of the specific gravities of upwards of eighty samples of olive oil. The following little table, due to *Thomson* and *Ballantyne*,[1] proves this conclusively :—

No.	Nature of Oil.	Free Fatty Acids.	Specific Gravity at 15·5° C. (Water at 15·5° C. = 1.)
		Per cent.	
1	Olive oil (Gioja) . . .	9·42	0·9156
2	Olive oil	3·86	0·9148
3	Olive oil	23·78	0·9147
4	Olive oil	5·19	0·9168
5	Olive oil	19·83	0·9160
6	Olive oil (for dyeing) . .	9·67	0·9154
7	Olive oil	11·28	0·9145
8	Olive oil (for cooking) . .	4·15	0·9151
9	Olive oil, No. 1, freed from fatty acids	0·0	0·9152

In order to obviate the uncertainty attaching to the determination of the specific gravity of rancid oils (containing free fatty acids), *Archbutt* has proposed to take the specific gravities of the liberated fatty acids. The fatty acids being, as a rule, solid at the standard temperature, the determinations must be made at the boiling point of water.

The following table gives some of the values found :—

Mixed Fatty Acids from	Specific Gravity at 100° C. (Water at 100° C. = 1.)
Olive oil	0·8758, 0·8739
Rape oil	0·8758
Cotton seed oil	0·8816
Niger seed oil	0·8886
Linseed oil	0·8925
Whale oil	0·8922

It should, however, be borne in mind that variations in the specific gravity of an oil do not depend exclusively on the amount of free fatty acids, but will also be caused, and perhaps to a greater extent, by oxidation of the glycerides of the unsaturated fatty acids. Thus *Allen* has found that a sample of porpoise oil, having originally the specific gravity 0·920, showed after having been kept for three years the spec. grav. 0·926, although there was no increase in the amount of free fatty acids.

The following table, given by *Thomson* and *Ballantyne*,[2] embodies

[1] *Jour. Soc. Chem. Ind.* 1890, 589. [2] *Ibid.* 1891, 30.

the results obtained on exposing several oils to the action of direct sunlight in uncorked bottles, the contents of which were agitated every morning for six months:—

Kind of Oil.	Specific Gravity at 15·5° C. (Water at 15·5° C. = 1.)						
	Original.	After 1 Month.	After 2 Months.	After 3 Months.	After 4 Months.	After 5 Months.	After 6 Months.
Olive . . .	0·9168	0·9187	0·9193	0·9208	0·9215	0·9227	0·9246
Castor . . .	0·9679	0·9681	0·9691	0·9700	0·9700	0·9685	0·9683
Colza . . .	0·9168	0·9183	0·9172	0·9185	0·9184	0·9200	0·9207
Cotton seed .	0·9225	0·9237	0·9241	0·9261	0·9278	0·9304	0·9320
Arachis . .	0·9209	0·9218	0·9221	0·9233	0·9239	0·9256	0·9267
Linseed . .	0·9325	0·9331	0·9336	0·9353	0·9359	0·9372	0·9385

ii. Solidifying (Congealing) Points of Fatty Oils.—Melting and Solidifying Points of their Mixed Fatty Acids

The solidifying point of oils is of little value, as the length of time the oils are exposed to low temperatures plays a very important part indeed.

Holde[1] showed that oils, the solidifying points of which have been given as below 0° by various observers, will solidify at 0° if allowed to stand for several hours at this temperature; stirring assists solidification, and the lower temperature stated by other observers appears to be due to the oils not having been stirred.

In the following table the solidifying (congealing) points of several oils are given :—

Solidifying (Congealing) Points of Oils

Kind of Oil.	Solidifying Point.			Melting Point of the Solidified Oils.
	Observer.			Observer.
	Paris Municipal Laboratory.	Chateau.[2]	Holde.	Glässner.
	°C.	°C.		°C.
Olive oil	+2	−2 to +4	0°	+2·5
Cod liver oil	0			
Rape oil	−3·75	−2 to −3	0° (after 8 hours)	−4
Colza oil	−6·25	−6 to −6·5	...	−6
Arachis oil	−7·0	−3 to −4	...	...
Almond oil	−10·0	−20 to −30	...	−20 to −25
Beechnut oil	−17·5	−15.5 to −17·5		
Cameline oil	−18·0	−18 to −19		
Poppy seed oil	−18·0	−18		
Linseed oil	−27·5	...	...	−16 to −20
Hemp seed oil	−27·5	...	...	−27
Castor oil	...	...	...	−18
Sunflower oil	...	...	...	−16
Sesamé oil	...	...	...	−5
Lard oil	...	...	...	+6 to +8
Cotton seed oil	...	−2[3]		
Ben oil	...	0		
Croton oil	...	−16		
Sheep's foot oil	...	0		
Hazelnut oil	...	−17 to −18		
Maize oil	...	−10		
Walnut oil	...	−27 to −28		
Peach nut oil	...	−12		
Plum kernel oil	...	−8 to −9		
White mustard seed oil	...	−16		
Black mustard seed oil	...	−18		
Spindle tree oil	...	−20		
Fir seed oil	...	−27·5		
Grape seed oil	...	−15		

[1] *Jour. Soc. Chem. Ind.* 1896, 122. [2] Chateau-Hartmann, *Die Fette*, p. 194.

[3] This can only refer to the liquid portion of cotton seed oil, as many kinds of cotton seed oil deposit "stearine" at +12° C.

The melting and solidifying points of the **mixed fatty acids** are, however, far more significant than those of the oils themselves.

The following table contains the melting and solidifying points of a number of mixed fatty acids determined by various observers :—

Melting and Solidifying Points of some Fatty Acids[1]

Mixed Fatty Acids from	Bach.		Bensemann.		Allen.		Hübl.		Lewkowitsch.
	Melting Point.	Solidifying Point.	Point of Incipient Fusion.	Point of Complete Fusion.	Melting Point.	Solidifying Point.	Melting Point.	Solidifying Point.	Titer Test.
	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
Olive oil	26·5–28·5	22	23–24	26–27	26·0	21·0	26·0	21·2	19·0–19·4
Cotton seed oil	38	35	39–40	42–43	35·0	32·0	37·7	30·5	32·2–35·2
Sesamé oil	35	32·5	25–26	29–30	23·0	18·5	26·0	22·3	21·2–23·8
Arachis oil	33	31·0	31–32	34–35	29·5	28·0	27·7	23·8	28·1–29·2
Sunflower oil	23	17·0	...	...	...	...	...	...	...
Rape oil	20·7	15·0	18–19	21–23	19·5	18·5	20·1	12·2	11·7–13·6
Castor oil	13·0	2·0	...	...	...	...	13·0	3·0	...
Almond oil	...	...	...	...	...	...	14·0	5·0	9·5–11·8
Linseed oil	...	...	...	...	...	...	17·0	13·3	19·0–20·6
Poppy seed oil	...	...	...	...	...	...	20·5	16·5	...
Hemp seed oil	...	...	...	...	...	...	19·0	15·0	15·6–16·6
Walnut oil	...	...	...	...	...	...	20·0	16·5	...

Not Below

[1] Cp. chap. xi.

Bach's method of determining the melting and solidifying points of the fatty acids was to stir the fatty acids, contained in a narrow thin-walled test-tube with a thermometer, and to heat gradually in a water-bath; the point at which the mass became completely clear was noted as the melting point, that point at which cloudiness was noticed around the mercury bulb was taken as the solidifying point.

The melting point of the mixed fatty acids from cotton seed oil is remarkably high; it will, of course, vary in proportion to the amount of "cotton stearine" separated from the oil before being brought into commerce (cp. table, chap. xi. p. 378).

In commercial analysis too much value must not be attached to the melting point of the mixed fatty acids, its indications being so uncertain, that even as large a quantity as 25 per cent of admixed oil cannot be safely recognised.

iii. Optical Methods of Examination

(*a*) *Spectroscopical Examination*

This method may be conveniently used in some cases for detecting an admixture of vegetable oils with oils of animal origin (cp. p. 113).

(*b*) *Refractometric Examination*

Leone and *Longi*[1] were the first to point out that the adulteration of olive oil with sesamé oil or cotton seed oil could be recognised by the altered refractive power of the sample.

Strohmer has determined the refractive indices of a number of oils by means of *Abbe's* refractometer; they are given in the following table:—

[1] *Gazz. Chimica*, 16. 393.

[TABLE

Kind of Oil.	Remarks.	Refractive Index.			Difference between Refractive Index of the Oil at 15° C. and Water at 15° C.
		At 16° C. n_D 16° C.	At 14° C. n_D 14° C.	At 15° C. Mean of *a* and *b* n_D 15° C.	
		a	*b*	*c*	*d*
Olive oil . .	Virgin oil, Trieste	1·4700	1·4696	1·4698	0·1368
Olive oil . .	Dalmatian	1·4702	1·4704	1·4703	0·1373
Sesamé oil . .	Freshly expressed	1·4748	1·4748	1·4748	0·1418
Sesamé oil . .	French, 9 years old	1·4755	1·4768	1·4762	0·1432
Cotton seed oil .	American, finest	1·4743	1·4761	1·4752	0·1422
Cotton seed oil .	"Marginis"	1·4729	1·4734	1·4732	0·1402
Cotton seed oil .	Trieste, 7 years old	1·4735	1·4751	1·4743	0·1413
Rape oil . .	Three years old	1·4733	1·4731	1·4732	0·1402
Rape oil . .	Freed from fatty acids	1·4718	1·4721	1·4720	0·1390
Rape oil . .	Refined, 7 years old	1·4727	1·4725	1·4726	0·1396
Rape oil . .	Winter rape seed	1·4747	1·4767	1·4757	0·1427
Castor oil . .	Cold expressed	1·4786	1·4803	1·4795	0·1465
Castor oil . .	Hot expressed	1·4809	1·4796	1·4803	0·1473
Linseed oil . .	Cold expressed	1·4834	1·4836	1·4835	0·1505
Poppy seed oil .	...	1·4779	1·4787	1·4783	0·1453
Cod liver oil .	"Möller"	1·4841	1·4862	1·4852	0·1522
Cod liver oil .	Pale	1·4791	1·4809	1·4800	0·1470
Cod oil . .	...	1·4785	1·4792	1·4789	0·1459
Fish oil . .	...	...	1·4790	1·4790	0·1460
Water . . .	...	1·3330	1·3330	1·3330	...
Kerosene . .	Sp. gr. 0·7897 at 15° C.	...	...	1·4376	0·1046
Mineral oil . .	Russian, sp. gr. 0·9058 at 15° C.	...	...	1·4942	0·1612
Mineral oil . .	Sp. gr. 0·9066 at 15° C.	...	...	1·4943	0·1613

Holde[1] has obtained the following results with *Abbe's* refractometer at about 20° C. :—

Kind of Oil.	Limits of Indices of Refraction.	Mean Index of Refraction.
Rape oil, refined .	1·4722 to 1·4736	1·4735
Rape oil, crude .	1·4735 to 1·4760	1·4744
Olive oil. . .	1·4670 to 1·4705	1·4698
Mineral oil . .	1·4776 to 1·4980	1·4923
Resin oil. . .	1·5274 to 1·5415	1·5344

The following table, due to *Thörner*,[2] gives the refractive indices of a number of oils and of their fatty acids determined by means of *Pulfrich's* refractometer at 60° C. :—

[1] *Jour. Soc. Chem Ind.* 1891, 166. [2] *Ibid.* 1895, 43.

Kind of Oil.	Refractive Index at 60° C.	
	of the Oil.	of its Mixed Fatty Acids.
Linseed . . .	1·4660	1·4546
Poppy seed . .	1·4586	1·4506
Sunflower . .	1·4611	1·4531
Cotton seed . .	1·4570	1·4460
Sesamé . . .	1·4561	1·4461
Rape (crude) . .	1·4667	1·4491
Castor . . .	1·4636	1·4546
Almond . . .	1·4555	1·4461
Arachis . . .	1·4545	1·4461
Olive . . .	1·4548	1·4410
Cod liver oil . .	1·4621	1·4521

Although *Strohmer* is of opinion that the refractometric method is of no use for analytical purposes, it will be seen from the tables that olive oil possesses the smallest refractive index, and furthermore that castor oil and the drying oils possess a greater refractive power than the non-drying oils. The refractive index varies according to the age of the oil and the manner in which it has been prepared.

Column *d* of *Strohmer's* table gives the differences between the refractive indices of the oils and water; these values are, therefore, free from the unavoidable errors attaching to the apparatus itself. Since the refractive indices of the oils are influenced to a greater extent by a change of temperature than the corresponding index of water, comparative determinations should be made at the temperatures given in the table.

Amagat and *Jean*, on the contrary, claim that the refractive power as determined by their oleo-refractometer (p. 119) affords a very valuable criterion in the examination of oils. Thus, ten samples of olive oil examined in their apparatus showed differences not exceeding one or two degrees.[1]

The following table contains a number of values, obtained by means of the oleo-refractometer by *Jean*, by *Lobry de Bruyn* and *van Leent*, and other observers. The values given are "degrees" (p. 119), + means deviation to the right, – to the left.

I have, following the system adopted in this work, arranged the oils and liquid waxes in the order of their iodine values, so that it may be seen at a glance whether a connection can be established between iodine number and refractive power. No definite relation, however, can be established. It is remarkable that the oils belonging to the class "Terrestrial Animal Oils" deviate to the left, and it would appear as if animal oils could be readily differentiated from vegetable oils by their behaviour in the oleo-refractometer (cp. p. 318, and chap. xi., butter fat and lard).

As will be seen, the values found by the different observers agree on the whole satisfactorily, with the exception of those for sesamé oil and seal oil.

[1] This is confirmed by a recent examination of eleven pure Californian olive oils, the refractive indices of which varied from 1·4710 to 1·4717 (Blasdale, *Jour. Soc. Chem. Ind.* 1896, 206).

Kind of Oil.	Specific Gravity.	Acidity.	Deviations of the Oil. Degrees + or −.		Remarks.	Observer.	Class of Oil.
			Commrl.	Purified.[1]			
Linseed oil . .	0·9335	1·5	+53	+54	...	Jean	Drying oils
,, ,, . .	0·9315	2.6	+48	+48	...	,,	
,, ,, . .	...	...	+49 to +51	...	...	Bruyn & van Leent	
,, ,, (crude) .	...	...	+48 to +52	...	3 samples Temp. 22° C.	Pearmain	
,, ,, (refined)	...	...	+50 to +54	...	5 samples Temp. 22° C.	,,	
Japan wood oil .	...	...	+75	...	,, ,,	,,	
Hemp seed oil .	0·9258	13·8	+30	+32	...	Jean	
,, ,, .	0·9254	...	+34	+32	...	,,	
,, ,, .	...	...	+34 to +37·5	...	4 samples Temp. 22° C.	Pearmain	
Walnut oil . .	...	...	...	+35	...	Jean	
,, ,, . .	0·9270	...	...	+36	Nice	,,	
,, ,, . .	0·9266	...	...	+35	...	,,	
Poppy seed oil .	...	...	+29	...	Laboratory sample	,,	
,, ,, .	...	...	+23·5	...	...	,,	
,, ,, .	0·9249	2·5	+25	...	...	,,	
,, ,, .	0·9366	2·6	+35	+38	Very old sample	,,	
,, ,, .	...	3·7	+29·5	...	...	,,	
,, ,, .	...	...	+30 to +35	...	3 samples Temp. 22° C.	Pearmain	
Niger seed oil .	...	...	+26 to +30	...	2 samples Temp. 22° C.	,,	
Sunflower oil . .	...	...	+35	...	,, ,,	,,	
Fish oil . . .	...	...	+38	...	...	Jean	Fish oils
Pilchard oil . .	...	...	+32 to +36	...	2 samples Temp. 22° C.	Pearmain	
Japan fish oil . .	0·9297	...	+53	...	...	Jean	
,, ,, . .	0·9312	...	+50	...	...	,,	
Cod liver oil . .	...	28·6	+45	...	...	Jean	Liver oils
,, ,, . .	...	11·2	+53	...	...	,,	
,, ,, . .	...	11·2	+38	+38	Pharmaceutical	,,	
,, ,, . .	...	11·0	+50	...	,,	,,	
,, ,, . .	...	...	...	+40 to +46	8 samples Temp. 22° C.	Pearmain	
Shark liver oil .	...	...	...	+29 to +35	3 samples Temp. 22° C.	,,	
Seal oil . . .	0·9168	4·6	+15	+15·5	Pale	Jean	Blubber oils
,, ,, . . .	0·9170	2·7	+ 8	+12·5	Brown	,,	
,, ,, . . .	...	...	+30 to +36	...	2 samples Temp. 22° C.	Pearmain	
Whale oil . .	...	...	+30·5	...	Northern oil	Jean	
,, ,, . .	...	...	+30·5	...	Southern oil	,,	
,, ,, . .	...	...	+42 to +48	...	2 samples	Pearmain	

[1] The purification had been effected by shaking the oils with alcohol to remove the free fatty acids.

Kind of Oil.	Specific Gravity.	Acidity.	Deviations of the Oil. Degrees + or −.		Remarks.	Observer.	Class of Oil.
			Commrl.	Purified.[1]			
Cameline oil . .	0·9240	...	+32	...	...	Jean	Semi-drying oils
Cotton seed oil .	0·9249	0·4	+20	...	Pale	,,	
,, ,, .	0·9250	0·3	+20	...	Yellow	,,	
,, ,, .	...	...	+12	...	Origin unknown	,,	
,, ,, (crude)	...	...	+16 to +17	...	3 samples Temp. 22° C.	Pearmain	
,, ,, (refined)	...	...	+17 to +23	...	6 samples Temp. 22° C.	,,	
Sesamé oil . .	0·9237	2	+18	...	...	Jean	
,, ,, . .	0·9210	4·1	+17·5	...	Bombay	,,	
,, ,, . .	...	...	+17	+17	Pale	,,	
,, ,, . .	...	...	+45	...	...	Bruyn & van Leent	
,, ,, . .	...	...	+13 to +17	...	5 samples Temp. +22° C.	Pearmain	
Beechnut oil . .	0·9206	...	+16·5	...	...	Jean	
,, ,, . .	0·9206	...	+18	...	...	,,	
Colza oil . .	...	...	+18	+18	...	,,	Rape oil group
,, ,, . .	0·9147	4·6	+17·5	...	...	,,	
,, ,, . .	0·9142	0·6	+16·5	...	French	,,	
,, ,, . .	0·9142	1·0	+18·5	...	French	,,	
,, ,, . .	0·9142	1·3	+16·0	+18·5	...	,,	
,, ,, . .	0·9142	1·0	+17·5	...	Cawnpore	,,	
,, ,, . .	0·9156	11·6	+17·5	+18	India	,,	
,, ,, . .	...	...	+15 to +16	...	...	,,	
Rape oil . . .	...	...	+16 to +20	...	8 samples Temp. 22° C.	Pearmain	
Ravison oil . .	...	...	+20 to +24	...	2 samples	,,	
Cabbage seed oil .	...	...	...	...	...		
Castor oil . .	...	6·3	+43	...	...	Jean	Castor oil group
,, ,, . .	...	1·4	+46	...	Commercial	,,	
,, ,, . .	...	2·0	+43·5	...	Pharmaceutical	,,	
,, ,, . .	...	...	+37	...	Javan	Bruyn & van Leent	
,, ,, . .	...	...	+40	...	Pharmaceutical	,,	
,, ,, . .	0·9637 to 0·9642	...	+41 to +42·5	...	Indian oils	Deering & Redwood	
,, ,, . .	...	...	+39 to +42	...	8 samples Temp. 22° C.	Pearmain	
Peach kernel oil .	...	...	+7·5 to +11·5	...	2 samples Temp. 22° C.	Pearmain	Non-drying oils
Almond oil . .	0·9177	...	+ 6	+ 6	...	Jean	
,, ,, . .	0·9180	...	+ 6	+ 6	Pharmaceutical	,,	
,, ,, . .	0·9198	3·3	+ 5	+ 6	,,	,,	
,, ,, . .	...	...	+ 7	...	...	Bruyn & van Leent	
,, ,, . .	...	...	+ 8 to +10·5	...	8 samples Temp. 22° C.	Pearmain	
Arachis oil . .	0·9167	...	+ 3·5	+ 3·5	Rufisque	Jean	
,, ,, . .	0·9154	...	+ 3·5	+ 4·5	...	,,	
,, ,, . .	0·9187	4·4	+ 4	+ 4·5	Gambia	,,	
,, ,, . .	0·9176	8	+ 5	+ 6·5	Boulam	,,	
,, ,, . .	0·9164	1·7	+ 3·5	+ 3·5	La Félicie	,,	
,, ,, . .	...	...	+ 4	...	...	Bruyn & van Leent	
,, ,, . .	...	...	+ 5 to +7	...	8 samples Temp. 22° C.	Pearmain	

[1] The purification had been effected by shaking the oils with alcohol to remove the free fatty acids.

Kind of Oil.	Specific Gravity.	Acidity.	Deviations of the Oil. Degrees + or −.		Remarks.	Observer.	Class of Oil.
			Commrl.	Purified.[1]			
Tea seed oil . .	...	...	+ 8·0	...	Temp. 22° C.	Pearmain	Non-drying oils
Olive oil . .	...	...	+ 0 to + 2	...	20 samples	Jean	
,, ,, . .	...	...	+ 9	...	very old	,,	
,, ,, . .	...	...	+ 0 to +1·5	...	...	Bruyn & van Leent	
,, ,, . .	...	...	+1·0 to +3·5	...	105 samples Temp. 22° C.	Pearmain	
Sperm oil . .	0·8780	5	−17·5	−17	...	Jean	Liquid waxes
,, ,, . .	0·883	3·3	−12·0	...	...	,,	
Arctic sperm oil (Bottlenose oil) .	...	...	+50	...	...	Pearmain	
Lard oil . .	...	...	+ 5·5	...	...	Jean	Terrestrial animal oils
,, ,, . .	...	...	− 0 to +1·0	...	6 samples Temp. 22° C.	Pearmain	
Sheep's foot oil .	0·9184	...	0	0	...	Jean	
Horse's foot oil .	...	...	−12	...	...	,,	
,, ,, .	0·9205	1	−13	...	...	,,	
,, ,, .	0·9202	...	−13	...	...	,,	
,, ,, .	0·9225	...	− 6	...	...	,,	
Neat's foot oil .	0·9163	...	− 4	...	...	,,	
,, ,, .	...	...	− 3·5	...	American	,,	
,, ,, .	...	...	− 3	...	French	,,	
,, ,, .	...	...	− 1 to −3·0	...	2 samples	Pearmain	
Tallow oil . .	0·9210	...	−15	...	...	Jean	
,, ,, . .	...	...	−1·0 to −5·0	...	2 samples Temp. 22° C.	Pearmain	
Resin oil . .	0·9732	...	+78	...	...	Jean	

[1] The purification had been effected by shaking the oils with alcohol to remove the free fatty acids.

The following table, collated by the writer, shows that gross adulterations may be detected by means of the oleo-refractometer :—

[TABLE

Kind of Oil.	Adulterated with	Deviation of the Oil.	Observer.	Class of Oil.
		Degrees + or −		
Linseed oil	20 % of resin oil . .	+67·0	Jean	Drying oils
,, ,,	20 % of hemp seed oil .	+47·0	,,	
Walnut oil	linseed oil . . .	+40·5	,,	
Whale oil	resin oil . . .	+60·0	Jean	Blubber oil
Almond oil	20 % of poppy seed oil .	+14·0	Jean	Non-drying oils
,, ,,	poppy seed oil . .	+16·0	,,	
,, ,,	cotton seed oil . .	+ 9·0	,,	
,, ,,	20 % of cotton seed oil .	+13·0	,,	
Olive oil .	10 % of poppy seed oil .	+ 6·5	,,	
,, ,, .	20 % ,, ,, ,, .	+10·0	,,	
,, ,, .	10 % of cotton seed oil .	+ 3·0	,,	
,, ,, .	20 % ,, ,, ,, .	+ 5·0	,,	

If a mixture of two oils be given, and the deviations of the individual oils be known, it is possible to calculate the proportions of the two oils in the mixture from the deviation observed in the oleo-refractometer, as *Jean* has shown. Let m be the quantity of the one oil having the deviation d, and n the quantity of the other having the deviation d', and let D be the deviation of the mixture, then we have the two equations—

$$n+m=100$$

$$\frac{m}{100}d+\frac{n}{100}d'=\mathrm{D}$$

from which n and m may be calculated.

The deviations obtained by means of *Zeiss's* refractometer will be given in chap. xi.

(c) *Polarimetric Examination*

From the remarks made on this subject in chap. v. p. 120, and the table given there, it will be evident that very little information of a discriminative nature can be gained from the polarimetric examination of the oils. Croton and castor oils only have distinct rotatory powers, these having shown, on examination in a saccharimeter, a rotation to the right of + 43° and + 40·7° respectively.

A strong deviation to the right may reveal the presence of resin oils, and for this reason the polarimetric examination is of great help in the examination of linseed oil (chap. xi. p. 343).

iv. Viscosimetric Examination

The viscosimetric examination of fatty oils does not lead to results of a discriminative nature; sperm oil, a liquid wax, alone is very characteristic in this respect (chap. xi. p. 646). The application in the examination of butter will be described (chap. xi. p. 630).

The following tables give the viscosities of sperm oil and a number of fatty oils, some of which are largely used for lubricating purposes :—

Kind of Oil.	Number of Seconds required at			Observer.
	15·5° C.	49° C.	82° C.	
Sperm oil . .	47	30·5	25·75	J. Veitch Wilson[1]
Olive oil . . .	92	37·75	28·25	,,
Lard oil . . .	96	38	28·5	,,
Rape oil . . .	108	41·25	30	,,
Neat's foot oil . .	112	40·25	29·25	,,
Tallow oil . .	143	37	25	,,
Engine tallow . .	Solid	41	26·5	,,

Kind of Oil.	Specific Gravity at 15·5° C.	Number of Seconds required at			Observer.
		15·5° C.	50° C.	100° C.	
Sperm oil . . .	0·881	80	47	38	Allen[2]
Seal oil (pale) . .	0·924	131	56	43	,,
Northern whale oil .	0·931	186	65	46	,,
Menhaden oil . .	0·932	172	40	...	,,
Sesamé oil . . .	0·921	168	65	50	,,
Arachis oil . . .	0·922	180	64	...	,,
Cotton seed oil (refined)	0·925	180	62	40	,,
Niger seed oil . .	0·927	176	59	43	,,
Olive oil . . .	0·916	187	62	43	,,
Rape oil . . .	0·915	261	80	45	,,
Castor oil . . .	0·965	2420	330	60	,,

Kind of Oil.	Specific Gravity at 17·5° C.	Viscosity (Engler) at				Observer.
		20° C.	50° C.	100° C.	150° C.	
Rape oil, crude .	0·920	9·03	4·0	1·78	1·34	Künkler[3]
Rape oil, refined .	0·911	11·88	4·9	2·05	1·40	,,
Olive oil . . .	0·914	10·3	3·78	1·80	...	,,
Castor oil . .	0·963	...	16·46	3·01	...	,,
Linseed oil . .	0·930	6·36	3·2	1·76	...	,,
Tallow . . .	0·951	...	5·19	2·50	1·73	,,
Neat's foot oil . .	0·916	11·63	4·44	1·92	...	,,

[1] Allen, *Com. Organ. Analys.* ii. 195 (1886). [2] *Ibid.*
[3] *Jour. Soc. Chem. Ind.* 1890, 198; *Dingl. Polyt. Jour.* 1889, 282.

Kind of Oil.	Number of Seconds required (Redwood) at									Observer.
	60° F.	70° F.	80° F.	90° F.	100° F.	120° F.	150° F.	200° F.	250° F.	
Rape oil, refined	540	405	326	360	213·5	147	95·5	58·5	43·25	Redwood
Sperm oil . .	177	136	113	90	80·5	60·5	49	42	34·75	,,
Neat's foot oil .	470	366	280	219·25	174·75	126	75·5	50·4	44	,,
Beef tallow .	..	..	..	..	..	..	..	54·75	40	,,
Water . .	25·5									,,

v. The Difference in the Solubility of Oils as a means of Identification

In some cases it is possible to differentiate oils by means of their solubilities in alcohol and acetic acid.

Fatty oils are nearly insoluble, or very sparingly soluble in alcohol, with the exception of *castor oil*, *croton oil*, and *olive kernel oil*. These three oils dissolve easily even in cold alcohol.

Oils containing a large proportion of glycerides of the lower fatty acids, such as cocoa nut oil, palm nut oil [butter fat], porpoise oil, are, comparatively, easily soluble in alcohol. The same property is possessed by oils consisting to a large extent of glycerides of linolic and linolenic acids, as *e.g.* linseed oil.

The following table, due to *Girard*, gives the solubilities of some oils in 1000 grms. of absolute alcohol at 15° C. :—

1000 *Grms. of Absolute Alcohol dissolve at* 15° C.

Kind of Oil.	Grms.
Rape oil	15
Colza oil	20
Mustard seed oil	27
Hazelnut oil	33
Olive oil	36
Almond oil	39
Sesamé oil	41
Apricot kernel oil	43
Walnut oil	44
Beechnut oil	44
Poppy seed oil	47
Hemp seed oil	53
Cotton seed oil	64
Arachis oil	66
Linseed oil	70
Cameline oil	78

Castor oil is sharply distinguished from all other oils by its comparative insolubility in petroleum ether and paraffin oil. (Compare p. 425.)

Valenta[1] classifies the fatty oils and solid fats (the latter are also considered here so as to avoid repetition) into three groups according to their solubility in acetic acid. The test is carried out by thoroughly mixing equal volumes of oil and glacial acetic acid of specific gravity 1·0562 in a test-tube, and warming the mixture if no solution has taken place.

1*st Class.*—Completely soluble at the ordinary temperature (14° to 20° C.) are: Olive kernel oil and castor oil.

2*nd Class.*—Completely soluble or nearly so at temperatures ranging from 23° C. up to the boiling point of glacial acetic acid: Palm oil, laurel oil, nutmeg butter, cocoa nut oil, palm nut oil, bassia oil, olive oil, cacao butter, sesamé oil, pumpkin seed oil, almond oil, cotton seed oil, arachis oil, apricot kernel oil, beef tallow, bone fat (American), beef stearine, and cod liver oil.

3*rd Class.*—Not completely dissolved—even at the boiling point of glacial acetic acid—are oils obtained from seeds of the *Cruciferæ:* Rape seed oil, mustard seed oil, hedge mustard oil.

The oils belonging to the second class may be further differentiated, by gradually warming the sample with an equal volume of glacial acetic acid in a test-tube with frequent shaking until complete solution is effected. A thermometer is then introduced into the liquid, and the temperature noted at which turbidity appears. According to *Valenta*, the fats of the second class may be subdivided into two groups: the one embracing the following fats—palm oil, laurel oil, nutmeg butter, cocoa nut oil, palm nut oil, and bassia oil; the remaining oils of that class forming the second group. The temperatures found by *Valenta* are given in the following table.

Allen's[2] observations, however, are not in agreement with those published by *Valenta*. *Hurst*,[3] who has also studied *Valenta's* test, finds the method unreliable—a conclusion in which *Ellwood*[4] and also *Thomson* and *Ballantyne*[4] concur.

In the following table the results of *Valenta's*, *Allen's*, and *Hurst's* experiments are placed side by side:—

[1] *Jour. Soc. Chem. Ind.* 1884, 643.
[2] *Ibid.* 1886, 69; 282.
[3] *Ibid.* 1887, 22.
[4] *Ibid.* 1891, 233.

[TABLE

Solubility of Fatty Oils and Solid Fats in Acetic Acid

Kind of Oil or Fat.	Temperature of Turbidity for equal Volumes of Fat and Glacial Acetic Acid, spec. grav. 1·0562.		
	Valenta.	Allen.	Hurst.
	°C.	°C.	°C.
Palm oil	23	83	
Laurel oil	26-27	40	
Nutmeg butter	27	39	
Cocoa nut oil	40	7·5	
Palm nut oil	48	32	
Bassia oil	64·5		
Yellow olive oil	111	...	28, 47, 62, 65, 71, 76
Green olive oil (of second expression)	85	...	
Cacao butter	105	Insoluble	
Sesamé oil	107	87	
Pumpkin seed oil	108		
Almond oil, sweet	110		
Cotton seed oil	110	90	53, 63
Niger seed oil	...	49	
Linseed oil	...	57-74	36, 36, 36, 41, 41
Arachis oil	112	87	72, 92
Apricot kernel oil	114		
Beef tallow	95		
Bone fat (American)	90-95		
Tallow stearine (M. P. 55·8°)	114		
Cod liver oil	101	79	65
Menhaden oil	...	64	
Shark liver oil	...	105	95
Porpoise oil	...	40	84, 74, 74
Whale oil	...	38, 86	48, 53, 65, 71
Seal oil	...	72	34
Lard	...	96·5	
Butter fat	...	61·5	
Oleomargarine	...	96·5	
Lard oil	...	...	69, 73, 76
Tallow oil	...	...	47
Neat's foot oil	...	102	65, 85
Arctic sperm oil	...	102	
Sperm oil	...	98-103	85

The following table, comprising oils belonging to *Valenta's* third class, more clearly demonstrates the same point :—

Kind of Oil.	Specific Gravity at 15·5° C. (water at 15·5 = 1).	Observer.		
		Valenta.	Allen.	Hurst.
Rape oil	0·9145	Insoluble	Insoluble	88
Rape oil	0·9168	,,	,,	86
Rape oil	0·9132	,,	,,	85
Rape oil	...	,,	,,	73
Colza oil	0·9162	,,	,,	99
Colza oil	0·9131	,,	,,	97
Colza oil	...	,,	,,	94
Colza oil	...	,,	,,	94
Colza oil	0·9132	,,	,,	82

Thomson and *Ballantyne*, experimenting with acetic acids of different strengths, arrived at the following numbers :—

Kind of Oil.	Free Acid calculated as Oleic Acid.	Temperature of Turbidity with Glacial Acetic Acid of		
		Sp. Gr. 1·0542.	Sp. Gr. 1·0552.	Sp. Gr. 1·0562.
	Per cent.	°C.	°C.	°C.
Olive oil (Gioja)	9·42	65	80	91
Same oil, freed from free acid	none	87	...	...
Olive oil (Syrian)	23·88	42	...	...
Olive oil	5·19	78	96	...
	3·86	85	100	111
Arachis oil (commercial)	6·20	76	92	112
Arachis oil (French, refined)	0·62	96	114	Not completely dissolved
Rape oil	2·43	110	Not completely dissolved	...
	4·54	105	...	...
Linseed oil	0·76	61	78	90
Linseed oil (Baltic)	3·74	42	59	71
Linseed oil (East India)	0·79	57	...	...
Linseed oil (River Plate)	1·21	56	...	...

The indications of the last table prove that the amount of free fatty acid in fats considerably influences the indications of *Valenta's* test, a fact which has also been brought out by *Hurst's* experiments.

Notwithstanding these serious discrepancies, *Valenta's* test may, in conjunction with other tests, afford some valuable hints in the examination of an oil.

According to *Bach*,[1] reliable results are obtained by examining the behaviour of the mixed *fatty acids* prepared from the oils under examination. The solvent recommended by *Bach* is identical with the alcohol-acetic acid mixture proposed by *David*. The solvent (prepared as described p. 197) is treated with 1 to 2 grms. of stearic acid, and the clear supernatant liquor only is used. One operates as follows :— Place 1 c.c. of the mixed fatty acids in a test-tube divided into $\frac{1}{10}$ cubic centimetres, add 15 c.c. of the alcohol-acetic acid mixture, agitate well, and allow to stand at a temperature of 15° C. The mixed acids from pure *olive oil* give a clear solution, whereas the mixed *cotton seed oil* fatty acids remain undissolved. However, on dissolving the latter, by gently warming the mixture and allowing to stand, a white gelatinous mass is obtained when the temperature falls to 15° C. The fatty acids from *sesamé* and *arachis oils* behave similarly. *Sunflower oil* acids dissolve in the mixture, but give on standing at 15° C. a granular precipitate. *Rape oil* acids do not dissolve at all, but float on the top as an oily layer. *Castor oil* acids behave like olive oil acids. Olive oil containing 25 per cent of cotton seed or sesamé oil deposits a granular

[1] *Pharm. Centralhalle*, 1883, 159.

precipitate. Smaller quantities of the admixed oils, however, cannot be detected. In the case of rape oil having been used as an adulterant the limit is 50 per cent.

The following modification of Valenta's test has been proposed by *Jean*:[1]—Place 3 c.c. of the fat in a graduated test-tube of 1 cm. diameter, and immerse the tube in water of 50° C. Remove, by means of a finely drawn-out pipette, so much oil that exactly 3 c.c. remain at the temperature of 50° C. Next introduce, by means of a graduated pipette, 3 c.c. of acetic acid, specific gravity 1·0565 at 15° C. (prepared from glacial acetic acid by adding the requisite amount of water), measuring off the acid at 22° C., warm the contents of the tube in the water for a few minutes, then cork well, and agitate thoroughly. Allow the mixture to settle out at 50° C. until two distinct layers are noticeable, and read off the volume of the undissolved acetic acid. The volume of the acid dissolved in the fat is then easily calculated. *Jean* has found the following proportions for the oils and fats given in the table :—

Kind of Oil or Fat.	Acetic Acid (sp. gr. 1·0565 at 15° C.) dissolved. Per cent.
Arachis oil (Boulam)	41·65
Arachis oil (Gambia)	43·66
Colza oil	30·00
Ravison oil	33·30
Almond oil, sweet	33·00
Olive oil	35·00
Walnut oil	36·60
Cameline oil	36·60
Castor oil	100·00
Maize oil	100·70
Beechnut oil	53·3
Poppy seed oil (Indies)	63·3
Poppy seed oil, French	43·3
Neat's foot oil	43·3
Sheep's foot oil	36·66
Horse fat	30·08
Lard	26·66
Veal tallow	26·66
Butter, 9 samples of different origin	63·33[2]
Cotton seed stearine	40·00
Butterine	31·60
Margarine	26·66
Palm oil	100·00
Cocoa nut oil	100·00

For further information the reader is referred to the article on "Butter Fat," chapter xi. p. 619.

The behaviour of some fats with carbolic acid has been studied by

[1] *Corps gras industriels*, 1892 [19], 4.

[2] Besides these nine samples, all of which gave 63·33 per cent, two abnormal butters were examined, giving 58·7 and 73·0 respectively.

Salzer,[1] after the same solvent had been utilised by *Crook* for the discrimination of butter fat (p. 618) from other animal fats. The test is carried out by adding the oil drop by drop to 10 c.c. of phenol (of the specified strength) contained in a graduated cylinder with constant shaking, until the turbidity no longer disappears. In liquefied phenol of more than 91 per cent most oils seem to be equally soluble, important differences appearing with the employment of weaker solutions. In the following table *Salzer's* results are reproduced :—

Kind of Oil.	Dissolved are by 10 c.c. of Phenol of		
	91 per cent.	87 per cent.	83 per cent.
	c.c.	c.c.	c.c.
Almond oil	...	Min. 2·5 Max. 3·5	
Olive oil	...	Min. 2·0 Max. 3·0	
Rape oil	4	...	
Linseed oil	...	...	3
Poppy seed oil	...	6·8	Min. 2
Croton oil	16	8·5	4·0
Arachis oil	11·5	4·3	0·8
Cotton seed oil	10·5	5·5	1·0
Sesamé oil	10	3·8	0·8
1 part of olive oil + 1 pt. of poppy seed oil	...	4·8	
3 parts of olive oil + 1 pt. of poppy seed oil	...	3·4	
3 parts of olive oil + 1 pt. of arachis oil	...	3·0	
1 part of olive oil + 1 pt. of arachis oil	...	3·8	
9 parts of olive oil + 1 part of rape oil	...	2·1	
Croton oil	...	Distinct turbidity with 2·3	

Salzer claims to be able to detect adulteration with mineral oil in almond oil, cod liver oil, etc. The figures recorded in the table are not of the kind to inspire great confidence in this method ; moreover, free fatty acids increase the solubility. *Salzer's* method can, therefore, at best only serve as a preliminary test.

vi. Other Physical Properties

Several other physical methods have been proposed for the examination of liquid fats, but hitherto they have been of little use for practical purposes, and need only be enumerated for the sake of completeness.

Tomlinson and also *Hallwachs*, state that every kind of oil furnishes characteristic figures when allowed to fall on the surface of water so as to spread out into a thin film. These figures—the so-called **cohesion figures**—are said to be sufficiently characteristic of each

[1] *Arch. d. Pharmac.* 227. 433.

particular oil to serve for identification or detection of adulterations. Without going any further into the subject, it may be said that definite results can only be obtained by a very long and exhaustive series of experiments, without, however, yielding as satisfactory results as other physical methods.

According to *Girard*, the method of examining the cohesion figures may be of some use for the detection of castor and croton oils, these two oils rendering the surface of the water strongly iridescent.[1]

Wynter Blyth has studied the figures or patterns which drops of various fats assume under certain conditions, and states that each fat appears to have its own distinctive pattern and can be identified by this pattern alone. But as every alteration of the experimental condition modifies more or less the pattern, it is evident that this "pattern test" must be considered as only of use in the hands of an observer with special experience in this branch of examination.

The **electrical conductivity** was made use of by *Rousseau* and afterwards by *Palmieri* in the examination of olive oil, but this method has not met with any extended application in the commercial analysis of oils.

Recently, however, the electrical conductivity has been proposed again by *Herlant* (chap. v. p. 121) for detecting adulteration in butter (see chap. xi. p. 630).

The following numbers have been obtained by *Herlant* for the oils enumerated in the table. A few values for butter and margarine are added here, as this chemist believes that the method will be useful in the examination of butter. The third and fourth columns are added in order to show that the conductivity stands in direct relation to the refractive index and critical temperature :—

Oil or Fat.	Specific Conductivity at 18° C.	Refractive Index. Degrees in Leiss's Butyro-refractometer at 35° C.	Critical Temperature of Dissolution. °C.
Cotton seed . .	0·008629	63	115-116
Arachis I. . .	0·008700	58·25	115-116
,, II. . .	0·008741	60·25	123
Sesamé . . .	0·008779	63	120·5
Olive	0·009927	57·25	123
Butter 1 . . .	0·006457	98-103	44·5
,, 2 . . .	0·006500		45
,, 3 . . .	0·006507		45
,, 4 . . .	0·007010		48
Margarine 1 . .	0·008221	122-123	52·5
,, 2 . .	0·008459		56·5
,, 3 . .	0·008472		54
,, 4 . .	0·008489		58

[1] The "pattern test" has recently been applied to butter fat and margarine (J. Hoffmann, *Chem. Zeit.* 1897, 572) without any useful result.

vii. Critical Temperature of Dissolution

There have not yet been collected sufficient data to allow definite conclusions to be drawn as to the value of this constant (cp. chap. v. p. 122) in the examination and discrimination of oils.

The observations obtained hitherto are collated in the following table :—

Critical Temperatures obtained with Alcohol, Specific Gravity 0·8195, *at* 15·5° *C.*

Substance.	No. of Samples.	°C.	Observer.
Japanese fish oil	...	108	Crismer and Motteu [1]
Cotton seed oil	...	115-116	Herlant [2]
Colza oil	...	132-135	Crismer and Motteu
Sesamé oil	...	120·5	Herlant
Arachis oil	1	115-116	,,
Arachis oil	2	123	,,
Olive oil	...	123	,,
Animal oil	...	120	Crismer and Motteu
Sheep's foot oil	...	102	,,
Neat's foot oil	...	95	,,
Lard oil	...	104	,,
Cocoa nut oil	...	71-75	Crismer [3]
Cacao butter	...	126	,,
Butter	14	98-102	Crismer
Butter	4	98-103	Herlant
Margarine	...	122-126	Crismer
Carnaüba wax	...	154	Crismer
Beeswax	from various sources	129-133	,,
Ozokerit	...	175	Crismer
Paraffin wax	according to constitution and melting points	140-160	,,
Oil of turpentine	...	14	,,

By using more dilute alcohol higher values are obtained for the critical temperatures, as will be seen from the following table, due to *Asbóth* [4] :—

[1] *Jour. Soc. Chem. Ind.* 1896, 300.
[2] *Ibid.* 1896, 562.
[3] Cp. chap. v. p. 123.
[4] *Chem. Zeit.* 1896, 685.

Critical Temperatures with Alcohol of 90 *per cent by volume, Specific Gravity* 0·8332

	No. of Samples.	Becomes perfectly clear at °C.	Commences to become cloudy at °C.	Commences to form 2 layers at °C.	Critical Temperature. °C.
Butter[1] . .	7	119-134	117·5-131	113·5-120	111·5-115
Fresh Butter	1	124	121	116	115
Margarine[2].	2	140-151	138-148	135-144·5	133·5-142

If absolute alcohol be employed, an open tube may be used. The results obtained for butter will be given in chap. xi. under "Butter."

B. Application of Chemical Methods in the Identification of Individual Oils and Recognition of their Purity

The fixed oils may be subdivided according to their chemical behaviour into the following four large classes:—

i. **Liquid Waxes.**—These oils, occurring solely in marine animals, contain but small quantities of glycerides, if any, and consist chiefly of compound ethers of fatty acids of monovalent alcohols. They yield, therefore, on saponification large quantities of "unsaponifiable matter." They absorb but little oxygen from the atmosphere, do not dry, and yield elaïdin.

ii. **Fish Oils, Liver Oils, and Blubber Oils.**[3]—These oils are liquid glycerides occurring in marine animals. They absorb large quantities of oxygen, without, however, drying into varnishes; they yield but little or no elaïdin.

iii. **Drying Oils.**—The drying oils consist for the most part of glycerides of linolic and linolenic acids. They absorb large quantities of oxygen, and also of iodine, and dry into varnishes on exposure to the air in a thin layer. The drying oils do not yield elaïdin.

iv. **Non-drying Oils.**—These oils, containing large proportions of olein, do not dry on exposure to the atmosphere, at any rate not at the ordinary temperature, absorb but little oxygen, assimilate less iodine than the drying oils, and yield elaïdin.

As an intermediate class between classes iii. and iv. there may be interposed the Semi-drying Oils (see p. 366).

i. Liquid Waxes

The liquid waxes—of which but two true representatives are yet known, viz. sperm oil and Arctic sperm oil—are readily distinguished

[1] Cp. more detailed results, chap. xi. p. 628. [2] Chap. xii. p. 679.

[3] These three groups of oils, as also the liquid waxes, are comprised in German under the term "Thrane," the English equivalent of which—"train oils"—only denotes blubber oils. To avoid confusion, the term "train" oil is not used in this work.

from all other fixed oils by their yielding a large proportion of unsaponifiable matter. Whereas most oils yield 95 per cent of fatty acids on saponification, the remainder forming glycerol, the liquid waxes contain but 60 to 65 per cent of fatty acids, the remaining 40 to 35 per cent consisting of monovalent aliphatic alcohols. The proportion of glycerides, and consequently of glycerol, in the liquid waxes is but very small (cp. chap. xi. p. 643).

Their physical properties also admit of their being readily distinguished from other oils, their specific gravities being very low, and their viscosity much less influenced by variation of temperature than is the case with other oils.

The following table gives a few constants of the two liquid waxes :—

Name of Oil.	Source.	Fatty Acids.	Monovalent Alcohols.	Sponific. Value.	Iodine Value.	Specific Gravity.	
		Per cent.	Per cent.			At 15°-16° C.	At 98°-99° C.
Sperm oil .	*Physeter macrocephalus* (Sperm whale, or cachelot)	61-58·5	39-41·5	123·4-147·4	84·3	0·875-0·884	0·822-0·830
Arctic sperm oil (or bottle-nose oil), doegling oil . . .	*Hyperoodon rostratus* (Bottle-nose or doegling whale)	60-65	40-35	123·0-134	80·4	0·876-0·881	0·823-0·828

Dolphin oil (from *Delphinus globiceps ;* spec. grav. 0·922 at 15°-16° C.) contains large quantities of waxes, but will be classed, on account of its proportion of glycerides, amongst blubber oils.

ii. Fish Oils, Liver Oils, and Blubber Oils

The fish, liver, and blubber oils are easily distinguishable from other liquid fats by their fishy smell and taste. According to some chemists they are further characterised by the intense colourations they give with caustic soda, sulphuric acid, nitric acid, and phosphoric acid.

The phosphoric acid test was proposed by *Schaedler* as the most characteristic, enabling one to detect even 0·1 per cent of these oils. The best results were stated to be obtained by warming five measures of the oil under examination with one volume of syrupy phosphoric acid, when all oils belonging to this class, both in their pure state or in admixture with other oils, were said to show intensely red, reddish-brown, or brownish-black colourations. *Holde*[1] states that the phosphoric acid test is uncertain, for on the one hand resin oils produce red colourations with this acid, and on the other hand distinct

[1] *Jour. Soc. Chem. Ind.* 1890, 419.

colourations only appear when large quantities of marine animal oils are present in other oils. The writer,[1] after extensive examination of these colour reactions, has come to the conclusion that they are not exclusively characteristic of these oils, but are due to impurities which can be removed by proper modes of refining. Thus, a sample of horses' foot oil (not refined), prepared in the laboratory, gave, with the above-mentioned reagents, reactions which might be considered as typical of marine animal oils. Also *old* samples of linseed and cotton seed oils behaved similarly.

The same conclusion holds good of the chlorine test, which is stated to blacken these oils, whereas vegetable oils are bleached by chlorine.

The liver oils contain notable proportions of *cholesterol*.

The nature of the fatty acids in these oils is very imperfectly known. Some of them have high *Reichert values*, pointing to the presence of large quantities of volatile acids. Most of these oils consist of glycerides of unsaturated fatty acids, as is shown by their high iodine values, ranging, as they do, from 120 upwards. The physetoleic acid of the earlier authors could not be detected by *Fahrion*[2] on examining various fish oils. He thinks, however, that he has proved the presence of an unsaturated acid $C_{18}H_{30}O_2$—jecoric acid—(cp. p. 62), and infers the presence of an unsaturated acid of the composition $C_{17}H_{32}O_2$—asellic acid—from the dihydroxyasellic acid obtained on oxidising the fatty acids of sardine oil.

An investigation of the fatty acids of the oils belonging to this class is still a desideratum, especially since *Heyerdahl* claims to have discovered two new unsaturated fatty acids in cod liver oil, viz. jecoleic acid (p. 59), and therapic acid (p. 63).

Owing to the large amount of unsaturated fatty acids they contain, they develop a considerable amount of heat when treated with sulphuric acid (*Maumené* test) or with bromine (see p. 301).

iii. iv. Drying and Non-drying Oils

Although the extremes of these two groups, as represented by linseed oil and, say, olive oil, are sharply defined in that the former easily "dries up" to a varnish on exposure to air, even at the ordinary temperature, whereas the latter remains comparatively unchanged under the same conditions, there exist so many gradations between these two extremes, that a sharp line of demarcation cannot be drawn. The gradual transition from the true drying oils to the decidedly non-drying oils admits of the interposition of an intermediate class of semi-drying oils (cp. chap. xi.), but as the process of drying into a varnish may occupy in some cases as much as several months, it is evident that a strict subdivision cannot be based on the more or less defined drying properties.

It should be noted that the distinction drawn here is based on the behaviour of the oils at the ordinary temperature, for according

[1] *Jour. Chem. Soc. Ind.* 1894, 617. [2] *Ibid.* 1893, 938; 935.

to *Livache* (cp. p. 288) all oils, even solid fats, are oxidised on exposure to air at higher temperatures.

Some preliminary tests, admitting of an approximate discrimination of the various oils belonging to these groups, are the **Elaïdin test**, the **Sulphur Chloride test**, the **Oxygen Absorption test**, and the **Thermal tests**. The most reliable methods, however, of distinguishing the oils are furnished by the quantitative reactions. A workable principle of classification appears to be the iodine-absorbing power of these oils, and this principle will be adopted in chap. xi.

1. Elaïdin Test

This test is based on the fact that olein is converted into the solid isomeric elaïdin by nitrous acid, whilst the glycerides of linolic, linolenic, and isolinolenic acids remain liquid under the same conditions. The non-drying oils yield therefore solid masses, whereas the semi-drying and the drying oils give more or less liquid products (cp. chap. i. p. 13, *Lidoff*).

This test was proposed first by *Poutet* in 1819 for the examination of adulterated olive oil; his original directions have been modified by many experimenters. *Poutet's* test, as practised in the Paris Municipal Laboratory, is carried out in the following manner:—10 grms. of the oil under examination, 5 grms. of nitric acid of spec. gravity 1·38 to 1·41, and 1 grm. of mercury, are placed in a test-tube, and the mercury dissolved by shaking continuously for three minutes. The mixture is then allowed to stand for twenty minutes, when it is shaken again for one minute. The behaviour of different oils after that time is recorded in the following table:—

Kind of Oil.	Consistency.
Olive oil	Solidified after 60 minutes.
Arachis oil	,, ,, 80 ,,
Sheep's foot oil	,, ,, 120 ,,
Sesamé oil	,, ,, 185 ,,
Colza Oil	,, ,, 185 ,,
("Saponified" oleine	Assumes the consistency of dough after 120 minutes.)
Linseed oil	Forms a red, dough-like scum.
Cod liver oil	Becomes doughy, red, and forms a scum.
Whale oil	Same appearance.
Hemp seed oil	Remains unchanged.

For mercury copper may be substituted. 10 c.c. of oil are placed together with 10 c.c. of 25 per cent nitric acid and 1 grm. of copper wire in a test-tube, and allowed to stand.

The various modifications proposed of the elaïdin test have been discussed by *Archbutt*,[1] who has made a thorough examination of them. His results point to the following conclusions:—

(1) That the test must be made at a temperature not lower than 25° C., and that the temperature must be uniform throughout the experiment.

[1] *Jour. Soc. Chem. Ind.* 1886, 304.

(2) That the length of time required for solidification is of far greater importance than the ultimate consistency of the elaïdin formed.

Archbutt prepares and applies *Poutet's* reagent in the following manner:—18 grms. of mercury are placed in a dry stoppered 50 c.c. cylinder, and 15·6 c.c. of nitric acid of 1·42 spec. gravity are added from a burette. The nitrous acid is entirely absorbed with production of a green colouration; as long as the reagent retains its green colour it is fit for use. 8 grms. of the reagent are shaken up with 96 grms. of the oil in a wide-mouthed stoppered bottle, placed in water of the required temperature, and again shaken at intervals of ten minutes during two hours.

When tested in this manner, the more important oils may be arranged according to *Allen*[1] in four groups:—

(*a*) *A solid, hard mass* is yielded by: Olive oil, almond oil, arachis oil, lard oil, sperm oil, and sometimes neat's foot oil.

(*b*) *A butter-like mass* is yielded by: Neat's foot oil, Arctic sperm oil, mustard seed oil, and sometimes by arachis, sperm, and rape oils.

(*c*) *A pasty or buttery mass, separating from a fluid portion*, is yielded by: Rape oil, sesamé oil, cotton seed oil, sunflower oil, Niger seed oil, cod liver oil, seal oil, whale oil, and porpoise oil.

(*d*) *Liquid products* are yielded by: Linseed oil, hemp seed oil, walnut oil, and other drying oils.

Archbutt has also experimented with a reagent prepared by passing dry sulphur dioxide into cold nitric acid of spec. gravity 1·42. By this reagent cotton seed oil and rape oil also are solidified; the product yielded by pure cotton seed oil is red, that given by rape oil deep red; but 10 per cent of either of these oils in olive oil does not sensibly colour the white elaïdin yielded by the latter oil.

The hardest elaïdins are obtained from olive oil, arachis oil, and lard oil. The elaïdin test has been specially applied to the examination of olive oil (cp. p. 461).

The elaïdin test cannot, however, be made to serve as a quantitative reaction. It has been shown by *Hübl* that the most serious errors may be committed, when an attempt is made to draw conclusions as to the composition of an oil from differences in the time required for the formation of elaïdin, and from observations of the consistency and colour of the solidified mass, since the mode of preparing the nitrous acid, the mode of mixing the acid and oil, the shape of the vessel, and chiefly the temperature, influence the results to a very considerable extent.[2] Nor should it be forgotten that the age of an oil and the manner in which it has been kept

[1] *Comm. Org. Analysis*, ii. 58.

[2] The same conclusions have been re-stated by Wellemann, *Jour. Soc. Chem. Ind.* 1891, 800.

(exposure to air and light) have an important bearing on the results of the elaïdin test. Thus *Gintl* has shown that an olive oil after exposure to sunlight for a fortnight did not yield any elaïdin at all.

In order to obtain trustworthy results, it will be found best to institute side by side with the oil under examination a test with standard oils of known purity under exactly the same conditions.

2. Sulphur Chloride Test

E. Bruce Warren states that *drying oils*, on treatment with sulphur chloride, S_2Cl_2, yield solid masses, insoluble in carbon bisulphide, whereas *non-drying oils* on the same treatment give soluble products. On this reaction he bases a mode of discriminating between drying and non-drying oils. He determines the amount of drying oils in mixtures of fatty oils in the following manner:—

The reagent employed is sulphur chloride, diluted with an equal volume of carbon bisulphide. The sulphur chloride is obtained from the commercial yellow sulphur chloride, or "chloride of sulphur," by fractional distillation, rejecting the portion boiling below 137° C. [The portions having a lower boiling point may be digested with a moderate excess of sulphur and fractionated again.] The sulphur chloride is mixed with an equal volume of carbon bisulphide, and the reagent is kept in bottles closed by corks coated with paraffin wax. The exact quantity required for a test is withdrawn by means of a pipette. To perform a test, 5 grms. of the oil under examination are mixed in a porcelain crucible of about 120 c.c. capacity with 2 c.c. of the reagent and 2 c.c. of carbon bisulphide, and warmed on the water-bath, with constant stirring, until reaction sets in. The mass soon becomes hard. The product must be broken up with a glass rod as completely as possible, in order to allow thorough expulsion of the volatile substances, and is dried until constant weight is obtained. The appearance of the product, both before and after drying—especially its colour and consistency—should be noted. The dried mass is then finely powdered and exhausted with carbon bisulphide, the solution evaporated to dryness, and the residue weighed. The quantity of the insoluble portion is found by difference. [It should be noted that every trace of moisture must be rigorously excluded.]

Thus *Warren* has obtained the following figures on examining poppy seed and linseed oils:—

5 grms. of	Solid insoluble Product.	Liquid soluble Product.
	Grms.	Grms.
Poppy seed oil gave .	6·46	1·96
Linseed oil ,, .	6·36	0·78

Warren's method is based on older observations made by *Rochleder*,[1] *Roussin*,[2] *Perra*,[3] and *Mercier*.[4] His results, however, do not agree with *Rochleder's* statement that olive oil, eminently a *non-drying* oil, yields an insoluble product, and are further contradicted by *Sommer*[5] and by *Henriques*.[6] The experiments carried out by the latter prove conclusively that there exists no relationship between the drying power of an oil and the proportion of sulphur chloride it requires to form a solid product.

Also work, undertaken by the writer (with a view to converting the sulphur chloride test into a quantitative reaction) proves the unreliableness of Warren's statements, as is shown in the following table :—

Oils and Fats treated with S_2Cl_2 ; *5 grms. of fat with 2 c.c.* S_2Cl_2, *and 2 c.c.* CS_2 (*Lewkowitsch*)

A. *Product completely soluble in Carbon Bisulphide*

Class of Oil.	Kind of Oil.	Mass thickens after Minutes.
Liquid waxes	Sperm oil, No. 1	20
	Sperm oil, No. 2	45
	Arctic sperm oil, No. 1	45
	Arctic sperm oil, No. 2	55
	Arctic sperm oil, No. 3	30
Vegetable fats	Palm oil	Does not thicken.
	Palm nut oil	
	Cocoa nut oil	
	Mowrah seed oil	
Animal fats	Beef tallow	
	Mutton tallow	
	Lard	
	Butter fat	

[1] *Dingl. Polyt. Jour.* 111. 159.
[2] *Ibid.* 151. 136.
[3] *Ibid.* 151. 138.
[4] *Compt. rend.* 84. 916.
[5] German Patent, No. 50,282.
[6] *Jour. Soc. Chem. Ind.* 1894, 47.

B. *Products not completely soluble in Carbon Bisulphide*

Class of Oil.	Kind of Oil.	Solidifies after Minutes.		Soluble in CS_2.
		In the Cold.	On the Water-bath.	
				Per cent.
Drying oils	Linseed oil	10	2	14·4
	Hemp seed oil	11	...	9·2
	Poppy seed oil	21	...	10·6
Fish oils	Japan fish oil	9	...	12·4
Liver oils	Cod liver, pure	15	...	4·4
	Cod liver, rancid	1½	...	6·4
Blubber oils	Seal oil	11	...	4·4
	Whale oil	13	...	3·0
Semi-drying oils	Cotton seed oil	20	4	24·0
	Sesamé oil	21	...	18·4
	Colza oil	23	...	2·8
	Rape oil	12	2	4·2
	Croton oil	18	...	25·4
	Castor oil	½	at once	3·8
Non-drying oils	Peach oil	26	...	4·8
	Almond oil, sweet	27	...	4·0
	Almond oil, bitter	28	...	3·4
	Arachis oil	30	...	6·0
	Olive oil	22	4	4·2
	Sheep's foot oil	36	...	6·0
	Horses' foot oil	20	...	13·6
	Neat's foot oil	23	...	9·4
	Lard oil	10	...	15·0
	Tallow oil	12	...	29·8

I have further found a remarkable difference in the action of sulphur chloride on vegetable oils on the one hand, and on their mixed fatty acids on the other. Whereas in the case of the former the reaction takes place quickly with the formation of a solid product, the free acids react more slowly, yielding but semi-solid, viscous products.

The reaction that takes place, when sulphur chloride is allowed to act on oils, appears to consist in an absorption of the elements of sulphur chloride, much as iodine is absorbed in *Hübl's* test. In fact, *Henriques* has shown that oils after treatment with sulphur chloride have a far lower iodine absorption value than before. *Ulzer* and *Horn*, and afterwards also *Henriques*, have proved that the products of reaction contain sulphur and chlorine in approximately the same proportion as sulphur chloride (S_2Cl_2). Thus, the action of sulphur chloride on oils appears to consist in the conversion of unsaturated fatty acids or their glycerides into saturated compounds. Further research will be required to show whether a separation of saturated from unsaturated glycerides can be effected by means of this reagent. In this connection the difference is remarkable between lard and tallow on the one hand and their oleines on the other.

Much light has been further thrown on the rationale of the

chemical reaction involved by researches of *C. O. Weber*.[1] Further information on that subject will be given under "Rubber Substitutes" (p. 742).

For the thermal reaction with sulphur chloride cp. p. 299.

3. Oxygen Absorption Test. Livache Test

The drying of an oil not being complete before the lapse of several months, a convenient method of distinguishing drying and semi-drying oils from non-drying oils cannot be based on the determination of the increase in weight which oils attain on being exposed to the atmosphere in thin layers.

Casselmann has therefore proposed to shorten the period of exposure by heating 3 to 4 grms. of an oil for three hours daily up to 150° C. His results are tabulated below :—

Kind of Oil.	Behaviour on heating to 150° C. for Three Hours daily.
Linseed oil	Dried up after 1½ to 2 days.
Poppy seed oil	,, ,, ,, 4 to 5 days.
Hemp seed oil	,, ,, ,, a few more days.
Sunflower oil	Gives a viscid, gelatinous mass after three months.

It is evident that no reliable results can be obtained by proceeding in this manner.

The following table, due to *Kissling*,[2] shows the gain in weight of several oils, 10 grms. of each, spread out so as to cover a surface of 35 sq. cm., having been exposed to the air for ten days at the ordinary temperature.

Kind of Oil.	Gain in Weight of 100 parts in Ten Days at ordinary Temperature.
Olive oil	0·0
Rape oil, crude	0·05
Rape oil, refined	0·0
Neat's foot oil, refined	0·065
Cotton seed oil	0·545
Linseed oil, crude	1·130
Linseed oil, boiled	3·400
Triolein	0·0

Experiments carried out by the same author at temperatures from 100° to 105° C. show a different result[3] :—

[1] *Jour. Chem. Soc. Ind.* 1894, 11. [2] *Ibid.* 1891, 778.

[3] On passing air through linseed oil at 100° C. for 6 days *Kissling* (*Jour. Soc. Chem. Ind.* 1895, 479) found that 0·87 per cent of oxygen was taken up daily, 0·41 per cent of which remained in the oil, whilst 0·46 were carried away as volatile gases consisting of 15 per cent CO_2 and 85 per cent of volatile acids of the methane series and other organic substances.

Kind of Oil.	Gain (+) or Loss (−) in Weight of 100 parts after exposure to Air for			
	2 Hours.	22 Hours.	42 Hours.	Remarks.
Crude Rape oil, fresh . . .	+0·12	+1·08	...	Moderate skin
Crude Rape oil, old	−0·14	+0·55	...	Moderate skin
Crude Rape oil, very old . . .	−0·02	+0·42	...	Moderate skin
Refined Rape oil	−0·13	+0·57	...	Moderate skin
Refined Rape oil, old . . .	−0·10	+0·51	...	Moderate skin
Olive oil	−0·15	−0·77	...	Slight skin
Crude Neat's foot oil, German . .	−0·67	−1·40	...	No skin
Crude Neat's foot oil, partially refined	−0·23	+0·06	...	Moderate skin
Crude Neat's foot oil, refined American	−0·08	−0·40	−0·27	Moderate skin
Crude Lard oil, American . . .	−0·21	−1·44	...	No skin
Refined Lard oil, American . .	−0·08	−0·56	...	Moderate skin
Cotton seed oil, old	−0·52	−0·43	−0·96	Strong skin
Crude Linseed oil	...	+0·19	...	Strong skin
Boiled Linseed oil	+0·26	+0·97	...	Strong skin
Triolein	−0·53	−3·34	...	No skin

It will be observed from these data, that the better drying an oil is, the more oxygen it absorbs, and consequently the greater the gain in weight after a certain time.

The rate of absorption of oxygen is very much accelerated, according to *Livache*,[1] by addition of finely divided lead. Thus, linseed oil reaches, in consequence of this treatment, the maximum of absorption within a few days, whereas under ordinary conditions the same result is only arrived at after several months. The lead-powder is prepared by precipitating a lead salt with zinc, washing the precipitate rapidly in succession with water, alcohol, and ether, and finally drying in a vacuum.

In actual testing one operates as follows :—Spread about 1 grm. of the lead, weighed off accurately, on a somewhat large watch-glass in a thin layer, and then allow to fall on to it from a pipette 0·6 to 0·7 grms. (not more) of the oil to be tested, placing each drop on a different portion of the lead, and taking care that the drops do not run into one another. Then allow the watch-glass to stand at the ordinary temperature at a place exposed to light.

Drying oils will be found to have absorbed the maximum quantity of oxygen after eighteen hours, or in some cases after three days, whereas non-drying oils do not gain any weight before four or five days.

The free fatty acids, with the notable exception of cotton seed oil fatty acids, behave like their glycerides, *i.e.* their increase in weight corresponds to the gain in weight of the corresponding neutral oils. *Livache's* results are recorded in the subjoined table :—

[1] *Jour. Soc. Chem. Ind.* 1886, 494.

Kind of Oil.	Gain in Weight of 100 parts		
	Of Oil after		Of Fatty Acids after
	2 Days.	7 Days.	8 Days.
Linseed oil . . .	14·3	...	11·0
Walnut oil . . .	7·9	...	6·0
Poppy seed oil . .	6·8	...	3·7
Cotton seed oil . .	5·9	...	0·8
Beechnut oil . .	4·3	...	2·6
Colza oil . . .	0·0	2·9	2·6
Rape oil . . .	0·0	2·9	0·9
Sesamé oil . . .	0·0	2·4	2·0
Arachis oil . . .	0·0	1·8	1·3
Olive oil . . .	0·0	1·7	0·7

In order to obtain a correct estimation as to the drying properties of an oil, regard must be had not only to the increment in weight, but also to the length of time required. Thus, of the two oils, the drying powers of which are given in the following table :—

No. of Oil.	Weight of Oil.	Weight of Lead.	Gain in Weight of 100 parts after			
			1 Day.	3 Days.	6 Days.	9 Days.
1	3·246	1·012	14·4	15·7	unchanged	...
2	3·154	0·653	2·45	12·0	15·9	unchanged

the oil No. 1 must be considered the better drying, although both oils [evidently both linseed oils] finally reach the same absorption of oxygen.

Jean has used *Livache's* method for the examination of the following oils, allowing them to stand for three days in a dry atmosphere (under a desiccator over sulphuric acid); there are added *Tortelli's*[1] numbers, obtained by the same method :—

Kind of Oil.	Gain in Weight of 100 parts	
	after 3 Days (Jean).	until weight remained constant (Tortelli).
Whale oil	8·266	7·62
Japan fish oil . . .	8·194	
Cod liver oil . . .	6·383	5·43
Menhaden oil . . .	5·454	
Sperm oil	1·629	
Sardine oil	...	4·22
Neat's foot oil . . .	...	1·19

[1] *Annali del Lab. Chim. Centr. delle Gabelle*, iii. 1897, 211.

Long before *Livache*, the amount of oxygen absorbed by oils was used by *van Kerkhoff* in the examination of rape oil. His method, which can only claim historical interest, was to run the oil from a burette into a known volume of a permanganate solution [1] until it was decolourised. Thus he has found that—

15 *c.c. of permanganate solution were reduced by*

3·21 c.c. of rape oil.
1·01 „ cameline oil.
1·00 „ linseed oil.

Fox has modified *Livache's* process by heating 1 grm. of the oil to be tested with 0·5 grm. of precipitated lead to 105° C. (220° F.) in a sealed tube, and measuring the quantity of oxygen absorbed. His results are tabulated below :—

Kind of Oil.	c.c. of Oxygen absorbed.
Linseed oil (Baltic)	191
Linseed oils from other sources	126-186
Cotton seed oil	24·6
Rape oil	20
Olive oil	8·2-8·7

O. Bach has adopted Fox's method for the examination of lubricating oils (see p. 714).

As will be seen from Fox's table, even olive oil, the type of a non-drying oil, absorbs oxygen at an elevated temperature. *Livache* [2] has shown recently that rape oil and olive oil behave like drying oils when they are kept at a sufficiently high temperature (120°-160° C. with or without previous treatment with litharge or manganese borate), and become finally transformed into a solid substance, viz. *Mulder's* "linoxyn" (see p. 337). Further experiments of *Livache* demonstrate that all fatty substances without exception, whether of vegetable or animal origin, even solid animal fats, can be converted into "linoxyn," the rapidity of the change depending on the temperature used and the previous treatment to which the fatty substance has been subjected. It will therefore be evident that the subdivision of oils into drying, semi-drying, and non-drying oils (see p. 277) is only admissible on the understanding that this distinction holds good for the ordinary temperature.

Fahrion [3] has recently proposed to determine the oxygen absorption of oils by impregnating a strip of chamois leather with the oil under examination, and exposing it, suspended from a brass hook, to the atmosphere. Side by side with it is suspended a similar strip of leather, serving as a blank test, so as to eliminate the influence of evaporation of moisture from the leather, etc.

Fahrion's results are tabulated below ; the absorption of oxygen has been calculated to per cents of oil used :—

[1] This method has been proposed again by *Crauzel* (*Jour. Soc. Chem. Ind.* 1895, 316) for detection of fatty oils in vaseline.

[2] *Jour. Soc. Chem. Ind.* 1895, 811.

[3] *Ibid.* 1894, 405.

	Iodine Value.	Absorption of Oxygen in 100 parts of Oil after													Maximum.	Absorption according to Livache.	Calculated from the Iodine Value. I×0·063.
		1 Day.	2 Days.	3 Days.	4 Days.	5 Days.	6 Days.	7 Days	8 Days.	9 Days.	10 Days.	14 Days.	21 Days.	28 Days.	56 Days.		
Blank test .	..	0·0	1·0	1·3	0·9	1·4	−0·6	1·3	0·0	0·5	1·8	−0·5	1·1	3·3	−2·5	..	..
Olive oil .	82·1	0·2	1·0	1·2	0·9	1·4	−0·4	1·1	−0·1	0·5	1·7	−0·5	0·7	3·5	−2·5	0·2	5·2
Sesamé oil .	110·2	0·1	1·2	0·9	0·5	1·1	−0·5	1·0	0·0	0·7	2·0	1·1	4·7	6·6	−0·5	3·6	7·0
Rape oil .	102·4	0·1	1·1	1·3	1·0	1·8	0·5	2·5	2·0	2·8	4·6	2·3	3·2	6·3	−0·2	2·8	6·5
Cotton seed oil	109·2	−0·1	0·8	1·4	1·2	3·1	2·2	5·0	4·7	5·7	7·4	2·5	1·6	5·2	−1·4	5·6	6·9
Poppy seed oil	135·9	0·3	2·0	3·2	4·3	7·1	7·3	9·7	7·0	7·3	8·0	3·3	2·7	6·7	−0·3	8·4	8·6
Walnut oil .	149·2	−0·2	2·0	4·4	7·1	9·7	8·4	9·6	7·2	7·3	8·3	4·0	4·2	8·4	−1·3	9·0	9·4
Linseed oil .	175·8	0·1	1·5	2·0	3·8	12·3	11·8	13·2	10·4	11·3	11·8	7·9	8·2	12·6	4·5	12·4	11·1
Cod liver oil .	171·0	−0·6	1·1	8·1	10·0	10·9	8·0	10·4	8·0	8·5	10·1	6·8	6·3	11·8	4·3	9·5	10·8

In order to obtain more rapid oxidation *Bishop*[1] spreads the oil on precipitated silica, and adds a little manganese resinate obtained from the commercial product by extraction with petroleum ether or common ether. *Bishop* proceeds as follows: 5 to 10 grms. of the oil are placed in a dish and mixed on the water-bath with exactly 2 per cent of manganese resinate, until the latter is completely dissolved. Meanwhile 1 grm. of calcined precipitated silica is weighed out into a flat-bottomed dish, and 1·02 grm. of the resinated oil, drop by drop, by means of a pipette, is added. The mass is intimately mixed by means of a glass rod, carefully spread over the bottom of the dish so as to offer a large surface to the air, and then left at a temperature of 17°-25° C. for drying oils, and at 20°-30° C. for other oils. The dish is weighed after six hours, and twice again in the twenty-four hours, a fresh surface being exposed after each weighing by stirring the mass. The maximum increase in weight, calculated to per cents, is termed by *Bishop* the *degree of oxidation.*

The following table contains the results obtained by *Bishop*:—

Oils.	Specific Gravity.	Absorption of Oxygen in Per Cent "Degrees of Oxidation."	Mean Values.
Linseed oil, French	0·9327	17·70-16·40	17·05
,, ,, La Plata	0·9304	15·45-15·00	15·20
Hemp seed oil	0·9287	14·55-14·30	14·40
Poppy seed oil, French	0·924	14·50-13·90	14·20
Walnut oil, French	0·924	13·70	13·70
Cotton seed oil	0·924	8·60	8·60
,, ,, without stearine	0·923	9·60-9·30	9·45
Sesamé oil, Senegal	0·9215	8·95-8·50	8·70
,, ,, Indian	0·921	7·40	7·40
Arachis oil, African	0·916	6·70	6·70
,, ,, white	0·916	6·50	6·50
Colza oil, French	0·9142	6·40 (?)	6·40 (?)
,, ,, Indian	0·9137	5·90-5·80 (?)	5·85 (?)
Olive oil	0·9155	5·30 (?)	5·30 (?)

The chemical changes occurring during the drying of oils are but very imperfectly understood, and further experiments are required to elucidate this important question (cp. "Boiled Oil," p. 738). The drying properties of an oil seem to stand in direct ratio to the proportion of glycerides of linolic and linolenic acids in the oil. Therefore, in a general way, the rule holds good that the higher the iodine value the better drying is an oil (Japanese wood oil seems to form an exception, p. 345). It should, however, be borne in mind that oleic acid, although an unsaturated acid, possesses no drying properties. Therefore a direct proportionality between the quantities of oxygen and of iodine, which drying oils assimilate, cannot be established, inasmuch as two atoms of iodine absorbed should correspond to one atom of oxygen. Still, a certain proportionality does exist, as will be seen from the following table, in which the percentage of

[1] *Jour. Pharm. et Chimie*, 1896, 55; *Jour. Soc. Chem. Ind.* 1896, 475.

oxygen actually absorbed is compared with the quantity of oxygen calculated from the iodine absorption value by multiplying the latter by $\frac{16}{254} = 0{\cdot}063$.

Kind of Oil.	Oxygen absorbed.	
	Determined by Analysis.	Calculated from Iodine Value.
Linseed oil . . .	14·3	11·0
Walnut oil . . .	7·9	9·0
Poppy seed oil . .	6·8	8·6
Cotton seed oil . .	5·9	6·7

Hübl obtained values in better agreement with the iodine numbers by using finely-divided copper instead of lead.

If a correct method of determining accurately the oxygen absorbed were known, it would be possible to class the determination of the drying power, or, as it might be called, of the "oxygen value," amongst the quantitative reactions.

The absorption of oxygen from the atmosphere is of great practical importance for the industry of paint oils, and has a very important bearing on the liability of oils to cause spontaneous combustion when spread in a finely-divided state on fibrous organic substances (cp. chap. xii. p. 706).

4. Thermal Tests

(*a*) *Thermal Reaction with Sulphuric Acid: Maumené Test*

Maumené[1] has found that, on mixing concentrated sulphuric acid with drying oils, a higher temperature is produced than is the case with non-drying oils, and he proposed therefore the sulphuric acid test as a useful reaction in the examination of fats.

Fehling, *Casselmann*, *Allen*, *Archbutt*, and others have confirmed *Maumené's* observation, and proved that comparable results are obtained if the experiments are carried out under exactly the same conditions. It is therefore necessary to *always* use sulphuric acid of precisely the same strength (the acid must be kept carefully protected from access of air), to cool the oil and the reagent to exactly the same temperature before commencing the operation, and even to use the same vessel for each determination.[2] (*Archbutt*, however, thinks that it is unnecessary to work at some constant initial temperature.)

Maumené[3] has found that sulphuric acid heated to 320° C., and used immediately after cooling, gave a different temperature reaction to that given by acid that had not been so treated. This is due to partial dissociation of the sulphuric acid having taken place. Since, according to *Lunge* and *Naef*, sulphuric acid of 99 per cent and 96

[1] *Compt. rend.* 35. (1882), 572. [2] *Jour. Soc. Chem. Ind.* 1891, 234.
[3] *Compt. rend.* 92. 721.

per cent of SO_4H_2 possess the same specific gravity, it is best to ascertain the strength of the sulphuric acid by titration (*Archbutt* [1]).

The influence of the concentration of the acid on the result is shown in the following table due to *Archbutt* (cp. also below, *Thomson* and *Ballantyne's* table) :—

Kind of Oil.	Rise of Temperature observed with Acid containing per cent of SO_4H_2.						
	97·38.	96·71.	95·72.	94·72.	93·75.	92·73.	91·85.
	°C.	°C.	°C.	°C.	°C.	°C.	°C.
Olive oil, genuine .	43·25 42·25	42	39	36·5	34·5	31	28 29·25
Rape oil, genuine .	63, 62	61	58	54	50·25	47	40·5, 43
Olive oil, impure .	48·5 48·5	47, 47·5	43·75 44·25	40·75 40·25	38·5, 39	35·5 35·5	32·5 32·5

It should also be noted that on using weak acid the rise of temperature is very slow.

Archbutt recommends the following method of operating: 50 grms. of the oil to be tested (weighed accurately to within 10 to 20 milligrms.) are placed in a beaker of 200 c.c. capacity. The bottle of acid and the beaker of oil are then placed in a large vessel of water until both liquids have acquired the same temperature, which should be about 20° C. The beaker containing the oil is then removed, wiped outside, and placed in a "nest" of cardboard, having hollow sides stuffed with cotton wool, or in a larger beaker lined with cotton wadding. A thermometer is then immersed in the oil, and the temperature having been read off, 10 c.c. of the concentrated sulphuric acid are rapidly withdrawn from the bottle with a pipette and run into the oil, the time allowed for the emptying of the pipette occupying one minute. During this time the oil should be stirred with the thermometer, and the stirring continued until no further rise of temperature is observed. The highest point is easily noticed, as the temperature remains constant for some little time before it begins to fall.

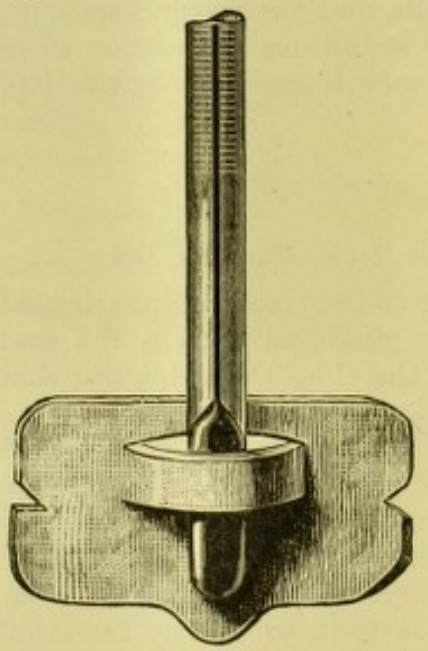


Fig. 42.

In order to secure a more perfect admixture of oil and acid, *Allen* fastens the thermometer to a tin plate, bent into the shape of a screw-paddle. This piece of apparatus, shown in Fig. 42, forms an efficient stirrer, producing a complete intermixture of the two liquids.

[1] *Jour. Soc. Chem. Ind.* 1886, 304.

The following table, compiled by *Allen*,[1] from the observations of various chemists, gives the rise of temperature by *Maumené's* test for various oils. The writer has re-arranged the table according to the iodine values, and has added the last column in order to show the correlation of the thermal reaction and the iodine absorbing power of the oils. Further numbers will be found in chap. xi., where the individual oils will be described.

Kind of Oil.	Rise of Temperature with Sulphuric Acid. °C.						Class of Oils.
	Maumené.	Baynes.	Dobb.	Archbutt.	Allen.	Wiley.	
Linseed oil .	103	104-124	...	...	104-111	...	Drying oils
Hemp seed oil	98	...	...	...	...	...	
Walnut oil .	101	...	...	...	...	...	
Poppy seed oil	74	...	...	86-88	...	...	
Niger seed oil	...	82	...	...	81	...	
African fish oil	...	...	156	...	...	...	Liver, fish, and blubber oils
Menhaden oil	...	...	...	123-128	126	...	
Cod liver oil .	102-103	116	...	...	113	...	
Shark liver oil	...	...	...	...	90	...	
Seal oil .	...	...	...	...	92	...	
Whale oil, northern	...	...	...	...	91	...	
Whale oil, southern	...	...	85-86	92	...	...	
Porpoise oil .	...	...	...	...	50	...	
Cotton seed oil, crude	...	84	61	70	67-69	79	Semi-drying and non-drying oils
Cotton seed oil, refined	...	77	...	75-76	74-75	...	
Sesamé oil .	68	...	...	65	...	...	
Beechnut oil	65	...	...	...	...	...	
Rape and Colza oils	57-58	60-92	54-60	55-64	51-60	...	
Castor oil .	47	...	...	46	...	...	
Almond oil .	52-54	35	...	...	...	...	
Olive oil .	42	40	39-43	41-45	41-43	...	
Arachis oil .	67	...	...	47-60	...	69	
Cocoa nut oleine	...	..	...	...	26-27	...	
Neat's foot oil	...	...	...	43	...	...	Terrestrial animal oils
Horses' foot oil	51	...	...	...	...	...	
Lard oil .	...	...	...	...	41	54	
Tallow oil .	41-44	...	...	...	...	...	
Sperm oil .	...	...	...	51	45-47	...	Liquid waxes
Arctic sperm oil	...	...	...	42	41-47	...	
Oleic acid .	...	...	...	37·5	38·5		

[1] *Comm. Org. Analysis*, ii. 56 ; Thorpe, *Dictionary of Applied Chemistry*, iii. 36.

There is undoubtedly a correlation between the rise of temperature in *Maumené's* test and the iodine value of an oil; the higher the temperature rises the higher is the iodine number (cp. chap. xi. under "Olive Oil," p. 461). However, this correlation cannot be expressed by a constant factor, for *Hehner* and *Mitchell*[1] derived from

	Iodine number / Maumené test.
9 observations, made by one and the same observer, on lards, the factor	1·748
10 observations on olive oils, the factor	2·1837
203 observations on olive oils, the factor	2·314

Even on applying the last-named factor to other oils examined by the same observers, discordant results were obtained.

Oils causing a very high rise of temperature should be diluted, according to *Maumené*, with a measured quantity of olive oil. *Bishop*[2] recommends mineral oil for the same purpose. The rise of temperature, which the original oil would show, is then calculated from the observed rise of temperature in the following way, which, however, is not quite correct. Let 67° C. be the rise of temperature obtained with 10 grms. of cod liver oil, 10 grms. of mineral oil, and 20 grms. of sulphuric acid; if the rise of temperature of the mineral oil alone be 14° C., then the figure for cod liver oil would be $2(67 - 14) = 106°$ C. (*Bishop*).

Bishop obtained in this way the following results:—

Kind of Oil.	Rise of Temperature calculated. °C.
Cod liver oil, white	100
Cod liver oil, pale	102
Cod liver oil, brown	102·5
Arachis oil	66
Mixture consisting of 80 parts of cod liver oil, pale, and of 20 parts of arachis oil . .	97
Mineral oil	14

Ellis[3] has also recommended mineral oil as a diluent. Having found that no concordant results were obtained when the maximum temperature was much over 60° C. (which seems to indicate that above that temperature further reactions set in between sulphuric acid and the oil), *Ellis* considers it necessary to dilute each oil, if required, with mineral oil in such proportions that the highest temperature attained may be below 60° C. For his mode of calculation and his results the original paper must be consulted.

Jean[4] determines the heat evolved in *Maumené's* test by means of a special form of apparatus, styled by him "Thermelæometer." This

[1] *Analyst*, 1895, 147.
[2] *Jour. Phar. Chem.* 20. 302.
[3] *Jour. Soc. Chem. Ind.* 1886, 150; 361.
[4] *Ibid.* 1890, 113.

apparatus (Fig. 43) consists of a small vessel, A, 4 cm. wide and 6 cm. high, graduated for the reception of 15 c.c. of oil, and of the acid holder B. The latter is fitted with a hollow glass-stopper C, to which is attached the india-rubber tube R. The neck of the acid holder is fastened to a clamp, to which a thermometer is fixed.[1]

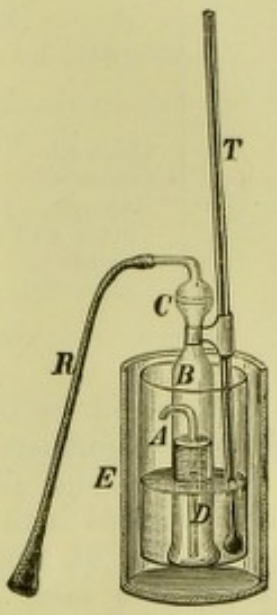


Fig. 43.

The mode of operation is as follows: 15 c.c. of oil, previously warmed to about 40° to 50° C., are placed in A, and 5 c.c. of concentrated sulphuric acid of specific gravity 1·819 are introduced into B. Vessel B is then placed in A, and the apparatus allowed to cool to 30° C., the thermometer being used to stir the oil occasionally. To prevent further cooling, A is placed in the felt-lined brass case E. The acid is then forced out of B through the small syphon tube into A by blowing through R, and the mixture of oil and acid is well stirred until the maximum temperature is reached. Drying oils should be mixed with 5 c.c. of mineral oil.

If the oils are much oxidised they must be treated with alcohol before testing; a better plan still is to prepare the fatty acids and test the latter. *Jean* has obtained the following results with his "thermelæometer":—

Kind of Oil.	Rise of Temperature of the	
	Neutral Oil. °C.	Fatty Acids. °C.
Olive oil	41·5	45
Linseed oil . . .	61	109
Colza oil, French . .	37	44
Colza oil, India . . .	37	46

The numbers obtained by *Jean* are, of course, not directly comparable with those given in the table, p. 293.

Exposure to light and air with its concomitant oxidation increases the temperature reaction with sulphuric acid. Thus *Archbutt* records for a sample of olive oil, which, kept in the dark, gave a Maumené test of 41·5° C., after exposure, the higher figure 52·5° C.

This fact is brought out more prominently by *Ballantyne's* results:—

[1] Another apparatus, offering no special feature, has been used by *Wiley* (cp. Wiley, *Lard and Lard Adulterations*, Washington, 1889).

Kind of Oil.	Rise of Temperature.	
	Original Oil. °C.	After Exposure. °C.
Olive oil	44	67
Castor oil	73	78·5
Rape oil	61·5	72·5
Cotton seed oil . . .	75·5	100
Arachis oil	73·5	90
Linseed oil	113·5	131

It should be noted that the reverse holds good for the iodine absorption numbers.

Thomson and *Ballantyne*[1] propose to refer the rise of temperature obtained with 50 grms. of oil and 10 c.c. of sulphuric acid to the rise of temperature which 50 grms. of water give under exactly the same conditions in the same vessel. The quotient $\frac{\text{Rise of temperature with oil}}{\text{Rise of temperature with water}}$ is termed by them "specific temperature reaction"; it expresses, therefore, the rise of temperature compared with water as unity. In the following table the results are multiplied by 100 in order to dispense with decimals. By recording the results in this way the discrepancies obtained on testing with sulphuric acids of varying strengths are, of course, considerably reduced, as will be seen from the following table :—

Kind of Oil.	Sulphuric Acid of 95·4 per cent.		Sulphuric Acid of 96·8 per cent.		Sulphuric Acid of 99 per cent.	
	Rise in Temperature. °C.	Specific Temperature Reaction.	Rise in Temperature. °C.	Specific Temperature Reaction.	Rise in Temperature. °C.	Specific Temperature Reaction.
Olive oil . .	36·5	95	39·4	95	44·8	96
Olive oil . .	...	...	39	94	43·8	94
Rape oil . .	49	127	...	...	58	124
Castor oil . .	34	88	37	89	...	...
Linseed oil .	104·5	270	...	...	125·2	269
Water . .	38·6	100	41·4	100	46·5	100

The following specific temperature reactions are given by *Thomson* and *Ballantyne*, and by *Jenkins*[2] :—

[1] *Jour. Soc. Chem. Ind.* 1891, 234. [2] *Ibid.* 1897, 194.

Kind of Oil.	Specific Temperature Reaction. Water=100.		Class of Oil.
	Thomson and Ballantyne.	Jenkins.	
Japanese wood oil	...	372	Drying oils
Linseed oil, Baltic	349	...	
,, ,, East India	320	...	
,, ,, River Plate	320	...	
,, ,, raw	...	313	
,, ,, boiled	...	248	
Menhaden oil	306	...	Fish oils
Cod liver oil, medicinal	272	...	Liver oils
,, ,, Scotch	246	...	
,, ,, Newfoundland	243	...	
Seal oil	...	278	Blubber oils
,, ,, tinged	229	...	
,, ,, cold drawn, pale	225	...	
,, ,, Norwegian	223	...	
,, ,, steamed, pale	212	...	
Whale oil, pale	157	...	
Cotton seed oil, refined Egyptian	170	...	Semi-drying oils
,, ,, ,, ,,	169	...	
,, ,, crude Egyptian	163	...	
Ravison rape oil	...	162	
Rape oil	144	...	
,, ,,	135	...	
,, ,,	133	...	
,, ,,	...	130	
,, ,,	127	...	
,, ,,	125	...	
Castor oil, commercial	89	105	
Sperm oil, southern	100	...	Liquid waxes
Arctic sperm oil (Bottlenose)	93	103	
Arachis oil, commercial	137	...	Non-drying oils
,, ,, French, refined	105	...	
Olive oil, Malaga	94	...	
,, ,, Mogador	93	...	
,, ,, Mytilene	93	...	
,, ,, Syrian	93	...	
,, ,, commercial	92	94	
,, ,, Candia	92	...	
,, ,, Gioja	89	...	
Neat's foot oil	...	87	Animal oils
Blown cotton seed oil	...	164	Manufactured oils
Blown rape oil	...	153	

The writer arranged the values in the order of their magnitude, and, as was to be expected, the same order obtains for the different classes of oils as in the table given above, p. 293.

Although the *Maumené* test is not accurate enough to admit of its being classed among the "quantitative reactions," it must be considered a valuable test which, in conjunction with other reactions, notably the "quantitative reactions" (see below), renders valuable services in detecting sophistications. Thus, adulterations practised on olive oil may be detected with comparative ease, olive oil having the lowest rise in temperature, with the exception of animal oils. This reaction may further be used with advantage in the examination of linseed oil for its drying power.

Archbutt recommends that every observer should construct a table for himself, using oils of known purity, and whenever a sample of oil is tested, compare the results with those furnished by the standard samples.

H. D. Richmond proposes a modification of the *Maumené* test by introducing the Relative Molecular Maumené figure (R.M.M.), that is, the total heat evolved per mean molecule. As his paper does not give experimental values, and bears the character of a preliminary note, the reader must be referred to the original paper.[1]

(*b*) *Thermal Reaction with Sulphur Chloride*

Fawsitt[2] proposed to measure the heat evolved by the action of sulphur chloride on various oils, with a view to discriminating between drying and non-drying oils, after the manner of *Maumené's* test (see p. 291). Since, however, this procedure offers no advantage over *Maumené's* test, or the bromine heat test (p. 300), it may suffice to briefly describe the *modus operandi*, and to record the values obtained in the table given below.

30 grms. of the sample are weighed out in a small beaker, which is then placed in a larger beaker, the space between the two beakers being packed with cotton wool. A thermometer is then inserted into the oil, the temperature observed, and the sulphur chloride poured in slowly, with constant stirring. The time is then taken, the thermometer kept stationary until the temperature ceases to rise, and both highest temperature and time noted.

[1] *Analyst*, 1895, 58.

[2] *Jour. Soc. Chem. Ind.* 1888, 552.

[TABLE

Class of Oil.	Kind of Oil.	Number of c.c. S_2Cl_2 added.	Rise in Temperature.	Time in Rising.	Rise per Minute.	Final Condition of Oil.
			°C.	Min.	°C.	
Drying oils .	Linseed	2	57	5	11·4	Liquid, viscous
	,,	3	79	3	26·3	Liquid, very viscous
	,,	4	97	2	48·7	Solid, sticky
Liver oils . .	Cod liver	2	55	4	13·7	Liquid, viscous
	,,	3	82	3	27·3	Solid, very sticky
	,,	4	103	3	34·3	Solid, dry
Blubber oils .	Seal	2	45	10	4·4	Liquid, more viscous
	,,	3	79	6	13·2	Solid, sticky
	,,	4	112	5	22·4	Solid, dry
	Whale	2	57	6	9·4	Liquid, more viscous
	,,	3	71	5	14·1	Liquid, very viscous
	,,	4	91	3	30·2	Solid, dry
Semi-drying oils	Cotton seed	2	49	11	4·4	Liquid, more viscous
	,,	3	64	9	7·1	Liquid, very viscous
	,,	4	93	6	15·4	Solid, sticky
	Rape	2	53	10	5·3	Liquid, more viscous
	,,	3	66	7	9·3	Solid, slightly sticky
	,,	4	89	6	14·8	Solid, dry
	Castor	2	56	2	27·7	Liquid, very viscous
Non-drying oils	Olive	2	52	6	8·7	Liquid, viscous
	,,	3	69	5	13·7	Liquid, very viscous
	,,	4	94	4	23·5	Solid, dry
Liquid waxes .	Sperm	2	37	16	2·3	Liquid
	,,	3	54	11	4·9	Liquid, more viscous
	,,	4	71	8	8·8	Liquid, more viscous
	,,	5	86	6	14·2	Liquid, very viscous
Animal oils .	Neat's foot	2	51	7	7·3	Liquid, more viscous
	,,	3	66	5	13·2	Liquid, very viscous
	,,	4	82	4	20·5	Solid, sticky
	Lard	2	40	16	2·4	Liquid, very viscous
	,,	3	62	9	6·9	Solid, got dry on standing
	Oleic Acid	2	53	6	10·6	Liquid, viscous
	,, ,,	3	74	5	14·9	,, ,,
	,, ,,	4	99	6	16·5	,, ,,
	Stearic Acid	2	5[1]	7	0·7	Solid
	,, ,,	4	8[1]	5	1·6	Solid
	Glycerol	4	21	7	3·0	Liquid

[1] Initial temperature.

(c) *Thermal Reaction with Bromine or Heat of Bromination Test. Bromine Thermal Value*

The action of bromine on fats and oils is attended with considerable evolution of heat. *Hehner* and *Mitchell*[1] proved by their researches that the measurement of the heat thus evolved leads to results furnishing more definite data than those obtained in the Maumené test.

Hehner and *Mitchell* proceed as follows:—

One grm. of the oil under examination is placed in a Dewar vacuum-jacketed test-tube[2] and dissolved in 10 c.c. of chloroform, the diluent being used to moderate the action. Exactly one c.c. of bromine, measured by means of a pipette (provided at its upper end with a narrow tube filled with caustic lime, and having an asbestos plug at each end), and previously brought to the same temperature as the oil in the vacuum tube, is run in, and the rise of temperature due to the instantaneous reaction is measured by means of a correct thermometer divided into fifths of a degree centigrade.

The whole operation occupies only a few minutes. Fatty acids are dissolved in glacial acetic acid instead of chloroform, and treated as above.

Hehner and *Mitchell* compared the numbers obtained for the rise of temperature of various fats and oils with their iodine numbers, with a view to elucidating the correlation, if any, existing between these two values. As will be seen from the following table, given by *Hehner* and *Mitchell*, the factor 5·5 serves to express the relation with considerable accuracy for the majority of the fatty substances examined by them under their particular conditions. The column headed "Deviation" has been added by the writer.

[1] *Analyst*, 1895, 148.

[2] The oil may be weighed in the tube, suspended obliquely, by means of platinum wire, from the arm of the balance. (Cp. Archbutt, *Jour. Soc. Chem. Ind.* 1897, 310.) In their earlier experiments *Hehner* and *Mitchell* employed an ordinary test-tube packed with cotton wool into a beaker; the results thus obtained are, *cæteris paribus*, two degrees centigrade lower.

[TABLE

I. Oil or Fat.	II. Heat of Bromination. °C.	III. Iodine Number. Experiment.	III. Iodine Number. Calculated from Column II. by multiplying by 5·5.	IV. Deviation. Absol.	IV. Deviation. Per Cent.
Lard, No. 1	10·6	57·15	58·3	+1·15	+2·00
,, 2	10·4	57·13	57·2	+0·07	+0·12
,, 3	11·2	63·11	61·6	−1·51	−2·40
,, 4	11·2	61·49	61·6	+0·11	+0·18
,, 5	11·8	64·69	64·9	+0·21	+0·32
,, 6	11·8	63·96	64·9	+0·94	+1·50
,, 7	10·2	57·15	56·1	−1·05	−1·90
,, 8	10·4	57·80	57·2	−0·60	−1·05
,, 9	9·0	50·38	49·5	−0·88	−1·70
,, 10	11·0	58·84	60·5	+1·66	+2·7
,, +10 per cent cotton seed oil	11·6	64·13	63·8	−0·33	−0·52
Lard fatty acids	10·4	59·60	57·2	−2·40	−4·20
,, ,,	11·0	59·15	60·5	+0·35	+0·57
Mutton fat (kidney)	8·1	44·48	44·5	+0·02	+0·05
,, ,, (flare)	7·6	39·70	41·8	+2·10	+5·0
Butter, No. 1	6·6	37·07	36·3	−0·77	−2·1
,, 2	7·0	38·60	38·5	−0·10	−0·27
,, fatty acids	6·2	36·50	34·1	−2·40	−7·04
Almond oil	17·6	96·64	96·68	+0·04	+0·041
Olive oil	15·0	80·76	82·50	+1·74	+2·1
Maize oil	21·5	122·	118·20	−3·80	−3·2
Cotton seed oil	19·4	107·13	106·70	−0·43	−0·4
Castor oil	15·0	83·77	82·50	−1·27	−1·5
Linseed oil, No. 1	30·4	160·7	167·20	+6·5	+3·9
,, ,, 2	31·3	154·9	172·00	+17·1	+10·0
Rape oil, No. 1	18·4	88·33	101·20	+12·87	+12·7
,, ,, 2	17·6	77·2	96·80	+19·6	+20·0
Cod liver oil	28·0	144·03	140·00	−4·03	−2·9
Commercial oil	19	108·5	104·5	−4·00	−3·8
,, ,,	19·2	105·7	105·6	−0·01	−0·009
,, ,,	18·9	105·7	103·9	−1·8	−1·7

It should be distinctly understood that the factor 5·5 must not be taken as an absolute one, but as depending on the particular vacuum-tube and the *modus operandi* adopted by *Hehner* and *Mitchell*. It is therefore absolutely necessary that each chemist using this method should ascertain the factor applying to his individual case by determining the heat of bromination of a non-drying oil, the iodine value of which has been fixed by means of Hübl's method.

Thus *Jenkins*[1] obtained the constant factor 5·7, and *Archbutt*[2] found it to vary in the case of tallow, olive oil, rape oil, and linseed oil from 5·7 to 6·2. In the latter case the variation may be partly due to the fact that the weight of substance taken was not the same in every instance.

[1] *Jour. Soc. Chem. Ind.* 1897, 194.
[2] *Ibid.* 1897, 310. Cp. also Wilson, *Chem. News*, 1896, 27.

Notwithstanding the considerable differences shown in the case of linseed and rape oils, *Hehner* and *Mitchell* considered that the determination of the iodine number by Hübl's method may be replaced by that of the heat of bromination. They even went so far as to express the opinion, that the *calculated* iodine values of linseed and rape oils examined are more correct than those found by Hübl's method. In the writer's opinion this is tantamount to begging the question, and a larger number of experiments is required to substantiate so far-reaching conclusions. This is all the more necessary as further serious deviations have been stated by *Jenkins* for Japanese wood oil, and for "blown oils."

On account of the exceeding simplicity of this test, and the rapidity in its execution, the heat of bromination test will prove a very useful auxiliary test, especially where a large number of specimens of the same kind have to be examined in a short time. It will be no less useful as a sorting test (*Hehner*), affording rapid information as to the class an oil belongs to. (Of course, if accuracy is required the iodine value must be determined as described above, p. 172.)

The great rapidity being one of the chief recommendations in favour of using this test, *Wiley's*[1] modification to employ a chloroformic solution of bromine would seem to complicate matters, all the more so as a lowering of temperature takes place when bromine is dissolved in chloroform. The latter fact has already led to the suggestion to substitute carbon tetrachloride for chloroform. In the case of oils giving a very violent reaction, as linseed oil, *Archbutt*[2] suggests to work with 0·5 grm. of oil, and to multiply the result by 2, whilst in the opposite case, viz. of solid fats, which develop but little heat, to take 2 grms., and divide the result by 2.

5. The Discrimination of the Different Oils by "Quantitative Reactions"

The values obtained by the methods described in chap. vi. pp. 148-180, *i.e.* by the so-called quantitative reactions, furnish the most valuable indications as to the nature and purity of an oil.

We consider here the following quantitative values:—

(*a*) Saponification values.
(*b*) *Hehner* values.
(*c*) *Reichert* (*Meissl*) values.
(*d*) Iodine (and Bromine) values.
(*e*) Acetyl values.

(*a*) *Saponification Values*

The subjoined table contains the saponification values of a number of oils and liquid waxes, as determined according to *Köttstorfer's*

[1] *Jour. Soc. Chem. Ind.* 1896, 384. [2] *Ibid.* 1897, 310.

method by *Allen*,[1] *Moore*,[2] *De Negri* and *Fabris*,[3] *Lewkowitsch*,[4] and other observers. The figures given in the column headed "Mean value" do not always represent the actual means of the highest and lowest values recorded; in the case of the better known oils, the mean value is the number most frequently found.

The classification in the following table is that adopted in the preceding pages, with subdivisions according to the plan arranged in chap. xi.:

Saponification Values of Oils and Liquid Waxes

Kind of Oil.	1 Grm. of Oil requires for Saponification Mgrms. KOH.			Class of Oil.
	Minimum.	Maximum.	Mean Value.	
Sperm oil	123	147	135	Liquid waxes.
Arctic sperm oil (Bottlenose)	123	134	128·5	
Menhaden oil	...	...	192	Fish oils.
Sardine oil	...	...	185·5	
Japan fish oil	189·8	192·1	190·9	
Pilchard oil	186	187	186·5	
Cod liver oil	171	213·2	185	Liver oils.
Haddock liver oil	...	...	188·8	
Skate liver oil	...	...	185·4	
Shark liver oil	140	197·6	168	
Seal oil	191·2	196	193·5	Blubber oils.
Whale, northern oil	188·5	224	206	
Whale, southern oil	...	...	193·1	
Dolphin, body, oil	...	...	197·3	
Dolphin, jaw, oil	...	...	290	
Porpoise, jaw, oil	...	...	143·9	
Porpoise, fluid portion, oil	253·7	272·3	263	
Linseed oil	187·4	195·2	193	Drying oils.
Japanese wood oil	155·6	211	193	
Lallemantia oil	...	...	185	
Hemp seed oil	...	...	193·1	
Walnut oil	...	...	196	
Poppy seed oil	192·8	194·6	193·7	
Niger seed oil	189	191	190	
Sunflower oil	...	...	193	
Fir seed oil	...	...	191·3	
Madia oil	...	...	192·8	
Garden rocket oil	...	...	191·8	
Henbane seed oil	...	...	170·8	
Celosia oil	...	...	190·5	
Indian laurel oil	...	...	170	
Cameline oil	...	...	188	Semi-drying oils.
Soja bean oil	192·5	192·9	192·7	
Pumpkin seed oil	...	...	188·1	
Maize oil	188	193·4	190·7	
Kapok oil	...	...	181	
Cotton seed oil	191	210·5	192·5	
Sesamé oil	187·6	192·2	190	
Beechnut oil	191·1	196·3	193·7	
Brazil nut oil	...	...	193·4	

[1] *Jour. Soc. Chem. Ind.* 1883, 50.
[2] *Chem News*, 50. 268.
[3] *Annali del Laboratorio delle Gabelle*, 1893.
[4] Cp. tables, chap. xi.

Saponification Values of Oils and Liquid Waxes—continued.

Kind of Oil.	1 Grm. of Oil requires for Saponification Mgrms. KOH.			Class of Oil.
	Minimum.	Maximum.	Mean Value.	
Garden-cress oil	...	...	178	Semi-drying Oils: Rape oil group.
Hedge mustard oil	...	...	174	
Rape oil	175	179	177	
Black mustard oil	174	174·6	174·3	
White mustard oil	170·3	171·4	170·8	
Radish seed oil	...	...	178	
Jambo oil	...	...	172·26	
Charlock oil	176	177	176·5	
Croton oil	210	215	212·5	Castor oil group.
Curcas oil	210·2	230·5	220·3	
Grape seed oil	178·4	179	178·7	
Castor oil	176	186	183	
Cherry kernel oil	193·4	195	194·2	Non-drying oils.
Cherry laurel oil	...	...	194	
Apricot kernel oil	192·2	193·1	192·7	
Plum kernel oil	...	...	191·5	
Peach kernel oil	189·1	192·5	190·8	
Wheat meal oil	...	...	166·5 (?)	
Acorn oil	...	...	199·3	
Almond oil	187·9	190·4	191	
Sanguinella oil	...	...	192	
Californian nutmeg oil	...	...	191·3	
Arachis oil	190·1	197	193·5	
Rice oil	...	...	193·2	
Tea seed oil	194	195·5	194·8	
Pistachio oil	191	191·6	191·3	
Hazelnut oil	191·4	197·1	194·2	
Olive oil	185·2	196	193	
Olive kernel oil	...	...	188·5	
Coffee berry oil	165·1	173·4	169·3	
Ungnadia oil	191	192	191·5	
Strophantus oil	...	...	187·9	
Secale oil	...	...	178·4	
Sheep's foot oil	...	...	194·7	Terrestrial animal oils.
Horses' foot oil	195	196·7	195·8	
Egg oil	185·2	186·7	186	
Neat's foot oil	191	194·3	192·6	
Lard oil	191	196	193·5	

A glance at the table shows that the saponification values, as given by different observers, do not agree very well, and further series of determinations, carried out with genuine oils, are required to ascertain within what limits the values vary for each kind of oil. Definite variations found could then be safely attributed to differences of soil, climate, etc.

In the above table an attempt has been made to arrange the oils according to the system which appears to the writer to be the nearest approach to a natural one.

Artificial classifications based on the saponification number are hardly of any value, if strictly carried through. Still, if judiciously used, the saponification value may give useful hints as to the class to which an oil of unknown origin may belong.

The majority of oils have a saponification value of 193. A considerably lower number—such as 178—will justify the suspicion that the oil giving it belongs to the rape oil group. True, castor oil and grape seed oil are also distinguished by similarly low values, but they are easily differentiated from the oils of the rape oil group by their solubility in alcohol and acetic acid respectively, and chiefly by their acetyl values. The lower saponification values of these oils are easily explained by the large proportion of higher fatty acids they contain. Thus, rape oil is characterised by the glyceride of erucic acid, and castor and grape seed oils by glycerides of hydroxy acids.

The low saponification values of the liquid waxes are so characteristic that they afford a ready means of distinguishing them from other oils. On the other hand, the high saponification values of the fluid portions of dolphin and porpoise oils (used for lubricating purposes) single them out in such a manner as to make their recognition comparatively easy. Croton and curcas oils also are remarkable for their high numbers.

With a view to eliminating the variations in the saponification values due to the presence of free fatty acids in the oils, *Valenta* has proposed to determine the saponification values of all the fatty acids, *i.e.* the total acid values. Obviously, the values so obtained will only refer to the *insoluble* fatty acids of the oils. Therefore, the characteristic differences due to the presence of glycerides of *soluble* fatty acids will disappear. Thus, to choose a striking example, the difference of the saponification values of the fatty acids from butter and oleomargarine respectively will be far less remarkable than the saponification values of the corresponding neutral fats.

If, however, the differences of the saponification values of two oils under examination are due to a difference in the molecular weights of the fatty acids, the determination of the saponification values of the free acids will afford useful indications as to the nature of the oil.

Thus, *Valenta* has obtained the following values :—

Fatty Acids from	Milligrms. KOH.	Molec. Weight calculated.
Cotton seed oil	203·9	275·1
Olive oil	203·0	276·0
Sesamé oil	199·3	281·5

The mean molecular weight of the rape oil fatty acids is 314.

These molecular weights, however, must not be confounded with Allen's *Saponification Equivalents* (p. 152), which are calculated from the saponification value, K, by dividing 5610 by K, the proportion of glycerol in the fat being disregarded. As already pointed out, Allen's *Saponification Equivalents* furnish no further quantitative information than is given by the saponification values, and for this reason they are altogether omitted in this treatise.

(*b*) *Hehner Values*

The *Hehner* values of the majority of the fatty oils are about 95. Only croton and curcas oils give lower numbers, viz. 88·9 and 87·9.

With regard to the *Hehner* values of the liquid waxes compare chap. x. p. 329.

(*c*) *Reichert* (*Meissl*) *Values*

Most of the naturally-occurring fats contain but small quantities of soluble, *i.e.* volatile fatty acids, therefore their *Reichert* values are very low. As a rule they are below 1. It is evident, therefore, that a somewhat higher *Reichert* (*Meissl*) value will be characteristic of an oil, and that very valuable indications as to the nature of an oil may be obtained by the determination of the volatile acids. Subjoined is a table containing those oils which possess *Reichert* or *Reichert-Meissl* values above 1. It must be understood that such oils as olive oil, cotton seed oil, etc., naturally fall outside the range of this list.

Kind of Oil.	Reichert Value, for 2·5 grms.	Reichert-Meissl Value, for 5 grms.	Observer.
Sperm oil	1·3	...	Allen
Arctic Sperm oil . . .	1·4	...	,,
Whale oil	3·7	...	,,
Whale oil	12·5	...	,,
Dolphin oil, body . .	5·6	...	Moore
Dolphin oil, jaw . . .	65·92	...	,,
Porpoise oil	11-12	...	Allen
Porpoise oil	...	46·9	Steenbuch
Porpoise oil, jaw oil, skimmed and strained	47·77-56·00	...	Moore
Porpoise oil, jaw oil, skimmed and strained	...	131·6	Steenbuch
Porpoise oil, jaw oil, not skimmed	2·08	...	Moore
Croton oil	...	13·42[1]	Lewkowitsch

The extraordinarily high values of dolphin and porpoise oils are due to the presence of a large proportion of the glyceride of isovaleric acid.

[1] Cp. also p. 313.

(*d*) *Iodine* (*and Bromine*) *Values*

The subjoined table contains the iodine values of some oils as determined by the earlier observers *Hübl* and *Moore*:—

Kind of Oil.	Iodine Value.		
	Hübl (mean values).	Moore.	
Linseed oil	158[1]	155·2[1]	Drying oils
Hemp seed oil	143	...	
Walnut oil	143	...	
Poppy seed oil	136	134	
Pumpkin seed oil	121	...	Semi-drying oils
Cotton seed oil	106	108·7	
Sesamé oil	106	102·7	
Arachis oil	103	87·4	
Rape oil	100	103·6	
Apricot oil	100	...	Non-drying oils
Almond oil (sweet)	98·4	98·1	
Mustard seed oil	...	96·0	
Castor oil	84·4	...	
Olive oil	82·8	83·0	
Olive kernel oil	81·8	...	
Bone oil	68·0	...	

As will be seen from this table, the drying oils, headed by linseed oil, are characterised by the highest iodine values, whereas the non-drying vegetable oils and bone oil, like other oils of terrestrial animals, possess distinctly lower values. The semi-drying oils occupy an intermediate place.

The high absorptions of the drying oils are due to their containing large amounts of the glycerides of the linolenic acids and of linolic acid, which absorb 18 atoms and 12 atoms of iodine respectively, whereas the glycerides of oleic acid, the chief constituents of the non-drying oils, assimilate but 6 atoms of iodine.

Consequently, the determination of the iodine value affords a very valuable and easily ascertainable characteristic in the examination of oils. Provided fish, liver, and blubber oils, possessing high iodine values but no drying properties, be absent, the mere determination of the iodine value allows of the discrimination of a drying oil from a non-drying one.

It has, therefore, become customary, since the publication of *Hübl's* very useful method, to determine in the first instance the iodine absorption of an oil under examination. Numerous determinations done by a great number of chemists prove that the iodine values of all oils are constant within narrow limits. Thus, *Dieterich*, on examining 200

[1] Compare the correct value of the following table.

samples of olive oil, has found no greater variations than from 81 to 84·5. In the case of linseed oil greater differences have been observed; but the apparent discrepancies have for the most part disappeared since it has been shown by *Benedikt* that a larger excess of iodine solution was required than had been used by *Hübl* and *Moore*. Besides, it must be borne in mind that the iodine values of linseed oil depend greatly on the age of the oil (comp. "Linseed Oil," chap. xi p. 341).

In the following table I give the iodine values of oils and liquid waxes compiled from the publications of numerous observers, of whom the following may be mentioned:—*Hübl*, *Moore*, *Dieterich*, *Wilson*, *Erban*, *Herz*, *Spüller*, *Horn*, *Richter*, *Kremel*, *Beringer*, *Benedikt*, *Archbutt*, *Micko*, *De Negri* and *Fabris*, and *Lewkowitsch*. There are also added the bromine absorptions, as determined by *Mills*, *Snodgrass*, *Akitt*, and *Maben*; these values have been calculated to iodine values by multiplying by $\frac{127}{80}$ in order to facilitate comparison.[1] The oils have been arranged, as in the table given by *Hübl*, according to the magnitude of their iodine values, subject, however, to the keeping together of the members of some natural groups. This order has been carried through systematically by the writer for the members of the several groups in chap. xi., this system suggesting itself as the most natural one.

Morawski and *Demski* (cp. p. 180) proposed to determine the iodine values of the mixed fatty acids. It has been pointed out already (p. 180) that a close correspondence between the iodine values of the oils and their (insoluble) fatty acids cannot be expected. It has, however, become customary in the commercial examination of fats and oils to ascertain also the iodine absorptions of the (insoluble) fatty acids as obtained on saponification. Therefore we have added in the subjoined table the iodine values of the mixed fatty acids. Compare also tables, chap. xi.

[1] It must be, however, understood that, *a priori*, these calculated iodine values need not be identical with those obtained by Hübl's process, the disagreement being no doubt due to the varying amount of substitution. This will be clearly seen from the following table containing the bromine and iodine values of a number of seal oils, determined by Chapman and Rolfe (*Jour. Soc. Chem. Ind.* 1894, 843), to which I have added the calculated iodine values:—

Seal Oil, No.	Bromine Value.	Iodine Value Experiment.	Iodine Value calculated.
1	69·6	129·5	110·5
2	77·6	133·0	122·6
3	77·2	136·4	122·6
4	80·0	137·4	127·0
5	78·2	139·0	124·1
6	79·8	141·0	126·7

On the whole, the iodine values show greater regularity than the bromine values.

Iodine Values of Oils and Liquid Waxes, and of their Mixed Fatty Acids

Kind of Oil.	Oils.					Mixed Fatty Acids.			Class of Oil.
	Bromine Absorption.	$\frac{Br \times 127}{80}$	Iodine Absorption.			Iodine Absorption.			
			Minim.	Maxim.	Mean.	Minim.	Maxim.	Mean.	
Linseed, fresh	76	120·8	170	181	175	..	..	..	Drying oils.
,, commercial	..	..	148	181	170	155·1	182	179	
Japanese wood	..	..	156	166	161	..	..	150	
Lallemantia	..	..	..	..	162	..	..	166	
Garden rocket	..	..	145·9	155·3	155·1	..	..	157	
Hemp seed	..	..	142	158	150	122	141	131·5	
Walnut	..	..	132	152	146	..	..	150·5	
Poppy seed	56·5	89·9	134	142	138	116	..	139	
Henbane seed	..	..	..	..	138	..	..	..	
Niger seed	35·1	55·8	..	..	133	..	..	..	
Sunflower	54·3	86·2	122	133	128	124	134	129	
Celosia	..	..	..	..	126	..	..	..	
Fir seed	..	..	118·9	120	119·5	..	..	121·5	
Madia	..	..	117·5	119·5	118·5	..	..	120·7	
Candle nut	..	..	..	..	118	..	..	..	
Indian laurel	..	..	..	..	118·6	..	..	..	
Sardine	..	..	..	..	193	..	..	..	Fish oils.
Menhaden	..	..	148	160	154	..	..	..	
Japan fish	..	..	96	122	109	..	..	..	
Cod liver	81·6-86·7	129·5-137·6	126	166·6	146·3	..	..	..	Liver oils.
Skate liver	..	..	..	..	157·3	..	..	..	
Haddock liver	..	..	..	..	154·2	..	..	..	
Coal fish liver	..	..	123	137	130	..	..	..	
Shark liver	84·36	133·3	90	114·6	102·3	..	..	..	
Ling liver	82·4	131	..	..	..	..	..	..	
Seal	57·3-59·9	91-95	125	152	138·5	..	..	..	Blubber oils.
Whale	30·9	49	109·2	126·7	117·9	..	..	..	
Blackfish, body	..	..	..	..	99·5	..	..	..	
,, jaw	..	..	..	..	32·8	..	..	..	
Porpoise, skimmed	..	..	30·9	49·6	40·2	..	..	..	
,, not skimmed	..	..	..	..	76·8	..	..	..	
Cameline	..	..	132·6	135·3	133·9	..	..	136·8	Semi-drying Oils.
Soja bean	..	..	121·3	122·2	121·7	115	122·2	118·6	
Pumpkin seed	..	..	..	..	121	..	..	..	
Maize	66·5-74·4	105·5-118·1	111·2	119·9	115·6	113	125	119	
Kapok	..	..	..	..	116	..	..	108	
Cotton seed	50	79·5	102	111	108	110·9	115·7	113·3	
Sesamé	47·4	75·2	103	112	108	108·9	112	110·5	
Beechnut	65·2	103·5	104·4	111·2	107·8	..	..	114	
Brazil nut	..	..	..	..	106·2	..	..	108	
Garden cress	..	..	108	108·8	108·4	..	..	111·4	Rape oil group.
Hedge mustard	..	..	..	..	105	..	..	..	
Rape	69·4	110·4	99	105	101	96	105	100·5	
Black mustard	..	..	96	106	101	..	..	109·6	
White mustard	..	..	92·1	97·7	94·9	94·7	95·9	95·3	
Charlock	..	..	96	97	96·5	..	..	..	
Radish seed	..	..	95·6	95·9	95·7	..	..	97·1	
Jambo	..	..	95·2	95·6	95·4	96·1	96·2	96·1	
Croton	46·7	74·1	101·7	104·7	103	..	..	..	Castor oil group.
Curcas	..	..	100·9	127	113·9	..	..	105·5	
Grape seed	..	..	94	96·2	95·6	98·6	99	98·8	
Castor	58·3	92·7	83·6	85·9	84·7	86·6	93·9	90·2	

Iodine Values of Oils and Liquid Waxes, and of their Mixed Fatty Acids—continued

Kind of Oil.	Oils.					Mixed Fatty Acids.			Class of Oil.
	Bromine Absorption.	$\frac{Br \times 127}{80}$	Iodine Absorption.			Iodine Absorption.			
			Minim.	Maxim.	Mean.	Minim.	Maxim.	Mean.	
Cherry kernel	..	..	110·8	114·3	112·5	104·3	114·3	109·3	Non-drying Oils.
,, laurel	..	..	..	..	118·9	..	..	112·1	
Apricot kernel	70	111·1	100	108	104	102·6	103·8	103·2	
Plum ,,	..	..	100·2	100·4	100·3	102	104·2	103·1	
Peach ,,	25·4	40·4	92·5	99·7	96·6	94·1	101·9	98	
Wheat meal	..	..	..	..	101·5	..	..	..	
Pine nut	..	..	..	..	101·3	..	..	..	
Acorn	..	..	..	..	100·7	..	..	..	
Almond	26·3-33·7	41·8-85·3	93	101·9	97·4	93·5	96·5	95	
Sanguinella	..	..	..	..	100·8	..	..	102·7	
Californian nutmeg	..	..	..	..	94·7	..	..	..	
Arachis	46·2	73·3	85·6	101·3	93·5	95·5	103	99·2	
Rice	..	..	..	..	96·4	..	..	..	
Tea seed	..	..	..	..	88	..	..	..	
Pistachio	..	..	86·8	87·8	87·4	..	..	88·9	
Hazelnut	..	..	83·2	88·5	85·8	..	..	90·1	
Olive	54-60·6	85·9-96·4	79·2	88·7	82·8	86·1	90·2	88·1	
,, kernel	..	..	..	..	81·8	..	..	..	
Coffee berry	..	..	85·89	87·34	86·5	88·8	90·4	89·6	
,, ,,	..	..	..	..	78·65	..	..	81·8	
Ben	50·89-52·95	80·8-84·1	..	..	..	..	..	..	
Ungnadia	..	..	81·5	82·0	81·7	..	..	..	
Strophantus seed	..	..	..	..	73	..	..	..	
Secale	..	..	..	..	71	..	..	..	
Sperm	54·5	86·5	..	..	84	83·2	85·6	84·4	Liquid waxes.
Arctic sperm (Bottlenose)	48·7	77·4	80·4	82·1	81·3	82·2	83·32	82·7	
Lard	..	..	72·8	85	79	..	..	..	Terrestrial animal oils.
Sheep's foot	..	..	74·0	74·4	74·2	..	..	..	
Horses' foot	..	..	73·7	73·9	73·8	..	..	..	
Egg	..	..	68·5	81·6	70	..	..	73	
Neat's foot	38·3	60·8	69·3	70·4	69·8	..	..	62	
Bone	..	..	67	70	68	..	..	..	

The important place the iodine value occupies in the commercial examination of oils will be best illustrated by the following quotation from *Hübl's* classic paper:—

"The determination of the iodine absorption furnishes a ready means of ascertaining the nature of an oil under examination, as it affords a standard by which we can gauge its purity, and by allowing conclusions to be drawn as to its qualitative composition; it will even permit it in some cases to be inferred approximately in what proportions two oils have been mixed.

"If it be required to identify an oil or fat, the iodine value will indicate the class to which it belongs, and it will then, as a rule, not be difficult to distinguish it from other oils and fats belonging to the same class by other characteristic reactions. It should, however, be

borne in mind that it is quite possible, nay, even likely, that some kinds of oils or fats may occur the iodine values of which may not lie within the limits given, since the values given above have been derived from but a limited number of samples. In such cases the connection existing between the iodine value and the melting point of the mixed free fatty acids will afford some indications as to the nature of the oil.

"If a mixture of two oils is under examination, one constituent of which is unknown, as in the case of an adulterated oil, or if the nature of either constituent be unknown, it will, of course, be required to utilise all those methods that are likely to throw some light on the nature of the components of the mixture. But even in such a case the iodine value of the mixture will furnish the first clue as to the order in which further tests, such as determination of the melting and solidifying points of the mixed fatty acids, of the saponification value, of the solubilities, and of other chemical and physical constants, have to be undertaken.

"If the nature of two oils in a mixture be known, or if we have succeeded in identifying them, it is possible to approximately calculate the proportions of both oils in the sample if they belong to two different classes. Let x be the percentage of one oil and y the percentage of the other oil in the sample under examination, consequently $x + y = 100$, and further, let m be the iodine value of the oil x in the pure state, and n the corresponding value of the oil y, then we find from the iodine value J of the sample—

$$x = \frac{100(J - n)}{m - n}.$$

"The age does not materially affect the iodine absorption as long as the oil has not undergone any important change. Samples of linseed and rape oils, even fifteen years old, gave correct values. If, however, an oil has become thickened and rancid on exposure to light and air, the iodine absorption is diminished in a corresponding degree. Thus, an exposed linseed oil yielded 130, and an exposed olive oil but 75.[1] Oils thus changed are, however, characterised by their greater solubility in acetic acid, and by abnormally high percentages of free fatty acids."

Ballantyne[2] has studied the influence of exposure to light and air on the iodine values of some oils. His results are recorded in the following table :—

[1] An exposed olive oil, examined by the writer, absorbed 70 per cent of iodine.

[2] *Jour. Soc. Chem. Ind.* 1891, 31.

Kind of Oil.	Original Value.	After Six Months' Exposure to Sunlight.	
		Protected against Access of Air.	Exposed to Air.
Linseed oil . .	173·46	172·88	166·17
Cotton seed oil .	106·84	106·40	100·12
Rape oil . . .	105·59	105·27	102·13
Arachis oil . .	98·67	97·60	93·20
Castor oil . .	83·63	83·27 (after 2 months)	83·27
Olive oil . . .	83·16	82·64	78·24

The same fact is brought out by comparing the iodine values of the "blown oils" with those of the original oils (cp. table, chap. xii. p. 734).

It is apparent that the action of both light and air is required to reduce the iodine value (cp. p. 11).

Just as in the examination of a fat of unknown composition it is expedient to separate its constituents into a solid and into a liquid portion, it will be found useful to break up the fatty acids of an oil into a solid and a liquid part. For it is quite possible that two oils may absorb the same amount of iodine, whereas their liquid fatty acids may have very different iodine values. Such cases may be represented by two oils, one of which consists chiefly of triolein, and the other of trilinolin, tristearin, and tripalmitin.

Wallenstein and *Finck*[1] have determined for a number of oils the iodine values of the liquid fatty acids (for which they propose the term "inner" or "absolute" iodine value of the oil (this term is not used in this work, as it may lead to confusion). Their numbers, contrasted with the iodine numbers of the oils themselves, are given in the following table:—

Oil.	Iodine Value of Oil.	Iodine Value of the Liquid Fatty Acids.
Niger seed oil	133·5	147·5
Maize oil	122	140·7
Cotton seed oil—American .	107·8-108	147·3-147·5
,, ,, Egyptian .	106·5-108	146·8-148·2
,, ,, Peruvian .	106·8	147·8
Rape oil	101·1	120·7
Arachis oil	98·9	128·5
Tallow oil	...	92·2-92·7
Lard oil—European[2] . .	...	95·2-96·2
,, American . .	...	103-105
Cocoa nut oil	8·4	54·84

[1] *Jour. Soc. Chem. Ind.* 1895, 97.

[2] *Ibid.* 1897, 503.

(e) *Acetyl Values*

The determination of the acetyl value is especially suitable for the detection of castor oil, grape seed oil, and the "blown oils."

The following acetyl values have been recorded by *Lewkowitsch* [1] :—

Kind of Oil.	Acetyl Value.	
	(a) By Distillation Process.	(b) By Filtration Process.
Castor—I. . . .	150·5	149·6
,, II. . . .	149·9	149·4
,, III. . . .	...	146·7
[2]Croton—I. . . .	19·61	20·02
,, I. . . .	19·78	19·84
Maize—I. . . .	8·75	8·25
,, I. . . .	...	8·21
,, II. . . .	7·81	7·9
Cotton seed—I. . .	24·76	25·1
,, II. . .	...	21·1
,, III. . .	...	21·9
Olive	12·78	13·48
,, ...	...	13·62
Colza	17·2	16·6
Linseed . . .	6·85	6·92
,, . . .	7·03	
Fish	41·0	
Shark liver . . .	...	17·83
Animal . . .	22·04	22·38
Horses' foot . . .	...	14·40

6. Qualitative Reactions

Various colour reactions have been proposed from time to time, and are still being proposed, for the recognition of oils.

A very complete synopsis of the older methods has been given by *Chateau* in his work *On Fats.*[3] The following tests may be mentioned in chronological order :—

Heydenreich (1848) first employed concentrated sulphuric acid for the examination of oils ; his test consists in letting fall five drops of the oil under examination on the surface of pure concentrated sulphuric acid in a porcelain basin, and observing the colours developed during the first three minutes.

Penot introduced sulphuric acid saturated with potassium bichromate as a general reagent, the various colours obtained with different oils being considered as characteristic for those oils.

Behrens used a mixture of equal parts of sulphuric and nitric acids.

[1] *Jour. Soc. Chem. Ind.* 1897, 503.

[2] The apparent acetyl values (p. 166) of croton oil, having a high Reichert value (p. 306), were found 40·68 and 40·85, from which 21·07 had to be deducted for the volatile acids.

[3] Chateau, *Die Fette, bearbeitet von H. Hartmann.* Leipzig, 1864.

Fauré (1839) has stated that vegetable oils can be distinguished from animal oils by gaseous chlorine, the latter oils—with the exception of foot oils from terrestrial animals—becoming black on treatment with this reagent (p. 279). The same chemist also employed ammonia as a general reagent.

Hauchecour-Yvetot proposed hydrogen peroxide as a general reagent.

Crace Calvert's (1854) method has for a long time been in vogue. This chemist examined the colour reactions noticeable on treating oils with the following reagents: (1) caustic soda, 1·340 spec. grav.; (2) sulphuric acid, 1·475 spec. grav.; (3) sulphuric acid, 1·530 spec. grav.; (4) sulphuric acid, 1·635 spec. grav.; (5) nitric acid, 1·180 spec. grav.; (6) nitric acid, 1·220 spec. grav.; (7) nitric acid, 1·330 spec. grav., and subsequently caustic soda, 1·340 spec. grav.; (8) syrupy phosphoric acid; (9) mixture of equal volumes of nitric acid, 1·330, and sulphuric acid, 1·345; (10) aqua regia, consisting of 25 measures of hydrochloric acid and 1 measure of nitric acid, 1·330, and subsequent treatment with caustic soda. In the older text-books *Crace Calvert's* results are presented in a tabular form; for reasons stated below the table is omitted in this work.

Chateau, in his book *On Fats*, has published very extensive tables, in which an attempt is made to distinguish the oils by systematic application of the following reagents: (*a*) calcium polysulphide, (*b*) zinc chloride, (*c*) concentrated sulphuric acid, (*d*) fuming stannic chloride, (*e*) syrupy phosphoric acid, (*f*) phosphoric acid, (*g*) mercuric nitrate, with subsequent addition of sulphuric acid, (*h*) mercuric nitrate alone. All these tests must, on the whole, be considered of very little value, and are therefore not recorded here.

Later on *Glaessner* also proposed a systematic course for the examination of oils, using as reagents caustic potash, fuming nitric acid, and concentrated sulphuric acid.

In order to avoid a rise of temperature with the last-mentioned acid, whereby some characteristic colour reactions may become indistinct, or the oil may become partially charred, *Finkener* dilutes the oils with carbon disulphide. This solvent is said to be specially adapted to the test, since no thermal reaction takes place on mixing it with concentrated sulphuric acid.

All colour reactions must be used with the greatest caution, small quantities of resinoid or albuminoid substances, or other foreign matters, such as cholesterol, influencing the tints to such an extent that in most cases it will remain doubtful whether the reactions are due to the oils themselves or to the presence of small quantities of foreign substances. A notable example of a serious mistake of this kind was the reddish-brown colour obtained on treating imperfectly purified tallow with nitric acid being erroneously attributed to the presence of cotton seed stearine.

The colour reactions were resorted to chiefly for want of better methods; they have been in most cases superseded by the "quanti-

tative reactions." It should be borne in mind that many colour reactions quoted in older text-books, and perpetuated in even more recent treatises, were not always obtained with typical samples, little or no regard having been paid to their source, their age, their mode of purification, and all that host of circumstances that have a vital influence on the colour the reagents produce. With the progress of technology a number of impurities, the very substances that gave origin to the colours supposed to be characteristic, have ceased to occur in commercial samples.

A colour reaction can only be of value if it be produced by a well-defined substance, naturally occurring in an oil, and characteristic of it to such an extent that the oil may be identified by that reaction. Of course, these characteristic substances occurring only in minute quantities must not be easily removable by the process usually applied in practice.

As a type of a most valuable reaction of this kind we may refer to *Baudouin's* test for sesamé oil which has recently obtained its scientific explanation and confirmation by the isolation of the colour-producing principle in that oil (cp. "Sesamé Oil," p. 389). The colour reaction for cholesterol, although highly characteristic, requires more circumspection, as other substances also give the same or a very similar colouration (p. 84).

Group reagents, such as are used in inorganic analysis, do not exist, and every new reagent recommended as such must be received with great suspicion.

The writer[1] has carefully examined four of the so-called group reagents, viz. concentrated sulphuric acid, gaseous chlorine, syrupy phosphoric acid, and phospho-molybdic acid. From his experiments the following conclusions have been arrived at :—

Sulphuric Acid.—This reagent enables, at best, with a good deal of practice, to discriminate between drying oils, semi-drying, and non-drying oils, if the acid be applied to the oil direct. The first-named oils may be recognised by their forming dark clots, when, say, two drops of concentrated acid are stirred into twenty drops of oil. A discrimination between semi-drying and non-drying oils, however, is more difficult and indeed scarcely possible in every case.

The better drying an oil is, the darker it will be coloured by the acid, so that it may be possible, judging from the depth of the colour, to distinguish between oils standing at the extreme ends of these classes, such as cotton seed oil and olive oil, whereas it is impossible to differentiate by this test alone, *e.g.* rape oil from cotton seed oil. The colour reactions obtained with a solution of the oil in carbon bisulphide cannot be said to yield more reliable results, the dilution tending to obliterate the otherwise sharp distinction between the eminently drying and the other oils.

In the case of liver oils, the blue and purple colourations due to the presence of cholesterol and colouring principles—lipochromes—are very characteristic ; they are best observed if the oil is previously

[1] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1894, 617.

dissolved in carbon bisulphide. But the value of this test is greatly diminished by the fact that some blubber oils (perhaps due to an accidental admixture with liver oils) show the same reaction, but chiefly for the reason that rancidity seems to destroy the chromogenetic substances.

Chlorine gas cannot be admitted as a group reagent for marine animal oils, the black colour being influenced by the state of purity and rancidity of the oil, so that even vegetable oils or terrestrial animal oils may give stronger colourations than pure liver oils.

Phosphoric acid appears to indicate only impurities that may be eliminated by refining, or that are products of oxidation or rancidity.

Phospho-molybdic Acid.—This reagent has been proposed by *Welmans.*[1] The test is performed as follows: 1 grm. (or 25 drops) of an oil or fat is dissolved in 5 c.c. of chloroform in a test-tube, and agitated with 2 c.c. of a freshly prepared solution of phospho-molybdic acid,[2] or of sodium phospho-molybdate and a few drops of nitric acid. After standing for a short time the chloroformic layer becomes colourless, whereas the upper layer shows, in the case of a vegetable oil and of cod liver oil, according to *Welmans*, a green colour. On adding ammonia or a fixed alkali a beautiful blue colour appears, the intensity of which corresponds to that of the green tint noticed before. Animal fats—with the above stated exception of cod liver oil—were said to cause no reduction, and consequently to produce no green with subsequent blue colouration.

The writer's experiments,[3] however, demonstrate that such a distinction cannot be upheld. Several kinds of olive oil, as also almond, arachis, and peach oils, showed far less distinct colours than tallow oil, and even lard oil. Amongst the large numbers of oils and fats of undoubted genuineness and belonging to all classes of oils and fats he has examined, only pure, freshly rendered lard left the phospho-molybdic acid unreduced, so that it remained colourless on being supersaturated with ammonia. But a slightly rancid lard behaved almost like a vegetable oil in *Welmans'* test (cp. "Lard," p. 580). Moreover, mineral oil and resin oil gave deep colourations; the phospho-molybdic acid test can, therefore, only rank amongst preliminary tests.

Special colour reactions, useful in some instances for the identification of an oil or for the detection of an adulterant, will be exhaustively dealt with in the chapter treating of the distinctive properties of the individual oils and fats.

[1] *Jour. Soc. Chem. Ind.* 1892, 548.

[2] The reagent is prepared by precipitating a solution of ammonium molybdate with sodium phosphate, washing the precipitate thoroughly and dissolving it in a warm solution of sodium carbonate. The solution is boiled down to dryness and the residue heated. If the residue becomes coloured blue, add a few drops of nitric acid and heat again. Then boil the residue with water, add nitric acid until strongly acid, and dilute so as to obtain a 10 per cent solution. Filter if necessary and keep the reagent protected from dust.

[3] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1894, 619.

Distinction between Oils of Animal and Vegetable Origin

A frequently occurring problem in commercial fat analysis is to detect vegetable oils in oils of animal origin.

It has been shown in the preceding pages that the colour reactions are of very limited value. The methods described below may, however, in some cases lead to definite results if used judiciously. They are based on the fact that (*a*) the vegetable oils, with the exception of olive oil, contain appreciable quantities of phytosterol, whereas animal fats—butter fat, however, excepted—are free from it, they in their turn being characterised by presence of cholesterol; and (*b*) that all vegetable oils and also the vegetable fats hitherto examined contain linolic acid, yielding on oxidation sativic acid; whereas oils of animal origin—excepting the fish, liver, and blubber oils—as a rule contain no other unsaturated acid than oleic acid. This rule, however, breaks down in the case of oils from animals fattened with oleaginous substances (as linseed cakes, maize), notably so in the case of American lard oil (cp. also p. 332).

(1) *Cholesterol or Phytosterol Test.*[1]—50 grms. of the sample are saponified with alcoholic potash; the soap solution is diluted with 1000 c.c. of water and exhausted with ether. When the two layers have separated, the aqueous layer is run off and the ethereal liquid filtered and evaporated to a small bulk. To ensure complete absence of unsaponified fat, it is best to saponify again with alcoholic potash, and to repeat the exhaustion with ether. The ethereal layer is then washed with water and the ether evaporated in a deep basin.

This method being somewhat cumbersome, it will be found preferable to boil out 50 grms. of the sample twice with 95 per cent alcohol, using 75 c.c. each time, then to pour off the alcoholic layers and to saponify only the dissolved portion.[2] The saponified mass is then extracted with ether.

The residue left after evaporating off the ether is next dissolved in hot alcohol, the solution boiled down to 1 to 2 c.c., and the residue allowed to cool. If phytosterol or cholesterol be present, crystals will separate out. They are dried on unglazed porcelain and their melting points determined.

If the sample consisted of a mixture of animal and vegetable oils, as a rule, almost pure phytosterol, melting point 132°-134° C., will be obtained. In the case of, say, an unadulterated cod liver oil the crystals will be pure cholesterol, melting point 146° C. A cod liver oil adulterated with vegetable oils will yield crystals melting at, say, 139°-140° C.; in this case microscopic examination is necessary, and the colour reaction with sulphuric acid (p. 315) must be resorted to.

(2) *Iodine Value of the Liquid Fatty Acids.*[3]—Provided fish, liver, and blubber oils are absent (which may be ascertained by the absence of the peculiar smell and taste of these oils), the determination of the

[1] Salkowski, *Jour. Soc. Chem. Ind.* 1888, 37.

[2] Forster and Riechelmann, *Zeits. öffentl. Chemie*, 3, 10; cp. also Lewkowitsch, *Jour. Soc. Chem. Ind.* 1892, 136; and above, chap. vii. p. 230.

[3] Muter and Koningh, *Analyst*, 1889, 61; and Wallenstein and Finck, *Jour. Soc. Chem. Ind.* 1895, 79.

iodine value of the liquid fatty acids of the sample will furnish the information whether vegetable oils are present. As will be seen from the table giving the iodine values of the liquid fatty acids (p. 312), the vegetable oils, with the exception of cocoa nut oil and palm nut oil, give higher numbers than the animal oils. Tallow oils [1] have almost the theoretical value of oleic acid—90—whereas lard oils vary from 95 to 105 according to their origin.[2] Now, if the iodine value of the liquid fatty acids of a sample be found above 105, it is certain that vegetable oils are present. If numbers lying between 95 and 105 be found, there may be an admixture of a vegetable oil; in such a case *Wellman's* reaction may perhaps be of some help. But if the iodine value of the liquid fatty acids be below 90, then there must be an admixture of cocoa nut oil, provided no unsaponifiable oil be in the sample to a notable extent (cp. "Edible Fats," chap. xii., and "Detection of Cotton Seed Oil in Lard"). It will thus be seen that the opinion held for some time that terrestrial animal oils contain oleic acid only is erroneous, and that we must therefore assume the presence of small quantities of less saturated fatty acids. This has become a certainty since *Kurbatoff* [3] has proved the presence of linolic acid in the fat from the common hare, the white hare, the Caspian seal, the sturgeon, and the shad-fish, and, furthermore, since *Fahrion* has obtained sativic acid from lard—cp. (3), and *Amthor* and *Zink* have discovered drying fats (p. 331).

(3) *Sativic Acid Test. Benedikt* and *Hazura's* method.—50 grms. of the *liquid* fatty acids are oxidised with potassium permanganate (p. 141); the solution is then acidified, the liberated fatty acids extracted with ether, and boiled out repeatedly with water.

A turbidity appearing in the filtrates on cooling does not necessarily prove the presence of sativic acid, since small quantities of soap retained by the precipitated acids may have passed into the filtrate causing opalescence. Again, if a few drops of dilute sulphuric acid have been added to the water employed for washing, in order to decompose the soap, a little dihydroxystearic acid, the oxidation product of oleic acid, will be dissolved. The latter, however, may be easily distinguished from sativic acid by its melting point and crystalline habitus.

Benedikt and *Hazura* were unable to obtain sativic acid from lards rendered by themselves, although they very carefully looked for this substance. The specimen of lard examined by *Fahrion* yielded, however, sativic acid; this confirms the observation frequently made that the food taken by an animal has a considerable influence on the composition of its fat.

Further research must decide whether vegetable oils can be readily distinguished from animal oils by means of the *oleo-refractometer* (cp. p. 263).

[1] Fileti and Baldracco (*Chem. Zeit.* 1896, 239) could not obtain from tallow oleic acid the tetrachlorostearic acid readily yielded by almond oil "oleic" acid.

[2] American lards show higher iodine values than European lards, because in America hogs are fattened with maize.

[3] *Berichte*, 25, Abstracts, 506.

CHAPTER X

APPLICATION OF PHYSICAL AND CHEMICAL METHODS TO THE SYSTEMATIC EXAMINATION OF SOLID FATS AND WAXES

THE fats and waxes considered in this chapter may be recognised chiefly by the following definite characteristics :—

1. Specific gravities.
2. Melting and solidifying points of the fats or waxes.
3. Melting and solidifying points of their fatty acids.
4. Behaviour with solvents.
5. *Hehner* values.
6. *Reichert* (*Meissl*) values.
7. Saponification values.
8. Iodine values.

Further information may be gathered from the acetyl values, thermal tests, and refractive indices.

The consistency, colour, degree of transparency, etc., will, as a rule, give some clue as to the nature of a fat.

As to the *consistency* at ordinary temperature, the various gradations between the butters, lards, and hardest fats will help to limit conveniently the range of substances to which examination may extend.

The *colour* of most fats is almost white or yellowish. However, palm oil in its crude state will always be easily recognisable by its red colour, shea butter by its grey or greenish-grey colour, and laurel oil by its yellowish-green colour.

The examination of the *unsaponifiable matter* will also furnish valuable information in many instances, as notably in the case of waxes.

Many semi-solid or solid fats may be separated by pressure, at the ordinary or slightly higher temperature, into a fluid portion and a solid fat, possessing a higher melting point than the original substance. The separate examination of the two constituents may lead to important conclusions, especially in the case of adulterated samples (see "Beef Tallow").

Reactions affording means of detecting vegetable oils in animal fats have been pointed out above (p. 317). The most reliable method consists in the determination of the iodine value of the liquid

fatty acids.[1] The sativic acid method is more tedious. It may be mentioned that *Benedikt* and *Hazura* have obtained from the liquid fatty acids of palm oil and cacao butter 0·6 and 0·5 per cent respectively of sativic acid. It should, however, be noted that palm oil, in contradistinction to most vegetable oils, is free from phytosterol.

1. Specific Gravities of Solid Fats and Waxes

The recorded specific gravities of fats vary to a considerable extent, as will be seen from the values given for each individual fat in the following chapter. In order to give a synopsis I subjoin several tables.

The following table summarises the results obtained by *Hager* and *Dieterich* for some solid fats and allied substances likely to be met with (as adulterants) in fats :—

Specific Gravities of Solid Fats and Waxes at 15° C.

Kind of Fat.	Hager.	Dieterich.	
Beef tallow	0·925-0·929	0·952-0·953	Fats
Butter fat (clarified)	0·938-0·940	...	
,, ,, (several months old)	0·936-0·937	...	
Artificial butter	0·924-0·925	...	
,, ,,	0·925-0·930	...	
Lard (fresh)	0·931-0·932	...	
,, (old)	0·940-0·942	...	
Mutton tallow	0·937-0·940	0·961	
Mixed beef and mutton tallow (equal parts)	0·936-0·938	...	
Cacao butter (fresh)	0·950-0·952	0·980-0·981	
,, ,, (very old)	0·945-0·946	...	
Nutmeg butter	0·965-0·966	...	
Japan wax	0·977-0·978	0·975	
,, ,, (very old)	0·963-0·964	...	
Beeswax (yellow)	0·959-0·962	0·963-0·964	Waxes
,, (African)	0·960	...	
,, (white)	0·919-0·925	0·973	
Spermaceti	0·960	...	
Stearic acid (fused)	0·964	0·971-0·972	Solid substances met with as admixtures.
,, ,, (crystallised)	0·967-0·969	...	
Ceresin (perfectly white)	0·905-0·908	0·918	
,, (half white)	0·923-0·924	0·920	
,, (yellow)	0·925-0·928	0·922	
Paraffin wax	0·913-0·914	...	
Ozokerit (crude)	...	0·952	
Pine resin (purified)	...	1·045	
Colophony (American)	1·100	1·108	
,, (French)	...	1·104-1·105	

[1] This statement must be qualified, since "drying" animal fats (cp. chap. xi. p. 331) have been detected.

For the reasons stated (chap. v. p. 128) it is more convenient to determine and compare the specific gravities of the solid fats at higher temperatures, *i.e.* in their liquid state.

The following table, due to *Allen*, gives the specific gravities of solid fats and waxes arranged according to their specific gravities at the boiling point of water :—

Class of Fat, Wax, etc.	Specific Gravity at 98° C.-100° C. (Water 15·5° C. = 1.)			
	0·750 to 0·800.	0·800 to 0·855.	0·855 to 0·863.	0·863 to 0·867.
Vegetable fats .	...	..	Palm oil Cacao butter	Palm nut oil Cocoa nut oil Japan wax Myrtle wax *Manufactured.* Cocoa nut stearine Cotton seed stearine
Animal fats .	...	...	Tallow Lard Bone fat *Manufactured.* Oleomargarine Butterine	Butter fat
Waxes . .	...	Spermaceti Beeswax Chinese wax Carnaüba wax		
Fatty acids .	...	Stearic acid Palmitic acid Oleic acid		
Hydrocarbons .	Paraffin wax Ozokerit	Shale products Petroleum products	Vaseline	

Dividing the fats into two groups, according to presence or absence of glycerides of soluble fatty acids, we obtain the two following tables. The values are due to *Allen* and to *Königs*.

[TABLE

A. *Fats, Free from Glycerides of Soluble Fatty Acids*

Class of Fat.	Kind of Fat.	Specific Gravities at 100° C. (Water at 15° C. = 1.)
Vegetable Fats . . .	Cacao butter	0·857
	Palm oil	0·857
	Japan wax	0·8755
Animal Fats . . .	Lard	0·861
	Tallow (beef and mutton)	0·860
	Horse fat	0·861
	Oleomargarine	0·859

B. *Fats, containing Glycerides of Soluble Fatty Acids*

Class of Fat, Wax, etc.	Kind of Fat.	Specific Gravities at 100° C. (Water at 15° C. = 1.)
Vegetable fats . . .	Cocoa nut oil	0·8736
	Palm nut oil	0·8731
Animal fats	Butter fat	0·865-0·868

On comparison, it will be seen that the specific gravities of the fats belonging to group B are higher than those of group A.

Allen has determined the specific gravities of a number of fats at two distant temperatures, and calculated from them the differences per 1° C., by means of which specific gravities determined at temperatures other than the normal temperatures may be reduced to the latter. As pointed out already, *Allen* has calculated the expansion coëfficients of the fats from these differences.

Specific Gravities of Melted Fats, Waxes, etc., at 40° *to* 90° C., *and at* 98°-99° C.

Kind of Fat, Wax, etc.	°C.	Specific Grav. (Water at 15·5° C. = 1.)	°C.	Specific Grav. (Water at 15·5° C. = 1.)	Difference per 1° C.
Palm oil	50	0·8930	98	0·8586	0·000717
Cacao butter	50	0·8921	98	0·8577	0·000717
Japan wax	60	0·9018	98	0·8755	0·000692
Tallow	50	0·8950	98	0·8626	0·000675
Lard	40	0·8985	98	0·8608	0·000650
Oleomargarine	40	0·8982	98	0·8592	0·000672
Butter fat	40	0·9041	99	0·8677	0·000617
Cocoa nut oil	40	0·9115	99	0·8736	0·000642
Palm nut oil	40	0·9119	99	0·8731	0·000657
Spermaceti	60	0·8358	98	0·8086	0·000716
Beeswax	80	0·8356	96	0·8221	0·000750
Carnaüba wax	90	0·8500	98	0·8422	0·000975
Stearic acid (commercial)	60	0·8590	98	0·8305	0·000750
Oleic acid (commercial)	15·5	0·9032	99	0·8484	0·000656
Paraffin wax	60	0·7805	98	0·7530	0·000724

2. Melting and Solidifying Points of Solid Fats and Waxes

The melting and solidifying points recorded in the following tables vary considerably; these variations may be due to the varying condition of the fats, the irregularities during the melting and solidifying, and, lastly, discrepancies inherent to the methods employed.

The following table contains the observations of *Wimmel*, *Rüdorff*, *Bensemann*, *Allen*, and others. (Cp. also the tables given, chap. xi., for the individual fats.)

Melting and Solidifying Points of Fats and Waxes

Kind of Fat, Wax, etc.	Wimmel.			Rüdorff.[1]			Bensemann.	Bach.	Allen.		Terreil.		De Negri and Fabris.	
	Melting Point. °C.	Turbidity sets in at °C.	Temp. rising to °C.	Melting Point. °C.	Solidifying Point. °C.	Temp. rising to °C.	Melting Point. °C.	Solidifying Point. °C.	Melting Point. °C.	Solidifying Point. °C.	Melting Point. °C.	Solidifying Point. °C.	Melting Point. °C.	Solidifying Point. °C.
Beef tallow, fresh	43	33	36-37	43·5-45	27-35	Several degrees	..	44-49	..	..	46	36	..	..
Beef tallow, old	42·5	34	38	..	..	..	..	..	..	..	..	..	..	..
Mutton tallow, fresh	47	36	40-41	46·5-47·4	32-36	Several degrees	..	..	..	..	52	37	..	..
Mutton tallow, old	50·5	39·5	44-45	..	..	..	..	..	..	..	..	..	..	..
Lard	41·5-42	30	32	..	..	..	..	42	44	39	36	32	..	..
Butter, fresh	31-31·5	19-20	19·5-20·5	..	..	..	34-35	..	..	..	..	..	..	..
Butter, old	32·5	24	25·5	..	..	..	..	..	..	..	..	..	..	..
Japan wax	52·5-54·5	40·5-41	45·5-46	50·4-51	..	50·8	..	..	56	53	..	..	..	..
Myrtle wax	..	..	..	..	..	..	..	..	47·5	46	..	..	..	..
Cacao butter	24·5	20-20·5	22-23	33·5	..	27·3	25-26 28-29	..	..	..	..	..	..	..
Laurel oil	..	..	..	..	..	..	..	..	..	..	..	..	32-34	25
Palm oil, fresh, soft	30	21	21·5	..	..	..	..	..	50	45·5	..	..	..	..
Palm oil, fresh, hard	36	24	35	..	..	..	..	..	..	..	..	..	..	..
Cocoa nut oil	..	..	..	..	..	..	..	..	24	20·5	..	..	23-28	14-20
Nutmeg butter	43·5-44	33	41·5-44	47-48	..	41·7-41·8	..	..	..	..	..	..	..	..
Beeswax, yellow	62-62·5	Solidify immediately below melting point without rise of temperature.		63·4	61·5 62·6 62·3	..	..	..	..	..	..	..	..	..
Beeswax, white	..			61·8	61·6	..	..	..	..	..	64	63	..	..
Spermaceti	44-44·5			43·5	43·4	..	..	..	..	..	..	..	..	..
Carnaüba wax	..	..		44·1-44·3	44·2	..	..	..	..	..	85·5	78	..	..
Stearic acid, commercial	..	..	..	53·3 56·2-56·6 56-56·4	55·2 55·8 55·7	..	..	..	..	..	59	..	..	..
Paraffin wax	..	..	..	49·6 52·5-54 53 52·7-53·2	49·6 53·0 52·9 52·7	..	..	..	..	..	45	43	..	..

[1] Rüdorff considers as melting point the temperature at which the warmed fat drops off the bulb of a thermometer coated with it.

Further data regarding melting points will be found in the following chapter.

3. Melting and Solidifying Points of the Mixed Fatty Acids from Fats and Waxes

It has been repeatedly pointed out that the determination of the melting and solidifying points of the mixed fatty acids gives more information as to the nature of a fat than the determination of the melting and solidifying points of the fat itself. I subjoin several tables giving the melting points of mixed fatty acids recorded by several observers. (Cp. also the tables given, chap. xi., for the individual fats.)

[TABLE

Melting and Solidifying Points of Mixed Fatty Acids

Mixed Fatty Acids from	Hübl.		Bensemann.		Terreil.[1]		Rüdorff.		De Negri and Fabris.	
	Melting Point. °C.	Solidifying Point. °C.	Point of Incipient Fusion. °C.	Point of Complete Fusion. °C.	Melting Point. °C.	Solidifying Point. °C.	Melting Point. °C.	Solidifying Point. °C.	Melting Point. °C.	Solidifying Point. °C.
Mutton tallow	...	...	49-50	53-54	54	47				
Beef tallow	45	43	43-44	46-47	49·5	43·5				
			42-43	45-46						
Palm oil	47·8	42·7								
Cacao butter	52	51	48-49	51-52						
			49-50	52-53						
Nutmeg butter	42·5	40								
Lard	...	...	43-44	46-47	43	39				
Oleomargarine	42	39·8								
Artificial butter, Dutch	...	...	39-40	42-43						
Butter	38	35·8	41-42	43-44						
			41-42	44-45						
			42-43	44-45						
Goose fat	...	...	37-38	40-41						
Laurel oil	27	22								
Cocoa nut oil	24·6	20·4	...	...	...	...	...	...	25-27	16-18
Wool fat	41·8	40								
Stearic acid (commercial)	...	...	...	...	59 58	53·5 52	55·3 56·2-56·6 56·0-56·4	55·2 55·8 55·7		

[1] *Jour. Soc. Chem. Ind.* 1890, 744.

The melting and solidifying points of the mixed fatty acids of the most important commercial fats, as tallow and palm oil, will be dealt with in the following two chapters (cp. p. 519).

The writer recommends as the most reliable method, especially for the commercial valuation of fats, the determination of the "titer test." The following table gives the results collated from a very large number of observations made by the writer during a number of years :—

Titer Tests of Mixed Fatty Acids (Lewkowitsch)

Class of Fat.	Kind of Fat.	Titer Test.	Remarks.
Vegetable fats	Cotton seed stearine	34·9 –35·1	
	Chaulmoogra oil	39·5 –39·6	
	Laurel oil	14·3 –15·1	
	Mowrah seed oil	38·3 –38·5	
	Shea butter	53·75–53·8	
	Vegetable tallow[1]	52·1 –53·4	
	Palm oil, Bonny	35·8 –35·9	
	,, Bassam	38·0 –38·47	
	,, Lagos	43·8 –43·925	
	,, Old Calabar	44·3 –44·6	
	,, Salt Pond	44·3 –44·475	
	,, New Calabar	45·4 –45·55	
	,, Congo	44·9 –45·05	
	Macassar oil	51·6 –53·2	
	Sawarri fat	46·0 –47·0	
	Nutmeg butter	35·5 –35·95	
	Cacao butter	48·0 –48·27	
	Palm nut oil	20·0 –20·5	Lowest
	,, ,,	24·6 –25·5	Highest
	Cocoa nut oil, commercial	21·2 –22·55	Lowest
	,, ,,	24·8 –25·2	Highest
	,, Cochin	24·8 –25·2	
	Japan wax	58·8 –59·4	
Animal fats	Horse fat	33·6 –33·7	
	Horse marrow	38·4 –38·55	
	Lard	41·45–42·0	
	Beef tallow, English	38·45–38·7	Lowest
	,, ,, ,,	45·0 –45·1	Highest
	,, ,, North American	38·9 –41·1	Lowest
	,, ,, ,, ,,	43·3 –44·15	Highest
	,, ,, South American	42·75–42·95	Lowest
	,, ,, ,, ,,	45·7 –46·25	Highest
	,, ,, Australian	37·9 –38·3	Lowest
	,, ,, ,,	43·05–43·3	Highest
	Mutton tallow, English	40·15–41·5	Lowest
	,, ,, ,,	47·5 –48·3	Highest
	,, ,, Australian	41·65–42·35	Lowest
	,, ,, ,,	47·8 –48·05	Highest
	Beef marrow	37·9 –38·0	

[1] Commercial.

4. Behaviour with Solvents

Dubois and *Padé* have studied the solubility of some solid fats in benzene and of their mixed fatty acids in absolute alcohol. Their observations are given in the following two tables :—

Solubility of Solid Fats and Benzene

Kind of Fat.	100 grms. of Benzene dissolve at 12° C.
	Grms.
Mutton tallow	14·70
Beef tallow	15·89
Veal tallow	26·08
Lard	27·30
Butter fat	69·61
Margarine	12·83

Solubility of Mixed Fatty Acids in Absolute Alcohol

Mixed Fatty Acids from	100 Grms. of absolute Alcohol dissolve	
	at 0° C.	at 10° C.
	Grms.	Grms.
Mutton tallow	2·48	5·02
Beef tallow	2·51	6·05
Veal tallow	5·00	13·78
Lard	5·63	11·23
Butter fat	10·61	24·81
Margarine	2·37	4·94

The indications furnished by *Valenta's* test are less characteristic than those recorded in the last two tables. *Valenta's* turbidity temperatures for some of the solid fats have been given already (p. 271). (Cp. also "Butter Fat," p. 619).

5. Hehner Values

The *Hehner* value for the majority of solid fats lies between 95 and 96. The following fats containing considerable quantities of glycerides of soluble fatty acids form notable exceptions :—

Kind of Fat.	Hehner Value.
Butter fat	87·5
Cocoa nut oil	89·6
Palm nut oil	91·1
Mocaya oil[1]	—

[1] Although the *Hehner* value has not been determined, yet there can be no doubt but that the value in this case will lie in the neighbourhood of 90.

On saponifying **waxes**, such as beeswax and wool wax, the fatty substance separating on acidulating the alcoholic solution consists of a mixture of fatty acids and (unsaponifiable) insoluble alcohols. Therefore, in these cases an apparent *Hehner* value of more than 100 will be found, water having been assimilated during the saponification. In order to find the real *Hehner* value, it is necessary to separate, by shaking with ether, the alcohols from the soap solution, and to acidulate the latter. The *Hehner* value, however, is not taken in the case of waxes, other characteristics more readily enabling us to distinguish them from glycerides.

6. Reichert-Meissl Values

The *Reichert-Meissl* value of most fats and waxes lies below 1; the following exceptions are notable, the *Reichert-Meissl* value serving in these cases as a most valuable means of identifying and readily distinguishing them from other fats.

Kind of Fat.	Reichert-Meissl Value.
Butter fat	28
Cocoa nut oil	7
Mocaya oil	7
Palm nut oil	5

7. Saponification Values

Most solid fats have saponification numbers varying from 195 to 197, only the saponification values of butter fat, cocoa nut oil, probably also Mocaya oil, and palm oil are exceptionally high. The four fats forming the exception are recorded in the following table :—

Kind of Fat.	Mean Saponification Value.
Butter fat	227
Cocoa nut oil	255
Palm nut oil	247
Mocaya oil[1]	—

The saponification values of all the waxes are considerably lower, as shown in the following table :—

Kind of Wax.	Mean Saponification Value.
Insect wax	63
Carnaüba wax	79-95
Beeswax	97-107
Wool wax	102·4
Spermaceti	129

8. Iodine (and Bromine) Values

The iodine (and bromine) values of the solid fats and waxes, and their mixed fatty acids, as far as they have been determined, are collated in the following table. The means given do not always represent the actual means (cp. p. 303) :—

[1] Not determined yet, but it is very likely that the value will be about 250.

Iodine (and Bromine) Values of Solid Fats and Waxes, and of their Mixed Fatty Acids

Kind of Fat.	Bromine Value.	$\frac{Br \times 127}{80}$	Iodine Values of						Class of Fat or Wax.
			Fat or Wax.			Fatty Acids.			
			Minim.	Maxim.	Mean.	Minim.	Maxim.	Mean.	
Cotton stearine	...	...	88·7	93·6	91·2	...	...	94·3	Vegetable Fats
Chaulmoogra oil	...	...	...	...	90·6	...	...	86·0	
Carapa oil	...	...	...	...	72·1	...	...	...	
Laurel oil	...	...	49	80	64	...	...	...	
Mowrah seed oil	...	...	50·1	62·0	56·1	...	...	56·7	
Shea butter	...	...	56·2	56·9	56·5	56	57	56·5	
Vegetable tallow	...	...	52·2	52·53	52·3	54·1	54·8	54·4	
Vegetable tallow, commercial	...	...	32·1	45·2	38·6	34·2	47·0	40·6	
Palm oil	35·44	56·2	51·5	52·4	52·0	...	...	...	
Macassar oil	...	...	48·3	53	50·5	49·7	50·7	50·2	
Sawarri fat	...	...	...	...	49·5	...	...	51·5	
Mafura tallow	...	...	44·8	46·1	45·5	46·9	48·2	47·5	
Nutmeg butter	...	...	31	52	41·5	...	...	...	
Rambutan tallow	...	...	...	...	39·4	...	...	41·0	
Mkanyi fat	...	...	...	...	38·6	...	...	...	
Cacao butter	...	...	32	36·6	34·3	...	...	39·1	
Kokum butter	...	...	...	...	33·1	...	...	...	
Borneo tallow	...	...	...	...	(31 ?)	...	...	...	
Dika oil	...	...	30·9	31·3	31·1	...	...	...	
Mocaya oil	...	...	...	...	24·6	...	...	...	
Palm nut oil	...	...	10·3	17·5	13·5	...	...	12·1	
Cocoa nut oil	...	...	8	9·3	8·7	8·4	9·3	8·9	
Myrtle wax	6·34	10·7	...	...	...	...	...	...	
Ucuhuba fat	...	...	...	...	9·5	...	...	...	
Japan wax	1·53-2·33	2·4-3·7	4·2	6·6	5·8	...	...	...	

Iodine (and Bromine) Values of Solid Fats and Waxes, and of their Mixed Fatty Acids—continued.

Kind of Fat.	Bromine Value.	$\frac{Br \times 127}{80}$	Iodine Values of						Class of Fat or Wax.
			Fat or Wax.			Fatty Acids.			
			Minim.	Maxim.	Mean.	Minim.	Maxim.	Mean.	Animal Fats.
Blackcock fat	..	..	..	..	121·1	..	..	120	(Drying fat)
Hare fat	..	..	..	..	102·2	..	..	93·3	,,
Wild rabbit fat	..	..	..	..	99·8	..	..	101·1	,,
Wild goose fat	..	..	..	..	99·6	..	..	..	
Wild duck fat	..	..	..	..	84·6	..	..	..	
Starling fat	..	..	..	..	83·7	..	..	79·4	
Pigeon fat	..	..	..	..	82·3	..	..	..	
Turkey fat	..	..	..	..	81·15	..	..	70·7	
Fox fat	..	..	..	..	79·7	..	..	65·4	
Horse fat	35·67	56·7	71·4	86·1	78·7	74·4	84	81·0	
Wild boar fat	..	..	..	..	76·6	..	..	81·2	(Drying fat)
Badger fat	..	..	..	..	71·3	..	..	73	
Pine marten fat	..	..	..	..	70·2	..	..	53	
Tame rabbit fat	..	..	..	..	67·6	..	..	64·4	
Goose fat	..	..	66·4	71·5	67	..	..	65·3	
Chicken fat	..	..	..	..	66·7	..	..	64·6	
Polecat fat	..	..	..	..	62·8	..	..	60·6	
Human fat	..	..	..	..	61·5	..	..	64	
Lard	..	..	..	70·4	59	..	..	64·2	
Dog fat	..	..	..	..	58·5	..	..	50·2	
Wild cat fat	..	..	..	..	57·8	..	..	58·8	
Domestic cat fat	..	..	..	..	54·5	..	..	54·8	
Beef marrow	..	..	55·2	55·6	55·4	..	..	55·5	
Bone fat	..	..	46·3	55·8	51·0	55·7	57·4	56·5	
Beef tallow	..	..	35·4	44	40	25·9	41·3	41	
Mutton tallow	..	..	32·7	46·2	42	..	..	..	
Elk fat	..	..	..	..	35	..	..	27·8	
Roebuck fat	..	..	..	..	32·1	..	..	27·9	
Butter fat	..	..	19·5	38·0	30	..	..	..	
Fallowbuck fat	..	..	..	..	26·4	..	..	28·2	
Chamois fat	..	..	..	..	25	..	..	24·4	
Stag fat	..	..	20·5	25·7	23	..	..	23·6	
Carnaüba wax	33·5	53·2	..	..	13·5	..	..	..	Vegetable Wax
Wool wax	..	..	25·8	28·9	27·3	..	..	17	Animal Waxes
Beeswax	0·0-0·54	0·0-0·86	8·3	11·0	9·6	..	..	..	
Spermaceti	..	..	..	..	(3·7)	..	..	..	

The liquid fatty acids of the animal oils were until recently considered to consist of oleic acid only, and this was thought naturally to constitute an important difference between vegetable and animal fats. It has, however, been proved that some animal fats contain less saturated fatty acids than oleic, notably so, lard, and especially American lards. It is very likely that the less saturated acid is linolic acid, as *Fahrion* obtained sativic acid on oxidising the liquid fatty acids from lard.

In the case of hare fat, in which also linolic acid has been proved to be present by *Kurbatoff*, the iodine value is as high as 102·2, and in the case of blackcock fat it rises to 121·1. It is therefore not surprising that the hare fat should exhibit drying properties; blackcock fat, however, although possessing the higher iodine number, has less marked drying properties than hare fat. Also two other animal fats, viz. that of the wild rabbit and of the wild boar, dry on exposure to the air, so that in a similar fashion to the subdivision of oils into drying and non-drying oils we may classify the animal fats into drying fats and non-drying fats. The former would in some sense correspond to the oils of marine animals. Nor is there wanting a fat forming, as it were, the intermediate link between the drying and the non-drying fats. This is represented by wild boar fat, whereas the ordinary lard has no drying properties whatever at the ordinary temperature. The high iodine values of the American lards are due to the mode of fattening the hogs in the United States. The iodine values of fats from cattle fed on oil cakes is higher than those fed on grass, from which one may conclude that domestic animals yield fats richer in olein than wild animals. The contrary, however, appears to be true, judging from several determinations made by *Amthor* and *Zink*.[1] These are given in the following table:—

Fat from	Iodine Value.
Rabbit, wild	101·1
,, tame	64·4
Goose, wild	99·6
,, wild, held in captivity 2 years	67·0
,, domestic	67·6
Duck, wild	84·6
,, domestic	58·5
Hog, wild boar	76·6
,, domestic	63 (max.)
Cat, wild	57·8
,, domestic	54·5

The iodine value of the liquid fatty acids has become of the greatest importance in the examination of the animal fats used as edible fats. For this reason the numbers given in the following table will be found useful:—

[1] *Zeits. f. analyt. Chemie*, 1897, 1.

Kind of Fat.	Iodine Value of Liquid Fatty Acids.	Observer.
Cocoa nut oil . .	54·0	Wallenstein and Finck
Tallow, beef . .	92·2-92·7	,, ,, ,,
Lard, European . .	95·2-96·6	,, ,, ,,
,, home rendered .	90	Dieterich
,, American . .	103-105	Wallenstein and Finck
,, ,, . .	97·8-103·2	Raumer

9. Acetyl Values

The determination of the acetyl values is hitherto of little use in the examination of solid fats. The following numbers have been determined by *Lewkowitsch*[1] :—

Fat.	Acetyl Value.
Cocoa nut oil	0·0
Beef marrow	4·2
Tallow	5·4
Butter	0·0
Horses' foot oil	9·1-10·3

Thermal Tests.—*Maumené's* thermal reaction test is but rarely employed in the examination of solid fats. It has, however, been used with advantage for the detection of vegetable oils in lard and butter fat. The heat of bromination test is likely to supersede the Maumené test on account of the shorter time required to carry out the operation (cp. p. 300).

For the **sulphur chloride test** compare chap. ix. p. 282, and under "Lard," chap. xi. p. 582.

The **refractive indices** of several fats and of their fatty acids, determined by *Thörner*,[2] are given in the following table :—

Kind of Fat.	Refractive Index at 60° C.	
	of the Fat.	of the Mixed Fatty Acids.
Palm oil . .	1·4510	1·4441
Cacao butter .	1·4496	1·4420
Palm nut oil .	1·4431	1·4310
Cocoa nut oil .	1·4431	1·4295
Lard . . .	1·4410	1·4395
Tallow, Beef .	1·4539	1·4375
,, Mutton .	1·4510	1·4374
Butter . .	1·445-1·448	1·437-1·439
Margarine . .	1·443-1·453	1·443-1·444

For further information under this head cp. "Lard" (p. 577) and "Butter" (p. 623).

[1] *Jour. Soc. Chem. Ind.* 1897, 506. Other acetyl values recorded for fats have been omitted as being evidently incorrect (cp. Butter Fat, p. 604). [2] *Ibid.* 1895, 43.

CHAPTER XI

DESCRIPTION OF NATURAL FATS AND WAXES: METHODS OF EXAMINING THEM AND DETECTING ADULTERATIONS

We now come to the consideration of the individual natural fats and waxes, arranging them according to the classification adopted in the two preceding chapters. The tables appended will be found to give in a handy form the physical and chemical constants of each fat and wax, as recorded by the various observers, and also the variations, within narrow limits, of these constants as found in the examination of different specimens of the same kind of fat or wax,—due to the difference of age, source, mode of preparation, etc. It is hoped that by following this plan the analyst will have placed in his hand a ready means of identifying any unknown fat or wax that he may have to examine.

The methods followed in testing for adulteration will also be found fully described in each case.

It should be mentioned that the writer has very carefully examined the various colour reactions that have been proposed from time to time (see chap. ix. p. 313), and, as the result of his investigations, many of those reactions usually found in text-books have been omitted as worthless.

As the order in which the fats and waxes are enumerated here is determined by the iodine value, a number of these values had to be ascertained by the writer.

The subject matter will be found arranged under two principal divisions and a number of subdivisions.

A. OILS AND FATS. GLYCERIDES

I. OILS OR LIQUID FATS

1. VEGETABLE OILS

(1) Drying Oils
(2) Semi-drying Oils
(3) Non-drying Oils

2. ANIMAL OILS

(1) Marine Animal Oils

α. **Fish Oils**

β. **Liver Oils**

γ. **Blubber Oils**

(2) Terrestrial Animal Oils

II. SOLID FATS

1. Vegetable Fats

2. Animal Fats

B. WAXES. NON-GLYCERIDES

I. LIQUID WAXES

II. SOLID WAXES

1. VEGETABLE WAXES

2. ANIMAL WAXES

A. OILS AND FATS. GLYCERIDES

I. OILS OR LIQUID FATS

1. VEGETABLE OILS

(1) Drying Oils

The general characters of drying oils have been described already (p. 279). The following are the most important drying oils conveniently arranged according to their iodine values, as approximately indicating the order of their drying powers: Linseed oil, Japanese wood oil, Lallemantia oil, hemp seed oil, walnut oil, poppy seed oil, Niger seed oil, sunflower oil, fir seed oil, madia oil, candle nut oil. Lesser known oils are: Isano oil, Mohamba oil, garden rocket oil, henbane seed oil, celosia oil, Indian laurel oil, tobacco seed oil, weld seed oil.

LINSEED OIL

French—*Huile de lin.* German—*Leinoel.*

For tables of constants see pp. 338-340.

Linseed oil is obtained from the seeds of the flax plant, *Linum usitatissimum*, L. The principal countries where it is grown and whence the seed is shipped to this country are Russia and India. Two qualities of Russian seed are recognised in the trade, and known, according to their source, as Baltic and Black Sea seed; hence Baltic linseed oil and Black Sea linseed oil. The oil expressed from Indian seed is known as East India oil. The Baltic linseed oil, yielding the best drying oil, is the first, the East Indian the lowest in quality; this is explained by the fact that the Baltic seed is the purest, whereas in Black Sea seed 5 per cent of hemp seed or ravison seed is usually present, and that Indian seed is always mixed with mustard, rape, and cameline seed, owing to the plants yielding the latter being grown along with the flax plant. For it has been proved by experiments that if the linseed was carefully separated from the foreign seeds and then expressed, the oil was possessed of as good drying properties as best Russian oil. The addition of hemp seed or ravison seed to Black Sea oil has, however, been recently abandoned, and it is hoped that more attention will be paid in India to this growing industry. South American seed, yielding the River Plate oil, has recently been imported into this country, as also Canadian oil, in small quantities.

Linseed oil expressed from the seed in the cold has a golden yellow colour; the oil obtained at a higher temperature is of a yellowish-brown hue.

The taste and odour are peculiar, that of the oil obtained by hot pressure being more pronounced and more acrid than the cold-drawn oil.

On exposure to the air linseed oil turns easily rancid with absorption of oxygen; when spread in a thin film on a large surface it dries to a neutral substance insoluble in ether, termed linoxyn, the nature of which has not hitherto been ascertained. The linoxyn in its turn is further oxidised to a liquid substance (chap. xii. p. 738).

Linseed oil contains about 10 to 15 per cent of glycerides of solid fatty acids—stearic, palmitic, and myristic—and 90 to 85 per cent of liquid glycerides. The liquid fatty acids consist, according to *Hazura* and *Grüssner*,[1] of about 5 per cent of oleic, 15 per cent of linolic, 15 per cent of linolenic, and 65 per cent of isolinolenic acids.

Pure linseed oil, prepared by *Moerk*[2] from pure seed, dissolved in 5 parts of absolute alcohol; by the purification of the oil with sulphuric acid the solubility is decreased. *Girard's* figure has been stated above (p. 269), as also the solubility in acetic acid (p. 271).

The amount of free acid in commercial linseed oil has been determined by *Nördlinger*,[3] *Thomson* and *Ballantyne*,[4] and *Deering*.[5] The following table gives their results:—

Free Fatty Acids in Linseed Oil

Observer.	No. of Samples.	Free Acid as Oleic Acid.
		Per cent.
Nördlinger	10	0·41-4·19
Thomson and Ballantyne .	4	0·76-3·74
Deering	5	0·75-1·60

The proportion of unsaponifiable matter in linseed oil has been found by *Thomson* and *Ballantyne* to vary between 1·09 and 1·28 per cent.

For the purposes of ascertaining the purity of linseed oil and its drying power, and for the detection of adulterations, its specific gravity and iodine value are determined, and the thermal tests (p. 291) and *Livache's* (p. 285) test applied.

Linseed oil possesses a higher **specific gravity** than any fatty oil that would be used as an adulterant with the exception of Japanese wood oil. A lower gravity than 0·930 would point to the presence of fish oils or mineral oils; a higher gravity would indicate probable adulteration with resin oils. According to *Allen*, linseed oil, intended for the manufacture of boiled oil, should possess a specific gravity of not less than 0·935.

[1] *Jour. Soc. Chem. Ind.* 1888, 506. [2] *Ibid.* 1888, 330.
[3] *Ibid.* 1889, 806. [4] *Ibid.* 1891, 236.
[5] *Ibid.* 1884, 541.

Physical and Chemical Constants of Linseed Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
12	0·939	Saussure	– 16 (after several days' standing)	Gusserow	– 16 to – 20	Glaessner	187·6	Dieterich	170-181	Benedikt
15	0·9347	Schübler	...	...	...	...	189-195	Allen	173·5-187·7 [1]	Thomson and Ballantyne
,,	0·9325	Souchère	...	...	...	...	190·2-192·7	De Negri and Fabris	171-175	Lewkowitsch
,,	0·932-0·937	Allen	– 27	Chateau	...	...	195·2	Moore	172-180	Holde
,,	0·9315-0·9345	Thomson and Ballantyne	...	...	...	...	201-221	Coreil	177-178	Thoerner
,,	0·9342	De Negri and Fabris	...	...	...	...	190-192	Thoerner	183-188 [1]	Williams
18	0·9299	Stilurell								
25	0·930	Saussure								
50	0·921	,,								
94	0·881	,,								
99 (water at 15·5 = 1)	0·8809	Allen								

[1] These numbers must be accepted with reserve, as the iodine was allowed to act on the oil far too long a time.

Physical and Chemical Constants of Linseed Oil—continued

Acetyl Value.		Thermal Tests.				Refractive Index.		
		Maumené Test.		Heat of Bromination.				
	Observer.	°C.	Observer.	°C.	Observer.	At °C.		Observer.
6·85-7·03	Lewkowitsch	103	Maumené	30·4-31·3	Hehner and Mitchell	15	1·4835	Strohmer
		61	Jean			60	1·4660	Thoerner
...	...	104-124	Baynes	31·4-32·5[1][2]	Archbutt		Oleo-refractometer.	
...	...	104-111	Allen	29·8-30·5[1][3]	,,		"Degrees."	Observer.
...	...	122-126	De Negri and Fabris				+48 to +53	Jean
		Specific Temperature Reaction.					+48 to +52	Bruyn and van Leent
		320 to 349	Thomson and Ballantyne				+50 to +54 (at 22° C.)	Pearmain
		313	Jenkins					

[1] The rise of temperature observed multiplied by two, as 0·5 grm. of oil only was used. [2] Baltic oil. [3] East India oil.

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60 °C.	Observer.
15·5	0·9233	Allen	13·3	Hübl	17	Hübl	198·8	Dieterich	283	Williams	178·5	Williams	1·4546	Thoerner
99 (water at 15·5 = 1)	0·8612	,,	17·5	Allen	24	Allen	196	Thoerner	307·2	Allen	159·85	De Negri and Fabris		
			13·5	Thoerner	Below 13	Dieterich					179-182	Lewko-witsch		
100 (water at 100 = 1)	0·8925	Archbutt	16-17	De Negri and Fabris	20-21	De Negri and Fabris					155	Thoerner		
			Titer Test.											
			19·0-19·4	Lewko-witsch										
			20·2-20·6	,,										

Linseed oil, being the best drying oil, next to Japanese wood oil, possesses the highest **iodine value** of all known fatty oils. Unfortunately the published values disagree to a considerable extent, the older numbers being much too low, owing to too small an excess of iodine solution having been used by the earlier experimenters (*Benedikt*[1]). Thus *Hübl* had found 156-160, *Moore* 155·2, *Dieterich* 161·9-180·9, and *Wilson* 148·1-149·1. Since then the more correct values, registered in the above given tables, have been obtained. Some chemists, however (*Thomson* and *Ballantyne*, *Williams*, *Filsinger*), go further, and allow the iodine to act 18 and more hours on the oil, and, consequently, obtain higher numbers. Such arbitrary alteration of a standard method is, however, not admissible.

Fahrion[2] has pointed out that the iodine value of linseed oil does not reach the figure calculated for its composition as given by *Hazura* and *Grüssner* (see above), and he assumed, therefore, that raw linseed oil is partly polymerised during the process of manufacture. The fact, however, that, according to their own showing, *Hazura* and *Grüssner's* results represent but an approximation to the true values, should be sufficient to overthrow *Fahrion's* hitherto unsubstantiated assumption.

The iodine value of fresh linseed oil should, therefore, as a rule, be above 170. A decrease of this value consequent upon exposure to the air has been shown to take place by *Ballantyne*.[3] This observer obtained for a sample of linseed oil, originally absorbing 173·46 per cent of iodine, after exposure to sunlight in an uncorked bottle and daily agitation, the following numbers :—

After one month . . .	171·8
„ two months . . .	171·78
„ five „ . . .	169·07
„ six „ . . .	166·17

Another sample of the same oil, but kept in a corked bottle, though exposed to sunlight, possessed after that time very nearly the original value, viz. 172·88.

A sample of linseed oil, that had been kept by the writer for seven years in a stoppered bottle, absorbed 162·3 per cent of iodine.

The following results given by *Thomson* and *Ballantyne*[4] for various brands of linseed oil are also instructive, being made under the same conditions :—

Kind of Linseed Oil.	Iodine Value.
Baltic	187·7
East India	178·8
River Plate	175·5
„ „	173·5

The **temperature reaction** of linseed oil with sulphuric acid—*Maumené* test—is also very characteristic, linseed oil giving the

[1] *Zeit. f. angew. Chemie*, 1887, 213. [2] *Ibid.* 1892, 172.
[3] *Jour. Soc. Chem. Ind.* 1891, 31. [4] *Ibid.* 1891, 236.

highest rise of temperature with the exception of some fish oils (cp. p. 293). The better a linseed oil for varnish-making, the more pronounced is the thermal reaction, as shown by the following short table due to *Baynes*[1]:—

Kind of Linseed Oil.	Rise of Temperature. °C.
Baltic, two years old	124
,, similar sample	123
English, old sample	115
Russian	113
River Plate	112
East Indian, fresh	104

The **bromine thermal value** is, in correspondence with the *Maumené* test and the iodine value, also the highest on record.

The values obtained are given in the following table:—

Kind of Linseed Oil.	I. Bromine Thermal Value °C.	II. Hübl Iodine Value.	I×5·5.	I×5·7.	I×6·0.	Observer.
...	30·4	160·7	167·2	...	...	Hehner & Mitchell
...	31·3	154·9	172·0	...	...	,, ,,
Raw linseed	30·55	174·3	...	173·9	...	Jenkins[2]
Old sample	28·5	167·1	...	...	171·0	,,
...	28·8	177·0	...	...	172·8	Archbutt[3]
American (?)	29·6	177·0	...	...	177·6	,,
...	29·7	177·8	...	...	178·2	,,
East Indian	29·8	178·7	...	...	178·8	,,
,, ,,	30·45	183·3	...	..	182·7	,,
Baltic	31·35	188·5	...	...	188·1	,,
,,	31·4	188·8	...	...	188·4	,,
,,	31·75	188·8	...	...	190·5	,,
,,	32·5	192·5	...	...	195·0	,,

Livache's test yields the highest numbers for linseed oil (see p. 285), as also does, of course, the oxygen absorption test proposed by *Fahrion* (p. 288). Therefore the commercial value of a sample of linseed oil intended for the manufacture of varnish is best ascertained by determining its oxygen absorption power.

Linseed oil is further characterised by not yielding a solid elaïdin.

The colour reactions, such as *Brullé's*, *Heydenreich's*, *Hauchecorne's*, are not characteristic enough to be used as a means of distinguishing linseed oil from other oils, or to ascertain its presence in mixtures of oils, the concentrated sulphuric acid test (p. 315) excepted. On allow-

[1] Allen, *Com. Org. Analys.* ii. 123. [2] *Jour. Soc. Chem. Ind.* 1897, 194.
[3] *Ibid.* 1897, 311.

ing 2 drops of concentrated sulphuric acid to fall into 10 drops of linseed oil, a reddish-brown clot is produced ; if other oils are present the linseed oil (and other drying oils) only is resinified, and the brown clots are readily observed as they float in the unresinified oil.

Adulteration of Linseed Oil. — Linseed oil being one of the cheapest fatty oils—sometimes even cheaper than cotton seed oil—a fraudulent admixture of a *vegetable* oil will seldom occur. However, presence of vegetable oils, of the *rape* oil and *cotton seed* oil group, would be revealed at once by the considerably lower iodine value of the sample. *Rape oil* would be indicated by a lower saponification value than the normal one (p. 305) [in the absence of unsaponifiable matter], and *cotton seed oil*, perhaps, by the colour test with nitric acid, etc. (see "Cotton Seed Oil," p. 381).

The presence of vegetable oils belonging to the drying oils, such as *hemp seed oil* or *Japanese wood oil*, would not be pointed out unmistakably by the iodine value, their iodine absorptions being too close to those of pure linseed oil. Admixture of Japanese wood oil, if such should occur, would most likely be ascertained by the determination of the viscosity of the sample.

As some *fish oils* assimilate fully as much iodine as linseed oil, the iodine test would be of no practical use for the detection of such oils. The presence of *fish oils* would, however, be recognised by the characteristic smell of the oil, especially on warming, and perhaps also by the intensity of the phospho-molybdic acid colour reaction (see p. 475).

According to *Livache*[1] linseed oil fatty acids are frequently used as an adulterant. Their presence in linseed oil would be detected by a considerable acid value of the sample ; the acids could be separated from the oil by agitating the sample with alcohol, in which linseed oil is but sparingly soluble.

Adulteration with *mineral oils* and *resin oils* is frequently practised. If only one of these two oils be the adulterant used, the specific gravity of the sample would indicate the line of examination. A judiciously prepared mixture of both oils, however, might possess the specific gravity of linseed oil. The presence of either adulterant, however, is recognised by the estimation of the *unsaponifiable matter* (p. 218). This determination yielding unmistakable results, the tests proposed by *Coreil*[2]—viz. action of gaseous chlorine and determination of the saponification value, and subsequent calculation on the basis of assumed average values—are altogether superfluous. If the further examination of the unsaponifiable matter be desired, especially with a view to ascertaining the presence of either *mineral* oil or *resin* oil, the methods pointed out above must be resorted to (p. 225).

Aignan[3] states that the French linseed oils are, as a rule, adulterated with resin oil, and recommends the polarimetric method for its detection. Linseed oil being optically inactive (or at all events almost so for all practical purposes) he employs a saccharimeter (or

[1] *Vernis et Huiles Siccatives*, Paris, 1896, p. 158.
[2] *Jour. Soc. Chem. Ind.* 1892, 550. [3] *Ibid.* 1890, 903.

any other polarimetric apparatus), a deviation to the right indicating resin oil.

Resin itself is best detected in linseed oil by applying the *Liebermann-Storch* reaction (p. 226). If the oil be very dark in colour, extraction of resin with alcohol may be resorted to. The amount of resin can be determined quantitatively by titration of the sample of oil with aqueous normal alkali, using phenolphthalein as an indicator, subtracting, however, from the amount of alkali used the small quantity of alkali required for free acid in the linseed oil (from 0·4 to 4 per cent). Test experiments instituted in the writer's laboratory proved the correctness of this method (cp. p. 239).

Linseed oil is used as stock material for soft soaps ; its principal application, however, is found in the manufacture of boiled oil for paints and varnishes. On treatment with yellow sulphur chloride a rubber-like mass is obtained, used as a rubber substitute ; on heating with sulphur the official *oleum lini sulf.* is obtained.

Boiled oil and the rubber substitute obtained from linseed oil will be described in the following chapter (pp. 736, 742).

JAPANESE WOOD OIL [1]

French—*Huile de bois.* German—*Oelfirnissbaumoel, Tungoel.*

Physical and Chemical Constants of Japanese Wood Oil

Specific Gravity.			Solidifying Point.		Hehner Value.		Saponification Value.		Iodine Value.		Thermal Tests.		Refractive Index.	
											Maumené Test.		Oleo-refractometer.	
At °C.		Observer.	°C.	Observer.	Per Cent.	Observer.	Mgrms. KOH.	Observer.	Per Cent.	Observer.	Specific Temp. Reaction.	Observer.	"Degrees."	Observer.
15	0·940	Davies & Holmes [2]	below −17	Jenkins	96·4	Jenkins	211	Davies & Holmes	155·84	Deering	372	Jenkins	+75	Pearmain
15	0·9405	Deering	..	..	..	..	194	Jenkins	160·4–163·7	Henriques	Heat of Bromination.			
15	0·9361	De Negri & Sburlati	..	..	..	..	155·63	De Negri & Sburlati	165·7	Jenkins				
15·5	0·9385	Jenkins	..	..	..	..	172·4	,,	159·2	De Negri & Sburlati	23·4° C.	Jenkins		
							191·2	Deering	161·3					

[1] Prepared by these observers from the seeds. [2] *Pharm. Jour.*, 1885, 634, 636. [3] Commercial oil.
[4] Calculated from bromine value.

[1] Japanese wood oil must not be confounded with the ethereal wood oil or Gurjun balsam.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Thermal Test. Heat of Bromination.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per Cent.	Observer.	°C.	Observer.
34	Jenkins	37	Jenkins	188·8	D. N. & S.	150·1	Jenkins	26	Jenkins
31·2	D. N. & S.[1]	43·8[1]	D. N. & S.	..	..	159·4	D. N. & S.[1]		

Japanese wood oil is obtained from the seeds of *Aleurites cordata* —(its Japanese names are *Abura giri*, and *Jani*, *Kiri*)—(*Elæococca vernicia*), a tree indigenous to China [2] and Japan.

The cold-drawn oil is pale yellow, whereas the oil obtained by hot pressure is dark brown, and has an unpleasant taste and odour. It thickens at −18° C. without, however, solidifying. A specimen examined by *Jenkins*,[3] contained 3·84 per cent of free acid calculated as oleic acid, and another specimen, examined by *Deering*, 5·9 per cent. The former specimen contained 0·44 per cent of unsaponifiable matter.

The oil does not give the elaïdin reaction; by this test an oily layer was obtained resting on a lower, nearly solid product; when stirred up, the whole mass would flow. Tested in *Redwood's* viscosimeter, 50 c.c. took 1433 seconds to run through (water, 28 seconds). In *Valenta's* test the temperature of turbidity was 47° C. In the sulphur chloride test 5 grms. of the oil treated in the cold with 2 c.c. of S_2Cl_2 and 2 c.c. of CS_2 gave in $1\frac{1}{2}$ minutes a thick and stiff jelly. The refractive index is very high, approaching that of resin oil.

Japanese wood oil consists, according to *Cloëz*,[4] of the glycerides of oleic and elæomargaric acids (p. 60). The existence of the latter acid has been confirmed by *De Negri* and *Sburlati*.

Japanese wood oil possesses even more strongly pronounced drying powers than candle nut oil, and is consequently the best drying oil known. In thin layers the oil dries completely within 20 hours (linseed oil 20 hours). In an experiment made by *Jenkins*, 4 grms. of oil exposed in the boiling-water oven in a shallow porcelain dish, 7 cm. diameter, showed after $\frac{1}{4}$ hour evidence of a skin commencing to form round the edges. In two hours the oil would not flow, and was entirely covered by a crinkled skin. The average gain of weight during four hours' exposure was 0·36 per cent per hour. (Raw linseed oil treated similarly showed after four hours no evidence to skin.) Heated with lead oxide and red lead, the oil gelatinises within fifteen minutes to a light brown mass.

[1] Prepared by these observers from seeds. [2] Cp. *Jour. Soc. Chem. Ind.* 1897, 684.
[3] *Ibid.* 1897, 194. [4] *Bulletin Société Chimique*, 26. 286; 28. 23.

According to these experiments, one would expect Japanese wood oil to absorb more iodine than linseed oil. It appears likely that if the freshly expressed oil were examined, wood oil may be found to have so high an iodine value as to take its place before linseed oil. But it should be pointed out that the heat of bromination test leads to a calculated iodine value of 133·4 only, whereas the Hübl test indicates 165·7. This difference, however, disappears when the fatty acids are examined, the bromo-thermal test giving by calculation 148·3 instead of the observed iodine number 150·1.

Concentrated sulphuric acid gives a black clot with the oil. When 1 grm. of the oil is dissolved in 5 c.c. of chloroform, and 5 c.c. of a saturated solution of iodine in chloroform are added and the mixture stirred, the whole is converted into a stiff jelly after about 2 minutes. If 2 grms. of the oil be employed under the same conditions, the jelly is so stiff that it can be granulated. On heating the oil to 250° C., contact with air being carefully excluded, it is converted into a clear, solid, elastic substance; this body is insoluble in the ordinary solvents of oils, and shows no tendency to melt, on being again heated to 250° C.

Wood oil has not yet been imported to Europe as a commercial article, but is at present attracting some attention. In China and in Japan it is produced in enormous quantities, and is used there chiefly as a natural varnish for wood, and also for lighting.

LALLEMANTIA OIL [1]

French—*Huile de Lallemantia.* German—*Lallemantia Oel.*

Physical and Chemical Constants of Lallemantia Oil

Specific Gravity at 20° C.	Solidifying Point.	Hehner Value.	Reichert Value.	Saponification Value.	Iodine Value.
0·9336	− 35° C.	93·3	1·55	185	162·1

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.	Iodine Value.
11° C.	22·2° C.	166

Lallemantia oil is obtained from the seeds of *Lallemantia iberica*, a plant belonging to the *Labiatæ*, growing wild in the Caucasus, and cultivated in Russia (near Kieff).

[1] Richter, *Jour. Soc. Chem. Ind.* 1887, 825; *Zeitsch. f. Chem. Ind.* 1887, 230.

As will be seen from the iodine value, the oil belongs to the best drying oils, and surpasses in this respect, according to *Richter*, even linseed oil. A sample of the oil spread on a watch-glass dried after 9 days to a thick resin-like skin. If the oil was heated to 150° C. for 3 hours, complete drying took place after 24 hours. The absorption of oxygen, determined according to *Livache*, using copper powder, was for the oil 15·8 per cent after 24 hours, and for the mixed fatty acids 14 per cent after 8 days. 10 grms. of the oil at 18° C. mixed with 2 grms. of concentrated sulphuric acid rose to a temperature of 120° C.

In the elaïdin test 10 grms. of the oil, 5 grms. of nitric acid, specific grav. 1·4, and 1 grm. of mercury, gave after shaking for 3 minutes a dark red dough-like mass.

Lallemantia oil is used for illuminating purposes. It should prove an excellent material for varnishes.

HEMP SEED OIL

French—*Huile de chènevis, Huile de chanvre.* German—*Hanfoel.*

For tables of constants see p. 349.

Hemp seed oil is obtained from the seeds of the hemp plant, *Cannabis sativa*. The colour of the freshly expressed oil is light green to greenish-yellow, becoming brownish-yellow on keeping. It possesses a characteristic smell, has a mild taste, and dries easily. Hemp seed oil is soluble in 30 volumes of cold alcohol; from a solution of the oil in 12 volumes of boiling alcohol "stearine" is deposited on cooling.

The fatty acids of the liquid glycerides of hemp seed oil consist, according to the researches of *Bauer*, *Hazura*, and *Grüssner*, principally of linolic acid and of smaller quantities of oleic, linolenic, and isolinolenic acids. The solid glycerides in hemp seed oil are: stearin and palmitin.

Pure hemp seed oil may be easily identified by its high **iodine absorption**. Mixtures of the same iodine value can only be prepared with the help of linseed (or Lallemantia) oil. The price of the latter, however, being against it, linseed oil is rather adulterated with hemp seed oil (and Lallemantia oil). This used to happen regularly until recently in the case of Black Sea linseed oil, as the growers had been in the habit of mixing hemp seed with the linseed.

Hemp seed oil is used as a paint oil, though less frequently in this country than on the Continent, where considerable quantities are also employed for making soft soaps, characterised by a dark green colour. Although not drying so quickly as linseed oil (cp. chap. ix. p. 287), it is used in the manufacture of varnishes.

Physical and Chemical Constants of Hemp Seed Oil

Specific Gravity.		Solidifying Point.	Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index. Oleo-refractometer.	
At 15° C.	Observer.	°C.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	"Degrees."	Observer.
0·9255	Souchère	Thickens at −15 and solidifies at −27	193·1	Valenta	143	Hübl	98	Maumené	+30 to +34	Jean
0·925-0·931	Allen		192·8	De Negri and Fabris	157·5	Benedikt	95-96	De Negri and Fabris	+34 to +37·5 at 22° C.	Pearmain
0·9276	Fontenelle		190-191·1	Lewkowitsch	140·5	De Negri and Fabris				
0·9270	Chateau	...	...	...	148	Lewkowitsch				
0·9255	Massie									
0·9280	De Negri and Fabris									

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
15	Hübl	19	Hübl	122·2-125·2	Morawski and Demski
16 } 14-15 }	De Negri and Fabris	18-19 } 17-18 }	De Negri and Fabris	141	De Negri and Fabris
Titer Test.					
15·6-16·6	Lewkowitsch				

WALNUT OIL—NUT OIL

French—*Huile de noix.* German—*Nussoel, Wallnussoel.*

For tables of constants see p. 351.

This oil is obtained from the seeds of the common walnut-tree, *Juglans regia.* The fruit intended for the preparation of the oil must be allowed to ripen fully and be kept two to three months before being pressed, as the fresh seeds yield a very turbid oil, difficult to clarify. The cold-drawn oil is very fluid, almost colourless, or of a pale yellowish-green tint, and has a pleasant smell and an agreeable nutty taste; the hot-pressed oil has a greenish tint and an acrid taste and smell.

One part of walnut oil dissolves in 188 parts of cold, or in about 60 parts of boiling alcohol. On cooling, crystals separate from the solution.

The solid glycerides of walnut oil contain myristic and lauric acids; the liquid fatty acids of the oil consist chiefly of linolic acid, and of smaller quantities of oleic, linolenic, and isolinolenic acids.

Walnut oil is a very good drying oil, and at least equal, if not superior in that respect to linseed oil (cp. chap. ix. p. 287). Its greater cost acts as incentive to its adulteration with linseed oil. The latter is detected by an **iodine value** higher than the normal one. Presence of other vegetable oils, such as *sesamé* oil, *arachis* oil, can be recognised by the lower iodine absorption. Walnut oil, in its turn, is used as an adulterant for olive oil, its higher iodine absorption being compensated by the addition of lard oil.

Walnut oil is chiefly used by artists for paints, as it dries into a varnish less liable to crack than the linseed oil varnish. The better brands of walnut oil being almost colourless, it is preferred to any other oil for white paints.

[TABLE

Physical and Chemical Constants of Walnut Oil

Specific Gravity.			Solidifying Point.	Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index.	
At °C.		Observer.	°C.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.		Observer.
12	0·928	Saussure	Thickens at −15, and solidifies at −27·5	196·0	Valenta	143	Hübl	101	Maumené	1·4804	Blasdale
15	0·926	Souchère		188·7	Dieterich	147·9-151·7	Dieterich	96	De Negri and Fabris	Oleo-refractometer.	
15	0·9264	Maben									
15	0·925-0·926	Allen		194·4	Maben	145·7	Hazura	110	Blasdale	"Degrees."	Observer.
15	0·9265	De Negri and Fabris									
15	0·9256	Blasdale [1]								+35 to +36	Jean
25	0·919	Saussure	...	193·81-197·32	De Negri and Fabris	143·3	Peters				
94	0·871	Saussure	...	...	...	144·5-145·1	De Negri and Fabris				
				194·4	Blasdale	132·1	Blasdale				

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
16	Hübl	20	Hübl	150·05	De Negri and Fabris
		16-18	De Negri and Fabris		
		15	Blasdale		

[1] *Blasdale* (*Jour. Soc. Chem. Ind.* 1896, 206). Oil from *Juglans regia* grown in California.

POPPY SEED OIL

French—*Huile d'œillette, Huile blanche, Huile de pavot de pays.*
German—*Mohnoel*

For tables of constants see p. 353.

Poppy seed oil is obtained from the seeds of the poppy, *Papaver somniferum*, by pressing. The cold-drawn oil, the oil of the first pressing, is almost colourless or very pale golden yellow; this is the "white poppy seed oil" of commerce. The second quality, expressed at a higher temperature, is much inferior, and constitutes the "red poppy seed oil" of commerce.

Poppy seed oil has little or no odour and a pleasant taste, so that it is largely used as salad oil, especially as it does not easily turn rancid. The oil of unsound quality, however, possesses an acrid taste.

Poppy seed oil dissolves in 25 volumes of cold, or in 6 volumes of boiling alcohol.

The glycerides of myristic and lauric acids are absent; the fatty acids of the solid glycerides are: stearic and palmitic acids. The liquid fatty acids of poppy seed oil consist chiefly of linolic acid (65 per cent) and smaller quantities of oleic acid (30 per cent); the less saturated linolenic acids are present only in small quantities (5 per cent).

Poppy seed oil contains varying quantities of free fatty acids, as shown in the following table:—

Kind of Oil.	Free Fatty Acids calculated to Oleic Acid.	Observer.
	Per cent.	
...	2·09	Rechenberg
...	2·29	Salkowski
Salad oil, 26 samples	0·70-2·86	Nördlinger
Commercial oil, expressed, 5 samples	12·87-17·73	,,
Commercial oil, extracted, 5 samples	2·15-9·43	,,

Poppy seed oil is but rarely adulterated with other oils; the adulterant chiefly used is *sesamé oil*. The latter can be detected by the lower **iodine absorption** of the sample, and by the characteristic *Baudouin* colour reaction (cp. "Sesamé Oil," p. 390).

Poppy seed oil is in its turn fraudulently added to olive oil (cp. p. 460); the high iodine value in conjunction with the comparatively high specific gravity chiefly indicate the adulteration.

The finer qualities of oil are used for culinary purposes, and also for the best quality of paints for artists, because of its excellent drying properties (see chap. ix. p. 290). A mixture of equal volumes of "sun-bleached" poppy seed oil and bleached poppy seed oil varnish is extensively used for white pigments (*Lotter*[1]). A solution of fused gum mastic and Japan wax in poppy seed oil is obtainable in commerce as "wax oil." On account of its high price but the lowest qualities can be employed for making soft soaps.

[1] *Jour. Soc. Chem. Ind.* 1895, 168.

Physical and Chemical Constants of Poppy Seed Oil

Specific Gravity.			Solidifying Point.		Hehner Value.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index.	
At °C.		Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	At 60° C.	Observer.
15	0·924	Souchère	−18	Girard	95·38	Dietzell and Kressner	194·6	Valenta	136	Hübl	74	Maumené	1·4586	Thoerner
,,	0·924-0·937	Allen	..	..	..	..	192·8	Moore	134	Moore	86-88	Archbutt	Oleo-refractometer.	
,,	0·9262	Clarke	..	..	..	..	197·7	Dieterich	137·6-143·3	Dieterich	87-88·5	De Negri and Fabris		
,,	0·924	Massie	..	..	..	..	193·6	De Negri and Fabris	139-141	Peters			"Degrees."	Observer.
,,	0·927	De Negri and Fabris	..	..	..	..	192-195	Oliveri	134-135	Souchère			+23·5 - 29	Jean
18	0·9245	Stilurell	..	..	..	..	190·1	Lewkowitsch	136·8-137·6	De Negri and Fabris			+35[1]	,,
98-99 (water at 15·5 = 1)	0·8738	Allen	..	..	..	..	193-194	Thoerner	133-138	Oliveri			+30 to +35 at 22° C.	Pearmain
									132·6-136	Lewkowitsch			Butyro-refractometer.	
									134-135	Thoerner			At 25° C.	Observer.
													74·5	Mansfeld
													72	Beckurts and Seiler

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Refractive Index.	
At 100° C. Water at 100° = 1	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
0·8886	Archbutt	16·5	Hübl	20·5	Hübl	199	Thoerner	139	De Negri and Fabris	1·4506	Thoerner
		15·4-16·2	Lewkowitsch	20-21	De Negri and Fabris						
		16·5	Thoerner	20·5	Thoerner	..	..	116·3	Thoerner		

[1] Very old sample.

NIGER SEED OIL

French—*Huile de Niger.* German—*Nigeroel.*

For tables of constants see p. 355.

Niger seed oil is expressed from the seeds of *Guizotia oleifera*, a plant cultivated in the East and West Indies, and also in Germany.

The oil is yellow, has a nutty taste, and has poorer drying powers than the preceding oils. According to *Allen* it dries rapidly at 100° C.

Niger seed is crushed in this country (Hull), and the oil obtained is used as a substitute for linseed oil, and for adulterating rape oil.

Physical and Chemical Constants of Niger Seed Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index Oleo-refractometer.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	"Degrees."	Observer.
15·5 99 (water at 15·5 =1)	0·9270 0·8738	Allen ,,	− 9 ...	Allen ...	189-191 ...	Stoddard ...	132·9 133·5	Archbutt Wallenstein and Finck	82 81	Baynes Allen	+26 to 30 at 22° C.	Pearmain

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.		Iodine Value of the Liquid Fatty Acids.	
At 100° C. (Water at 100=1.)	Observer.	Per cent.	Observer.
0·8886	Archbutt	147·5	Wallenstein and Finck

SUNFLOWER OIL

French—*Huile de soleil, Huile de tournesol.*
German—*Sonnenblumenoel.*

For tables of constants see p. 357.

This oil, obtained from the seeds of *Helianthus annuus*, is a limpid, pale yellow oil of mild taste and pleasant smell.

A sample of sunflower oil was found to contain 0·31 per cent of unsaponifiable matter; free fatty acids and volatile acids were absent; another sample prepared by *Holde*[1] from sunflower seed by extraction with petroleum ether contained 5·6 per cent of free fatty acids calculated to oleic acid. The liquid fatty acids consist chiefly of linolic acid, oleic acid being present in small quantities only.

This oil dries more slowly than those already described. The absorption of oxygen, according to *Hübl's* method, using copper powder as an oxygen carrier, took place at the following rate:—

Absorption of Oxygen.	After 2 days.	After 7 days.	After 30 days.
	Per cent.	Per cent.	Per cent.
Sunflower oil	1·97	5·02	...
Sunflower oil fatty acids . . .	0·85	3·56	6·3

Sunflower oil is chiefly cultivated in Russia,[2] where the cold-drawn oil serves for culinary purposes; the oil expressed at a higher temperature is employed in soap-making and for the manufacture of varnishes. It is added fraudulently to olive oil (*Allen*), and recently also, in place of cotton seed oil, to margarine (*Jolles*[3]). The nitric acid test has been found reliable for distinguishing sunflower oil from cotton seed oil in mixtures with other oils; whereas the latter becomes brown on treatment with this reagent (see "Cotton Seed Oil," p. 381), sunflower oil does not change its colour.

[1] *Jour. Soc. Chem. Ind.* 1894, 892. [2] *Ibid.* 1892, 470.
[3] *Ibid.* 1893, 935.

[TABLE

Physical and Chemical Constants of Sunflower Oil.

Specific Gravity.			Solidifying Point.		Hehner Value.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index.	
At °C.		Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	At 60° C.	Observer.
15	0·9262	Chateau	−16 to −18·5	Bornemann	95	Spüller	193-194	Bornemann	129	Spüller	72-75	De Negri & Fabris	1·4611	Thoerner
,,	0·924-0·926	Allen	at −17	Holde	..	..	193-193·3	Spüller	122·5-133·3	Dieterich			Oleo-refractometer.	
,,	0·9258	Spüller	par-	..	..	..	188-189	De Negri & Fabris	119·7-120·2	De Negri & Fabris	67·5	Spüller	"Degrees."	Observer.
,,	0·926	De Negri & Fabris	tially solid	..	..	..	193	Holde	135	Holde			+35 at 22° C.	Pearmain
,,	0·936	Dieterich											Butyro-refractometer.	
,,	0·9240	Holde											At 25° C.	Observer.
90	0·919	,,	..	..	..	..	193-194	Thoerner	129	Thoerner			72·2	Beckurts and Seiler

Physical and Chemical Constants of the Mixed Fatty Acids.

Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Refractive Index.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
17	Bach	23	Bach	201·5	Spüller	133·2-134	Spüller	1·4531	Thoerner
18	Dieterich	23	Dieterich			124	De Negri & Fabris		
18	De Negri & Fabris	17-22	Peters	201·6	Thoerner				
		22-24	De Negri & Fabris	..	..	133-134	Thoerner		
17	Thoerner	23	Thoerner						

FIR SEED OIL

French—*Huile de Pignon.* German—*Fichtensamenoel.*

For tables of constants see p. 359.

Fir seed oil is obtained from the seeds of several kinds of pine-trees —*Pinus sylvestris* (Scotch fir seed), *Pinus Picea*, and *Pinus Abies.*[1]

This oil is limpid and of pale yellow colour (Scotch fir seed oil brownish-yellow—*Allen*), and has a sweet taste.

Fir seed oil dries easily, and is therefore used in the preparation of varnishes.

The following are the constants of the oils obtained from the different seeds :—

[1] The fatty oil from *Pinus monophylla* (?) is described as *Pine nut oil* by Blasdale (*Jour. Soc. Chem. Ind.* 1896, 205). It is a brown, drying oil with an unpleasant odour and taste. The following constants are given :—

Physical and Chemical Constants of Pine Nut Oil.

Spec. Grav. at 15° C.	Saponification Value.	Iodine Value.	Maumené Test.	Refractive Index.
0·933	192·8	101·3	71°	1·4769

Physical and Chemical Constants of the Mixed Fatty Acids.

Melting point	19° C.

[TABLE

Physical and Chemical Constants of Fir Seed Oil

Source.	Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.	
	At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
Pinus sylvestris .	0·9312	De Fontenelle	– 27 to – 30	De Fontenelle						
Pinus Abies .	0·9285	De Fontenelle	– 27	Schaedler						
,, ,, .	0·9288	Schaedler	...	...						
Pinus Picea .	0·9250	Schaedler	– 27	Schaedler	191·3	De Negri and Fabris.	118·9-120	De Negri and Fabris.	98-99	De Negri and Fabris.
,, ,, . .	0·9215	De Negri and Fabris	– 18 to – 20	De Negri and Fabris						

Physical and Chemical Constants of the Mixed Fatty Acids

Source.	Solidifying Point.		Melting Point.		Iodine Value.	
	°C.	Observer.	°C.	Observer.	Per cent.	Observer.
Pinus Picea, expressed . .	10-15	De Negri and Fabris	16-19	De Negri and Fabris	121·5	De Negri and Fabris
,, ,, extracted . .	12-16	,, ,,	17-19	,, ,,		

MADIA OIL

French—*Huile de Madia.* German—*Madiaoel.*

For tables of constants see p. 361.

Madia oil is obtained from the seeds of the Chilian plant *Madia sativa*. It has been also cultivated successfully in South Germany.

This oil is dark yellow, and possesses a characteristic, not unpleasant odour. It dissolves in 30 volumes of cold or 6 volumes of hot alcohol (*Schaedler*).

Madia oil occupies an intermediate place between drying and semi-drying oils. Treated with nitrous acid (elaïdin test) it remains liquid; for this reason, and on account of its high iodine value, it is placed amongst the drying oils. It absorbs, indeed, considerable quantities of oxygen, becoming thereby viscid.

The oil is chiefly used for burning and also for soap-making.

[TABLE

Physical and Chemical Constants of Madia Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
0·926-0·928	Hartwich	−10 to −11 (by hot pressure)	Schaedler	192·8	De Negri and Fabris	117·5-119·5	De Negri and Fabris	95-99	De Negri and Fabris
0·9285	De Negri and Fabris	−25 (cold-drawn)	,,						
0·9286	Schaedler	−12 to −15	De Negri and Fabris						

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
20-22	De Negri and Fabris	23-26	De Negri and Fabris	120·7	De Negri and Fabris

CANDLE NUT OIL

French—*Huile de noix de chandelle.* German—*Candlenussoel, Bankulnussoel.*

Candle nut oil is obtained from the seeds of the tropical plant *Aleurites moluccana*. The constants recorded for this oil are of a somewhat conflicting nature, owing, no doubt, to different observers having had under examination oils from different sources. A sample of oil examined by *Cloëz* had a specific gravity of 0·9232 at 15° C.

The cold-drawn oil is limped, colourless or yellowish, and has a pleasant odour and taste (*Bornemann*); on account of its purging properties, however, it cannot be used for edible purposes. A sample of candle nut oil, three years old, contained 56·5 per cent of free fatty acids (*Nördlinger*[1]).

Candle nut oil possesses powerful drying properties; on boiling, a good varnish is obtained, drying far better than the oil itself. Candle nut oil varnish surpasses even boiled linseed oil as a rapidly drying oil.

The oil is also used for soap-making, especially in France, and is said to be a good substitute for cocoa nut oil.

Lach[2] has examined a sample of candle nut oil (perhaps candle nut "stearine"). The consistency was that of a salve, its colour light yellow, and its smell nauseous. On exposure to light and air it dried to a horny mass. It dissolved sparingly in alcohol, easily in petroleum ether. The alcoholic solution had an acid reaction, owing, no doubt, to the large percentage of free fatty acids (see above).

The following constants were determined by *Lach* for this sample:—

Hehner value	94·56
Solidifying point of the mixed fatty acids . .	56° C.
Melting ,, ,, ,, ,, . .	65·5° C.
Iodine value	118

The fatty acids were amorphous, consequently the fat was unsuitable for candle-making.

Lesser Known Drying Oils

ISANO (UNGUEKO) OIL[3]

Isano (I'Sano) oil is obtained from the seeds of the I'Sano[4] or Ungueko,[5] a large tree of the family *Oleaceæ*, growing in the French Congo. The ground and dried seeds yield 60 per cent of oil.

[1] *Jour. Soc. Chem. Ind.* 1889, 806.
[2] *Chem. Zeit.* 1890, 871.
[3] Hébert, *Jour. Soc. Chem. Ind.* 1896, 660.
[4] Local name in Loango.
[5] Local name.

The specific gravity of the oil is 0·973 at 23° C. It is liquid even at – 15° C., is reddish in colour, has an insipid flavour and fishy smell. The oil is viscous and possesses strong drying powers. Tested by Maumené's test it gives a thermal reaction of 115° C. The bromine value is stated to be double that of oleic acid.

It is further stated that the oil contains 86 per cent of liquid fatty acids (the lead salts being entirely soluble in ether), consisting of 15 per cent oleic acid, 75 per cent linolic acid, and 10 per cent of isanic acid (chap. iii. p. 63).

On saponification from 12 to 13 per cent of glycerol are said to be obtained.

MOHAMBA OIL [1]

The seeds yielding Mohamba oil are very similar to those of the Isano tree, but after drying they give only 12 per cent of oil.

The oil has a specific gravity of 0·915 at 23° C.; it remains liquid at – 15° C., is of yellow colour, fairly fluid, inodorous, and of insipid taste.

The thermal reaction—Maumené's test—gave a rise of 55° C.

On saponification about 9 per cent of glycerol and 90 per cent of brown liquid unsaturated fatty acids are obtained from the oil. From the lead salts of the acids, which are entirely soluble in ether, there was obtained, on separating the free acids, a white fatty acid, soluble in alcohol and ether, and crystallising from the latter in laminæ, melting at 34°-35° C. This acid absorbs about as much bromine as oleic acid, and would therefore belong to the oleic series, but does not seem to correspond with any known acid. The liquid acids appear to consist of oleic acid, as they absorb an amount of bromine corresponding to oleic acid and give the elaïdin reaction.

GARDEN ROCKET OIL [2]—DAME'S VIOLET OIL

French—*Huile de julienne.* German—*Rothrepsoel.*

For tables of constants see p. 364.

This oil is expressed from the seeds of the garden rocket, *Hesperis matronalis.* When fresh it is of green colour, becoming brownish on keeping. It is an odourless oil possessing a somewhat bitter taste.

Rocket garden oil is expressed in France and Switzerland, and used as a burning oil.

[1] Hébert, *Jour. Soc. Chem. Ind.* 1896, 660.

[2] De Negri and Fabris, *Annali del Laborat. Chim. delle Gabelle,* 1891-92, 151.

Physical and Chemical Constants of Garden Rocket Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
0·9282	Schübler	− 22 to − 23	Schaedler	191·8	De Negri and Fabris	154·9-155·3	De Negri and Fabris	125-127·5	De Negri and Fabris
0·9315	Villon								
0·9335	De Negri and Fabris.								

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.	Iodine Value.
°C.	°C.	Per cent.
16-14	20-22	157

HENBANE SEED OIL [1]

German—*Bilsenkrautsamenoel.*

Henbane seed oil is obtained from the seeds of *Hyoscyamus niger.* This oil is yellow, somewhat viscous, slightly fluorescent, and readily drying.

Physical and Chemical Constants of Henbane Seed Oil

Spec. Gravity at 15° C.	Saponific. Value.	Reichert Value.	Hehner Value.	Iodine Value.
0·939	170·8	0·99	94·7	138

CELOSIA OIL [2]

This oil is obtained from the seeds of *Celosia cristata ;* it is a greenish-brown, drying oil, sparingly soluble in alcohol.

Physical and Chemical Constants of Celosia Oil

Solidifying Point.	Saponific. Value.	Iodine Value.
– 10° C.	190·5	126·3

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.
21°-19° C.	27°-29° C.

INDIAN LAUREL OIL [3]

The fruits from *Laurus indica* yield a brown, viscous oil, having the constants given in the following table. The specimen examined contained 33 per cent of free fatty acids.

Physical and Chemical Constants of Indian Laurel Oil

Spec. Grav. at 15° C.	Solidifying Point.	Saponific. Value.	Iodine Value.
0·926	Thickens at – 15° C., but does not solidify.	170	118·6

[1] Mjöen, *Jour. Soc. Chem. Ind.* 1897, 340.
[2] De Negri and Fabris, *Chem. Zeit.* 1896, Rep. 161. [3] *Ibid.*

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.
19°-18° C.	24°-26° C.

TOBACCO SEED OIL

French—*Huile de Tabac.* German—*Tabaksamenoel.*

Specific gravity 0·9232 at 15° C., solidifies at −25° C. Colour—pale greenish-yellow.

The oil dries easily.

WELD SEED OIL

German—*Resedasamenoel.*

This oil is obtained from the seeds of the dyer's weld, *Reseda luteola.* Owing to the presence of chlorophyll the oil has a dark greenish tint. Specific gravity 0·9058. Solidifying point −20° C. It has a bitter taste and nauseous odour. The oil dries easily on exposure to air, and is used for burning and making varnishes.

(2) Semi-drying Oils

The oils comprised in this class form an intermediate link between the drying and the non-drying oils (cp. also chap. ix. p. 279). This finds its readiest expression in the iodine values. For this reason these oils are described in the order of their iodine values.

The members of this class appear to range themselves naturally into three groups—

α. The cotton seed oil group.
β. The rape oil group.
γ. The castor oil group.

α. The Cotton Seed Oil Group

The members of the group possess distinct drying properties. although less pronounced than in the case of the true drying oils. The group takes its name from its most prominent member, which may be considered as the type of a semi-drying oil.

We shall describe the following oils: Cameline oil, soja bean oil, pumpkin seed oil, maize oil, kapok oil, cotton seed oil, sesamé oil, basswood oil, beechnut oil, Brazil nut oil.

CAMELINE OIL (GERMAN SESAMÉ OIL)

French—*Huile de Camelina.* German—*Deutsches Sesamoel, Leindotteroel.*

For tables of constants see p. 368.

Cameline oil is obtained from the seeds of *Myagrum sativum* (or *Camelina sativa*), belonging to the *Cruciferæ.*

The oil has a golden-yellow colour and a pungent taste and smell.

On exposure to air it dries slowly. Boiled with litharge or manganese borate it yields a slowly drying varnish.

The low saponification value of the oil points to the presence of glycerides of erucic acid. The oil prepared by expression is free from sulphur, like all the oils drawn in the cold from seeds of the *Cruciferæ* (cp. "Rape Oil," p. 406).

On account of its low price the oil is not likely to be adulterated. It is used, however, for the adulteration of rape oil, in which it may be detected by the high iodine value. Cameline oil is naturally present in linseed oil expressed from East Indian seed (cp. 336).

The cold-drawn oil is sometimes employed for culinary purposes. Its chief use, however, is for soap-making, yielding as it does a very soft soap, which suitably replaces linseed oil in winter. In summer, however, cameline oil cannot be used alone, the soap being liquid at a temperature below 20° C.

Physical and Chemical Constants of Cameline Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index. Oleo-refractometer.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	"Degrees."	Observer.
0·9329	Clarke	−18	Chateau	188	De Negri and Fabris	132·6	Girard	117	De Negri and Fabris	+32	Jean
0·9260	Cristiani	...	...	...	...	135·3	De Negri and Fabris	82	Jean		
0·9259	Massie										
0·9228	Schaedler										
0.9252	Schübler										
0·9260	De Negri and Fabris										
0·9200	Levallois										
0·9240	Jean										

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
14-13	De Negri and Fabris	18-20	De Negri and Fabris	136·8	De Negri and Fabris

SOJA BEAN OIL

French—*Huile de Soya.* German—*Sojabohnenoel.*

For tables of constants see p. 370.

This oil is obtained from the seeds of *Soja hispida*, a plant indigenous in China and Japan, where the oil is used for culinary purposes.

A sample of the oil extracted with ether by *Morawski* and *Stingl* gave 0·22 per cent of unsaponifiable matter, and 2·28 per cent of free acid calculated to oleic acid.

On exposure to air it dries slowly with formation of a thin skin.

[TABLE

Physical and Chemical Constants of Soja Bean Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Hehner Value.		Iodine Value.		Maumené Test.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.	°C.	Observer.
0·9270	Morawski and Stingl	+15 to +8	De Negri and Fabris	192·9	Morawski and Stingl	95·5	Morawski and Stingl	122·2	Morawski and Stingl	61	Morawski and Stingl
0·9242	De Negri and Fabris	...	...	192·5	De Negri and Fabris	...	...	121·3	De Negri and Fabris	59	De Negri and Fabris

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
25	Morawski and Stingl	28	Morawski and Stingl	115·2	Morawski and Stingl
25-23	De Negri and Fabris	27-29	De Negri and Fabris	122	De Negri and Fabris

PUMPKIN SEED OIL

French—*Huile de pepins de citronelle.* German—*Kürbissamenoel.*

Physical and Chemical Constants of Pumpkin Seed Oil

Specific Gravity.			Solidifying Point.		Hehner Value.		Saponification Value.		Iodine Value.	
At °C.		Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0·9231	Schaedler	−15	Schaedler	96·2	Schattenfroh	188·1	Schaedler	121	Hübl
20	0·923	Schattenfroh	−16	Schattenfroh	...	...	188·7	Schattenfroh	121·5	Henriques
									113·4	Schattenfroh

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Mean Molecular Weight.	
°C.	Observer.	°C.	Observer.		Observer.
24·5	Schaedler	28	Schaedler	284·7	Schattenfroh

Pumpkin seed oil is expressed from the seeds of *Cucurbita pepo*. The cold-drawn oil is used for culinary purposes; it is stated that the oil from the large cucumber grown on the Slave Coast far exceeds in flavour the finest olive oil. The lower qualities serve for burning. This oil dries very slowly.

MAIZE OIL—CORN OIL[1]

French—*Huile de maïs.* German—*Maisoel.*

For tables of constants see p. 374.

This oil is obtained from the seeds of the maize plant, *Zea Mays*, either by expressing the seed before it is employed for the manufacture of starch, or, where they have been used for production of alcohol, by recovering it from the residue of the fermentation vats.

Maize oil prepared by the former process is of a pale yellow or golden-yellow colour, whereas the oil furnished by the second process is reddish-brown. The latter oil will most likely be characterised by a large proportion of free fatty acids. Thus the sample of oil examined by *Hart*,[2] being reddish-brown, contained 0·75 per cent of free fatty acids, whereas the sample analysed by *Spüller*,[3] was absolutely neutral.

The oil dissolves readily in acetone and more sparingly in alcohol and glacial acetic acid. The following table, due to *Smith*,[4] gives the volumes of oil dissolved by 100 volumes of these three solvents :—

Solubility of Maize Oil in 100 volumes of				
Absolute Alcohol.		Acetone, commercial.	Glacial Acetic Acid.	
At 16° C.	At 63° C.	At 16° C.	At 16° C.	At 63° C.
2	13	24	3	9

Maize oil is, notwithstanding its high iodine value,[5] almost devoid of drying powers. No decided drying properties are imparted to it by subjecting it to the process of "boiling," or by addition of lead oxide. If, however, a current of air is passed through it at 150° C., it will, on addition of manganese borate, acquire to a small extent

[1] So termed in the United States.
[2] *Jour. Soc. Chem. Ind.* 1894, 257.
[3] *Dingl. Polyt. Jour.* 264. 626.
[4] *Jour. Soc. Chem. Ind.* 1892, 505.
[5] *Rokitansky* (*Jour. Chem. Soc.* 1895, Abstr. i. 509) describes a maize oil obtained from the yellow Italian maize plant, grown in Southern Russia as a yellow, neutral oil of 0·836 specific gravity, and the (Hübl) iodine number 75·8. These numbers differ so much from those given in the table, that they have not been embodied therein.

drying properties, and a thin film on lead dries in ten to twenty hours, but not completely.

Maize oil appears to contain no stearin, since no stearic acid crystals could be obtained from a specimen of maize oil by *Hehner* and *Mitchell's* method (chap. viii. p. 198).

Like cotton seed oil, maize oil yields in the elaïdin test a mass having a pasty or buttery consistency.

The unsaponifiable matter in maize oil consists mostly of phytosterol. *Spüller* found 1·35 and *Hart* 1·55 per cent of unsaponifiable matter.

The colour reactions (*Wellmann's*, *Becchi's*) are not sufficiently characteristic to identify the oil, or to detect it in admixtures with other oils.

Adulteration of maize oil with mineral oil or resin can be easily recognised by the quantitative determination of the unsaponifiable matter and by the *Liebermann-Storch* reaction (p. 226).

Maize oil is used as a burning and lubricating oil, and also for soap-making. Latterly it is being used extensively in place of cotton seed oil for the adulteration of lard.

[Table

Physical and Chemical Constants of Maize Oil

Specific Gravity.		Solidifying Point.		Hehner Value.		Saponification Value.		Reichert Value.		Iodine Value.	
At 15° C.	Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.
0·9215	Bornemann	−10	Schaedler	96·67	Lloyd	188-189	Spüller	0·33	Spüller	119·4-119·9	Spüller
0·9244	Smith	−10 to −20	Smith	94·7	Spüller	193·4	Smith	2·5[1]	Smith	116·3	Smetham
0·9160	Lloyd	−10 to −15	De Negri and Fabris	95·7	Hart	190·4	De Negri and Fabris	...	...	122·9	Smith
0·9215-0·9220	De Negri and Fabris	...	...	...	...	...	...	...	...	111·2-112·6	De Negri and Fabris
0·9239	Hart	...	...	...	...	...	...	...	...	117	Hart
										122	Wallenstein

Physical and Chemical Constants of Maize Oil—continued

Acetyl Value.		Thermal Tests.			
		Maumené Test.		Heat of Bromination.	
	Observer.	°C.	Observer.	°C.	Observer.
7·8-8·75	Lewkowitsch	56	Spüller[2]	21·5	Hehner and Mitchell
...	...	86	De Negri and Fabris[3]		
...	...	89	Smith[4]		
...	...	60·5	Hart[2]		
...	...	79	Jean[3]		

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.		Saponification Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.
16-14	De Negri and Fabris	18-20	De Negri and Fabris	125	Spüller	198·4	Spüller
		20	Jean	113-115	De Negri and Fabris		
				Iodine Value of the Liquid Fatty Acids.			
				140·7	Wallenstein and Finck		

[1] The volatile acids from 108 grms. of oil required 0·56 grm. KOH (*Jour. Soc. Chem. Ind.* 1892, 505).
[2] By Maumené's method, p. 291. [3] By Jean's method, p. 295. [4] 15 grms. of oil and 5 c.c. of sulphuric acid.

KAPOK OIL

German—*Kapokoel.*

Physical and Chemical Constants of Kapok Oil [1]

Specific Gravity at 18° C.	Hehner Value.	Saponification Value.	Iodine Value.	Maumené Test.
0·9199 0·936 (Schaedler).	94·9	181	116 117·9-119·4	95° C.[2]

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.	Solidifying Point.	Melting Point.	Saponification Value.	Iodine Value.	Mean Molec. Weight.
0·9162	23-24	29	191	108	293

Kapok oil is obtained by pressing the seeds of *Eriodendron anfractuosum* (or *Bombax pentandrum*), a tree indigenous to the tropics and related to the cotton plant.[3]

The oil is very similar to cotton seed oil, but has better lubricating properties.

The oil has a greenish-yellow colour and a not unpleasant taste and odour. The nitric acid test, so characteristic of cotton seed oil, gives a similar colour reaction with kapok oil, but the tint is more greenish-brown than reddish-brown, as in the case of cotton seed oil; if samples of kapok oil and cotton seed oil are tested side by side, the difference is said to be easily noticeable.

Kapok oil is imported from the Dutch Indies into Holland, where it is used in soap-making as a substitute for cotton seed oil. In its home (East Indies, West Indies) the oil is also employed for culinary purposes.

COTTON SEED OIL

French—*Huile de Coton.* German—*Baumwollensamenoel, Cottonoel.*

For tables of constants see pp. 376-378.

Cotton seed oil is obtained from the seeds of the various kinds of the cotton-tree, *Gossypium.* The kind cultivated extensively in the United States and in Egypt is *Gossypium herbaceum.*

[1] Henriques, *Jour. Soc. Chem. Ind.* 1894, 258.
[2] By *Archbutt's* process, p. 292.
[3] *Jour. Soc. Chem. Ind.* 1893, 923; 1894, 147.

Physical and Chemical Constants of Cotton Seed Oil

Specific Gravity.			Solidifying Point.		Hehner Value.		Saponification Value.		Iodine Value.	
At °C.		Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0·922-0·930	Allen	0 to −1	Benedikt	95·87	Bensemann	191-196·5	Allen	106	Hübl
,,	0·9228	Valenta	Below 12° "stearine" separates out from the oil.		96·17	Lengfeld and Paparelli	195	Valenta	108·7	Moore
,,	0·9165	Levallois			...	...	191·2	Moore	102-108·5	Dieterich
,,	0·9216-0·9230	Del Torre			...	...	196	Dieterich	106-110	Wilson
,,	0·9222	Thomson and Ballantyne	...	...	...	...	211 (?)	Leone and Longi	106·8-108·3	Thomson and Ballantyne
,,	0·923-0·925	De Negri and Fabris	...	...	...	...	191·6-193·5	Thomson and Ballantyne	100·9-116·9	Wiley
17	0·923	Scheibe	...	...	...	...	191·8-193·8	De Negri and Fabris	106·9-110	De Negri and Fabris
18	0·9203	Long	...	...	...	...	191-195·5	Oliveri	104-108	Oliveri
,,	0·9230	Stilurell	...	...	...	...	...	...	107·8-108[1]	Wallenstein and Finck
99 (water 15·5 = 1)	0·8725	Allen	...	...	...	...	194-195	Thoerner	106·5-108[2]	,,
									106·8[3]	,,
100	0·8672	Leone and Longi								

[1] American oil. [2] Egyptian oil. [3] Peruvian oil.

Physical and Chemical Constants of Cotton Seed Oil—continued

Acetyl Value.		Thermal Tests.				Refractive Index.		
		Maumené Test.		Heat of Bromination.				
	Observer.	°C.	Observer.	°C.	Observer.	At °C.		Observer.
21·1-24·8	Lewkowitsch	77	Baynes	19·4	Hehner and Mitchell	15	1·4743-1·4752	Strohmer
...	...	75-76	Archbutt			60	1·4570	Thoerner
...	...	74-75	Allen			Oleo-refractometer.		
...	...	68-70	Del Torre					
...	...	80-90	Wiley			"Degrees."		Observer.
...	...	50-53	De Negris and Fabris			+20		Jean
		Specific Temperature Reaction.				+16 to +17 [1] at 22° C.		Pearmain
		169-170	Thomson and Ballantyne			+17 to +23 [2] at 22° C.		,,
						Butyro-refractometer.		
						"Degrees."		Observer.
						67·8		Beckurts and Seiler
						67·6-69·4		Mansfeld

[1] Crude oil.

[2] Refined oil.

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Mean Molec. Weight.		Iodine Value.		Refractive Index.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60°C.	Observer.
15·5 (water 4 = 1)	0·92055-0·9219	Crampton	32	Allen	35·2	Allen	203·9	Valenta	275	Valenta	110·9-111·4	Morawski and Demski	1·4460	Thoerner
40 (water 4 = 1)	0·90497-0·90612	,,	35·5	Valenta	38·3	Valenta	208	Dieterich	289	Williams	115·7	Williams		
50 (water 4 = 1)	0·89861-0·89972	,,	30·5	Hübl	35	Hübl	201·6	Thoerner	..	..	112·8-113	De Negri and Fabris		
100 (water 4 = 1)	0·86542-0·86774	,,	35	Bach	38	Bach					112-115	Thoerner		
99 (water 15·5 = 1)	0·8467	Allen	36	Dieterich	38·5	Dieterich					Iodine Value of the Liquid Fatty Acids.			
100 (water 100 = 1)	0·8816	Archbutt	39-40	Bensemann[1]	42-43	Bensemann[1]								
			32-35	Thoerner	35-40	Thoerner					136	Muter and Koningh		
			Titer Test.								147·3-147·5[4]	Wallenstein and Finck		
			32·2-32·7[2]	Lewkowitsch	34-35	De Negri and Fabris					146·8-148·2[5]			
			33·3-34·1[2]	,,	35-37	,,					147·8[6]	,,		
			33·0-33·3[2]	,,	37-38	,,								
			34·4-35·2[2]	,,										
			33·3-35·0[2]	,,										
			35·6-37·6[3]	,,										

[1] Determined by his method as point of incipient fusion and complete fusion. [2] Part of the "stearine" taken out of the oil. [3] All the "stearine" left in the oil.
[4] American oil. [5] Egyptian oil. [6] Peruvian oil.

The crude cotton seed oil, as expressed from the seeds, has a ruby-red to almost black colour. The following table contains a few constants characteristic of crude cotton seed oil :—

Kind of Crude Oil.	Specific Gravity.		Iodine Absorption.		Saponification Value.	
	At 15° C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.
American	0·920-0·922	Crampton	109	Thomson and Ballantyne		
Egyptian	0·9274	Thomson and Ballantyne	...	...	190·9	Thomson and Ballantyne

On saponifying the crude oil with caustic potash, the upper layers exposed to the air become blue and afterwards violet—a very characteristic reaction of crude cotton seed oil. If alkali be used in insufficient quantity to produce complete saponification—as in the refining of cotton seed oil on a commercial scale—the alkali carries down along with the soap formed the colouring substances, the supernatant oil being but slightly yellowish. Concentrated sulphuric acid imparts to crude cotton seed oil a bright red colour.

The refined cotton seed oil, as obtained in commerce, is pale yellow and possesses a pleasant, nutty taste. Even at the ordinary temperature it deposits "stearine" on standing (see "Cotton Seed Stearine," p. 506). The finer brands of cotton seed oil, intended for edible and culinary purposes, are freed from the "stearine" by chilling, or simply by allowing the oil to stand for some time in large storage tanks.[1]

Alkalis being the reagents used for refining, cotton seed oil is, of course, neutral in the fresh state. On keeping, however, the refined oil becomes rancid, with formation of free fatty acids. Those samples of oil which have been found by some chemists to contain small quantities of free fatty acids (*Salkowski*, *Nördlinger*, *Thomson* and *Ballantyne*) must, therefore, have been old ones and do not represent the typical oil.

Cotton seed oil contains the glycerides of stearic, palmitic, oleic, and linolic acids. The liquid fatty acids have been found to consist by *Hazura* of oleic and linolic acids in the proportion of about 3 : 4·5, and this view is supported by the high iodine value of the liquid fatty acids of cotton seed oil, and also of cotton seed oil itself. As the theoretical iodine number of a mixture of two molecules of linolic acid and one molecule of oleic acid is 151, whereas 147 to 148 was found by experiment, *Wallenstein* and *Finck* conjecture that the

[1] Examination by Hehner and Mitchell's method (p. 198) should decide whether the solid fatty acid of this "stearine" is stearic or palmitic acid.

basis of cotton seed oil is formed by a glyceride of the formula $C_3H_5(C_{18}H_{31}O_2)_2C_{18}H_{33}O_2$.

Cotton seed oil contains also hydroxy acids, the nature of which has not yet been investigated. A measure of their amount is given by the acetyl value of the oil (cp. table). *Fahrion*[1] has obtained from a sample of cotton seed oil, three years old and absorbing only 81·4 per cent of iodine, 3·6 per cent of hydroxy acids (?) insoluble in petroleum ether (cp. p. 204). On heating to 120° C. for three hours, the percentage of insoluble hydroxy acids increased to 9·4 per cent (comp. "Blown Oils," chap. xii. p. 734), the iodine value of the oil at the same time decreasing to 70·6.

The cotton seed oil fatty acids are distinguished by their high melting and solidifying points. This characteristic difference from other oils renders identification of cotton seed oil an easy operation, and also facilitates the detection of it in other oils and fats.

Its drying power corresponds to its high iodine value, and it may be considered as the type of a semi-drying oil. Whilst, however, cotton seed oil absorbs in the *Livache* test 5·9 per cent of oxygen after twenty-four hours, its mixed fatty acids absorb only 0·8 per cent, behaving indeed more like the mixed fatty acids of a non-drying oil.

In the **elaïdin test** a mass of pasty or buttery consistency is obtained.

Besides its legitimate use cotton seed oil is employed in immense quantities for the adulteration of olive oil, lard, butter fat, and in the manufacture of butter substitutes (cp. p. 678). The detection of cotton seed oil in these fats is consequently one of the most important objects of commercial fat analysis, and it is, therefore, not to be wondered at that the literature on that subject is very voluminous. Unfortunately, the opinions of the various writers as to the value of the one or the other process differ greatly, and agreement on this important question does not yet exist. The divergence of statements may be due in no small degree to differences of age and source in the samples examined (whether Egyptian or American, etc.) Another explanation may also be found in the fact that cotton seed oil is not easily obtainable in the retail trade.

The determination of the **iodine value** alone does not lead in every case to decided results, since the adulterator is only too careful to regulate the fraudulent admixture of cotton seed oil in such a manner as to obtain finally an iodine value not differing from the normal one to such an extent that sophistication can be established without doubt.

Most decisive results will be obtained by determining the iodine value of the liquid fatty acids (cp. p. 195, *Muter* and *de Koningh's* process), as will be seen from the following table[2]:—

[1] *Zeitsch. f. angew. Chemie*, 1892, 172.

[2] Cp. chap. ix. p. 312.

Liquid Fatty Acids from	Iodine Value.
Cotton seed oil	146-148
Niger seed oil	147·5
Maize oil	140·7
Arachis oil	128·5
Rape oil	120·7
Lard, European	96
,, American	105
Tallow	92·5

The colour reactions given below have been proposed for the detection of cotton seed oil in other fats.

1. *The Nitric Acid Test.*—On shaking oils containing cotton seed oil with an equal measure of nitric acid of specific gravity 1·37, a characteristic coffee-brown colouration is produced, the intensity of the colouration corresponding to the proportion of cotton seed oil present. *Holde*[1] states that nitric acid of specific gravity 1·37 does not give a characteristic reaction. This is an erroneous statement, the error perhaps being caused by the particular sample *Holde* operated upon. In the case of adulterated olive oil, at any rate, the nitric acid test is a most characteristic one, indicating, as it does, with the greatest facility as little as 2 to 3 per cent of cotton seed oil,[2] especially if the test be made side by side with a sample of pure olive oil treated in a similar fashion (cp., however, further below). This test is all the more valuable when contrasted with *Becchi's* test, as the nitric acid gives equally distinct results if the cotton seed oil has been heated previously to 240° C. *Zecchini* and *Souchère* recommend nitric acid of specific gravity 1·40 as more reliable, an acid of less density being said to produce colouration of insufficient distinctness. *Holde* experimented with nitric acid of specific gravity 1·41, and found that admixture of 20 per cent of cotton seed oil with olive oil could thus be ascertained, whereas 10 per cent could not be detected with certainty. Having obtained the brown colour also with a sample of refined rape oil, *Holde* decided that nitric acid of specific gravity 1·41 is a useless reagent. The writer's experiments, however, demonstrate the fact that nitric acid of specific gravity 1·375 gives more definite results than the more concentrated acid. A large number of samples of olive oil mixed with varying proportions of cotton seed oil on the one hand, and rape oil on the other, showed striking differences after twenty-four hours' standing. The samples containing cotton seed oil were of a pure brown colour, whereas those mixed with rape oil became more yellowish. Acid of specific gravity 1·4 did not yield decisive results. From this it is evident that if the presence of a small quantity of cotton seed oil be suspected in a sample it is best to allow the test-tube to stand for some time—say twenty-four hours—before the colour reaction is taken as final. More recent experience has shown that there are in commerce American cotton seed oils

[1] *Jour. Soc. Chem. Ind.* 1892, 637.

[2] In practice, adulterated samples will contain much more.

which give the nitric acid test so faintly that olive oils mixed with 10 per cent of cotton seed oil showed no brown colour. The impurity in cotton seed oil giving the brown colouration is therefore not characteristic of all cotton seed oils without exception, but fortunately such exceptionally pure cotton seed oils are rare (cp. also "Lard," p. 580).

2. *The Silver Nitrate Test.*—The silver nitrate test was proposed first by *Becchi*, and, although persistently condemned by several chemists, has been upheld by *Becchi*, and by a special committee appointed by the Italian Government to inquire into its value.[1] According to *Del Torre* the following two reagents are required :—

REAGENT I.

Silver nitrate	1·00 grm.
Alcohol, 98 per cent (by volume)	200·0 c.c.
Ether	40·0 c.c.
Nitric acid	0·1 grm.

REAGENT II.

Amyl alcohol	100 c.c.
Colza oil	15 c.c.

The test is carried out as follows :—10 c.c. of the oil under examination are mixed in a test-tube with 1 c.c. of reagent I., and then shaken with 10 c.c. of reagent II. The mixture is next divided into two equal portions, one of which is put aside for comparison later on, whereas the other is immersed in boiling water for a quarter of an hour. The heated sample is then removed from the water-bath and its colour compared with that of the first portion. Presence of cotton seed oil is indicated by the reddish-brown colouration of the heated portion. *De Negri* and *Fabris* lay stress on the necessity of using the purest alcohol. The colza oil used should be "cold-drawn" oil, and only slightly coloured; it should be filtered in a hot water oven before preparing the reagent. To guard against possible errors arising from the impurity of the reagents a blank test should be instituted side by side with the actual test.

Peruzzi, *Ridolfi*, *Roster*, and *Wiley* have tested *Becchi's* method in the case of over 200 samples of oil, and have found it thoroughly reliable, no other oil giving the brown colouration. *Holde*,[2] on the contrary, considers the test as absolutely valueless; but the experiments of *De Negri* and *Fabris*, and also tests made repeatedly by the writer (see below), prove that *Holde's* statements are too sweeping, and most likely too hastily deduced from the observations on the particular sample he examined.

The part played by the colza oil in this test is explained, according to *Becchi*, by the fact that whereas fresh cotton seed oils give the silver nitrate reaction without colza oil, old and rancid samples of oil, or

[1] *Annali del Laboratorio Chimico*, 1891-1892, 197.
[2] *Jour. Soc. Chem. Ind.* 1892, 637.

their mixed fatty acids, do not react with his reagent unless colza oil be added. Many chemists who apply *Becchi's* test to the detection of cotton seed oil in lards (as *Hehner*, *Stock*, *Pattinson*, *Ritsert*, *Wesson*, *Bishop*, *Ingé*, *Milliau*, *a.o.*) omit the addition of colza oil as unnecessary. The application of *Becchi's* test to the detection of cotton seed oil in lard will be detailed below (p. 580).

Milliau[1] finds that *Becchi's* method leads to fallacious results, besides having the drawback of introducing a serious cause of error with the colza oil, which may itself be impure. He modifies *Becchi's* test by adding the silver solution to the mixed fatty acids instead of to the neutral oil. *Milliau* proceeds as follows:—5 c.c. of the fatty acids of the sample are dissolved in 15 c.c. of 95 per cent alcohol and heated in the water-bath to 90° C., when 2 c.c. of a 30 per cent solution of silver nitrate are added, and the mixture heated until about one-third of the alcohol has evaporated. It will then be found, if the sample be cotton seed oil, or contain cotton seed oil, that the silver nitrate is reduced to a metallic state, producing a black or brown colour in the liquid, or giving particles of reduced silver. Even 1 per cent of cotton seed oil, as he states, can thus be detected. *Wiley*[2] considers this test a very useful one, whereas *Hehner*[3] sees no advantage in this modification of *Becchi's* test, an opinion in which I fully concur. In many samples, where cotton seed oil was present and was indicated by *Becchi's* test, no reaction was obtained. A test which yields such erratic results deserves no confidence. The fact that some chemists find *Milliau's* modification reliable can only be explained by the difference of the samples, and perhaps also by the circumstance, that when negative results were obtained the reducing principle had been destroyed during the preparation of the fatty acids.

The reduction of silver nitrate seems to be effected by a substance of an aldehydic nature, the properties of which have not yet been investigated.[4] It should be noted that this silver-reducing substance is destroyed or oxidised by heating cotton seed oil or its fatty acids to 240° C. (*Wesson*), or even by keeping the sample or the free acids for some time. Therefore, cotton seed oil heated to 240° C. cannot be identified or recognised in other fats by *Becchi's* or *Milliau's* tests.

Benedikt has found that some samples of cotton seed oil do not reduce *Becchi's* reagent either with or without the addition of colza oil. Since *Becchi* himself states that old samples of oil only reduce the silver when colza oil has been added, the value of all the modifications proposed becomes doubtful.[5] The writer has examined mixtures of fresh (Egyptian) cotton seed oil with olive oil, and finds that an

[1] *Compt. rend.* 106. 550 ; *Jour. Soc. Chem. Ind.* 1893, 716.

[2] *Lard and Lard Adulterations.* Washington, 1889, 467.

[3] *Analyst*, 13. 165.

[4] Dupont (*Jour. Soc. Chem. Ind.* 1895, 811) ascribes the Becchi reaction to the formation of silver sulphide, he having obtained on passing a current of steam through cotton seed oil a volatile substance yielding sulphuric acid on oxidation. But as the remaining oil still gave the Becchi test, the proof for *Dupont's* opinion is still wanting.

[5] Wilson also (*Chem. News*, 59. 99) states that cotton seed oil, after keeping for some time, loses its power of reducing silver nitrate.

admixture of 10 per cent of cotton seed oil can be detected with certainty; whereas in the case of 5 per cent the reaction becomes indistinct. The silver nitrate test can therefore only be relied upon as decidedly indicating presence of cotton seed oil if a positive reaction has been obtained. Absence of colouration, however, does not positively indicate absence of cotton seed oil. Since, according to *Wesson*, pure lard (p. 580) gives a slight colouration with silver nitrate, even the appearance of a brown colour should not be considered as absolute proof of adulteration with cotton seed oil.

The nitric acid test will therefore be found more reliable than the silver nitrate test.

3. *The Gold Chloride Test.*—*Hirschsohn*[1] has recommended gold chloride for the detection of cotton seed oil. The reagent is prepared by dissolving 1 grm. of crystallised gold chloride in 200 c.c. of chloroform. To 5 c.c. of an oil to be tested 5 to 6 drops of this reagent are added, and the mixture heated for twenty minutes in the water-bath. Cotton seed oil will give a beautiful red colour, even if only 1 per cent be present. *Moerk*,[2] however, states that the same colouration is produced by poppy seed, walnut, arachis, sesamé, and ben oils, whereas *Dieterich*,[3] contradicting *Moerk*, confirms the reliability of *Hirschsohn's* test.

Holde,[4] again, confirms *Moerk's* results, and adds hemp seed oil to the list of oils producing the same reaction. These conflicting statements must be due to differences in the oils used by the various writers.

However that may be, the value of *Hirschsohn's* test is considerably impaired by the fact that cotton seed oil heated to 240° C. does not give the red colour; besides, also free fatty acids and rancid lard interfere with the delicacy of the reaction (*Wesson*[5]). It is evident that any other reducing substance will produce *Hirschsohn's* reaction and that this test cannot claim any superiority over the two foregoing tests.

4. *Lead Acetate Test.*—*Bradford* (*Pharmacopœia of the United States*) recommends the use of basic lead acetate (vinegar of lead), which is said to produce a reddish colour when equal parts of cotton seed oil and lead solution are shaken together and allowed to stand for twelve to twenty-four hours. *De Negri* and *Fabris* reject this test as valueless, several samples of pure olive oil having given the same reaction.

Labiche[6] has modified the lead acetate test by mixing 25 c.c. of the sample (*e.g.* lard) with 25 c.c. of a 50 per cent solution of lead acetate and 5 c.c. of ammonia at a temperature of 35° C., and shaking until a homogeneous emulsion is formed. Cotton seed oil is stated to assume, under these circumstances, a reddish-orange colour, whilst olive, castor, almond, and other oils give a red colour. According to *Girard*,[7] however, this test is valueless.

[1] *Jour. Chem. Soc.* 1889, Abstr., p. 658.
[2] *Amer. Jour. of Pharmacy*, 1889, 65.
[3] *Helfenberger Annalen*, 1889, 106.
[4] *Jour. Soc. Chem. Ind.* 1892, 637.
[5] Wiley, *Lard*, etc., p. 502.
[6] *Jour. Soc. Chem. Ind.* 1888, 404.
[7] *Monit. Scientif.* 1889, 965.

Deiss[1] claims to be able to detect an admixture of even 5 per cent of cotton seed oil with olive oil by modifying *Labiche's* test in the following manner:—10 c.c. of the oil are dissolved in 10 c.c. of ether, the solution shaken with 5 c.c. of a concentrated solution of lead acetate, and again shaken after addition of 5 c.c. of ammonia. Since, however, the quantity of fraudulently admixed cotton seed oil, as a rule, exceeds 15 to 20 per cent, *Deiss* considers that the original method of *Labiche* will suffice for most cases. (According to *Bishop* and *Ingé*[2] old samples gave a more pronounced colouration than fresh ones.) *Dieterich*,[3] however, confirming *Labiche's* observations, condemns *Deiss's* method as valueless, having found that, besides cotton seed oil, poppy seed and walnut oils give an orange-red colour; under the same conditions, arachis, olive, sesamé, and sunflower oil gave orange to yellow colourations. Furthermore, cotton seed oil that has been heated to 240° C. remains absolutely white after treatment with lead solution, even after standing for several days. *Engler* and *Rupp*, again, do not consider the colourations reliable, these being influenced by the action of light, age of the oil, and especially the state of rancidity.

The writer is unable to see any advantage in *Labiche's* test, as on the one hand other vegetable oils give the same colourations, and on the other heated cotton seed oil is not affected. In lard, containing 10-15 per cent of cotton seed oil, the adulterant could not be detected. Besides, it is difficult to understand what the reagent is to indicate, and why such an enormous excess of the reagent—just as in *Milliau's* test—is used to detect a substance which can only be present in very minute quantities.

For the detection of cotton seed oil in other fats, compare also—"Olive Oil" (p. 463), "Tallow" (p. 597), "Lard" (p. 580), "Edible Fats" (chap. xii. p. 683).

Cotton seed oil being almost one of the cheapest fatty oils is hardly liable to adulteration. Still, if linseed oil is cheaper than cotton seed oil (as has happened occasionally) an admixture with linseed oil may occur. The iodine test, the oxygen absorption test, and the test with sulphuric acid would easily indicate presence of linseed oil.

Cotton seed stearine and cotton seed blown oils will be described p. 506 and p. 734.

SESAMÉ OIL (GINGILI OIL, TEEL OIL)

French—*Huile de sésame.* German—*Sesamoel.*

For tables of constants see pp. 387, 388.

Sesamé oil is obtained from the seeds of the sesamé plant, *Sesamum orientale* and *Sesamum indicum*, belonging to the family of *Bignoniaceæ*.

[1] *Chem. Zeit.* 1888, Rep. 191. [2] *Jour. Pharm. Chim.* 1888, 348.
[3] *Helfenberger Annalen*, 1890, 79.

The oil possesses a yellow colour, is free from odour, and has a pleasant taste, so much so, that the "cold-drawn" oil is considered equal to olive oil as an edible oil, and is even sometimes preferred to the latter on account of its peculiar taste.

Sesamé oil consists of the glycerides of stearic, palmitic, oleic and linolic acids. Judging from the iodine value, the proportion of linolic acid among the liquid acids of sesamé oil must be considerable.

Compared with cotton seed oil, its drying powers are very weak, the absorption of oxygen, in the *Livache* test, amounting to only 2·4 per cent after seven days for the oil, and to 2·0 per cent after eight days for the fatty acids.

The amount of free fatty acids in a number of samples of "sweet oil" and commercial oil has been determined by *Nördlinger* with the following result :—

Kind of Oil.	No. of Samples.	Free Fatty Acids in terms of Oleic Acid.
		Per cent.
Sweet oil	14	0·47 to 5·75
Commercial oil, expressed .	7	7·17 to 33·13
Commercial oil, extracted .	7	2·62 to 9·71

Tested with nitrous acid, sesamé oil becomes red after a short time, and later on acquires a dirty reddish-brown colour, yielding even after twenty-four hours' standing only a semi-fluid **elaïdin**.

[TABLE

Physical and Chemical Constants of Sesamé Oil

Specific Gravity.			Solidifying Point.		Hehner Value.		Reichert Value.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index.		
At °C.		Observer.	°C.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	At °C.		Observer.
15	0·9225	Souchère	−5	Girard	95·86	Bensemann	0·35	Medicus and Scherer	190	Valenta	106	Hübl	68	Maumené	15	1·4748-1·4762	Strohmer
15	0·923-0·924	Allen	−4 to −6	De Negri and Fabris	95·6	Dietzell and Kressner	..	..	194·6	Longi and Leone	102·7	Moore	65	Archbutt	60	1·4561	Thoerner
15	0·9230-0·9237	De Negri and Fabris	..	..	..		Reichert-Meissl Value.		187·6-191·6	Filsinger	108-111·7	Dieterich	65	Del Torre	Oleo-refractometer.		
18	0·9208-0·9212	Long	..	..	..	..			188·5-190·4	De Negri and Fabris	106·4-109	Filsinger	63-64	De Negri and Fabris			
23	0·919	Dieterich							189-190·5	Oliveri	104·9-105·3	Del Torre			"Degrees."		Observer.
35	0·9078-0·9098	Long	..	..	..	..	1·2	Thoerner	192-193	Thoerner	107-112	Peters			+17 to +18		Jean
											106·9-107·8	De Negri and Fabris			+13 to +17 at 22° C.		Pearnain
											105-107	Oliveri					
											103-105	Thoerner			Butyro-refractometer.		
															At 25° C.		Observer.
															69		Beckurts and Seiler
															67-68·2		Mansfeld

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Saponification Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
22·3	Hübl	26	Hübl	199·3	Valenta	286	Valenta	108·9-111·4	Morawski and Demski	1·4461	Thoerner
28·5	Dieterich	31·5	Dieterich	201·6	Thoerner	...	...	111·8-112	De Negri and Fabris		
18·5	Allen	23	Allen	...	...	...	...	110-111	Thoerner		
25-26	Bensemann [1]	29-30	Bensemann [2]								
		21-30	Peters								
20-22	De Negri and Fabris	24-26	De Negri and Fabris								
		25-32									
23·5	Thoerner		Thoerner								
Titer Test.											
22·9-23·55	Lewkowitsch										
23·7-23·8	,,										
21·2-22·93	,,										

[1] Point of incipient fusion.

[2] Point of complete fusion.

Sesamé oil is dextro-rotatory, a property which may be found useful as an additional means of identifying the oil. It should, however, be noted that only in the absence of castor, croton, and resin oils would the polarimetric observation be of any use (p. 120). The optical activity of the oil is no doubt due to that of the alcohol $C_{25}H_{44}O$, and to sesamin (see below).

Besides glycerides, sesamé oil contains a small quantity of foreign substances, which can be extracted by agitating the oil with glacial acetic acid. According to *Tocher*[1] glacial acetic acid extracts from sesamé oil two substances—

(*a*) A resinous substance which forms long crystalline needles (from alcohol), melting at 118° C. From a number of ultimate analyses and from determinations of the molecular weight (by *Raoult's* method in benzene and acetic acid) the formula $C_{18}H_{18}O_5$ is derived. This substance was named *sesamin*. Sesamin does not give *Tocher's* pyrogallol reaction[2] (see below) nor the *Baudouin* test (see below), but it assumes a green and then bright red colour with nitro-sulphuric acid (the colour reaction given by the U.S.P. for sesamé oil).

(*b*) A thick brown oil (composition unknown) which gives the characteristic colour reactions of sesamé oil.[2]

Villavecchia and *Fabris*[3] state that by extracting the oil itself with either acetic acid or alcohol, the chromogenetic substance cannot be wholly removed. By converting the oil into barium soap, and extracting the latter with alcohol, these chemists isolated from the alcoholic extract, by evaporating off the alcohol, and dissolving the residue in petroleum ether, three substances—

1. A higher alcohol of the formula $C_{25}H_{44}O$, melting point 137° C., and rotatory power $[a]_D^{20} = -34° 23'$, where $c = 5{\cdot}013$.[4]

2. A substance forming beautiful crystals of the formula $C_{11}H_{12}O_3$, melting point 123° C., and rotatory power $[a]_D = +68{\cdot}36$, where $c = 24{\cdot}45$ in chloroformic solution. This substance is called by the authors *sesamin*. It is apparently identical with *Tocher's* sesamin $C_{18}H_{18}O_5$, for theory requires for $C_{18}H_{18}O_5$, C = 68·79 per cent, H = 5·73, and for $C_{11}H_{12}O_3$, C = 68·75, H = 6·25. As *Tocher* found the molecular weight (by Raoult's method) of sesamin to be 311 (in benzene) and 312 (in acetic acid), the formula $C_{11}H_{12}O_3$ must be rejected.[5]

3. A thick, non-crystallisable oil, free from nitrogen. This oil contains the substance which produces the characteristic reaction with sugar and hydrochloric acid (see below), a very minute quantity

[1] *Pharm. Jour. and Trans.* 1891, 639; 1893, 700.

[2] Merkling's (*Jour. Soc. Chem. Ind.* 1888, 45) statement that it is the glacial acetic extract which gives the characteristic colour reaction of sesamé oil requires therefore correcting.

[3] *Jour. Soc. Chem. Ind.* 1894, 69.

[4] The authors do not state whether this alcohol is cholesterol; the data given above point with great probability to that substance. *Tocher* (private communication) states that he has isolated cholesterol from sesamé oil in 1890.

[5] Villavecchia and Fabris have since (*Annali del Lab. Chim. delle Gab.* iii. 1897, p. 22) found the molecular weight by Raoult's method in benzene to be 350, which they collate with 384, the number demanded by theory for $(C_{11}H_{12}O_3)_2$.

giving the crimson colour with those reagents (cp. *Tocher's* substance (*b*)).

The last-mentioned **colour reaction** is extremely characteristic of sesamé oil, and it may be detected thereby with certainty in mixtures with other oils. This test, due to *Camoin*, generally, however, known as the *Baudouin* reaction, is the only colour reaction which has hitherto been found absolutely reliable in the analysis of oils and fats (p. 315). True, *Schneider*[1] has stated that sugar and hydrochloric acid alone produce the same colouration, and that also castor, olive, almond, and croton oils behave similarly; but *Benedikt* has proved by experiments that *Schneider's* objection is unfounded. Pure olive oil, if care be taken not to heat the sample, gave no colouration whatever; on heating, the aqueous liquid acquired a brown colour, which, however, can by no means be mistaken for the crimson colour produced by sesamé oil.

Later, however, it has been shown that, in the case of some Tunisian and Algerian olive oils (*Domergue*,[2] *Burker*[3]) and also in the case of some Italian olive oils (*Lalande* and *Tambon*[4]), the aqueous liquid assumes, on applying this test, after a short time a violet colouration, which, although differing from the crimson colour characteristic of sesamé oil, may lead to error. *Villavecchia* and *Fabris*[5] confirmed this observation for some varieties of olive oil of undoubted purity[6] (obtained from the provinces of Bari, Brindisi, and Lecce); but they state that if *Baudouin's* test is applied in the following way, it is easy to distinguish even those anomalous olive oils from sesamé oil.

Baudouin's Test, as recommended by Villavecchia and Fabris.—Dissolve 0·1 grm. of sugar in 10 c.c. of hydrochloric acid of spec. grav. 1·19 in a test-tube, add 20 c.c. of the oil to be tested, shake thoroughly for one minute, and allow to stand. The aqueous solution separates almost immediately. In the presence of even the smallest quantity of sesamé oil it will be found coloured crimson. In the presence of pure olive oil, however, the aqueous layer will remain colourless for at least two minutes, and the oily layer has a greenish or yellowish colour, whereas the smallest quantity of sesamé oil will be indicated by a red colouration of the oil. In the case of those peculiarly behaving South Italian oils, it is rather the colouring of the oily layer than that of the aqueous solution which should be taken as an indication of the presence of sesamé oil.

Villavecchia and *Fabris*[7] attribute the chromatic reaction to the agency of levulose, or of substances produced by the action of hydrochloric acid on the latter; therefore glucose, maltose, and galactose

[1] *Commentary to the Austrian Pharmacopœia.*
[2] *Jour. de Chimie et Pharmac.* 1891, 34.
[3] *Die Seifen-, Oel-, u. Fettindustrie*, 2. 531.
[4] *Jour. de Chimie et Pharmac.* 1891, 234. [5] *Jour. Soc. Chem. Ind.* 1893, 67.
[6] Carlinfanti (*Selmi*, 1895, 49) states that the colouration given by pure olive oils may be removed by shaking the acid with three times its volume of water, whilst if the colour is due to only 0·5 per cent of sesamé oil, it is not affected by this treatment.
[7] *Jour. Soc. Chem. Ind.* 1894, 69.

cannot be used in place of saccharose. The main product of the interaction of levulose and hydrochloric acid being furfurol, these authors accordingly substitute the latter for the mixture of sugar and hydrochloric acid. Inasmuch as furfurol itself gives a violet tint with hydrochloric acid, it is necessary to use a dilute solution; it has been found best to employ a 2 per cent alcoholic solution of furfurol. The modified test is carried out in one of the following two forms:—

(*a*) Place 0·1 c.c. of the 2 per cent furfurol solution in a test-tube, add 10 c.c. of the oil to be tested, and 10 c.c. of hydrochloric acid of spec. grav. 1·19, shake the mixture for half a minute and allow to settle. In the presence of sesamé oil, even if it be less than 1 per cent, the aqueous layer will acquire a distinct crimson colour. In the absence of sesamé oil the lower layer is either colourless, or has at most, as in the case of a very rancid though pure olive oil, a dirty yellow colour.

(*b*) Mix, as above, 0·1 c.c. of the alcoholic furfurol solution with 10 c.c. of oil, and add 1 c.c. only of hydrochloric acid, agitate thoroughly and induce separation by addition of 10 c.c. of chloroform, when the aqueous layer will float on the top. Even less than 1 per cent of sesamé oil will be indicated by the crimson colouration of the liquid.

These two methods have been tried on a large number of olive and arachis oils obtained from various localities, and further on rape (colza), cotton seed, linseed, walnut, poppy seed, neat's foot, blubber, and fish oils, and their absolute reliability has been confirmed.[1]

Milliau[2] employs for the test, instead of the oil itself, the fatty acids derived from it, after drying them at 105° C., but there is no need for this complication.

Tocher's[3] reagent for the detection of sesamé oil, viz. a solution of 1 grm. of pyrogallol in 15 c.c. of concentrated hydrochloric acid, acts in a similar manner to furfurol. The pyrogallol solution is shaken with 15 c.c. of the oil in a separating funnel, and allowed to stand for one minute. The aqueous layer is drawn off and boiled for about five minutes. In presence of sesamé oil it becomes coloured, appearing red by transmitted, and blue by reflected light.

Considering the absolute reliability of the *Baudouin* reaction, all "modifications" and other colour reactions that have been proposed are of no importance. Therefore only a few will be mentioned.

Lalande and *Tambon*[4] shake 5 c.c. of nitric acid of spec. grav. 1·4 with 15 c.c. of the sample. A yellow colouration of the acid may be taken as an indication of presence of sesamé oil. This colouration, however, not being decisive, the nitric acid is carefully drawn off and diluted with water. In the case of pure sesamé oil a white flocculent precipitate is obtained; in mixtures of that oil with other oils, a turbidity only is noticeable, whereas in the case of pure olive,

[1] Further confirmation given by Wauters, *Jour. Chem. Soc. Ind.* 1896, 136.
[2] *Compt. rend.* 106. 550.
[3] *Pharm. Jour. and Transact.* 1891, 639. [4] *Jour. Pharm. Chim.* 1891, 234.

arachis, and cotton seed oils, the acid remains clear under the same conditions.

Bishop[1] uses hydrochloric acid of spec. grav. 1·18 in the proportion of two volumes of oil to three volumes of acid; for this test freshly expressed oil must not be used. If, however, the oil has been previously exposed to air and light for a few days, it gives with hydrochloric acid a green colour. After standing, the acid layer alone is found coloured. The intensity of the colour is proportional to the age of the oil. In the case of old oil bluish violet flakes deposit. Very old oil which has been exposed for years to air and light imparts to the acid an almost blue colour, and on standing a flocculent blue precipitate separates from the acid, the latter becoming of a clear green colour. When testing olive oil for sesamé oil, it is best to expose the sample to bright light for a few days. Sesamé oil, after this treatment with hydrochloric acid, still gives the *Baudouin* reaction.

Van Engelen's[2] reagent, viz. sodium molybdate and sulphuric acid, is useless in the case of mixtures of olive and sesamé oils, on this chemist's own showing.[3]

Sesamé oil is adulterated with poppy seed oil, arachis oil, cotton seed oil, and rape oil.

Poppy seed oil will be detected easily by the high iodine value and *Maumené's* test.

In the case of cotton seed, arachis, and rape oils, the iodine test will, of course, be of no use.

Cotton seed oil can be detected by the nitric acid and perhaps by *Becchi-Milliau's* tests. A higher value in the *Livache* test than the normal one, a higher melting point of the mixed fatty acids, and, no doubt, a higher iodine number of the liquid fatty acids than the normal one[4] will confirm the presence of this adulterant.

A lowering in the specific gravity of the oil may point to adulteration with **arachis oil**; this is ascertained by the isolation of arachidic acid (p. 445).

Rape oil, again, may be detected by deviation from the normal numbers of the specific gravity, the solidifying and melting points of the fatty acids, and notably the saponification value.

The better qualities of sesamé oil are largely used as an edible oil (in the manufacture of margarine[5]); the lower qualities find an outlet in the soap-making and perfumery trades. The lowest qualities are employed as burning oil.

[1] *Jour. Pharm. Chim.* 1889, 244. [2] *Bull. de l'Assoc. Belge*, 10. (1896), 161.

[3] The reagents proposed by *Cavalli* and by *Soltsien* are, in the writer's opinion, valueless. [4] This has not been determined yet.

[5] According to the latest German Margarine Act, margarine must be made to contain 10 parts of sesamé oil for 100 parts of fatty matter.

BASSWOOD OIL[1]

German—*Lindenholzoel.*

Physical and Chemical Constants of Basswood Oil

Specific Gravity.	Solidifying Point.	Saponific. Value.	Iodine Value.
At 15° C. (Water 15° C. = 1).	°C.	Mgrms. KOH.	Per cent.
0·938	−10	178·1	111

This oil was obtained from basswood (*Tilia Americana*) by extracting rasped wood with ether.

BEECHNUT OIL

French—*Huile de faines.* German—*Bucheckernoel.*

For tables of constants see p. 394.

Beechnut oil is obtained from the fruit of the red beech-tree, *Fagus sylvatica.* The cold-drawn oil is of pale yellow colour, limpid, and free from unpleasant taste. This quality of oil is used for culinary purposes, whereas the oil expressed at a higher temperature is employed as burning oil.

Beechnut oil is used in the adulteration of almond oil; its presence may be detected by determining the **iodine value** of the sample.

[1] Wiechmann, *Jour. Soc. Chem. Ind.* 1895, 665.

Physical and Chemical Constants of Beechnut Oil

Specific Gravity.		Solidifying Point.		Hehner Value.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index. Oleo-refractometer.	
At 15° C.	Observer.	°C.	Observer.	Per Cent.	Observer.	Mgrms. KOH.	Observer.	Per Cent.	Observer.	°C.	Observer.	"Degrees."	Observer.
0·9225	Chateau	− 17	Chateau	95·16	Girard	196·3	Girard	104·4	Girard	65	Maumené	+16·5 to +18	Jean.
0·920	Souchère	...	...	...	...	191·1	De Negri and Fabris	111·2	De Negri and Fabris	63	De Negri and Fabris		
0·9225	Schübler												
0·9205	Massie												
0·9220	De Negri and Fabris												

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
17	Girard	24	Girard	114	De Negri and Fabris
		23	De Negri and Fabris		

BRAZIL NUT OIL

French—*Huile de châtaignes du Brésil.* German—*Paranussoel.*

For tables of constants see p. 396.

Brazil nut oil is obtained from the seeds of the Brazilian nut tree —*Bertholletia excelsa.*

The oil is of pale yellow colour and odourless. Its taste is similar to that of the nuts themselves.

On standing, even at the ordinary temperature, the oil deposits "stearine"; it becomes easily rancid. Brazil nut oil is expressed from the nuts in South America for edible purposes. The nuts that have become mouldy in transit are expressed, and the oil thus recovered is used for soap-making or as a substitute for inferior kinds of olive oil.

Physical and Chemical Constants of Brazil Nut Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
0·9180	De Negri and Fabris	1	Schaedler	193·4	De Negri and Fabris	106·22	De Negri and Fabris [1]	50-52	De Negri and Fabris
0·9185	Schaedler	0-4	De Negri and Fabris						

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
31·1-32·25 [2]	Lewkowitsch	28-30	De Negri and Fabris	108	De Negri and Fabris

[1] The iodine value of Brazil nut oil extracted with solvents has been stated by *De Negri* and *Fabris* as 93·8-95·1.

[2] Titer test.

β. The Rape Oil Group

All the members of this group are obtained from seeds of plants belonging to the *Cruciferæ*.

Their drying powers are not of a marked character; the elaïdin obtained from them is a buttery mass.

Their most characteristic property is that they possess a much lower saponification value than any other vegetable oil (p. 305).

The opinion held for a long time that these oils contained sulphur has been shown to be erroneous; all the "cold-drawn" rape oils are free from sulphur, and absence of that element in an oil does not, therefore, prove absence of rape oil. Presence of sulphur, however, may point to a rape oil expressed at a high temperature.

We describe the following oils: Garden cress oil, hedge mustard oil, rape oil, black mustard oil, white mustard oil, radish seed oil, Jambo oil.

GARDEN CRESS OIL

French—*Huile de cresson alénois.* German—*Gartenkressensamenoel.*

For table of constants see p. 398.

Garden cress oil is obtained from the seeds of the garden cress, *Lepidium sativum.*

The high iodine value of the oil, and especially its exceptionally high thermal reaction, place this oil nearer to the oils from the two cruciferous plants mentioned before, viz. cameline oil (semi-drying oil) and garden rocket oil (drying oil), than to the other oils belonging to the rape oil group. Garden cress oil ranks, therefore, among the slowly drying oils.

Physical and Chemical Constants of Garden Cress Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
0·924 0·920	Schaedler De Negri and Fabris	−15	Schaedler	178	De Negri and Fabris	108-108·8	De Negri and Fabris	92-95	De Negri and Fabris

Physical and Chemical Constants of the Mixed Fatty Acids

Melting Point °C.	Iodine Value. Per cent.	Observer.
16-18	111·40	De Negri and Fabris

HEDGE MUSTARD OIL[1]

French—*Huile de raphanistre.* German—*Hederichoel.*

Physical and Chemical Constants of Hedge Mustard Oil

Specific Gravity at 15° C.	Solidifying Point. °C.	Saponific. Value. Mgrms. KOH.	Iodine Value. Per cent.
0·9175	−8	174	105 (Hübl)

This oil is obtained from the seeds of the common hedge mustard, *Raphanus Raphanistrum.* It possesses a characteristic taste, at first mild, then harsh.

Hedge mustard oil also closely resembles rape oil. It was expressed for the first time in 1880, with a view of substituting it for rape oil, and is therefore mostly admixed with the latter oil. It is detected in rape oil, according to *Valenta*, by treating 5 grms. of the sample with an amount of alcoholic potash, insufficient for complete saponification, filtering the soap solution from the unsaponified oil, and adding strong hydrochloric acid to the filtrate, when a green colour is said to indicate presence of hedge mustard oil.

RAPE OIL [COLZA OIL]

For tables of constants see pp. 401-403.

The various kinds of rape oil are obtained from the seeds of *Brassica campestris* and of several largely cultivated varieties of this species belonging to the natural order *Cruciferæ.* The oils from these plants are, especially in this country, indiscriminately termed rape oil or colza oil; on the Continent, however, two kinds of oils are distinguished under the last two names. Occasionally, also, three kinds are recognised under the following names:—

1. Colza oil (French—*Huile de colza;* German—*Kohlsaatoel*) from the seeds of *Brassica campestris.*

2. Rape oil (French—*Huile de navette;* German—*Rapsoel, Repsoel*) from the seeds of *Brassica campestris,* var. *Napus.*

3. [Rubsen oil] French—*Huile de rabette;* German—*Rüboel, Rübsenoel;* from the seeds of *Brassica campestris,* var. *Rapa.*

A further distinction of each of these three oils into a winter and a summer variety may be indulged in, as has been done by some chemists, but as it is impossible to distinguish these last-mentioned

[1] Valenta, *Dingl. Polyt. Jour.* 247. 36.

Physical and Chemical Constants of Rape Oil

Specific Gravity.			Solidifying Point.		Hehner Value.		Saponification Value.		Iodine Value.	
At °C.		Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0·9112-0·9175	Schaedler	− 2 to − 10	Schaedler	95·1	Bensemann	178·7	Köttstorfer	100	Hübl
,,	0·914-0·917	Allen	− 4 to − 6·25	Girard	95·0	Dietzell and Kressner	177	Valenta	103·6	Moore
,,	0·9142	Souchère [1]	...	...	...	...	175·3	Dieterich	98·5-105	Dieterich
,,	0·9151	,, [2]	...	...	...	...	175-179	Allen	100·4-102·8	Wilson
,,	0·9150-0·917	De Negri and Fabris [1]	0 (after 8 hours)	Holde	...	...	170-176·4	Archbutt [3]	100·8-102·4	Archbutt
15·5	0·9133-0·9168	Thomson and Ballantyne	...	...	...	...	170·6-175·3	Thomson and Ballantyne	99·1-105·6	Thomson and Ballantyne
,,	0·9132-0·9159	Archbutt [3]	...	...	...	...	175-177	De Negri and Fabris	97·65-102·1	De Negri and Fabris
18	0·9144-0·9168	Stilurell	...	...	...	...	177-178	Oliveri	99-106	Oliveri
23	0·910	Dieterich							101·1	Wallenstein and Finck
99 (water 15·5 = 1)	0·8632	Allen							97-102·2	Fraenkel

[1] Colza oil. [2] Rape oil. [3] Fifty-two samples. *Jour. Soc. Chem. Ind.* 1886, 310.

Physical and Chemical Constants of Rape Oil—continued

Reichert Value.		Thermal Tests.				Refractive Index.		
		Maumené Test.		Heat of Bromination.				
c.c. $\frac{1}{10}$ norm. KOH.	Observer.	°C.	Observer.	°C.	Observer.	At °C.		Observer.
0·25	Reichert	57-58	Maumené	18·4	Hehner and Mitchell	15	1·4720 to 1·4757	Strohmer
0·3-0·4	Medicus and Scherer	60-92	Baynes	17·6				
		54-60	Dobb	17·3	Jenkins	20	1·4735	Holde
		55-64	Archbutt	17·20·3	Archbutt	60	1·4667	Thoerner
...	...	51-60	Allen					
...	...	49-51	De Negri and Fabris					
						Oleo-refractometer.		
						"Degrees."		Observer.
						+15 to +18·5 +16 to +20 at 22 C.[1]		Jean Pearmain
		Specific Temperature Reaction.						
						Butyro-refractometer.		
		125-144	Thomson and Ballantyne			At 25° C.		Observer.
						68		Mansfeld.

[1] Ravison oil + 20 to + 24 at 22° C. (Pearmain).

Physical and Chemical Constants of the Mixed Fatty Acids.

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Mean Molecular Weight.		Iodine Value.		Acetyl Value.		Refractive Index.	
°C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.		Observer.	At 60 °C.	Observer.
99 (water 15·5 = 1)	0·8438	Allen	12·2	Hübl	20·1	Hübl	185	Thoerner	321·2	Allen	96·3-99·02	Morawski and Demski	17·2	Lewkowitsch	1·4991	Thoerner
100 (water 100 = 1)	0·8758	Archbutt	18·5	Allen	18·3-19·5	Allen			307	Williams	105·6	Williams				
			18-17	Bensemann [3]	21-22	Bensemann [4]			314	Valenta	99·8-103·1	De Negri and Fabris				
					18·5-21	Archbutt										
					16-19	De Negri and Fabris										
			16	Thoerner	20	Thoerner										
			Titer Test.								Iodine value of the liquid fatty acids.					
			12·7-13·6 [1]	Lewkowitsch							120·7	Wallenstein and Finck.				
			11·7-12·2 [2]	,,												

[1] Colza oil. [2] Rape oil. [3] Point of incipient fusion. [4] Point of complete fusion.

varieties by their chemical or physical properties, and furthermore as, in the trade, all three varieties are indiscriminately sold as *rape oil* or *colza oil*, we comprise within the two tables of the physical and chemical constants of the oil and its mixed fatty acids all the data that have been furnished by the several analysts who have examined the rape oils of commerce.

The refined oil of commerce is pale yellow, and possesses a characteristic smell [which may serve to identify the oil], and an unpleasant harsh taste. 100 parts of alcohol dissolve 0·534 parts of the oil.

Rape oil consists chiefly of the glycerides of stearic, oleic, and erucic acids. *Reimer* and *Will* [1] state that the liquid fatty acid of rape oil is not oleic acid, but rapic acid, to which they ascribed the formula $C_{18}H_{34}O_3$; it has, however, been shown by *Zellner* (p. 58) that rapic acid is an isomeride of oleic acid and has the composition $C_{18}H_{34}O_2$. Besides the erucic and rapic acids, *Reimer* and *Will* have also found behenic acid (p. 49) in rape oil. *Ponzio*,[2] confirming the occurrence of erucic and rapic acids in about equal proportions, states that what *Reimer* and *Will* termed behenic acid is in reality arachidic acid, present in rape oil to the extent of 0·4 per cent.

The high iodine value of rape oil points to the presence of an unsaturated fatty acid belonging to the series $C_nH_{2n-4}O_2$, or perhaps a lower series, the theoretical iodine values of the triglycerides of oleic, erucic, and rapic acids being 86·2, 72·2, and 81·6 respectively.

Halenke and *Möslinger* [3] have examined globular masses which had separated on standing from a sample of rape oil at the ordinary temperature, and obtained the following results :—

	Melting Point. °C.	Saponific. Value.
Fat	38·5	161·76
Fatty acids . .	34	160·05

The fat consisted, therefore, of almost pure trierucin.

Reimer and *Will*,[4] however, have found that the solid fat separating from older samples of rape oil is dierucin, the diglyceride of erucic acid. By dissolving the solid mass in ether, filtering and precipitating with alcohol, colourless needles having the melting point 47° C. are obtained.

Rape oil contains, according to *Allen* and *Thomson*, unsaponifiable matter (phytosterol, see below) to the extent of about 1 per cent. *Thomson* and *Ballantyne* found in five samples of oils 0·58 to 0·70 per cent of unsaponifiable matter.

[1] *Berichte*, 1887, 2388.
[2] *Jour. prakt. Chemie*, 1893, 487 ; *Jour. Soc. Chem. Ind.* 1894, 257.
[3] *Corresp. d. Vereins d. bayer. Chem.* No. 1. [4] *Berichte*, 1886, 332.

Commercial rape oil contains as a rule free fatty acids. In the following table some numbers found by various observers are recorded :—

Free Fatty Acids in Rape Oils

Description of Oil.	No. of Samples.	Free Fatty Acids in terms of Oleic Acid.	Observer.
		Per cent.	
...	1	4·28	Salkowski
...	1	6·64	Rechenberg
Sweet oil	3	0·53–1·82	Nördlinger
Commercial oil, expressed .	9	0·52–6·26	,,
,, ,, extracted .	2	0·77–1·1	,,
Commercial oil . . .	5	2·43–6·24	Thomson and Ballantyne
Commercial oil . . .	50	1·7–5·5	Archbutt
Commercial oil . . .	5	1·05–3·9	Deering

If the oil is to be used for burning, the proportion of free fatty acids should be as small as possible. The oils obtained by extraction are, as a rule, purer than those prepared by expression, a large amount of albuminoid and mucilaginous substances passing into the oil in the latter process.

Tested according to *Livache*, rape oil absorbs 2·9 per cent of oxygen after seven days, whereas the fatty acids absorb only 0·9 cent after eight days. (Cp. also p. 287.) The oil thickens and becomes rancid, without, however, drying. Rape oil may, therefore, be considered as representing a class of oils occupying an intermediate position between the semi-drying and the non-drying oils.

The **elaïdin test** does not yield characteristic indications.

Rape oil is largely adulterated with the following fatty oils : Linseed, hemp seed, poppy seed, cameline, cotton seed, fish oils, and hedge mustard oil ; paraffin and resin oils are also fraudulently added.

The unsaponifiable oils are easily detected by the estimation of the **unsaponifiable matter**. Addition of large quantities of *linseed*, *hemp seed*, *poppy seed*, *cameline*, and *fish oils*, would be indicated by the **iodine value** and by the determination of one of the following constants : specific gravity, melting point of the fatty acids, thermal tests, saponification value, and especially the viscosity of the oil.

The **specific gravity** of rape oil rarely exceeds 0·916, and this may be considered for practical purposes as the limit, although, as will be seen from the table given above, higher values have been recorded. Of the fifty-two samples examined by *Archbutt*—

7 samples had a specific gravity below 0·9140
27 ,, ,, ,, above 0·9139, but below 0·9150
18 ,, ,, ,, ,, 0·9149, ,, 0·9160

The specific gravities of the other fatty oils that may be used as adulterants are higher than 0·9160, so that a sample of oil the specific gravity of which exceeds that figure must be looked upon with suspicion. Of course, presence of an unsaponifiable oil cannot be detected by determination of the specific gravity.

The **melting point of the fatty acids**, or, better still, the **solidifying point** (titer test), will be higher than the normal one if cotton seed oil has been added; on the other hand, it will be lowered by the presence of linseed oil or of any of the other oils mentioned above.

The **temperature test** with sulphuric acid or bromine[1] will indicate admixture of linseed or other drying oils, or semi-drying oils, such as cotton seed oil.

The **saponification value** of the sample under examination will easily lead to a decision whether any other fatty oil, with *the exception of the oils belonging to the rape oil group, such as hedge mustard oil*, is present. In consequence of the large proportion of erucin in rape oil its saponification value is very low, lower than that of any of the fatty oils mentioned above. [Castor oil and grape seed oil, which are also characterised by low saponification values, need not be considered here, as their employment as an adulterant for rape oil is out of the question.] It should not be forgotten, however, that a low saponification value may also be found if unsaponifiable oils are present. If so, they must be first separated, and the saponification value of the fatty acids determined subsequently.

The following are the saponification values of the fifty-two samples examined by *Archbutt*:—

For	4	samples	170 to	171
	12	,,	171 ,,	172
	9	,,	172 ,,	173
	14	,,	173 ,,	174
	11	,,	174 ,,	175
	1	,,	175 ,,	176
	1	,,	176 ,,	177

It may be repeated that the other members of the rape oil class have also low saponification values.

The determination of the **viscosity** of rape oil is a very valuable means of ascertaining its purity. It will be found best to compare the sample with a standard rape oil of known purity, as the viscosity of rape oil is fairly constant. Since no other oil likely to be used as an adulterant possesses so high a viscosity as rape oil, the genuineness of the sample can be easily and quickly ascertained.

The **Valenta test** (p. 270) is very characteristic of rape oil, and will prove useful as an additional means of deciding whether a sample of rape oil is genuine or not.

Fish oils in rape oil may be recognised by their peculiar smell

[1] Cp. Archbutt, *Jour. Soc. Chem. Ind.* 1897, 311.

and taste, especially on warming, and perhaps also by the intensity of the phospho-molybdic acid reaction (p. 316).

There is, according to *Schweissinger*,[1] in commerce a specially prepared "refined fish oil" recommended as an adulterant for rape oil, which could not be detected in rape oil by the chlorine, and other antiquated colouring reactions for fish oils (p. 278). The determination of the iodine value, of the saponification value, and the detection of cholesterol, however, were quite sufficient to prove the addition of this adulterant. The figures collated in the following table for pure rape oil, this "refined fish oil," and a mixture of the two oils, demonstrate this clearly :—

	Rape oil.	"Refined Fish Oil."	Rape oil, containing 20 per cent of "Refined Fish Oil."
Specific gravity at 15° C. . . .	0·915	0·931	0·919
Saponification value	181	218	191
Iodine value	98	142	107
Melting point of the mixed fatty acids	21	26	23
Solidifying ,, ,, ,,	16	19	17

Besides these constants, the examination of the unsaponifiable matter furnishes a very valuable clue as to the nature of the adulterant. The unsaponifiable matter of rape oil consists of phytosterol, whereas the fish oils are characterised by cholesterol, which can be detected by the colour reactions given for the latter (p. 84).

As rape oil is refined with concentrated sulphuric acid, commercial oils should be tested for the presence of sulphuric acid by shaking the oil with warm water and examining the latter.

The detection of rape oil in *other oils* by means of *Mailho's* or *Schneider's*[2] reagents, purporting to show presence of sulphur, can no longer be considered as useful, since it has been proved that sulphur is not a constitutive element of the oils obtained from the seeds of *Cruciferæ*. The "cold-drawn" oils of commerce are completely devoid of sulphur, but oils extracted by means of carbon disulphide (as olive kernel oil, etc.) may retain some sulphur, the last traces of the solvent being extremely difficult to remove. Rape oil would be detected by its characteristic smell, or by the influence its presence exercises on the constants of the oil under examination, especially on the saponification value (cp. "Olive Oil," p. 461). The colour reaction proposed recently by *Palas*[3] for the detection of rape oil in olive oil (viz. agitation with rosaniline sulphite) is not characteristic of rape oil only, as any other oil containing silver-reducing substances, such as, *e.g.*, cotton seed oil, gives the same reaction. Experiments instituted by the writer proved that Palas' statement to the contrary is erroneous.

[1] *Pharm. Central-Halle*, 1890, 713. [2] Cp. page 463.
[3] *Jour. Soc. Chem. Ind.* 1897, 361.

BLACK MUSTARD OIL

French—*Huile de moutarde noire.* German—*Schwarzsenfoel.*

For table of constants see p. 408.

Black mustard oil is obtained from the seeds of *Sinapis nigra*. The oil has a brownish-yellow colour, and possesses a mild taste; it smells of the ethereal mustard seed oil.

In its chemical composition it closely resembles rape oil; like the latter, it contains the glycerides of erucic and behenic (or arachidic ?), and also of a liquid fatty acid [1] (rapic acid ?).

Nördlinger has found in two samples of the oil free fatty acids to the extent of 0·68 and 1·02 per cent, calculated to oleic acid.

The oil is a by-product; it is not so suitable for burning as the white mustard oil, and is therefore used for soap-making.

[1] Goldschmiedt, *Wiener Berichte*, 70.[2], 451.

Physical and Chemical Constants of Black Mustard Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
0·9170	Chateau	−17·5	Chateau	174·0-174·6	De Negri and Fabris	96	Moore	44	Girard
0·9183	Clarke			174·7	Blasdale	106·25-106·57	De Negri and Fabris	42-43	De Negri and Fabris
0·9180	Massie					103·07	Lengfeld and Paparelli	58·5 (!)	Lengfeld and Paparelli
0·916-0·920	Allen					103·6	Blasdale [1]		
0·9170-0·9175	De Negri and Fabris								
0·9161	Blasdale								

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
15·5	Girard	16	Girard	109·6	De Negri and Fabris
...	...	16-17	De Negri and Fabris		
		15	Blasdale		

[1] *Jour. Soc. Chem. Ind.* 1896, 206.

WHITE MUSTARD OIL

French—*Huile de moutarde blanche.* German—*Weisssenfoel.*

For tables of constants see p. 410.

White mustard oil is obtained from the seeds of *Sinapis alba* The oil is of a golden-yellow colour, and has a burning taste.

Most of its physical and chemical constants are almost identical with those of black mustard oil. The iodine values, however, appear to differ considerably.

The oil is used as a burning and lubricating oil.

Physical and Chemical Constants of White Mustard Oil

Specific Gravity.		Solidifying Point.		Hehner Value.		Saponification Value.		Iodine Value.		Maumené Test.	
At 15° C.	Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
0·9142	Chateau	−16·25	Chateau	96·7	Lengfeld and Paparelli	170·3-171·4	De Negri and Fabris	92·1-93·8	De Negri and Fabris	44-45	De Negri and Fabris
0·914-0·916	Allen	−8 to −16	Schaedler	..	..	173·9	Blasdale	97·68	Lengfeld and Paparelli	49·5	Lengfeld and Paparelli
0·9145	Schaedler							98·4	Blasdale		
0·9125-0·9160	De Negri and Fabris										
0·9151	Blasdale										

Physical and Chemical Constants of the Mixed Fatty Acids

Melting Point °C.	Iodine Value. Per cent.	Observer.
15-16	94·7-95·87	De Negri and Fabris
16	...	Blasdale

RADISH SEED OIL

French—*Huile de raifort.* German—*Rettigoel.*

For tables of constants see p. 412.

Radish seed oil, like the oils described last, closely resembles rape oil. The green colour, which is said to be characteristic of the soap solution of hedge mustard oil, is not obtained with this oil (*De Negri* and *Fabris*).

Physical and Chemical Constants of Radish Seed Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
0·9175	Schaedler	−10 to −17·5	Schaedler	178·05	De Negri and Fabris	95·6-95·9	De Negri and Fabris	51	De Negri and Fabris
0·9175	De Negri and Fabris								

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point °C.	Melting Point °C.	Iodine Value. Per cent.	Observer.
13-15	20	97·1	De Negri and Fabris

JAMBO OIL [1]

Physical and Chemical Constants of Jambo Oil

Specific Gravity at 15° C.	Solidifying Point. °C.	Saponification Value.	Iodine Value.	Maumené Test. °C.
0·9150-0·9158	−10 to −12	172·26	95·2-95·6	51-53

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.	Saponification Value.	Iodine Value.
°C.	°C.	Mgrms. KOH.	Per cent.
16-11	19-21	173·8-174	96·1-96·2

This oil, obtained from the seeds of a plant belonging to a variety of the genus *Brassica*, is closely related to rape oil. It is free from sulphur.

γ. Castor Oil Group

In this group are comprised four oils which, in consequence of their very weak drying properties, stand on the borderland between the semi-drying and the non-drying oils. Croton oil and curcas oil resemble castor oil in their medicinal properties and solubilities in alcohol—differing, however, from it in their chemical composition.

Castor oil and grape seed oil are remarkable as containing an extremely high proportion of hydroxy acids.

All four oils occupy a somewhat exceptionable position as regards their behaviour with solvents.

[1] De Negri and Fabris, *Annali del Laboratorio delle Gabelle*, 1891-92, 137.

CROTON OIL

French—*Huile de croton.* German—*Crotonoel.*

For table of constants see p. 415.

Croton oil is obtained from the seeds of *Croton Tiglium.*

The oil is of amber-yellow, or orange, or brown colour according to age, has a nauseous odour, a burning taste, and is a very powerful purgative. According to *Kobert*[1] there are some kinds of croton oil in commerce that are miscible with *alcohol* in every proportion. The solubility of different samples, however, varies so much that definite proportions cannot be given. Croton oil is soluble in *petroleum ether*, differing in this respect from castor oil. According to *Pèter* it is strongly dextro-rotatory.

Croton oil has not yet been exhaustively examined. Its chemical composition differs so widely from that of all other oils that its recognition by means of quantitative reactions is easy. The writer has found 0·55 per cent of unsaponifiable matter in various specimens of croton oil.

Croton oil contains the following fatty acids partly as free acids and partly as glycerides: Stearic, palmitic, myristic, lauric, valeric (isobutyl formic), butyric, acetic, formic, oleic, and tiglic. "Croton-oleic acid," which was said to constitute the purgative principle of the oil, and had been described as a non-volatile, unsaturated fatty acid, differing from oleic acid in that its barium salt was soluble in alcohol, is, according to *Dunstan* and *Bole*,[2] a resinous substance possessing extraordinary power as a vesicant.[3]

Croton oil is a weak drying oil; it thickens somewhat on exposure to air; it yields no elaïdin.

Castor oil is detected in croton oil, according to *Maupy*,[4] by heating 10 grms. of the sample in a silver dish with caustic potash; capryl alcohol escapes, recognisable by its characteristic smell, and sebacic acid crystallises from the aqueous solution obtained on boiling the residue with water.

[1] *Chem. Zeit.* 1887, 416. [2] *Jour. Soc. Chem. Ind.* 1895, 985.

[3] Its empirical formula is $C_{13}H_{18}O_4$; it is a hard, pale yellow, brittle resin, nearly insoluble in water, petroleum ether, and benzene, but easily soluble in alcohol, ether, and chloroform. On heating it softens gradually, and is quite fluid at 90° C. It has neither acid nor basic properties, and is decomposed by boiling with alkalis, yielding a mixture of acids, and losing its vesicating properties. This seems to point to this substance being a lactone or an anhydride.

[4] *Jour. Pharm. Chim.* 1894 [29], 362.

[TABLE

Physical and Chemical Constants of Croton Oil

Specific Gravity.		Solidifying Point.		Hehner Value.		Saponification Value.		Reichert-Meissl Value.		Iodine Value.		Acetyl Value.	
At 15° C.	Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.		Observer.
0·942	Schaedler	– 16	Schaedler	88·9	Lewkowitsch	215	Lewkowitsch	13·56	Lewkowitsch	74·1[3]	Mills	19·61-20·02	Lewkowitsch
0·9550[1]	,,	...	...	89·1	...	210·3	,,	13·27	,,	101·7-102	Lewkowitsch		
0·940-0·960[2]	,,	...	...	...	,,	...	...	..	...	103·9-104·7	,,		

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Saponification Value.	
°C.	Observer.	Mgrms. KOH.	Observer.
18·6-19	Lewkowitsch	201	Benedikt

[1] Old oil.

[2] *Arch. Pharm.* 1889, 357

[3] Calculated from bromine value 46·7.

CURCAS OIL (PURGING NUT OIL)

French—*Huile de médicinier.* German—*Curcasoel.*

For tables of constants see p. 417.

Curcas oil is obtained from the seeds of *Jatropha Curcas* (purging nut). It has a pale colour, but becomes yellow on exposure to air. Its odour is nauseous and slightly acrid. On account of its purging properties it is used in medicine. Of its chemical composition but little is known; it appears to contain ricinoleic acid. According to *Bouis* it contains the glyceride of isocetic acid (p. 45). Curcas oil differs from castor oil in its behaviour with solvents, being soluble in petroleum ether and insoluble in acetic acid. It is less soluble in alcohol than castor oil, requiring 100 parts of 96 per cent alcohol (*De Negri* and *Fabris*). According to *Arnaudon* and *Ubaldini*, curcas oil is soluble in cold alcohol, but when treated repeatedly with small quantities of this solvent a residue is left consisting of a solid fatty substance which requires a much larger proportion of alcohol for its solution. The oil obtained from the alcoholic solution, and from which the solid fat had been separated, was found to be more fluid and more readily soluble in alcohol than the original oil.

The **specific gravity** and also the **iodine value** serve to distinguish this oil from castor oil. Curcas oil has been used to adulterate olive oil (see p. 463).

Physical and Chemical Constants of Curcas Oil

Specific Gravity.		Solidifying Point.		Hehner Value.		Saponific. Value.		Iodine Value.		Reichert Value.	
At 15° C.	Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.
0·911	Girard	− 8	Girard	87·9	Horn	230·5	Horn	127	Horn	0·65	Horn
0·9192	Horn	9 to 0	Horn			210·2	De Negri and Fabris	100·9	De Negri and Fabris		
0·920	De Negri and Fabris [1]										
0·915	Arnaudon and Ubaldini [2]										

Physical and Chemical Constants of the Mixed Fatty Acids

Melting Point.		Iodine Value.	
°C.	Observer.	Per cent.	Observer.
24-26	De Negri and Fabris	105·05	De Negri and Fabris

[1] *Jour. Soc. Chem. Ind.* 1893, 453.

[2] *Ibid.* 1893, 934.

GRAPE SEED OIL

French—*Huile de raisins.* German—*Traubenkernoel.*

For tables of constants see p. 419.

Grape seed oil is obtained from grape seeds by expression or by extraction. The figures given in the tables refer to extracted oil.

The oil has a greenish-yellow colour, is transparent, and free from odour. It dissolves easily in glacial acetic acid at 70° C.; the solution becomes turbid at 66·5° C. In alcohol it dissolves only partially.

Grape seed oil does not dry on exposure to air.

The most prominent characteristic of this oil is its very high **acetyl value**, placing it, in this respect, in close relationship to castor oil. The occurrence of a large quantity of hydroxy acids renders *Fitz's* statement,[1] that grape seed oil contains largely erucic acid, more than doubtful. The sample examined by *Horn* had the acid value 16·2. Grape seed oil is expressed in various localities, and used as an edible oil and for burning. *Horn*[2] proposes to use this oil as a substitute for castor oil in the manufacture of turkey-red oil.

[1] *Berichte*, 1871, 444.
[2] *Mitth. des technolog. Gewerbe-Museums*, 1891, 185.

[TABLE

Physical and Chemical Constants of Grape Seed Oil

Specific Gravity.		Solidifying Point.		Hehner Value.		Reichert-Meissl Value.		Saponific. Value.		Iodine Value.		Maumené Test.		Acetyl Value.	
At 15° C.	Observer.	°C.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.		Observer.
0·926	Jobst	−11	Jobst	92·13	Horn	0·46	Horn	178·4	Horn	94	Horn	52-54	De Negri and Fabris	144·5[1]	Horn
0·9202	Schaedler	−15 to −17	Schaedler					178·5-179	De Negri and Fabris	95·8-96·2	De Negri and Fabris				
0·9561	Horn	−10 to −13	De Negri and Fabris												
0·935	De Negri and Fabris														

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Saponific. Value.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
20-18	De Negri and Fabris	23-25	De Negri and Fabris	187·4	Horn	98·65	Horn
...	...	...	...	...	...	98·9-99·05	De Negri and Fabris

[1] This value requires confirmation, having been determined by *Benedikt* and *Ulzer's* method.

CASTOR OIL

French—*Huile de ricin.* German—*Ricinusoel.*

For tables of constants see pp. 422-424.

Castor oil is obtained from the seeds of *Ricinus communis.* It is imported in large quantities from India, and is also produced on a commercial scale in Java.[1]

Castor oil is a colourless or pale greenish, transparent oil, having a taste at first mild, then harsh; this harsh taste is more pronounced in American than in Italian or French oils. It is very viscous, and thickens on exposure to air, finally forming a viscid mass, without, however, solidifying. It does not dry even when exposed in thin layers.

According to *Peter* (p. 120) it is strongly dextro-rotatory. Whereas *Allen* states that none of the samples examined by him were optically active, *Deering* and *Redwood* have recently observed a strongly marked rotatory power in the twenty-three samples of Indian castor oil they examined, the rotation caused by 200 mm. of oil varying from $+7{\cdot}6^\circ$ to $+9{\cdot}7^\circ$ in a *Hoffmann-Laurent* polarimeter. These observations, in conjunction with the fact that ricinoleic rotates the polarised light, leave no doubt as to the optical activity of castor oil.

If castor oil is allowed to stand in a very cool place, 3 to 4 per cent of a solid mass is deposited, consisting, according to *Krafft*,[2] of tristearin and triricinolein. Palmitic acid is absent, and a small quantity of sebacic acid found is, perhaps, due to a secondary reaction taking place on saponification. Amongst the fatty acids *Juillard* discovered dihydroxystearic acid (the first natural hydroxy fatty acid) to the extent of 1 per cent. Triricinolein is, according to *Krafft*, solid in its pure state, and the liquid state of castor oil must be ascribed to a state of superfusion of the oil. *Hazura* and *Grüssner*, however, have shown that the liquid fatty acids from castor oil consist of two isomerides, ricinoleic and ricinisoleic acids; perhaps *Krafft's* solid acid is identical with one of these acids (cp. also p. 65, *Mangold*). Olein does not occur in castor oil.[3] Castor oil may therefore be said to consist of a small quantity of tristearin, of the glyceride of dihydroxystearic acid, and the glyceride of ricinoleic acid, all the isomerides being comprised under that term.

The amount of free fatty acids in samples of castor oil has been determined by *Nördlinger*, *Thomson* and *Ballantyne*, and by *Deering* and *Redwood*. Their results are recorded in the following table:—

[1] *Jour. Soc. Chem. Ind.* 1895, 821.
[2] *Berichte*, 1888, 2730.
[3] Hazura and Grüssner, *Jour. Soc. Chem. Ind.* 1888, 681.

Free Fatty Acids in Castor Oil

Description of Oil.	No. of Samples.	Free Fatty Acids calculated to Oleic Acid.	Observer.
		Per cent.	
Expressed oil . .	9	0·68-14·61	Nördlinger
Extracted oil . .	5	1·18-5·25	,,
Commercial oil .	2	1·46-2·16	Thomson and Ballantyne
Indian oils . .	23	0·14-1·06	Deering and Redwood

The amount of unsaponifiable matter in the samples examined by *Thomson* and *Ballantyne* varied from 0·30 to 0·37 per cent.

The specific gravity of castor oil, its very high viscosity, and its behaviour with solvents, afford ready means of identifying it.

Castor oil has the highest **specific gravity** of any natural fatty oil. The "blown oils" only (p. 734) have such a high gravity acquired in the course of manufacture. According to *Allen*, any sample of castor oil having a less specific gravity than 0·958 must be regarded with suspicion. Resin oil of specific gravity 0·998 may have been added to mask the influence of a foreign fatty oil; it can be easily detected by determining the unsaponifiable matter (p. 218).

Of all known oils castor oil has the highest **viscosity**, only "blown oils" (p. 734) and resin oil approach it in this respect. The viscosity of the twenty-three samples examined by *Deering* and *Redwood* was from 1160 to 1190 seconds for 50 c.c. at 100° F.

Castor oil is miscible with **glacial acetic acid** in every proportion; it shares this property with croton and olive kernel oils (from which it can, however, be easily distinguished by its acetyl value).

Pure castor oil is miscible in every proportion with **absolute alcohol**; it also dissolves, at 15° C., in 2 volumes of 90 per cent, and in 4 volumes of 84 per cent alcohol. *Itallie*[1] has determined the solubility of five samples of castor oil (three of which, A, B, C, had been expressed by himself at the temperatures of 20° C., 50° C., and 80° C. respectively, whereas D and E were commercial oils) in 90 per cent alcohol, with the following result :—

10 c.c. of Oil	Require 90 per cent Alcohol at 20° C. c.c.
A	26·4
B	26·8
C	27·8
D	29·4
E	24·0

Though oleic acid, fraudulently added to castor oil, would also dissolve in alcohol, it would be easily recognised by the excessive amount of free fatty acids, and by the low specific gravity of the sample.

[1] *Chem. Zeit.* 1890, Rep. 367.

Physical and Chemical Constants of Castor Oil

Specific Gravity.*			Solidifying Point.		Reichert Value.		Saponification Value.		Iodine Value.	
At °C.		Observer.	°C.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
12	0·9699	Saussure	−17 to −18	Schaedler	1·4	Allen	181-181·5	Valenta	84·4	Hübl
15	0·9611	,,	−10 to −12[2]	...	...	...	176-178	Allen	83·4	Wilson
,,	0·9613-0·9736	Valenta	...	...	...	...	...	...	...	...
15·5	0·960-0·966	Allen	...	...	...	...	181	Dieterich	84-84·5	Dieterich
,,	0·9653-0·9679	Thomson and Ballantyne	...	...	...	...	180-183	Itallie	83·6-83·9	Thomson and Ballantyne
	0·9637-0·9642	Deering and Redwood[1]	...	...	...	...	178·6-180·2	Thomson and Ballantyne	83·8-85·9	Itallie
18	0·9667	Stilurell								
,,	0·9602	Long	...	...	...	...	176·7-179·1	Deering and Redwood[1]	83·7-85·3[4]	Deering and Redwood[1]
20	0·9589	,,								
,,	0·963-0·965	Itallie	...	...	...	...	185·9-186·6	Henriques[3]		
23	0·964	Dieterich	...	...	...	...	183·3	Lewkowitsch		
25	0·9575	Saussure	...	...	...	...				
,,	0·9555	Long								
30	0·9522	,,								
35	0·9488	,,								
94	0·9081	Saussure								
99 (water of 15·5 = 1)	0·9096	Allen								

[1] Twenty-three samples of Indian oil. *Jour. Soc. Chem. Ind.* 1894, 959.
[2] American oil, which is richer in solid glycerides than Indian or Italian oil.
[3] Java oil.
[4] Calculated from bromine values, 52·8-53·7.

Physical and Chemical Constants of Castor Oil—continued.

Acetyl Value.		Thermal Tests.				Refractive Index.		
		Maumené Test.		Heat of Bromination.				
	Observer.	°C.	Observer.	°C.	Observer.	At °C.		Observer.
149·9	Lewkowitsch	47	Maumené	15	Hehner and Mitchell	15	1·4795-1·4803	Strohmer
150·5	...	46	Archbutt	14·7	Jenkins	60	1·4636	Thoerner

Specific Temperature Reaction.		Oleo-refractometer.	
		"Degrees."	Observer.
89-92	Thomson and Ballantyne	+43 to +46 [1]	Jean
		+ 37	Bruyn and van Leent
		+40	,,
		+41 to +42·5	Deering and Redwood
		+39 to +42	Pearmain

[1] Java oil.

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.			Solidifying Point.		Melting Point.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
15·5	0·9509	Allen	3	Hübl	13	Hübl	290-295	Alder Wright	86·6-88·3	Morawski and Demski	1·4546	Thoerner
98-99	0·8960	,,	...	...	...	...	306·6	Allen	93·9	Williams		
							292	Williams	87-88	Thoerner		

Castor oil is nearly insoluble in **petroleum ether**, kerosene, and paraffin oils. At a temperature of 16° C. as little as 0·5 per cent of castor oil in these solvents causes a turbidity. However, castor oil gives a homogeneous solution with an *equal* measure of petroleum ether, or a volume and a half of kerosene or paraffin oil; if more of the solvents is used, any excess will float on the top of the mixture. This characteristic insolubility is lost at the ordinary temperature when castor oil is adulterated with a small quantity of a soluble oil.

For the rapid examination of castor oil (as by custom-house officers), *Finkener*[1] recommends agitation of 10 c.c. of the sample with 50 c.c. of alcohol, specific gravity 0·829 at 17·5° C., in a graduated cylinder. A strong turbidity, which does not disappear even at 20° C., shows that the oil is not pure; even 10 per cent of foreign oils (as sesamé, linseed, rape, cotton seed oils) may thus be detected. *Klie* employs 5 volumes of alcohol, of specific gravity 0·8371, for 1 volume of oil at the temperature of 22° to 26° C.

Castor oil is distinguished from all other oils—with the exception only of grape seed oil—by its very high **acetyl value**. The determination of this constant furnishes, therefore, the surest means of ascertaining its purity, and enables the analyst to estimate the amount of adulteration.

Also the **saponification value** (approaching that of the oils belonging to the rape oil group) and the **iodine value** will afford means of detecting fraudulently added oils. With regard to the saponification value it may be pointed out that *Henriques*[2] is of the opinion that castor oil is not so readily saponifiable as is generally believed, and that, therefore, the lower values are open to doubt (cp. table).[3] This is confirmed by the number given by the writer in the table, p. 422.

In the **elaïdin test** castor oil gives a whitish solid mass, due to the formation of ricinelaïdin

Rape oil, resin oil, and especially the "blown oils" prepared from rape, linseed, and cotton seed oils, are used as adulterants of castor oil.

Resin oil will be easily detected by determining the unsaponifiable matter. *Gilbert's*[4] test, viz. agitation of the sample with an equal volume of nitric acid of specific gravity 1·31, when castor oil thus adulterated is stated to assume a very dark colour, appears a somewhat doubtful method.

The "**blown oils**" simulate castor oil in specific gravity and viscosity, but they differ from it in having a smaller acetyl value, a higher saponification value (except those prepared from rape oil, cp. p. 305), and lesser solubility in alcohol.

Castor oil is easily detected in other oils by its acetyl value and behaviour with solvents (cp. "Olive Oil," p. 463).

[1] *Jour. Soc. Chem. Ind.* 1887, 148.

[2] *Zeit. f. angew. Chemie*, 1895, December.

[3] The saponification and iodine values given by Thoerner, viz. 201-203 and 93-94 respectively, are so abnormal that they have been omitted from the table.

[4] *Jour. Soc. Chem. Ind.* 1890, 112.

The following qualitative test for castor oil is given by *Draper*:—Heat a few drops of the oil with five to six drops of nitric acid, and after the action of the acid is over, neutralise with sodium carbonate. As soon as the smell of nitric acid has disappeared, œnanthylic acid may be recognised by its odour. It will be best to make a test side by side with a sample of genuine castor oil.

Castor oil is used in medicine, for soap-making, and in the manufacture of Turkey-red oil.

(3) Non-drying Oils

The general characters of the non-drying oils have been given already (p. 279). The oils described here have been arranged according to their iodine values, in the following order:—Cherry kernel oil, cherry laurel oil, apricot kernel oil, plum kernel oil, peach kernel oil, wheat meal oil, acorn oil, almond oil, sanguinella oil, Californian nutmeg oil, arachis oil, rice oil, tea seed oil, pistachio oil, hazelnut oil, olive oil, olive kernel oil, coffee berry oil, ungnadia oil, ben oil, strophantus seed oil, secale oil.

CHERRY KERNEL OIL

German—*Kirschkernoel.*

For tables of constants see p. 427.

The constants given in the tables refer to extracted oil.

Cherry kernel oil is obtained from the kernels of the cherry (*Prunus cerasus*). The oil has a golden-yellow colour when fresh, and a faint odour of almonds, which it loses in time, turning easily rancid.

With nitric acid of specific gravity 1·4 cherry kernel oil becomes dark reddish-brown; when tested with *Bieber's* reagent (p. 439), a brown colouration is obtained.

De Negri and *Fabris* have found a notable quantity of hydrocyanic acid in the extracted oil.

In South Germany (Württemberg) the "cold-drawn" oil is used as an edible oil; the oil expressed at a higher temperature serves as a burning oil, and also for soap-making. Owing to its property of turning easily rancid, cherry kernel oil cannot be used to any large extent for the adulteration of almond oil.

Physical and Chemical Constants of Cherry Kernel Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.	
At 15° C.	Observer.	°C	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C	Observer.
0·9184	Schaedler	– 19 to – 20	Schaedler	194·8-195	De Negri and Fabris	110·8-110·9	De Negri and Fabris	45	De Negri and Fabris
0·9235-0·9238	De Negri and Fabris	– 19 to – 20	De Negri and Fabris	193·4	Micko	114·3	Micko		
0·9285	Micko								

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Saponification Value.		Mean Molecular Weight.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.
15-13	De Negri and Fabris	19-21	De Negri and Fabris	189	Micko	296·2	Micko	114·3	De Negri and Fabris
...	...	16-20·6[1]	Micko	...	...	...	...	104·3	Micko

[1] Determined by the capillary tube method.

CHERRY LAUREL OIL[1]

German—*Kirschlorbeeroel.*

Physical and Chemical Constants of Cherry Laurel Oil

Specific Gravity.	Solidifying Point.	Saponific. Value.	Iodine Value.	Maumené Test.
At 15° C.	°C.	Mgrms. KOH.	Per cent.	°C.
0·9230	−19 to −20	194	108·9	44·5

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.	Iodine Value.
°C.	°C.	Per cent.
17-15	20-22	112·1

This oil has been extracted from the kernels of the cherry laurel (*Prunus laurocerasus*).

Cherry laurel oil is a transparent oil of golden-yellow colour ; its odour resembles that of bitter almonds. This oil also, like the preceding, contains appreciable quantities of hydrocyanic acid.

APRICOT KERNEL OIL

French—*Huile d'abricotier.* German—*Aprikosenkernoel.*

For tables of constants see p. 429.

Apricot kernel oil is obtained from the kernels of the apricot (*Prunus Armeniaca*).

The freshly expressed oil is almost colourless ; it becomes, however, yellow on keeping.

With nitric acid, spec. grav. 1·4, apricot kernel oil assumes an orange colour. With *Bieber's* reagent (p. 439) a peach-blossom colour is obtained ; this was formerly considered characteristic of peach kernel oil, and by means of this colour reaction apricot kernel oil was said to be detected if present in almond oil.

The sample of oil (extracted) examined by *Micko* had the acid value 0·64.

Apricot kernel oil is used as an edible oil, and in perfumery like almond oil ; it is also employed for adulterating the latter. Apricot kernel oil forms an important article of commerce.

[1] De Negri and Fabris, *Annali del Laboratorio Chimico delle Gabelle*, 1891-92, 173.

Physical and Chemical Constants of Apricot Kernel Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index. Butyro-refractometer.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	At 25° C.	Observer.
0·915	Schaedler	– 14	Schaedler	192·2-192·9	De Negri and Fabris	100	Hübl	46	Girard	65·6	Beckurts and Seiler
0·9191	Valenta	– 20	Maben	193·11	Micko	101	De Negri and Fabris	42·5	De Negri and Fabris	66·6	Mansfeld
0·9204	Maben	...	...	192·9	Valenta	108	Micko				

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Saponification Value.		Mean Molecular Weight.		Iodine Value.	
°C.	Observer.	°C.	Observer.	°C.	Observer.		Observer.	Per cent.	Observer.
0	Hübl	4·5	Hübl	194	Micko	288·6	Micko	103·8	De Negri and Fabris
...	...	2-3 / 3-5	De Negri and Fabris	...	...	...	...	102·6	Micko
..	...	13·4-18[1]	Micko						

[1] Determined by the capillary tube method.

PLUM KERNEL OIL

German—*Pflaumenkernoel.*

For tables of constants see p. 431.

The constants given in the tables refer both to expressed and extracted oils.

Plum kernel oil is obtained from the kernels of plums (*Prunus domestica* and *Prunus damascæna*). The oil is light yellow in colour, and possesses an agreeable, mild, almond-like taste.

With nitric acid, of specific gravity 1·4, plum kernel oil assumes an orange colour (like apricot kernel oil). With *Bieber's* reagent, consisting of equal parts (by weight) of concentrated sulphuric acid, fuming nitric acid, and water, a pink colouration is obtained.

The sample examined by *Micko* had the acid value 0·55.

The oil is chiefly used to adulterate almond oil.

Physical and Chemical Constants of Plum Kernel Oil

Specific Gravity		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
0·9127	Schaedler	– 8·7	Schaedler	191·48	De Negri and Fabris	100·4	De Negri and Fabris	44·5-45	De Negri and Fabris
0·9160	De Negri and Fabris	– 5 to – 6	De Negri and Fabris	191·55	Micko	100·2	Micko		
0·91949	Micko [1]								

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Saponification Value.		Mean Molecular Weight.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.
15-13	De Negri and Fabris	20-22	De Negri and Fabris	200·47	Micko	279·3	Micko	102	De Negri and Fabris
...	...	12·4-18·1 [2]	Micko	...	...	...	...	104·2	Micko

[1] *Jour. Soc. Chem. Ind.* 1893, 935.

[2] Determined by the capillary tube method.

PEACH KERNEL OIL

German—*Pfirsichkernoel.*

For tables of constants see p. 433.

Peach kernel oil (peach oil) is obtained from the kernels of the peach (*Amygdalus persica*).

The oil has a pale yellow colour, and is very similar to almond oil. With nitric acid peach kernel oil becomes first yellowish-brown, afterwards dirty orange. Tested with *Bieber's* reagent it remains unchanged for half an hour, and becomes brown after about one hour's standing.

This oil is chiefly used for adulteration of almond oil; in fact, according to *Schaedler*, the commercial "sweet almond oil" is nothing else than peach oil.

[TABLE

Physical and Chemical Constants of Peach Kernel Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index.					
											Butyro-refractometer.			Oleo-refractometer.		
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	At °C.		Observer.	At °C.	"Degrees."	Observer.
15	0·918	De Negri and Fabris	Below −20	Maben	189·1	Maben	92·5-93·5	De Negri and Fabris	42-43	De Negri and Fabris	25	67·2 [1]	Dieterich	22	+7·5 to +11·5	Pearmain
15	0·92147	Micko			192·5	De Negri and Fabris	99·7	Micko			,,	65·7 [2]	,,			
90	0·8899	Dieterich			191·1	Micko	109·7 [1]	Dieterich			,,	66·1	Beckurts and Seiler			
					163·1-166	Dieterich	98·6 [2]	,,			,,	66·5	Mansfeld			
											40	58·5 [1]	Dieterich			
											,,	57·0 [2]	,,			
											50	52·2 [1]	,,			
											,,	51·5 [2]	,,			

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Saponification Value.		Mean Molecular Weight.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.
		3-5	De Negri and Fabris	200·9	Micko	278·8	Micko	94·1	De Negri and Fabris
Titer Test.									
13-13·5	Lewkowitsch	10-18·9	Micko	...	...	...	...	101·9	Micko

[1] Freshly prepared oil. [2] Old oil.

WHEAT-MEAL OIL

German—*Weizenmehlfett.*

This oil was extracted from wheat flour.[1]

Physical and Chemical Constants of Wheat-Meal Oil

Specific Gravity at 100° (water 15° C. = 1).	Saponification Value.	Reichert-Meissl Value.	Iodine Value.	Refractive Index. At 25° C.
0·9068	166·5	2·8	101·5	1·4851
				Butyro-refracto-meter.
				92

ACORN OIL[2]

German—*Eicheckernoel.*

This oil is obtained by extracting the fruit of *Quercus agrifolia* with solvents. It is a deep brown fluorescent oil. On long standing it deposits wax.

Physical and Chemical Constants of Acorn Oil

Specific Gravity at 15° C.	Solidifying Point. °C.	Saponification Value.	Iodine Value.	Maumené Test. °C.	Refractive Index.
0·9162	10	199·3	100·7	60	1·4731

The melting point of the fatty acids is 25° C.

[1] Spaeth, *Analyst*, 1896, 234.
[2] Blasdale, *Jour. Soc. Chem. Ind.* 1896, 206.

ALMOND OIL

French—*Huile d'amandes.* German—*Mandeloel.*

For tables of constants see pp. 436-438.

Almond oil is expressed [or extracted] from sweet and bitter almonds, the seeds of the two varieties of the almond tree, *Prunus amygdalus*, var. *dulcis* and var. *amara*.

Almond oil is a thin oil, of a pale yellow colour and bland taste. The oils obtained from both varieties are very much alike, so much so, that no definite difference has been established by chemical means, as will be seen by glancing at the accompanying table. [The bitter almonds yield more oil than the sweet ones.]

Almond oil is very rich in olein. According to *Gusserow* it is free from stearin; this is confirmed by *Hehner* and *Mitchell*.[1] The iodine value points to the presence of glycerides of fatty acids belonging to a less saturated series than the oleic.

Almond oil easily turns rancid. A specimen examined by *Salkowski* contained 0·75 per cent of free fatty acids calculated to oleic acid.

Tested by the **elaïdin test**, almond oil from sweet almonds solidifies after about eight to nine hours, whereas the oil from bitter almonds is stated to become solid only after twenty-four hours. Since, however, various specimens of oil behave very differently no definite conclusion can be drawn from the behaviour of the oil in this test.

Almond oil is adulterated with the following oils: Poppy seed, sesamé, walnut, olive, lard, arachis, cotton seed, and (on a very large scale) peach and apricot kernel oils. The last two oils are used to such an extent that they are stated to be wholly substituted for almond oil, so much so, that "foreign almond oil" may be considered as wholly consisting of peach kernel or apricot kernel oil. The close relationship in which these two oils stand to almond oil renders it impossible to detect the adulteration by means of the quantitative reactions.

According to *Allen* many of these additions may be detected by observing the **absorption spectrum** of the sample, almond oil differing from most vegetable oils in giving neither a banded spectrum nor producing strong absorption in the red or in the violet.

Whereas the **specific gravity** of a sample may only indicate adulteration with heavier oils, the behaviour of the oil on **cooling** may lead to the detection of lard oil and also of olive oil, the latter two depositing "stearine" at -5° C. Lard oil is stated to be indicated by the odour on heating the sample.

[1] *Analyst*, 1896, 328.

Physical and Chemical Constants of Almond Oil

Specific Gravity.			Solidifying Point.		Hehner Value.		Saponification Value.	
At °C.		Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.
12	0·9168 [1]	Mills and Akitt	– 10	Girard	96·2	West-Knight	195·4	Valenta
,,	0·9154 [2]	,,	– 21	Maben	...	...	187·9	Moore
15	0·917-920	Chateau	– 10 to – 20	Schaedler	...	...	190·9	Dieterich
,,	0·914-920	Allen	...	...	...	...	187·9	Peters
,,	0·9180	Maben	...	...	...	...	190·5-191·2 [2]	De Negri and Fabris
,,	0·9186	Valenta	...	...	...	...	189·5-191·7 [1]	,,
,,	0·9183	Massie	...	...	...	...	...	...
,,	0·9190	Del Torre	...	...	...	...	...	...
,,	0·9190-0·9195 [2]	De Negri and Fabris						
,,	0·9175-9195 [1]	,,						

[1] From bitter almonds. [2] From sweet almonds.

Physical and Chemical Constants of Almond Oil—continued.

Iodine Value.		Thermal Tests.				Refractive Index.	
		Maumené Test.		Heat of Bromination.			
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	At 60° C.	Observer.
98·4	Hübl	52-54	Maumené	17·6	Hehner and Mitchell	1·4555	Thoerner
96·6-99·2	Beringer	53	Del Torre				
96·2-101·9	Dieterich	51-52 [2]	De Negri and Fabris				
97·5	Del Torre	51-53 [1]	,,				
98-99	Peters						
98·4 [2]	Moore						
93-95·4 [2]	De Negri and Fabris						
94·1-96·5 [1]	,,						

Oleo-refractometer.	
"Degrees."	Observer.
+ 6	Jean
+ 7	Bruyn and van Leent
+ 8 to + 10·5 at 22° C.	Pearmain

Butyro-refractometer.	
At 25° C.	Observer.
64·8	Beckurts and Seiler
64·0	Dieterich

[1] From bitter almonds.

[2] From sweet almonds.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Refractive Index.	
°C	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
5	Hübl	14	Hübl	204	Thoerner	93·5-95·5 [2]	De Negri and Fabris	1·4461	Thoerner
		13-14 [1 2]	De Negri and Fabris			94·1-96·5 [1]	De Negri and Fabris		
Titer Test.									
9·5-10·1 [2]	Lewkowitsch								
11·3-11·8 [1]	,,								

[1] From bitter almonds. [2] From sweet almonds.

The determination of the **melting point** of the mixed fatty acids also furnishes a valuable means of ascertaining the presence of foreign oils, almond oil being characterised by the low melting point of its mixed fatty acids. According to the German Pharmacopœia the mixed fatty acids of pure almond oil must remain liquid at 15° C. for an indefinite length of time; mixed with an equal volume of alcohol they must give a clear solution at 15° C., and not become turbid on adding twice the volume of alcohol. *Olive*, *sesamé*, *arachis*, and *cotton seed oils* may thus be recognised. *Peach* or *apricot kernel oils* will, however, escape detection.

A higher **iodine value** than the normal one will point to adulteration with *poppy seed* or *walnut oils*. (*Thoerner* gives for almond oil the iodine value 82-83, and for the mixed fatty acids 87-90. These figures being so exceptionally low, have not been entered in the table, pending confirmation.)

Cotton seed oil may be detected by the nitric acid or silver nitrate test; but the surest test will be afforded by the solidifying point of the mixed fatty acids.

Sesamé oil will be indicated by the furfurol reaction, **rape oil** by the decrease of the saponification value, and **arachis oil** by *Renard's* test (cp. "Arachis Oil," p. 445).

The detection of peach kernel, apricot kernel, and also plum kernel oils in almond oil is a very difficult problem, and is, as has been pointed out already, impossible by means of the quantitative reactions; nor would their presence be indicated by the organoleptic reactions (taste and odour).

The **nitric acid colour test** [1] and **Bieber's test**, however, are said to be useful for the detection of these oils. Whereas almond oil remains colourless with nitric acid of specific gravity 1·4, or becomes only slightly yellow, *plum* and *apricot kernel oils* assume an orange colour, and *peach kernel oil* becomes first yellowish-brown and afterwards dirty orange.

Bieber's [2] test is carried out by agitating one part of the oil under examination with five parts of a mixture consisting of equal parts (by weight) of concentrated sulphuric acid, fuming nitric acid, and water, when the following colour reactions are stated to appear:—

Pure almond oil gives a slightly yellowish-white liniment, changing to reddish.

Plum kernel oil is characterised by a pink colouration, *apricot kernel oil* by a peach-blossom colour [*Micko;* whilst *Bieber* ascribes this colouration to peach kernel oil], whereas *peach kernel oil* (according to *Micko*) gives no colour after half an hour, and only assumes a light brown colouration after that time.

If any *sesamé oil* be present [which is detected with certainty by the furfurol test] a pale yellowish-red colouration appears at first, changing to a dirty orange-red; in presence of sesamé oil, the

[1] Micko, *Jour. Soc. Chem. Ind.* 1893, 935.

[2] *Zeitsch. f. analyt. Chem.* 17. 264; cp. also Micko, *Jour. Soc. Chem. Ind.* 1893, 935.

detection of *peach kernel oil*, in any case a difficult task, would be impossible.

Maben[1] recommends for the discrimination of almond, peach kernel, and apricot kernel oils the colour reactions given in the following table:—

	Almond Oil.	Apricot Kernel Oil.	Peach Kernel Oil.
Elaïdin test; product	White, hard	Light yellow, hard	Lemon-yellow, soft
Nitric acid colour test (spec. grav. 1·42)	Slight action	Coffee-brown	Dark brown
Sulphuric acid colour test	Yellow to orange	Light brown to reddish-brown	Dark brown
Zinc chloride (5 drops of a saturated solution of ZnO in HCl and 10 drops of oil stirred together with a glass rod)	No change	Muddy brown, with shade of purple	Purple-brown

According to the German Pharmacopœia, no brown or reddish colouration should appear if five measures of pure almond oil are agitated with one measure of a mixture consisting of two parts of fuming nitric acid and two parts of water; after several hours' standing the fatty layer should form a solid white mass, and the aqueous liquid should be colourless.

SANGUINELLA OIL[2]

German—*Hartriegeloel.*

Physical and Chemical Constants of Sanguinella Oil

Specific Gravity at 15° C.	Solidifying Point. °C.	Saponific. Value. Mgrms. KOH.	Iodine Value. Per cent.	Maumené Test. °C.
0·921	−15	192·05	100·8	52

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point. °C.	Melting Point. °C.	Saponific. Value. Mgrms. KOH.	Iodine Value. Per cent.
31-29	34-37	195·1	102·75

This oil is obtained from the seeds of the dog-wood, *Cornus sanguinea*. It has a green-yellowish colour; its odour is similar to that of inferior olive oil.

[1] *Pharmac. Jour.* [3] 16. 797. [2] De Negri and Fabris, *Annali*, etc., 181.

CALIFORNIAN NUTMEG OIL [1]

Californian nutmeg oil is obtained from the fruit of *Tumion Californicum.*

Physical and Chemical Constants of Californian Nutmeg Oil

Specific Gravity at 15° C.	Saponific. Value. Mgrms. KOH.	Iodine Value. Per cent.	Maumené Test. °C.	Refractive Index.
0·9072	191·3	94·7	77	1·4766

The melting point of the fatty acids is 19° C.

ARACHIS OIL (PEANUT OIL, EARTHNUT OIL)

French—*Huile d'arachide.* German—*Erdnussoel, Arachisoel.*

For tables of constants see pp. 443, 444.

Arachis oil is obtained from the earthnuts, the seeds of *Arachis hypogæa* (Leguminosæ), a plant largely cultivated on the West Coast of Africa, in India, North America, South of Europe, etc. The "cold-drawn oil" of the first expression is nearly colourless, and has a pleasant taste resembling the flavour of kidney beans. It is used as salad oil. The oil obtained by second expression also serves as an edible oil or for burning. The third quality expressed at higher temperature is chiefly used for soap-making.

Of solid fatty acids, palmitic has been stated by *Caldwell* [2] to occur in arachis oil. *Kreiling* [3] could not detect this acid, without, however, having adduced absolute proof of its absence. The same chemist has shown that besides arachidic acid (melting point 74·5° C.), as proved by *Gössmann's* researches, another solid fatty acid, of the melting point 81° C., viz. lignoceric acid, occurs in combination with glycerol. Lignoceric acid, being less readily soluble in alcohol than arachidic acid, may be separated from the latter by means of this solvent.—A specimen examined by *Hehner* and *Mitchell* [4] gave 7 per cent of stearic acid crystals of the melting point 67° C.

The liquid fatty acids of arachis oil consist of oleic and linolic acids. *Gössmann* and *Scheven*,[5] and also *Schröder*,[6] claim to have found the unsaturated fatty acid—hypogæic acid (p. 53). *Schoen*,[7] however, having been unable to detect this acid, asserts that oleic acid is the

[1] Blasdale *Jour. Soc. Chem. Ind.* 1896, 206. [2] *Liebig's Annalen*, 101. 97.
[3] *Berichte*, 21. 880. [4] *Analyst*, 1896, 328. [5] *Liebig's Annalen*, 94. 230.
[6] *Ibid.* 143. 22. [7] *Ibid.* 244. 253; *Berichte*, 21. 878.

only unsaturated acid in arachis oil. *Hazura's*[1] conjecture that hypogæic acid may form a constituent of the unsaturated glycerides in arachis oil is confirmed by the fact that synthetical hypogæic acid has the same properties as the natural acid found in arachis oil by *Gössmann* and *Scheven*, and *Schröder* (cp. chap. iii. p. 53).

A number of samples of arachis oil, examined for the amount of free fatty acids, gave the following result :—

Description of Oil.	Number of Samples.	Free Fatty Acids in terms of Oleic Acid.	Observer.
		Per cent.	
Expressed salad oil . .	13	0·85 to 3·91	Nördlinger
Expressed commercial oil	12	3·58 to 10·61	,,
Extracted oil . . .	16	0·95 to 8·85	,,
Refined oil . . .	1	0·62	Thomson and Ballantyne
Commercial oil . .	1	6·20	,,

The last two oils in the preceding table contained 0·54 and 0·94 per cent of unsaponifiable matter respectively.

[1] *Wiener Monatshefte*, 10. 242.

Physical and Chemical Constants of Arachis Oil

Specific Gravity.			Solidifying Point.		Hehner Value.		Saponific. Value.		Iodine Value.		Maumené Test.		Refractive Index.	
At °C.		Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	At 60° C.	Observer.
15	0·9163	Chateau	−3 to −7	Schaedler	95·86	Bensemann	191·3	Valenta	103	Hübl	67	Maumené	1·4545	Thoerner
,,	0·9170	Souchère	−2·5	Schoen			196·6	Moore	87·3	Moore	58	Del Torre		
,,	0·922	Allen					190·1-197	Dieterich	95	Erban	44	Girard	Oleo-refractometer.	
,,	0·9193	Valenta					189·3[1]	Thomson and Ballantyne	87·3-90	Dieterich	49[3]	De Negri and Fabris		
,,	0·9173	Del Torre					192·1[2]	,,	96·7-98·7	Filsinger	51[4]	,,	"Degrees."	Observer.
,,	0·9171[1]	Thomson and Ballantyne					192·7-194·6	Schoen	101·3	Del Torre	46[5]	,,	+3·5[6] to +6·5[7]	Jean Bruyn and van Leent
,,	0·9209[2]	,,					190·2[2]	De Negri and Fabris	98·3	Merkling	45·5[2]	,,	+4	Pearmain
,,	0·917[2]	De Negri and Fabris					193·1[3]	,,	98·4-98·7	Thomson and Ballantyne	Specific Temperature Reaction.		+3 to +7 at 22° C.	
,,	0·9200[3,4]	,,					191·4-192[4]	,,	85·6-98·4	Schoen			Butyro-refractometer.	
,,	0·0165[5]	,,					189·4[5]	,,	95-95·4[3]	De Negri and Fabris	105[1]	Thomson and Ballantyne	At 25° C.	Observer.
22	0·911-0·916	Schoen					191-196	Oliveri	97·9-100[4]	,,	137[2]	,,	66·5	Beckurts and Seiler
23	0·917-0·918	Dieterich					194-196	Thoerner	92-92·7[5]	,,			65·8-67·5	Mansfeld
99 (water 15·5=1)	0·8673	Allen							92·4	,,				
									90·2	Lewkowitsch				
									101-105	Oliveri				
									98·9	Wallenstein and Finck				
									96·55-98·98	Schweitzer and Lungwitz				
									94-96	Thoerner				

[1] Refined oil. [2] Commercial oil. [3] From Pondichéry nuts. [4] From Coromandel nuts. [5] From Mozambique nuts.
[6] "Rufisque." [7] "Boulam."

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.			Solidifying Point.		Melting Point.		Saponific. Value.		Iodine Value.		Mean Molecular Weight.		Refractive Index.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.		Observer.	At 60° C.	Observer.
92·5	0·8436	Schoen	23·8	Hübl	27·7	Hübl	201·6	Thoerner	95·5-96·9	Morawski and Demski	281·8	Allen	1·4461	Thoerner
98·5	0·8468	..	28	Allen	27·8-29·5	Allen			103·42 [2]	De Negri and Fabris				
99 (water 15·5 = 1)	0·846	Allen	29-29·5	Dieterich	31·5-32	Dieterich			96·53 [4]	..				
					31-32 to 34-35	Bensemann [5]								
100	9·8475	Archbutt	33	Bach	31	Bach			96-97	Thoerner				
					30	Schoen								
			25-23 [1]	De Negri and Fabris	29-31 [1]	De Negri and Fabris								
			25-22 [2]	,,	28-30 [2]	,,			Iodine Value of the Liquid Fatty Acids.					
			24-22 [3]	,,	27-29 [3]	,,								
			25-23 [4]	,,	28-30 [4]	,,								
			29-30	Thoerner	30-32	Thoerner			128·5	Wallenstein and Finck				
			Titer Test.											
			28·1-29·2 [4]	Lewkowitsch										

[1] From Pondichéry nuts. [2] From Coromandel nuts.
[3] From Mozambique nuts. [4] Commercial oil.
[5] Bensemann's method.

Arachis oil is very similar to olive oil, so much so that it cannot be detected with certainty in the latter by the quantitative reactions, the differences in the iodine values of the two oils not being large enough. Nor are any chromatic reactions available for this purpose.[1] Arachis oil, if present in not too small a quantity in an oil, can however be detected with certainty by the isolation of arachidic acid. This test, proposed by *Renard*,[2] is carried out as follows :—Saponify 10 grms. of the oil, separate the fatty acids from the soap solution by hydrochloric acid, dissolve these in 90 per cent alcohol, and add a solution of lead acetate. I shorten the process by neutralising the excess of alkali with acetic acid, and precipitating with a lead salt without isolating the fatty acids.[3] Filter off the precipitated lead salts, and extract them with ether, thus separating the lead salts of the unsaturated acids from the lead palmitate and arachidate. Treat these latter salts with hydrochloric acid, separate the fatty acids when solidified, after cooling, from the lead chloride, and dissolve them in 50 c.c. of hot 90 per cent alcohol. If arachis oil is present in the sample, a crop of crystals consisting of arachidic acid will be obtained on cooling the alcoholic solution. No doubt the crystals will also contain the lignoceric acid discovered by *Kreiling*. Filter the crystals off and wash them on the filter, first with a measured quantity of 90 per cent, then with 70 per cent alcohol, which dissolves but small quantities thereof, and finally dissolve them by pouring boiling absolute alcohol on the filter, receiving the filtrate in a porcelain dish or in a flask. Evaporate to dryness and weigh the residue, consisting of crude arachidic acid. Add to the weight thus found the quantity dissolved by the 90 per cent alcohol used for washing, 100 c.c. of which dissolve 0·022 grm. at 15° C., or 0·045 grm. at 20° C. Finally determine the melting point of the crude arachidic acid, which should be from 71° to 72° C. *Renard* has isolated from 4·5 to 5·0 per cent, *Allen* 5·5, and *De Negri* and *Fabris* from 4·37 to 4·80 per cent of arachidic acid from genuine samples of arachis oil. Hence the amount of acid found will represent roughly a $\frac{1}{20}$ of the arachis oil present, and the latter may therefore be approximately calculated by multiplying the weight of the crude acid by 20.

Renard's method being a somewhat tedious one, several authors have proposed shorter processes. Thus *Souchère* dissolves the mixed fatty acids directly in boiling alcohol. The crystals obtained on cooling are recognised as arachidic acid by their characteristic nacreous lustre. *Marie*, and also *Peters*, proceed in a similar way. The method adopted in the Paris Municipal Laboratory is to saponify the sample with an equal weight of an alcoholic potash solution prepared by dissolving 200 grms. of solid caustic potash in 500 grms. of 90 per cent alcohol. The oil is heated with the alcoholic potash on the water-bath

[1] A. van Engelen's "molybdic" reagent (being a solution of 0·25 grm. of sodium molybdate in 20 c.c. of concentrated sulphuric acid) proposed recently (cp. p. 392) is valueless, on this chemist's own showing, in the case of a mixture of olive and arachis oils.

[2] *Compt. rend.* 73. 1330.

[3] Kreiss (*Jour. Soc. Chem. Ind.* 1895, 688) employs an *alcoholic* solution of lead acetate.

from 30 to 45 minutes, and allowed to cool down to a temperature between 0° and 6° C. In presence of as small a quantity as 5 per cent of arachis oil, there separate on the walls of the vessel granular masses of potassium arachidate which are insoluble in alcohol. Larger quantities of arachis oil are indicated by solidification of the whole mass.

De Negri and *Fabris*,[1] after having examined these abbreviated methods, state that they yield uncertain results, a conclusion which is also arrived at by *Holde*.[2] The original method of *Renard* is therefore recommended by these authors as giving the most reliable results.

The small quantity of arachin naturally occurring in olive oil does not interfere with the correctness of the method. *Ponzio* has recently stated that rape oil also contains arachidic acid (0·4 per cent, and not 4 per cent as given in the original paper in consequence of a clerical error). I have examined rape oil by *Renard's* test, but the quantities of arachidic acid were so small that they cannot vitiate this method for the detection of arachis oil.

De Negri and *Fabris* have examined mixtures of olive oil and arachis oil, obtaining the following numbers :—

Sample Containing		Arachidic Acid Found			Arachis Oil
Olive Oil.	Arachis Oil.	Weighed as Crystals.	Calculated as Dissolved.	Total.	Per cent.
Per cent.	Per cent.	Grms.	Grms.	Grms.	
70	30	0·107	0·0315	0·1385	29·08
80	20	0·0605	0·0315	0·0920	20·24
85	15	0·0385	0·0315	0·070	14·00
90	10	0·0200	0·0315	0·0515	10·30
90	10	non-weighable			
90	10	0·0280	0·0154	0·0434	9·54
90	10	non-weighable			

It will thus be seen that on employing 10 grms. of the sample, the limit is reached if it contain only 10 per cent of arachis oil. *Holde* recommends, therefore, that 40 grms. of the oil should be taken.

Herz[3] states that arachidic acid can be recognised with certainty under the microscope by the characteristic habitus of its crystals when allowed to crystallise from its alcoholic solution on an object glass. The safest plan will be to compare the crystals obtained with those similarly prepared side by side from a specimen of pure arachidic acid.

Arachis oil is adulterated with poppy seed, sesamé, cotton seed, and rape oils. *Poppy seed oil* would be detected by the specific gravity

[1] *Annali del Laboratorio Chimico delle Gabelle*, 1891-92, 123.
[2] *Jour. Soc. Chem. Ind.* 1891, 952.
[3] *Repert. Analyt. Chemie*, 1886, 604.

and the iodine value of the sample; *sesamé oil* by the furfurol reaction, *cotton seed oil* by the melting point of the fatty acids and perhaps also by the chromatic reactions, and *rape oil* by the saponification value of the oil and the melting point of its fatty acids.

RICE OIL[1]

German—*Reisoel.*

Saponification Value.	Iodine Value.
193·2	96·4

This oil, obtained from Rangoon rice meal by hydraulic pressure, had a dirty greenish colour, and in part solidified at the ordinary temperature.

The oil appears to be remarkable for the large proportion of free fatty acids it contains, viz. from 31·6 to 77·20 per cent.

Rangoon rice meal contains about 15 per cent of oil, common rice meal only 8-9 per cent.

TEA SEED OIL

German—*Theesamenoel.*

For table of constants see p. 448.

Tea seed oil is the oil obtained from the seeds of the tea plant, *Camellia theifera*, which is expressed on a large scale in China; the finest quality serves there as an edible oil, and the lower as burning oil and for soap-making. There are two varieties, viz. Chinese and Assam oil.

Tea seed oil is a limpid, straw or amber coloured yellow oil, closely resembling olive oil; like the latter it gives a hard elaïdin.

Similar to this oil is the fatty oil from *Camellia oleifera*, a plant largely cultivated in China for the sake of the pale bland oil prepared from its seeds. Its specific gravity is 0·9175 at 15° C. (*Schaedler*).

[1] Smetham, *Jour. Soc. Chem. Ind.* 1893, 848.

Physical and Chemical Constants of Tea Seed Oil

	Specific Gravity.		Solidifying Point.		Hehner Value.		Saponification Value.		Iodine Value.		Refractive Index. Oleo-refractometer.	
	At 15° C.	Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	"Degrees."	Observer.
Chinese oil .	0·917-0·927	Schaedler	−5	Schaedler	...	...	195·5	Davies	88	Itallie	+8 at 22° C.	Pearmain
Assam oil .	0·920	Itallie[1]	−12	Itallie	91·5	Itallie	194	Itallie				

[1] *Jour. Soc. Chem. Ind.* 1894, 79.

PISTACHIO OIL [1]

German—*Pistazienoel.*

Physical and Chemical Constants of Pistachio Oil

Spec. Grav.	Solidifying Point.	Saponification Value.	Iodine Value.	Maumené Test.
At 15° C.	°C.	Mgrms. KOH.	Per cent.	°C
0·9185	−8 to −10	191·0-191·6	86·8-87·8	44·5-45

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.	Iodine Value.
°C.	°C.	Per cent.
13 14-13	17-18 18-20	88·9

This oil is contained in the seeds of the pistachio nuts (from *Pistacia vera* or *P. lentiscus*). As it has no commercial value it may suffice to record the constants only.

HAZELNUT OIL

French—*Huile de noisette.* German—*Haselnussoel.*

For tables of constants see p. 450.

Hazelnut oil is prepared from the seeds of the hazelnut tree, *Corylus Avellana*, by pressing, or by extracting with solvents.

This oil has a golden-yellow colour; it is transparent, and has the odour of hazelnuts. For want of better methods this characteristic odour must be used for its detection in other oils.

According to *Schaedler* it contains a minute quantity of arachin. In the elaïdin test it yields a solid white mass.

Hazelnut oil resembles almond oil very closely, their mixed fatty acids behaving similarly with alcohol; its lower iodine value, however, may be used for discriminating it from almond oil.

According to *Filsinger* [2] hazelnut oil is used to adulterate chocolate. Hazelnut oil is used in perfumery. In its turn it is liable to adulteration with olive oil; this would be detected by the high solidifying point of the sample.

[1] De Negri and Fabris, *Jour. Soc. Chem. Ind.* 1893, 453.
[2] *Jour. Soc. Chem. Ind.* 1893, 51.

Physical and Chemical Constants of Hazelnut Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Hehner Value.		Reichert-Meissl Value.		Iodine Value.		Maumené Test.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
0·9243	Schaedler	– 20	Girard	197·1	Filsinger	95·5	Schoettler	0·99	Schoettler	88	Girard	38	Girard
0·9170	Massie	– 17	Schaedler	192·8	De Negri and Fabris	...	...	...	...	88·5	Filsinger	35-36	De Negri and Fabris
0·9146	Filsinger	– 10	Braconnot	191·4	Soltsien	...	...	...	...	86·2-86·8	De Negri and Fabris		
0·9170	De Negri and Fabris	...	...	187	Schoettler	...	...	...	...	83·2	Soltsien		
0·9164	Soltsien	...	...	...	...	...	...	...	...	87	Schoettler		
0·916	Schoettler												

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
9	Soltsien	17	Soltsien	90·1	De Negri and Fabris
...	...	25	Girard		
19-20	Schoettler	22-24	De Negri and Fabris		

OLIVE OIL

French—*Huile d'olive.* German—*Olivenoel.*

For tables of constants see pp. 454-456.

Olive oil is prepared from the fruits of the olive tree, *Olea europæa sativa*, by expression or by extraction.

The specimens of olive oil found in commerce vary to a considerable extent, their quality depending on many circumstances, such as the variety of the olive itself [Italy alone produces about 300 varieties of the olive tree], the degree of ripeness of the fruit, the manner of gathering it, the mode of expressing, and many others. The very finest oils, prepared from handpicked fruits—virgin oil, Provence oil, Aix oil—are used as best edible oils; next in quality rank the oils sold in this country as "Finest Tuscan cream." A somewhat inferior quality is also used as salad oil; the next lower grade oil serves as burning oil and for soap-making; for the latter purpose especially those oils are employed which have been recovered from the once or twice expressed marc, by mixing with a small quantity of water ("lavate" oils) and grinding it up, crushing at the same time the olive kernels. Lower grades still, partly obtained by extraction of the press residues with solvents (carbon bisulphide or petroleum ether), are met with in commerce under the name of *huiles de ressence*, *huiles d'enfer* (from marc fermented in pits), *sottochiari*, *sulpho-carbon oils*, etc. "*Tournant oil*" is a commercial product of the quality of the "*huiles d'enfer*," obtained from the fermented marc of expressed olives, and containing a large quantity (up to 26 per cent) of free fatty acids. It possesses, therefore, the property of giving a very complete emulsion with a solution of sodium carbonate, and this constitutes its value as Turkey-red oil (p. 464). Still lower qualities contain more fatty acids. Thus a sample of "olive oil grease" examined in the writer's laboratory had 48 per cent of free fatty acids.

The **colour** of olive oil naturally varies considerably, all shades from colourless to golden-yellow occurring; some kinds are always green, due to a small proportion of dissolved chlorophyll.

The **taste** of olive oil in its purest state is bland and pleasant, varying, however, with the locality where the fruit has been grown. Thus, the oils obtained from Tuscan fruits possess a decidedly more agreeable taste than those from Ligurian olives. Therefore purity alone is not sufficient for the valuation of a sample of olive oil. An oil may be free from adulteration and still be an inferior oil, on account of its rank and even nauseous taste.

Olive oil contains about 28 per cent of solid glycerides, consisting of palmitin and a minute proportion of arachin. *Hehner* and *Mitchell*[1]

[1] *Analyst*, 1896, 328.

did not obtain any stearic acid crystals from olive oil, therefore absence of stearin must be taken as proved.

The rest—about 72 per cent—was formerly considered to be practically pure olein (notwithstanding a conjecture of *Mulder's* as to the presence of an unsaturated fatty acid other than oleic), but *Hazura* and *Grüssner* have shown that the liquid portion contains, besides oleic acid, the less saturated linolic acid (approximately in the proportion of 93 oleic acid to 7 linolic acid). This fact is in complete harmony with the somewhat high iodine value of olive oil. Since, according to theory, pure olein absorbs only 86·2 per cent of iodine, the corresponding absorption of olive oil should be equal to 62 per cent for a proportion of 72 per cent of olein. Experiments, however, give far higher iodine absorptions (cp. table p. 455).

The **unsaponifiable matter** occurring in olive oil is cholesterol, whereas all other vegetable oils contain phytosterol. *Thomson* and *Ballantyne* found in 12 samples of oil the proportion of unsaponifiable matter between 1·04 and 1·42 per cent.

Varying amounts of **free fatty acids** have been found in commercial olive oils. The following table gives the results published by several chemists :—

Free Fatty Acids in Olive Oil

Description of Sample.	Number of Samples.	Free Fatty Acids as Oleic Acid.	Observer.
		Per cent.	
...	1	1·17	Salkowski
...	1	1·66	Rechenberg
Commercial oil . .	49	Less than 5	Archbutt
,, ,, . .	66	5-10	,,
,, ,, . .	44	10-15	,,
,, ,, . .	1	20-25	,,
,, ,, . .	11	3·86-11·28	Thomson and Ballantyne
,, ,, (Syrian)	1	23·88	,,
,, ,, (Californian	3	1·55-8·33	Moerck
,, ,, (European)	3	0·97-1·09	,,

Olive oils containing more than 5 per cent of free fatty acids are, according to *Allen*, not suitable for lubricating purposes; they are also unsuitable as burning oil, causing charring of the wick (*Archbutt*).

Olive oil must be considered as the type of a non-drying oil. Hence it gives in *Maumené's* test, as also in the heat of bromination test, of all vegetable oils the smallest rise of temperature, and shows also the lowest absorption of oxygen in *Livache's* test (p. 287).

On account of its comparatively high price olive oil is adulterated to an enormous extent. The oils mostly admixed with it are sesamé,

rape, cotton seed, poppy seed, and arachis oils. The olive oils sold under fancy names are, as a rule, adulterated. Thus a "sweet nut oil" consisted of a mixture of olive and arachis oil, and a "Union salad oil" was found to be almost pure cotton seed oil.

The importance of the examination of olive oil may justify our dealing with it at some length. At the same time the following lines may illustrate the way in which the methods, discussed in chap. ix., are employed for the commercial analysis of an oil, with a view to ascertaining the presence of adulterants.

[Table

Physical and Chemical Constants of Olive Oil

Specific Gravity.			Solidifying Point.		Hehner Value.		Reichert Value.		Saponification Value.	
At °C.		Observer.	°C.	Observer.	Per Cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Mgrms. KOH.	Observer.
12	0·9192	Saussure	At 2 turbid, at – 6, 26 per cent of "stearine" separate	Chateau	95·43	West-Knights	0·3	Medicus and Scheerer	191·8	Köttstorfer
15	0·9177	,,				Lengfeld and Paparelli			191·7	Valenta
15	0·9178 [1]	Clarke			94-96 [5]				191-196	Allen
15	0·9196 [2]	,,							185·2	Moore
15	0·9163 [1]	Paris Munic. Laborat.							188·7-203 [1]	Dieterich
									196-206 [3]	,,
15	0·9160 [3]	,,							185-196, [4]	De Negri and Fabris
15	0·916-0·918 [4]	De Negri and Fabris							generally 190	Oliveri
									190·5-195 [7]	Thomson and Ballantyne
15·5	0·914-0·917	Allen							189-192	Moerck
15·5	0·9141-0·9171	Thomson and Ballantyne							190-190·5 [5]	Blasdale [8]
15·5	0·91747-0·91797 [5]	Moerck							190·5-193·5 [5]	
18	0·9144	Stilurell								
18	0·9163	,,								
18	0·9199 [6]	,,								
18	0·9139-0·9141	Long								
19	0·9134	,,								
20	0·9127	,,								
21	0·9119-0·9121	,,								
22	0·9112-0·9114	,,								
23	0·9106-0·9117	,,								
23	0·912-0·914	Dieterich								
24	0·9101-0·9099	Long								
25	0·9094	,,								
25	0·9109	Saussure								
30	0·9060	Long								
35	0·9028	,,								
50	0·8932	Saussure								
94	0·8625	,,								

[1] "Virgin oil." [2] Gallipoli oil. [3] Commercial oil. [4] Derived from observations on 203 samples. [5] Californian oils. [6] Dark oil.
[7] Derived from observations on 106 samples. [8] *Jour. Soc. Chem. Ind.* 1895, 206.

Physical and Chemical Constants of Olive Oil—continued

Iodine Value.		Acetyl Value.		Thermal Tests.				Refractive Index.		
				Maumené Test.		Heat of Bromination.				
Per cent.	Observer.		Observer.	°C.	Observer.	°C.	Observer.	At °C.		Observer.
82·8	Hübl	12·8	Lewkowitsch	41·5-45·5	Archbutt	15	Hehner and Mitchell	15	1·4698	Strohmer
83	Moore			35 [1] [4] (mean)	De Negri and Fabris	14·3	Jenkins	15	1·4703 [5]	Guozdenovič
81·6-84·5	Dieterich			45-47 [2]	Blasdale	13·55 to 14·5	Archbutt	,,	1·4710-1·4716 [2]	Blasdale
79·18-82·3	Villavecchia							20	1·4670-1·4705	Holde
79-88, [1] generally 82	De Negri and Fabris			Specific Temperature Reaction.				60	1·4548	Thoerner
79-83·2 [3]	Oliveri							Oleo-refractometer.		
78·9-86·9	Thomson and Ballantyne			89-95	Thomson and Ballantyne			"Degrees."		Observer.
77·28-88·68 [2]	Lengfeld and Paparelli							+0 to 2		Jean
88·09-88·69 [2]	Moerck							+0 to +1·5		Bruyn and van Leent
80·4-86·5 [2]	Blasdale							+1 to +3·5 [6] at 22° C.		Pearmain
80·7-91·5 [5]	Guozdenovič							Butyro-refractometer.		
								At 25° C.		Observer.
								62-62·8		Mansfeld

[1] Derived from observations on 203 samples. [2] Californian oils. [3] Derived from observations on 106 samples. [4] By Jean's thermeläometer.
[5] Dalmatian oils (in one case even 92·8 was found as the iodine value). [6] 105 samples.

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.			Solidifying Point.		Melting Point.		Saponific. Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
99 (water 15·5 = 1)	0·8430	Allen	21·2	Hübl	26	Hübl	193	Thoerner	279·4	Allen	86·1	Morawski and Demski	1·4410	Thoerner
100 (water 100 = 1)	0·8749	Archbutt	21	Allen	26	Allen			286	Williams	90·2	Williams		
			Not below 22	Bach	22	Paris Munic. Lab.					87-88	Thoerner		
			23·5-24·6	Dieterich	23-24 to 26-27	Bensemann								
			22-17 [1]	De Negri and Fabris	26·5-28·5	Bach								
			21-22	Thoerner	26-28·5	Dieterich								
					24-27 [1]	De Negri and Fabris								
			Titer Test.		19-23 [5]	Moerck								
					Mostly below 28 [5]	Lengfeld and Paparelli								
			16·9-17·15	Lewkowitsch [2]	26-28	Thoerner								
			17·1-17·8		21-26 [5]	Blasdale [6]								
			18·6-19·7											
			19·45-20											
			23-25	,, [3]										
			20·1-21·2											
			19·75-20·8											
			21-21·87											
			21·5-22·9											
			18·4-19·2											
			18·9-19·8											
			25·2-26·4 [4]	,,										

[1] Derived from observations on 203 samples. [2] Finest Tuscan cream. [3] Commercial oil. [4] Gallipoli oil. [5] Californian oils.
[6] *Jour. Soc. Chem. Ind.* 1896, 206.

The **specific gravity** of olive oil ranges from 0·914 to 0·917 at 15° C., but may rise to 0·920, and even 0·925 in the case of commercial oils expressed at a higher temperature, owing to their larger proportion of palmitin. These oils are mostly recognisable by their darker colour. Free fatty acids in the oil cause, as a rule, a depression of the specific gravity. If the specific gravity of a pale olive oil be found higher than 0·917, it must be looked upon with suspicion, and as possibly adulterated with *sesamé*, *cotton seed*, or *poppy seed oil*. Sophistication with *rape* or *arachis oil* is, however, not indicated by the specific gravity, the differences in their respective gravities being too insignificant.

Special aræometers—oleometers—have been designed for the testing of olive oil, as those of *Lefèbre*, *Gobley*, *Fischer*, giving either the specific gravities directly or in "degrees" calculated in different ways (p. 124). Some of these aræometers bear also marks indicating the point to which the hydrometer dips in other oils.

Souchère[1] has determined by means of *Lefèbre's* oleometer (which is in use in France) the specific gravities of olive oil mixed with various proportions of other oils. His numbers are reproduced in the following table:—

Kind of Oil.	Specific Gravity at 15° C.					
	Pure Oil.	Olive Oil containing				
		10 Per cent.	20 Per cent.	30 Per cent.	40 Per cent.	50 Per cent.
Olive oil . .	0·9153	...	...	...	...	...
Colza oil . .	0·9142	0·91519	0·91508	0·91497	0·91468	0·91475
Sesamé oil .	0·9225	0·91602	0·91674	0·91741	0·91818	0·91890
Cotton seed oil	0·0230	0·91607	0·91684	0·91761	0·91838	0·91915
Arachis oil .	0·9170	0·91547	0·91564	0·91581	0·91598	0·91615

Souchère thinks that it is not only possible to discriminate olive oil from other oils by means of *Lefèbre's* oleometer, but also to determine quantitatively the proportion of the foreign oil added, provided the nature of the latter be known. This statement, however, is decidedly misleading as regards rape (colza) and arachis oils, and for the other oils is, to say the least, doubtful.

The **solidifying point** is also characteristic of olive oil. On referring to the table given on page 259 it will be seen that olive oil has of all vegetable oils the highest solidifying point. According to *Serra Carpi*,[2] the degree of hardness of the solidified olive oil may also serve for the detection of foreign oils, inasmuch as the latter are far softer than olive oil at −20° C. *Carpi's* test is carried out as follows:—The sample of oil is cooled down to −20° C., and kept at

[1] *Moniteur scientif.* 11. 791.

[2] *Zeitsch. f. analyt. Chemie*, 23. 566.

that temperature for three hours. A cylindrical iron rod, conical at the bottom, 1 cm. long and 2 mm. thick, is then placed, by suitable means, on the solidified fat, and weights are put upon it until it sinks in the oil.

His results are given in the following short table :—

Kind of Oil.	Weights required. Grms.
Purest olive oil	1700
Commercial olive oil . . .	Not quite 1000
Cotton seed oil	25

The apparatus designed by *Legler* might be advantageously used for this purpose (p. 103). It should, however, be noted that the solidifying point of mixtures of olive oil with other oils does not give any positive results.[1] As a rule a mixture of olive oil with other oils will have a lower melting point than either of these oils.

The **melting and solidifying points of the fatty acids** (or titer test) will also furnish useful indications as to the purity of the oil, as reference to the table given on page 260 will readily show. A good plan is to test the sample side by side with specimens of pure oils. *Bach* has determined the melting points of the mixed fatty acids from pure olive oil, and from mixtures of olive oil with other oils :—

Mixed Fatty Acids from	Melting Point. °C.	Solidifying Point. °C.
Pure olive oil	26·5-28·5	Above 22
80 parts olive oil, 20 parts sunflower oil .	24	18
80 ,, ,, 20 ,, cotton seed oil .	31·5	28
80 ,, ,, 33⅓ ,, rape oil . .	23·5	16·5

Dieterich, however, states that additions of foreign oils amounting to less than 25 per cent cannot be detected with certainty. Hence this method is not of much importance, since sophistication with so large quantities can be detected more easily by other means. *Dieterich* has recorded the melting points of the following mixtures of fatty acids from olive oil with the fatty acids derived from other oils :—

Mixed Fatty Acids from	Melting Point. °C.	Solidifying Point. °C.
Pure olive oil (mean of 17 samples) . . .	26-28·5	23·5-24·6
75 parts of olive oil and 25 parts of arachis oil .	29	26
75 ,, ,, ,, 25 ,, cotton seed oil	30	27·3
75 ,, ,, ,, 25 ,, sunflower ,,	25	20·5
75 ,, ,, ,, 25 ,, sesamé ,,	28	25
75 ,, ,, ,, 25 ,, linseed ,,	24·5	19·5
75 ,, ,, ,, 25 ,, rape ,,	23	19

[1] Cp. Goldberg, *Jour. Soc. Chem. Ind.* 1897, 447.

The **electrical conductivity** of olive oil being considerably less than that of any other vegetable oil—according to *Rousseau* 675 times less than that of the next oil in point of low conductivity—the determination of that physical constant should easily allow definite conclusions to be drawn as to the purity of a sample. *Palmieri's* "Diagometer" has been specially constructed for the examination of olive oil. This method, however, has not yet come into practical use, but it may be hoped that, since the determination of this physical constant has recently been introduced to chemical laboratories as a means of determining the constitution of chemical compounds, a simple apparatus may be devised for the examination of oils. A glance at the table given (p. 275) will show that *Herlant's* method (chap. v. p. 122) may prove of use in this direction.

Olive oil has also of all vegetable oils the smallest **refractive power** (cp. p. 262). *Leone* and *Longi* have proposed to examine olive oil for adulterants, especially for *cotton seed* and *sesamé* oils, by determining the refractive index of the oil. The results obtained will, however, hardly repay the trouble involved, inasmuch as only large proportions of foreign oils can be detected by this means, and other methods give much more definite indications.

Amagat and *Jean's* oleo-refractometer,[1] however, seems to lend itself with more advantage to the optical examination. As has been stated by *Oliveri*,[2] the deviation of a very large number of samples of olive oil ranged from + 1 and + 1·50. The following table contains *Oliveri's* results :—

Kind of Oil.	Deviation.
Olive (106 samples)	0 to 2
Cotton seed	18
Sesamé	15·5
Colza	26·5
Arachis	7·5
Poppy seed	28·5
Castor	41-44[3]

A sample consisting of two oils, having the deviations D and D_1, and mixed in the proportion of m and n per cent respectively, would have a deviation equal to

$$\frac{m}{100} D \times \frac{n}{100} D_1.$$

Thus a mixture of 80 parts of olive oil (deviation 1) with 20 parts of cotton seed oil (deviation 18) showed a deviation of $\frac{80}{100} + \frac{20}{100} 18 = 4{\cdot}4$. Mixtures of olive oil with any considerable quantity of the above-named oil will, as a rule, show deviations exceeding + 2, the limit stated above. Adulteration with arachis oil,

[1] *Gazz. Chimica*, 16. 393. [2] *Jour. Soc. Chem. Ind.* 1894, 45.

[3] Castor oil has been used to adulterate olive oil (*Di Vetere* and *Leonardi*). Cp. also *Jour. Soc. Chem. Ind.* 1894, 961, 981.

however, may still escape detection, since a mixture of 25 parts of arachis oil with 75 parts of olive oil—deviation 0·25—would produce a deviation of + 2°.

Zeiss's butyro-refractometer will, of course, prove itself equally useful.

According to *Guezdenovič*, Dalmatian oils appear to have abnormal refractive power (cp. also table, p. 455).

Behaviour with Solvents.—Olive oil being but slightly soluble in absolute alcohol (3·6 in 100), can be distinguished by means of that solvent from *castor* and *olive kernel oils;* its solubility in glacial acetic acid may help to detect rape or hedge radish oil.

The behaviour of olive oil fatty acids with a mixture of alcohol and acetic acid has been detailed above (p. 272). It should, however, be borne in mind that smaller quantities than 25 per cent of *cotton seed* or *sesamé* oil cannot be thus detected; if larger quantities be present in the sample granular precipitates are obtained. This test is less reliable still in the case of *rape* oil, addition of over 50 per cent only being recognisable. The insolubility of arachidic acid in cold alcohol allows its isolation from the other mixed fatty acids (cp. test for arachis oil).

Of the **quantitative reactions** the most important is the **iodine test**, constituting, as it does, the most valuable means of detecting adulteration. Olive oil has nearly the lowest iodine absorption of any oil that might be used for adulteration. As a rule, the iodine value of olive oil should be from 81·6 to 84·5. There are, however, undoubtedly genuine oils, the iodine number of which reaches 86 (from the Colombaio olive), and even 88, as in the case of *Californian* oil. Still these cases are notable exceptions, and an oil with an iodine value of more than 85 must be looked upon with suspicion.

The extraordinarily high iodine values of four Dalmatian oils (see table, p. 455) should stimulate further investigation.

If there is reason to exclude abnormal oils, a higher iodine absorption may indicate adulteration with as little as 5 per cent of a *drying oil* (poppy seed, hemp seed oil) or 15 per cent of *sesamé*, *cotton seed*, and *rape oils*. Less positive results are obtained in the presence of *arachis oil*, the lowest values recorded for that oil almost coinciding with the highest given for olive oil.

Paparelli[1] has studied the causes of the variability of the iodine values, and arrives at the following conclusions:—The more mature the olives are the higher is the iodine absorption of the oil. Old and rancid oil has generally a slightly lower number. The method of preparing the oil has also its influence. Oil from the pulp shows slightly lower iodine absorption than that obtained by grinding pulp and "pits" together; oils extracted by solvents show lower values than the same obtained by pressing; oils from pits are, again, characterised by higher numbers than those extracted from the fruit. The greatest variation, however, is found to be due to the variety of the olive from which the oil is made.

[1] *Jour. Soc. Chem. Ind.* 1892, 848.

It may be pointed out here that the iodine values of the semi-solid and the liquid portions into which olive oil separates on partial solidification almost coincide (*Goldberg*).[1]

The **saponification value** will only lead to definite results if large quantities of *rape oil* be admixed with the sample.

In the **elaïdin test** olive oil yields the hardest elaïdin of all oils, and also requires the shortest time for solidification. The effect of an addition of rape or cotton seed oil to olive oil is shown in the following table compiled from tables published by *Archbutt*:[2]—

Kind of Oil.	Minutes required for Solidification, at 25° C.	Consistency.
Olive oil	230	Hard, but penetrable
Olive oil + 10 per cent of rape oil .	320	Buttery
,, +20 ,, ,, .	From 9 to 11½ hours	Buttery
,, +10 ,, cotton seed oil .	From 9 to 11½ hours	Very soft butter
,, +20 ,, ,, .	More than 11½ hours	Very soft butter

The effect of a foreign oil on the hardness of the elaïdin can be measured quantitatively by using *Legler's* method (p. 103). It should, however, be borne in mind that, according to *Gintl* (p. 282), olive oil, after exposure to sunlight for a fortnight, no longer gives a solid elaïdin.

The **thermal reactions** give lower values than any other vegetable oil. *Lengfeld* and *Paparelli* assert that there exists a proportionality between the iodine number and the **Maumené test** of various olive oils. They obtained for fourteen oils numbers varying from 33·5° to 41° C. (compare also table, p. 455), the oil possessing the highest iodine absorption giving the greatest rise of temperature. Their results, arranged by the writer according to the iodine values, do not, however, bear out fully the correctness of this rule.

Olive Oil, No.	Iodine Value. Per cent.	Maumené Test. °C.
1	77·28	35
2	78·42	33·5
3	78·51	33·5
4	78·52	34
5	79·50	36
6	79·53	34·5
7	80·80	37
8	81·45	38
9	81·50	35
10	81·70	34
11	83·35	37·5
12	85·44	36·5
13	87·15	41

[1] *Jour. Soc. Chem. Ind.* 1897, 447. [2] *Ibid.* 1886, 308.

The proportionality between iodine number and **heat of bromination test** shows in a general way the same regularity, as will be seen from the numbers given in the following table (*Archbutt* [1]) :—

Olive Oil.	Iodine Value. Per cent.	Heat of Bromination. °C.
Malaga	78·4	14·2
...	78·7	13·55
...	78·9	13·8
Malaga	79·3	13·8
...	81·4	14·2
...	81·4	14·35
Gallipoli	82·0	14·4
,,	82·1	14·5
,,	82·5	14·5
...	84·2	14·45

The **unsaponifiable matter** in olive oil is, as a rule, below 1 per cent.[2]

The **phytosterol reaction** has been proposed by *Salkowski* as a means of detecting seed oils in olive oil, the latter containing but very minute quantities of phytosterol in contradistinction to the former. 50 grms. of olive oil do not yield a quantity of phytosterol sufficient for the determination of its melting point. *Hehner* recommends this test especially for the detection of *cotton seed oil*.

The **colour reactions** proposed by various authors are altogether unreliable and yield no definite results, with the exception of the colour test for *sesamé oil*, and perhaps also those for *cotton seed oil* (see below).

A curious reagent, consisting of egg-albumen and nitric acid, has been proposed by *Brullé* [3] for the rapid detection of seed oils. 0·1 grm. of egg-albumen, 2 c.c. of nitric acid (*specific gravity?*), and 10 c.c. of the sample, are placed in a test-tube and gently warmed over a spirit lamp, so that acid and oil have the same temperature. The albumen gradually dissolves in the oil. Whereas pure olive oil thus treated assumes a yellow colour with a faint greenish tint, an oil adulterated with only 5 per cent of a seed oil becomes distinctly amber-yellow, and, in the presence of larger quantities of the latter, dark orange. *Jean* states that this process gives reliable results, whilst *Holde* rejects it as absolutely untrustworthy. *Brullé* himself appears to have abandoned this "albumen test," as he adopts in his later publications a modification of *Becchi's* test for cotton seed oil. His colour reactions, however, stand greatly in need of confirmation, and the reader must therefore be referred to the original papers and table.[4]

[1] *Jour. Soc. Chem. Ind.* 1897, 311.

[2] It should be noted that in Germany commercial oil is denatured with rosemary oil, which of course increases the amount of unsaponifiable matter.

[3] *Jour. Soc. Chem. Ind.* 1888, 457.

[4] *Ibid.* 1890, 924 ; 1891, 390.

Green olive oils should be tested for **copper**, some specimens of "*Malaga* oil" being coloured green by admixture with copper acetate. *Cailletet*[1] detects the copper by agitating 10 c.c. of the sample with 5 c.c. of ether, in which 0·1 grm. of pyrogallol has been previously dissolved, when presence of copper will be indicated by the mixture becoming brown with separation of copper pyrogallate. Pure oils are not discoloured, nor do they become turbid. Copper may also be detected in the manner described above (p. 98).

In conclusion, we collate the tests useful for the detection of oils occurring as adulterants in commercial olive oils :—

1. **Arachis Oil.**—Iodine absorption ; as a rule, higher than that of normal olive oil. Detection of arachidic acid (see "Arachis Oil," p. 445).

2. **Sesamé Oil.**—Specific gravity ; solubility of fatty acids ; iodine absorption ; and, as most characteristic, *Baudouin's* test as modified by *Villavecchia* and *Fabris* (see "Sesamé Oil") in order to avoid errors that might possibly be caused by abnormal oils, such as Tunisian, etc.

3. **Cotton Seed Oil.**—Specific gravity ; melting point of fatty acids, behaviour of fatty acids with solvents, *iodine absorption*, *Livache* test ; nitric acid colour test ; *Becchi's* test (see "Cotton Seed Oil") ; phytosterol test (p. 317).

4. **Rape Oil.**—Iodine absorption ; melting and solidifying points of the mixed fatty acids ; behaviour of the mixed fatty acids with solvents ; saponification value. (*Palas'* colour reaction[2] cannot be recommended, cp. p. 406.)

Presence of *sulphur* will not always, as has been assumed until recently, indicate rape oil without fail, since on the one hand the "cold-drawn" oils from seeds of *Cruciferæ* are free from sulphur, and on the other hand olive oils extracted by carbon disulphide (sulpho-carbon oils) give the reactions characteristic of sulphur.

These sulpho-carbon oils possess a dark colour and an unpleasant smell, and dissolve easily in alcohol. They are thereby, and more especially by their iodine absorption, easily distinguished from rape oil.

Sulphur not being a constitutive element of rape oil, the colour test proposed by *Schneider*, and stated to detect the presence of even 2 per cent of rape oil in olive oil, is valueless. Besides, cotton seed oil may give a similar reaction. *Schneider's* test is as follows :—Dissolve one volume of the sample in two volumes of ether, and add 20-30 drops of a saturated alcoholic solution of silver nitrate ; the lower layer becomes brownish and at last black, if rape oil is present in large quantity, if in small quantity, distinctly brown after twelve hours' standing.

5. **Castor Oil.**—Specific gravity ; behaviour with solvents ; *acetyl value*.

6. **Curcas Oil** (used in Portugal, according to *Hiepe*, to adulterate olive oil).—Iodine absorption ; saponification value. Admixtures of even 10 per cent are said to be detected by the intense reddish-brown

[1] *Zeitsch. f. analyt. Chemie*, 18. 628. [2] *Jour. Soc. Chem. Ind.* 1897, 361.

colouration the sample will assume a short time after treatment with nitric acid and metallic copper.

7. **Lard Oil** (the price permitting).—Melting point of fatty acids; viscosity; odour of lard on warming.

8. **Drying Oils.**—Iodine value. Thermal tests. *Livache* test.

9. **Fish Oils.**—Iodine test; taste and smell.

10. **Hydrocarbons.**—Determination of unsaponifiable matter. Adulterants falling under this class are: colourless vaseline and mineral oils.

Turkey-red oil (Tournant oil) is tested for the percentage of free fatty acids, which should be present to the extent of about 25 per cent, calculated as oleic acid. Adulterations may be detected by the iodine test. A complete analysis of an adulterated Turkey-red oil is given below (chap. xiii. p. 811).

OLIVE KERNEL OIL

German—*Olivenkernoel.*

Physical and Chemical Constants of Olive Kernel Oil

Specific Gravity.		Saponification Value.		Iodine Value.		Acetyl Value.	
At 15° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.		Observer.
0·9202	Valenta	188·5	Valenta	81·8	Hübl	22·5	Benedikt

Olive kernel oil is the oil obtained by pressing or extracting from the seeds of the olive kernels.

This oil differs from olive oil by its dark greenish-brown colour, and by being more readily soluble in alcohol and acetic acid. [This is, no doubt, due to the large quantity of free fatty acids in the oils. Thus a sample examined by *Benedikt* had the acid value 90·1.] The oil is, however, not miscible with absolute alcohol in every proportion like castor oil. Thus a sample of olive kernel oil, on being mixed with 3·5 volumes of absolute alcohol, gave a clear solution, whereas with 4 volumes it gave a slight, and with 5 volumes a strong turbidity which, however, disappeared on adding more alcohol.

In other respects—elaïdin test, iodine absorption, etc.—the oil resembles olive oil closely. Olive kernel oil naturally occurs in those olive oils obtained from olive marc crushed with the kernels.

Physical and Chemical Constants of Coffee Berry Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Reichert-Meissl Value.		Iodine Value.		Maumené Test.	Refractive Index.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	°C.	At 25° C.	Observer.
0·9510-0·9525	De Negri and Fabris [1]	5 – 3 6 – 3	De Negri and Fabris	165·1-173·37 176·2-177·3	De Negri and Fabris Spaeth [2]	1·65-1·7	Spaeth	85·89-87·34 (78·65) 85·3-86·8	De Negri and Fabris Spaeth	53-55 [1]	1·4777-1·4778	Spaeth
											Butyro-refractometer.	
											79-79·25 at 25° C.	Spaeth

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.	Saponification Value.	Iodine Value.
°C.	°C.	Mgrms. KOH.	Per cent.
36 – 34 ...	38-40 ...	172-178 ...	88·82-90·35 (81·8)

[1] De Negri and Fabris, *Jour. Soc. Chem. Ind.* 1893, 454.

[2] Spaeth, *Chem. Zeit.* 1895, Rep. 292.

Coffee berry oil—extracted by means of ether from the coffee berries—has an intense greenish-brown colour; it possesses a faint odour of raw coffee. By roasting the berries the oil is very little changed.

The samples examined by *Spaeth* contained from 2·25-2·29 per cent of free acid, calculated as free acid.

According to *Hilger*, coffee berry oil consists of olein and small quantities of palmitin and stearin.[1]

UNGNADIA OIL[2]

Physical and Chemical Constants of Ungnadia Oil

Specific Gravity.		Solidifying Point.	Hehner Value.	Saponification Value.	Iodine Value.
At °C.		°C.	Per cent.	Mgrms. KOH.	Per cent.
15 100	0·9120 0·8540	−12	94·12	191-192	81·5-82

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.	Iodine Value.
°C.	°C.	Per cent.
10	19	86-87

Ungnadia oil is obtained from the seeds of *Ungnadia speciosa*, a tree indigenous in Texas.

The oil is limpid, and is remarkable (like ben oil) in not easily turning rancid.

[1] *Chem. Zeit.* 1895, 776 (Hehner and Mitchell's method was not known then).
[2] Schaedler, *Pharmac. Zeitung*, 1889, 340.

BEN OIL

French—*Huile de ben.* German—*Behenoel.*

Physical and Chemical Constants of Ben Oil

Specific Gravity.		Solidifying Point.		Iodine Value.[1]	
At 15° C.	Observer.	°C.	Observer.	Per cent.	Observer.
0·9120	Chateau	Solidifies completely at 0; deposits crystals at 7	Chateau	84·1[2]	Mills
0·9198[2]	Mills		...	80·8[3]	,,
0·9161[3]	,,				

Ben oil is prepared from the seeds of the ben nut from *Moringa oleifera.*

This oil has a slightly yellowish colour, is odourless, and has a sweet taste. On standing it separates into a solid and a liquid portion.

Ben oil consists of the glycerides of oleic, palmitic, and stearic acids, and of a solid acid of high melting point; according to *Völker*, this is identical with behenic acid, melting point 76° C. [arachidic acid ?]

It appears strange that, according to *Mills*, the specimen of oil containing much solid fat should absorb more iodine than the oil free from solid fat.

In the East ben oil serves as a cosmetic, and used to be employed in the "maceration" process for extracting perfumes from flowers, The liquid portion of the oil becomes rancid only after long exposure, and therefore this oil is very valuable for lubricating watch springs.

STROPHANTUS SEED OIL[4]

German—*Strophantusoel.*

Physical and Chemical Constants of Strophantus Oil

Specific Gravity at 13° C.	Hehner Value.	Saponification Value.	Reichert-Meissl Value.	Iodine Value.
0·9254	95·3	187·9	0·5	73·02

The melting point of the fatty acids was 28°-30° C.

This oil was obtained from the seeds of *Strophantus hispidus.*

[1] Calculated from bromine value. [2] Containing much solid fat.
[3] Containing no solid fat. [4] Mjöen, *Archiv. d. Pharmacie*, 1894 (234), 283.

SECALE OIL [1]

German—*Mutterkornoel.*

Physical and Chemical Constants of Secale Oil

Specific Gravity at 13° C.	Hehner Value.	Saponification Value.	Reichert-Meissl Value.	Iodine Value.
0·9254	96·3	178·4	0·20	71·08

The melting point of the fatty acids was 39·5°-42° C.
Secale oil was obtained from *Secale cornutum.*

2. ANIMAL OILS

Under this section we shall describe the oils obtained from animals, dividing them into two groups—

(1) Marine animal oils, and
(2) Terrestrial animal oils.

This subdivision is not made merely for the sake of convenience; it is based on striking chemical differences. Broadly speaking, these two groups may be compared with the two large groups of vegetable oils: the drying and the non-drying oils.

Like the drying oils the marine animal oils are characterised by very high iodine values, by their rapid absorption of oxygen, and by not yielding elaïdins.

On the other hand, the terrestrial animal oils compare with the non-drying oils in that they have low iodine values, do not easily absorb oxygen, and yield solid elaïdins.

Just as amongst the vegetable oils there are a number of oils occupying an intermediate position between the drying and the non-drying oils, viz. the semi-drying oils, we find among the marine animal oils gradations from the most pronounced type of easily oxidisable oils—the liver oils—to oils containing large quantities of glycerides of saturated fatty acids, thus approaching the chemical constitution of terrestrial animal oils.

[1] Mjöen, *Archiv. d. Pharmacie*, 1894 (234), 278.

(1) Marine Animal Oils

The oils belonging to this class are liquid at the ordinary temperature, yielding, however, on cooling, varying amounts of solid glycerides.

The classification of these oils is difficult, owing to our imperfect knowledge of them. The uncertainty of the colour reactions (p. 315) excludes them as a basis of subdivision.

The members of this class may conveniently be subdivided into the following three groups :—

α. Fish oils.
β. Liver oils.
γ. Blubber oils.

The term "train oil" has been avoided, as its German equivalent "Thrane" includes all three groups, and may therefore cause confusion. It must further be premised that, under blubber oils, those oils only are included that consist wholly or in greater part of glycerides. Therefore the liquid waxes—viz. sperm oil and Arctic sperm oil, although usually classed with blubber oils—are excluded from this group, as, according to their chemical constitution, they belong to the waxes proper.

The specific gravities of the marine animal oils do not vary much, lying, as they do, between 0·915 and 0·930. The saponification values of some of the blubber oils are notable for their great deviations from the normal value of about 195, according as they contain large amounts of spermaceti or of glycerides of volatile fatty acids; so that this constant, like the specific gravity, cannot be used for purposes of classification.

The liver oils, however, appear to form a natural group, characterised by notable amounts of cholesterol and other biliary substances. If, for the purposes of subdivision, we adopt the iodine value as basis, the liver oils may be interposed between the fish oils and the blubber oils.

The chemical constitution of the liquid fatty acids is as yet unknown (cp. p. 279). The high iodine values, especially those of the fish and liver oils, clearly point to the presence of acids belonging to a less saturated series than oleic acid. These hypothetical acids, however, cannot be identical with linolic acid or the linolenic acids, as the oils, although absorbing large amounts of oxygen (p. 287), do not dry like linseed oil.[1] The occurrence of acids belonging to the series $C_nH_{2n-2}O_2$, $C_nH_{2n-6}O_2$, and $C_nH_{2n-8}O_2$, has been made probable, although it is not proved yet, and therefore the existence of asellic (p. 54), jecoleic (p. 59), jecoric (p. 62), and therapic acids (p. 63) is open to doubt.

All the marine animal oils are easily recognised by their fishy taste and smell.

[1] The free fatty acids from seal and cod liver oil kept in stoppered glass bottles deposited after three months a resinous substance, which I intend to examine.

a. Fish Oils

The fish oils are obtained from all parts of the body of common fish—such as herring, sardine, salmon, etc.—by boiling. The livers of these fish contain, as a rule, very little oil, whereas the body of the liver oil-yielding fish, notably cod fish, gives so little oil, that it is not prepared commercially.

MENHADEN OIL

French—*Huile de Menhaden.* German—*Menhadenthran.*

For table of constants see p. 471.

Menhaden oil is an American fish oil, and, like other fish oils, is prepared from the heads and intestines of fish, especially of the menhaden, *Alosa Menhaden.*

The oil is of brownish colour, has a fishy odour, and absorbs oxygen readily.

Its composition is not known, but it may be considered to consist almost entirely of glycerides, as shown by the saponification value, its proportion of glycerol, and the small amount of "unsaponifiable matter."

Unsaponifiable Matter

Colour of the Oil.	Per cent.	Observer.
Pale yellow . . .	0·61	Fahrion
Red	0·82	,,
Yellowish-red (Levantine)	1·43	,,
Brown	1·60	Thomson and Ballantyne

Jean states that menhaden oil usually contains 0·02 per cent of iodine.

Menhaden oil is frequently adulterated with mineral oil.

Its principal use is in the currying trade, and for the manufacture of sod oil. The oil is employed for adulterating linseed oil.

[TABLE

Physical and Chemical Constants of Menhaden Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Reichert Value.		Iodine Value.		Maumené Test.	
°C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
15·5	0·927-0·933	Allen	– 4	Jean	192	Allen	1·2	Allen	147·9	Archbutt	126	Allen
,,	0·9311	Thomson and Ballantyne	...	...	189·3	Thomson and Ballantyne	...	...	160	Thomson and Ballantyne	123-128	Archbutt
									153·9	Schweitzer and Lungwitz		
											Specific Temp. Reaction.	
											306	Thomson and Ballantyne

SARDINE OIL

French—*Huile de Sardine.* German—*Sardinenthran.*

For tables of constants see p. 473.

This oil is obtained in the preparation of tinned sardines.

The Japanese sardine oil—Japan fish oil—prepared on a large scale in Japan, is extracted from the fish either by boiling with water or by allowing them to rot in heaps, when the greater part of the oil flows out, the remainder being obtained by pressure. This oil contains about 30 per cent of solid fat.[1] It is refined in Yokohama by heating to 50°-60° C. for an hour, and then run off into wooden vessels, where it soon separates into three layers. The upper layer is liquid and clear, the middle layer consists of solid fat,[1] and the lowest is water with albuminous substances and portions of the fish.[2] Some constants of this oil, which seems to differ from ordinary sardine oil, especially in its iodine absorption, have been recorded in the table given page 473.

Fahrion[3] has recently examined samples of sardine oil and Japan oil with a view to determining their ultimate constitution. Besides the values given in the table, we reproduce the following:—

[1] This solid fat, brought into commerce under the name "refined fish tallow," is chiefly used as a dégras substitute for currying leather. *Jour. Soc. Chem. Ind.* 1894, 894.

[2] Villon, *Jour. Soc. Chem. Ind.* 1887, 372.

[3] *Ibid.* 1893, 938; 935.

[TABLE

Physical and Chemical Constants of Sardine Oil

Specific Gravity.		Melting Point.		Hehner Value.		Saponification Value.		Iodine Value.		Refractive Index.	
15° C.	Observer.	Per cent.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Oleo-refractometer.	
0·933	Fahrion	...	...	94·5	Fahrion	...	...	193·2	Fahrion	" Degrees."	Observer.
Japanese Sardine Oil (Japan Fish Oil)										+50 to +53	Jean
0·916	Fahrion	20-22	Villon	95·93	Fahrion	189·8-192·1	Lewkowitsch	96 121·5	Fahrion Lewkowitsch		

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	
°C.	Observer.
27·6-28·2	Lewkowitsch

	Sardine Oil.	Japanese Oil.
Acid value	20·6	31·2
Unsaponifiable . . .	0·62-0·66 per cent	0·56-1·44 per cent
Hydroxy acids . . .	0·7 ,, ,,	0·5 ,, ,,
Solid hydroxy acids . .	0·2 ,, ,,	

The solid fatty acids of sardine oil were at first stated by *Fahrion* to consist of palmitic acid only; afterwards he modified this statement by allowing a small quantity of stearic acid, palmitic, however, preponderating. The liquid fatty acids do not contain physetoleic acid (p. 53), nor could any oleic, linolic, or either of the two linolenic acids be detected. The unsaturated fatty acid is said to be *jecoric acid*, $C_{18}H_{30}O_2$ (from *jecur*, liver; though sardine oil is not a liver oil), an acid isomeric with linolenic acid, but differing from it essentially in that it does not conform to *Hazura's* rule (p. 67), according to which it should yield, on oxidation with permanganate in alkaline solution, a hexahydroxy acid, whereas it is apparently broken up with formation of carbonic and volatile fatty acids. *Fahrion*, therefore, considers this sample of sardine oil to consist of

Tripalmitin, 14·3 per cent.
Trijecorin, 85·7 ,, ,,

The examination of the other Japanese oil mentioned by *Fahrion* gave an entirely different result, inasmuch as he could not detect any jecoric acid in it. [The low iodine value of this Japanese oil seems to confirm this.] He has, however, shown in an indirect way the occurrence of an unsaturated acid having seventeen carbon atoms in the molecule and belonging to the oleic series. This acid has been named asellic acid (p. 54).

In the present state of this difficult research no definite conclusions can be drawn, the less so as the various specimens seem to behave differently. The whole question must therefore be considered an open one, especially so as *Fahrion's* results have been severely criticised by *Weiss*.[1]

Japan fish oil has frequently been referred to by some chemists as a liver oil.

β. Liver Oils

The liver oils contain notable amounts of cholesterol and other unsaponifiable substances, giving rise to colour reactions (especially when the oils become rancid) which were formerly considered as characteristic. Only the sulphuric acid colour test can be looked upon as really decisive; in the case of pure and fresh liver oils the

[1] *Jour. Soc. Chem. Ind.* 1893, 937.

blue colour in the carbon bisulphide solution is very distinct; if the oils have become rancid a purple colouration takes the place of the blue. The examination of other liver oils than cod by *Tichomirow* and *Kaiser*[1] confirms this colour reaction to be a general one of the liver oils.

The intensity of the phospho-molybdic acid test is also remarkable. If the chloroformic solution of a liver oil, after shaking with the phospho-molybdic acid, be allowed to stand, there is formed a blue ring at the zone of contact of the two layers, no doubt due to the neutralising action of the bases in the oil. In this form the phospho-molybdic test may serve to identify a liver oil. Rancid liver oils, however, do not give a very distinct colour reaction.

The existence of jecoleic and therapic acids has been referred to already.

COD LIVER OIL

French—*Huile de foie de morue.* German—*Dorschleberthran, Leberthran.*

For tables of constants see pp. 477, 478.

Genuine cod liver oil is obtained from the liver of the cod, *Gadus morrhua* (and the dorsch, the young of *G. morrhua*, formerly considered as a separate species, *Gadus Callarias*).

The following three qualities of cod liver oil, as obtained by the natural decay of the livers (in the Lofoten islands), are known in commerce: (1) pale cod liver oil, (2) light brown oil, (3) brown oil.

Pale cod liver oil[2] and *light brown oil* are used in pharmacy. The former is the first product, the light brown oil forming a second product, after the putrefaction of the livers has proceeded further. At present large quantities of medicinal oil are prepared by heating the livers by means of steam, when the cell membranes burst and the oil exudes—"steam liver oil." The medicinal cod liver oil prepared in this country is exclusively obtained by the steam process. The livers must be absolutely fresh; they are taken from fish brought ashore alive and steamed the same day.

The *brown oil*—the "cod oil" of commerce—is also a genuine cod liver oil. As the fish cannot be brought alive to shore, they are opened in the boat and the livers collected. These are landed in a more or less putrid state, and the oil is therefore unfit for medicinal purposes. It is largely employed in the leather industry. The "unracked" cod oil is recovered by boiling the livers at a high temperature; this oil contains considerable quantities of "stearine," which is collected, especially in winter, and sold as "fish stearine" for soap-making or "fish tallow" for currying. "Norwegian cod oil" and "Newfoundland cod oil" are special brands of cod oil.

[1] *Chem. Zeit.* 1895, Rep. 310.

[2] The pale yellow colour is due, according to P. Möller, to a pigment (lipochrome) which is destroyed by the action of bright light—artificially bleached oils.

P. Möller[1] discerns four qualities: (1) raw medicinal oil; (2) pale oil; (3) light brown oil; (4) brown oil. As a rule, however, so little is obtained of oil (1) that it is not collected separately. Therefore the writer retains the subdivision into three qualities.[2]

The commercial "Coast cod oil" is a liver oil obtained from other fish besides cod, as hake (*Merluccius vulgaris*), haddock (*Merluccius æglefinus*), ling (*Molva vulgaris*), coal fish (*Gadus virens*), in fact any fish that is caught in the nets of the trawlers on the open sea. The livers from these fish are collected in barrels, and reach the works of the cod oil extractor in a very putrid state.

According to the temperature reached in the manufacture, cod liver oil contains larger or smaller quantities of "stearine" which is allowed to settle out. Therefore the solidifying point of different samples will be found to vary greatly.

[1] *Codliver Oil and Chemistry*, London, 1895.

[2] Complete details as to the manufacture of cod liver oil in Norway are given in P. Möller's book, *Codliver Oil and Chemistry*.

Physical and Chemical Constants of Cod Liver Oil

Specific Gravity.			Solidifying Point.		Hehner Value.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index.		
At °C.		Observer.	°C.	Observer.	Per cent	Observer.	Mgrms. KOH.	Observer.	Per cent	Observer.	°C.	Observer.	At °C.		Observer.
15	0·922-0·927	Kremel	0 to −10	Salkowski	95·3	Lewkowitsch	213·2	Valenta	123-141	Kremel	102-103	Maumené	15	1·4800-1·4852	Strohmer
,,	0·9257-0·9264	Bishop					182-187	Allen	139·6-152·6	Dieterich	116	Baynes	60	1·4621	Thoerner
,,	0·927	Fahrion					171-189	Kremel			113	Allen			
15·5	0·923-0·930	Allen					185·1-188·2	Thomson and Ballantyne	147·9	Fahrion			Oleo-refractometer.		
,,	0·9249-0·9265	Thomson and Ballantyne					175-185	Thoerner	141-143·4	Lewkowitsch					
99 (water 15·5 = 1)	0·8742	Allen					179-193·4	Parry and Sage	140·1	Heyerdahl	Specific Temperature Reaction.		"Degrees."		Observer.
									158·7-166·6	Thomson and Ballantyne					
									128-130	Thoerner	243-272	Thomson and Ballantyne	+38 to +53 +40 to +46 at 22° C.		Jean Pearmain
									153·5-168·4	Parry and Sage					
									144-151	Dulière			Butyro-refractometer.		
													At 25° C.		Observer.
													75		Mansfeld

Physical and Chemical Constants of the Mixed Fatty Acids

	Solidifying Point.		Melting Point of Solid Fatty Acids.		Saponification Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
	Titer Test.											
Medicinal .	17·5-18·4	Lewkowitsch	21-25	Parry and Sage	204·4	Dieterich	287·6-292·5	Parry and Sage	130·5	Thoerner	1·4521	Thoerner
Coast cod .	18·7-19·3	,,			207	Thoerner			164·9-170	Parry and Sage		
Norwegian .	13·3-13·9	,,										
Dark, unracked . .	22·5-24·3	,,	(cp. also below)									

The chemical composition of the glycerides in cod liver oil appears to be very complicated. As palmitic and stearic acids have been isolated, the occurrence of palmitin and stearin is certain. But the "stearine" separating from cod liver oil on cooling contains but little true "stearine," *i.e.* glycerides of stearic and palmitic acids, the cod liver oil stearine having a very high iodine value (113·4, *Heyerdahl;* 94, *Lewkowitsch*). The nature of the liquid fatty acids is but imperfectly understood as yet; the high iodine value points to the presence of large proportions of less saturated acids than those belonging to the oleic series.

Small quantities of glycerides of the lower fatty acids have been stated by various authors to occur in cod liver oil, such as glycerides of acetic, butyric, valeric, and capric acids. Thus *Allen* has found for a sample of oil a *Reichert* value of 1·1 to 2·1. According to *Salkowski* and *Steenbuch*, however, the volatile fatty acids found are but secondary products due to putrefaction of livers, which in the older processes of manufacture always occurred to a greater or less extent. The best medicinal liver oils prepared by steam are, indeed, free from volatile acids.

Fahrion,[1] examining the liquid fatty acids from a cod liver oil absorbing 175·5 per cent of iodine, could not identify amongst them jecoric acid with certainty, and assumes the presence of an acid, $C_{17}H_{32}O_2$, named asellic acid. Physetoleic acid (iodine value = 100), however, said to form the chief constituent of cod liver oil, could not be detected by this investigator.

The latest researches of *Heyerdahl*[2] led this chemist to the conclusion that the mixed fatty acids from cod liver oil, freed from its "stearine," contained amongst other acids, not identified hitherto, about 4 per cent of palmitic acid, 20 per cent of jecoleic acid (p. 59), and 20 per cent of therapic acid (p. 63). The presence of jecoleic acid is inferred from the existence of dihydroxyjecoleic acid prepared by oxidation of the mixed fatty acids by means of potassium permanganate, and that of therapic acid from the octobromide $C_{17}H_{26}Br_8O_2$ obtained on brominating the liquid fatty acids. No oleic acid has been found in cod liver oil, and the "stearine," no doubt, contains some unknown unsaturated acid or acids. In the fresh state cod liver oil contains no hydroxy acids, according to *Heyerdahl*. The peculiar composition of some of the fatty acids satisfactorily explains the extraordinary facility with which cod liver oil is oxidised and turns rancid. *Heyerdahl's* opinion, however, that rancidity is due to the formation of hydroxy acids requires confirmation.

A characteristic constituent of cod liver oil is **cholesterol,** which can be isolated by saponifying the oil and exhausting the soap with ether. The residue obtained on evaporating the ether is then crystallised from alcohol when the characteristic cholesterol crystals are deposited. The quantity of cholesterol, according to *Allen* and *Thomson*, is from 0·46 to 1·32 per cent; *Salkowski*[3] gives as an average 0·3 per cent. *Jean*[4] obtained 6 per cent of unsaponifiable

[1] *Jour. Soc. Chem. Ind.* 1893, 935.
[2] *Codliver Oil and Chemistry*, p. lxxxix.
[3] *Zeitsch. f. analyt. Chemie*, 26. 565.
[4] *Moniteur scientif.* 1885, 892.

matter from a sample, which must, in the opinion of the writer, be due to sophistication with shark liver oil. The figures recorded in the following table undoubtedly prove that 6 per cent is an exceptionally high figure :—

Unsaponifiable Matter in Cod Liver Oils

Description of Oil.	Colour.	Unsaponifiable.	Observer.
		Per cent.	
Steam cod liver oil, medicinal	Pale yellow	0·61	Fahrion [1]
,, ,, ,,	Almost colourless	0·64	,,
,, ,, ,,	Pale yellow	0·98	,,
Medicinal cod liver oil	Reddish yellow	0·54	,,
,, ,,	Yellow	1·08	,,
,, ,,	Pale yellow	1·44	,,
,, ,,	Yellow	0·87	Thomson and Ballantyne
Commercial oil, yellow	,,	0·65	Fahrion
,, ,,	,,	1·18	,,
,, English	Yellowish red	2·62	,,
,, ,,	Pale yellow	0·6-0·78	Lewkowitsch
,, Newfoundland	Red brown	1·50	Thomson and Ballantyne
Brown cod oil	Brown	1·82	Fahrion
,, ,,	,,	2·23	,,
,, ,,	,,	2·68	,,
,, ,,	,,	1·87	Thomson and Ballantyne

[1] *Jour. Soc. Chem. Ind.* 1893, 369.

Raw medicinal oil, *i.e.* the first oil exuding spontaneously from the livers, contains but very small quantities of ptomaïnes (*Heyerdahl*). In light brown cod liver oil, however, organic bases to the extent of from 0·035 to 0·050 per cent have been shown to occur by *Gautier* and *Morgues*.[1] The following bases have been isolated :—

Bases in Cod Liver Oil

Volatile.	Non-volatile.
Butylamine	Morrhuine, $C_{19}H_{27}N_3$
Isoamylamine	Aselline, $C_{25}H_{32}N_4$
Hexylamine	
Dihydrolutidine	

Besides these bases an acid containing nitrogen has been found. This acid, *morrhuic acid*, $C_9H_{13}NO_3$ (differing from tyrosine by H_2 only) is probably identical with *De Jongh's gaduine*.

Heyerdahl has isolated *trimethylamine* by means of its platinochloride. This base, however, must, like those mentioned above, be considered as a product of decomposition of the cellular tissue of the livers. Biliary colouring matters, as stated by earlier observers, are absent. According to *Salkowski* the colouring principle in cod liver oil belongs to the class of *lipochromes*.

As products of decomposition must also be considered small quantities of albuminoid substances occurring in cod liver oil. According to *Unger*,[2] there are combined with these latter minute quantities of *iron*, *manganese*, and *phosphoric acid* (a substance similar to lecithin, yielding phosphoric acid, glycerol, and the above-mentioned morrhuic acid, has been obtained by *Gautier* and *Morgues*). Also *calcium*, *magnesium*, and *sodium* have been found, and the metalloids chlorine, bromine, and iodine. The following amounts of iodine have been obtained by several chemists :—

Proportion of Iodine in Cod Liver Oil

Description of Oil.	Iodine.	Observer.
	Per cent.	
Pale . . .	0·020	Andres
Yellow . . .	0·031	,,
...	0·00138-0·00434	Stanford
...	0·0002	Heyerdahl

Formerly the *therapeutic value* of cod liver oil was supposed to be due to the small amount of iodine it contained (therefore cod liver oils are met with to which iodine or potassium iodide has been added fraudulently), or to any of the many "active principles" stated to

[1] *Compt. rend.* 107, 254 ; 626 ; 740. [2] *Pharmac. Centr. Halle*, 1889, 261.

occur by various writers. Thus, according to *Marpmann*,[1] it is due to a substance which may be precipitated by ether and alcohol, and is said to cause the cod liver oil to be completely emulsified on coming in contact with the gastric juice. The medicinal effect of cod liver oil, however, has rather to be looked for in the facility with which it is split up, or, as others will have it, digested, and it cannot be doubted that this property is caused by the peculiar constitution of the unsaturated fatty acids (therapic and jecoleic acids). According to *Heyerdahl*, that cod liver oil should be the best from the medicinal point of view which has been protected from oxidation.

Cod liver oil, becoming so easily rancid, contains varying amounts of *free fatty acids*. In fact, *Hosmann* states that cod liver oil is the only animal oil which is characterised by the presence of free acids even when freshly rendered. On testing a number of oils *Kremel* found the amounts of caustic potash required to saturate the free acids in 1000 grms. of each oil to vary from 0·62 grm. to 28·67 grms. The former number calculated to oleic acid corresponds to 0·312 per cent.

Heyerdahl has studied the influence that the length of time the livers are heated has on the proportion of free fatty acids in the oil produced. He found that, contrary to expectation, the percentage of free fatty acids decreased slightly but perceptibly as the time of heating was increased (from 20 to 80 minutes) and the temperature raised (from 62° to 85° C.). This result might be due to the volatilisation of free volatile acids at the higher temperature, or to the first portions of the extracted oil being richer in fatty acids, or to both causes together. Experiments, in which measured volumes of air were driven through samples of oil heated in the water-bath, proved that the free fatty acids decreased up to a certain point, and then slowly rose to or beyond the original percentage. The proportions of free fatty acids never exceeded 0·69 per cent calculated as oleic acid.

The oil obtained by passing steam directly into the livers is, according to the same chemist, practically devoid of volatile fatty acids, and their occurrence must therefore be due to some secondary process. This statement has been corroborated by the examination of liver oils from other species of fish (*Heyerdahl*).

How far the oil may thus be affected is shown in the following table :—

[1] *Chem. Centr. Blatt.* 19. 1213.

[TABLE

Free Fatty Acids in Cod Liver Oils, calculated as Oleic Acid

Description of Oil.	Colour.	Acid Value.	Free Fatty Acids.	Observer.
			Per cent.	
Raw medicinal oil . .	Pale	7·38	3·79	Heyerdahl
,, ,, . .	Somewhat darker	7·55	3·87	,,
,, ,, . .	Darkest	7·72	3·96	,,
Pale oil } obtained from	Pale	21·20	10·9	,,
Brown ,, } livers by decay	Brown	54·4	28·0	,,
Medicinal oil . . .	Yellow	...	0·36	Thomson and Ballantyne
Scotch cod oil . .	Brown	...	9·73	,,
Newfoundland cod oil .	Red-brown	...	23·31	,,
Medicinal oils . .	...	...	0·34-0·60	Parry and Sage

Examination of Cod Liver Oil

Cod liver oil is liable to be adulterated with not only the liver oils of other fish than those belonging to the "Gadus" family, but also with fish oils (such as Japan fish oil), and blubber oils (refined seal oil), the detection of which, in the present state of our knowledge, is extremely difficult. Colour alone is not the decisive characteristic, as oils are bleached artificially. In *Möller's* opinion, such oils are worse than brown oils. We are indebted to *Kremel*[1] for an exhaustive examination of this subject. His results are given in the following table, the inspection of which will show that the **specific gravity** affords us little help in identifying any of the oils mentioned when in admixture with cod liver oil :—

[1] *Pharmac. Centr. Halle*, 1884, 337.

[TABLE

No.	Description of Oil.	Specific Gravity.	Fatty Acids.		Melting Point of Solid Acids.	Acid Value.	Saponification Value.	Iodine Value.
			Liquid.	Solid.				
			Per cent.	Per cent.	°C.			
1	Cod liver oil, 1884 . .	0·922-0·927	...	...	...	0·62	171	131
2	,, ,, 1883 . .	,,	92·12	6·72	...	1·41	171	127
3	,, ,, ,, . .	,,	...	...	...	2·06	...	126
4	,, ,, ,, . .	,,	88·88	7·55	50·5	2·23	189	127
5	,, ,, ,, . .	,,	...	...	...	2·32	...	128
6	,, ,, ,, . .	,,	90·46	6·88	51	2·86	179	131
7	,, ,, 5 years old .	,,	...	...	...	1·47	178	140
8	,, ,, 10 ,, .	,,	...	...	...	28·67	...	...
9	,, ,, 10 ,, .	,,	...	...	...	5·03	...	129
10	Medicinal oil, pale, 1883-4 .	,,	...	9·60	48-49	9·59	173	139
11	,, ,, ,, ,, .	,,	...	...	...	11·29	174	138
12	,, ,, ,, ,, .	,,	...	...	...	11·57	173	141
13	,, ,, ,, ,, .	,,	92·72	5·25	52	8·66	181	...
14	,, ,, ,, ,, .	,,	87·00	12·75	51-52	6·78	181	135
15	,, ,, ,, ,, .	,,	...	...	...	10·46	...	136
16	Liver oil from *Merlangus*[1] .	0·925	75·32	19·04	55-56	1·26	177	137
17	,, ,, ,, .	0·926	...	12·22	53	1·23	177	137
18	,, ,, ,, .	...	...	...	...	1·29	179	129
19	,, ,, ,, .	0·925	74·20	20·6	...	1·49	181	126
20	,, ,, ,, .	0·927	70·00	21·34	52	1·68	181	123
21	Japan liver oil[2] . . .	0·908	87·6	10·52	50-51	..	...	120
23	Seal oil, 1883 . . .	0·925	85·02	10·23	57·5	1·95	178	127
24	,, ,, . . .	0·925	88·29	9·81	57	2·01	179	128

[1] This is the Danish "Sejthran."

[2] This is most likely Japan *fish* oil.

The amount of solid fatty acids in the liver oil from *Merlangus* is about twice as great as in cod liver oil. This, however, may be due to the "stearine" not having been allowed to settle out thoroughly. The solid fatty acids of seal oil have a somewhat higher melting point than those of the other oils.

Allen[1] also has pointed out that the specific gravity affords no reliable indication of the presence of fish oils in cod liver oil, as will be seen from the following table:[2]—

Specific Gravity of various Liver, Fish, and Blubber Oils (Allen)

Oil.	Specific Gravity at 15·5° C.
Cod liver oil	0·929
Hake liver oil	0·927
Skate liver oil	0·9327
Shark liver oil	0·9285
Mixed liver oils from cod, haddock, ling, whiting (prepared in Grimsby)	0·930
Haddock liver oil, Aberdeen	0·931
Ray liver oil	0·928
Herring oil	0·9326
Sprat oil	0·9284
Seal oil	0·9245
Whale oil	0·9301

According to *Kremel* the following **colour reaction** with fuming nitric acid is said to give reliable results. Place 10 to 15 drops of the sample on a watch-glass, and allow 3 to 5 drops of nitric acid, specific gravity 1·5, to flow in slowly from the side, when the following colourations will be observed:—

Oil.	Colour Reaction with Fuming Nitric Acid, Spec. Grav. 1·5.
Genuine cod liver oil	Red at the place of contact; on stirring, fiery rose, changing quickly to lemon-yellow.
Oil from *Merlangus*	Intense blue at the place of contact; on stirring, brown, and remaining so for two to three hours, and then changing to yellow.
Japan fish oil	Like the preceding, sometimes there appear red streaks as well as blue.
Seal oil	No change at first; turns brown after some time.

Kremel considers the reactions described so characteristic that 25 per cent of the three other oils may be detected with certainty in cod liver oil.

Meyer uses as reagent a mixture consisting of equal parts of concentrated sulphuric and nitric acids, with which he mixes 10 volumes of the sample. If the oil is genuine a fiery rose colour is obtained, which changes quickly to lemon-yellow. Other oils either do not give the change in such a distinct manner or cause a brownish-violet colouration.

[1] *Commercial Organic Analysis*, ii. 163.

[2] Cp. also table p. 489.

Roessler states that *seal oil* in cod liver oil can be detected by shaking the sample with aqua regia; genuine oil gives a greenish, dark yellow liniment, turning brown after half an hour, and remaining so; whereas in the case of pure pale seal oil, or of a mixture thereof with cod liver oil, a pale yellow colour is produced.

The experiments which the writer has made with pure samples prove that these colour reactions are valueless.[1]

Other qualitative reactions are the following:—The *Hager-Salkowski* cholesterol test (p. 84) gives with pure cod liver oil at first a violet-blue, then purple, then brownish-red colour, changing at last into a deep brown. According to *Salkowski* there participates in these colourations not only the cholesterol, but also a lipochrome and the cod liver oil acids. For if the unsaponifiable matter isolated from cod liver oil be dissolved at once in chloroform, without separating the cholesterol by crystallisation from alcohol, a clear, golden-yellow solution is obtained, giving a beautiful indigo-blue colour with sulphuric acid in the first instance, and afterwards the cholesterol reaction. The blue colour is due to a lipochrome.

The German Pharmacopœia prescribes as follows:—Dissolve one drop of oil in twenty drops of carbon bisulphide, and add one drop of concentrated sulphuric acid, when a beautiful violet-blue colour appears at once, changing afterwards into red and brown.—This test cannot serve as an identity reaction, as other liver oils, *e.g.* Arctic shark liver oil, gives the same *violet-blue* colour. Cod liver oil, as also other liver oils which have become rancid, do not show the violet-blue, but give at once the red colour (which is also shown by palm oil, see below).

Medicinal cod liver oils when poured carefully on nitric acid, of specific gravity 1·4, so as to form two separate layers, should, according to *Unger*, give a white ring, indicating albumen. This ring should appear, at latest, after five hours' standing. The writer could not obtain this reaction.

Of the **quantitative reactions** the acid value, the iodine value, the *Reichert* value, and the proportion of unsaponifiable matter, will give useful indications as to the quality and purity of the oil.

Steam cod liver oil contains, according to *Kremel*, *Salkowski*, and *Heyerdahl*, only from 0·3 to 1·5 per cent, medicinal oil, prepared by older processes, from 3·3 to 6 per cent of **free fatty** acids.

The free fatty acids may be determined by *Hofmann's* method:—0·5 to 7 grms. of oil (according to the proportion of free acids present) are dissolved in 20-40 c.c. of neutralised ether, and titrated with caustic potash, using an alcoholic solution of rosolic acid (1 : 1000) as an indicator, phenolphthalein giving unsatisfactory results (*Heyerdahl*).

Free volatile acids should not occur in a medicinal oil, as their presence would indicate that putrefied livers had been used in the preparation of the oil. These acids are detected by shaking the oil with water and examining the latter for acidity.

[1] Cp. also Jorissen, *Jour. Soc. Chem. Ind.* 1896, 460.

The higher the **iodine value** the better the oil; oil exposed to the atmosphere, or oil obtained from livers by the process of decay will show low numbers (cp. table p. 477).

The determination of the **Reichert value** would also indicate presence of volatile acids. No good oil should have a higher Reichert value than 0·20 (*Salkowski*).

The amount of **unsaponifiable matter** would possibly point to adulteration with (besides mineral oil) shark liver oil, this latter oil containing notable proportions of spermaceti, and consequently of ether soluble residue. Several samples of shark liver oil gave the following numbers:—

Shark Liver Oil.	Unsaponifiable.	Observer.
	Per cent.	
Yellow, steamed .	5·27	Fahrion
Red . . .	4·44	,,
Yellow . . .	1·24	,,
Yellowish-red .	0·93	,,
Japanese . .	2·82	Allen
Crude . . .	8·70	,,
Refined . . .	0·70	,,
	10·25	,,
	17·30	,,
	10·34	,,
Pale yellow, from *Scymnusborealis*	10·20	Lewkowitsch

The amount of **iodine** in *iodised* cod liver oils is ascertained, according to *Stanford*,[1] by saponifying 300 grms. of oil with 60 grms. of caustic soda (free from iodine), evaporating to dryness and burning the soap in a porcelain crucible. The charred mass is boiled out with water, filtered, and the filtrate evaporated to 300 c.c. 30 c.c. of this solution are then shaken with 12 c.c. of carbon bisulphide after a few drops of nitrosulphuric acid have been added (prepared by passing nitrous acid, evolved on heating starch or arsenious acid with nitric acid, into sulphuric acid). The amount of iodine dissolved in the carbon bisulphide is then estimated colorimetrically by comparing its depth of tint with that of another solution prepared similarly from a known amount of potassium iodide.

Andres[2] burns off 3 grms. of cod liver oil, previously mixed with 2 grms. of sodium carbonate in a porcelain crucible, then exhausts the mass with boiling water, and evaporates down to a few c.c. The solution is mixed with five to six drops of fuming nitric acid, agitated with carbon bisulphide, and the iodine dissolved in the latter titrated with a standardised solution of sodium thiosulphate.[3]

On shaking pure cod liver oil with water or alcohol no iodine passes into solution; fraudulently added potassium iodide can therefore be detected by this means.

[1] *Pharm. Jour.* (3) 14. 353. [2] *Chem. Zeit.* 1889, Rep. 106.
[3] Cp. also Gorges, *Jour. Pharm. Chim.* 1896 [16], 2.

Besides the oils already mentioned, the following are used for adulterating cod liver oil: Mineral oil, resin oils, and vegetable oils.

Mineral and *resin oils* may be detected by determining the amount of unsaponifiable matter and examining the latter.

Non-drying and semi-drying oils lower the iodine absorption and temperature in *Maumené's* test.

Drying oils, as poppy seed and linseed oils, may be recognised by spreading the sample in a thin layer on a glass plate. Cod liver oil becomes oxidised, but does not yield a solid skin like a typical drying oil, but, at most, becomes resinous. The *Livache* test would not be applicable in this case (cp. p. 287).

If the amount of seed oil present in a cod liver oil reaches 20 per cent the adulteration can be detected, according to *Salkowski*, by the phytosterol test (p. 317), the crystals obtained from the unsaponifiable matter melting, in the case of pure cod liver oil, at 146° C., and in the case of adulterated oil at from 139°-140° C. In the presence of rape or cotton seed oil the crystals of phytosterol may be recognised under the microscope; they are not so distinctly discerned in the case of linseed oil.

For the detection of *cod liver oil* in other oils *Salkowski* examines the liberated fatty acids. Cod liver oil fatty acids, dissolved in sufficient chloroform to yield a 5-8 per cent solution, assume on mixing with an equal volume of concentrated sulphuric acid a deep reddish-brown colour appearing dirty green in reflected light. If the mixture be allowed to settle half an hour and the colourless chloroform be poured off, the addition of a few drops of a mixture of sulphuric acid in a few c.c. of glacial acetic acid gives, after one to two hours' standing, a very beautiful reddish-violet colour, showing a dirty green reflection,[1] which remains for a few days. No seed oil shows this reaction with the mixture of sulphuric and acetic acids, oleic acid and the fatty acids from palm and linseed oils only giving a very faint indication.

A better and more characteristic test is the sulphuric acid test already described (only palm oil, and in very minute quantity, also cotton seed oil, contain a colouring substance producing a blue colouration with the mixture of chloroform and sulphuric acid).

Other liver oils are commercially of minor importance, and therefore need not be considered here individually. Some of these oils and their characteristics, as specific gravity, iodine values, etc., have been already referred to under cod liver oil. Shark liver oil appears to be no longer used in this country; at any rate it is not prepared here commercially. This oil is prepared in considerable quantities in Iceland, and exported to the Continent for use in tanning. The livers from any shark caught by the trawlers will no doubt be mixed with other livers, and therefore the "Coast Cod Oil" (p. 476) may

[1] Isocholesterol reaction?

contain varying quantities of shark liver oil. From the table given p. 487, it is apparent that shark liver oil contains a larger amount of unsaponifiable matter than cod liver oil.

I add here a few constants of several liver oils; the first three oils are undoubtedly genuine.[1]

Name of Oil.	Specific Gravity at 15° C.	Insoluble Fatty Acids.	Acid Value.	Saponification Value.	Iodine Value.	Acetyl Value.	Unsaponifiable.	Refractive Index. Oleo-refractometer. "Degrees" at 22° C.	Refractive Index. Oleo-refractometer. Observer.
		Per cent.					Per cent.		
Haddock liver .	0·92979	93.3	...	188·8	154·2	17·8	1·1	...	Lewkowitsch
Skate liver . . .	0·93069	94·7	...	185·4	157·3	...	0·97	...	,,
Shark liver, Arctic (from *Scymnus borealis*) . . .	0·91631	86·9	...	161·0	114·6	...	10·20	...	,,
Shark liver . . . (African ?)	0·9158	...	7·05	157·2	90	...	...	...	Eitner[1]
Shark liver . . .	...	...	...	...	...	...	...	+ 29 to + 35	Pearmain

[1] *Der Gerber*, 1893, 257.

[1] I am indebted for these oils to the kindness of Mr. W. Corder, South Shields.

γ. Blubber Oils

This group comprises oils of varying composition. Seal oil consists almost wholly of glycerides; whale oil and dolphin oil contain notable amounts of spermaceti, forming, as it were, intermediate members between true oils and liquid waxes.

We describe here the following oils: Seal oil, whale oil, dolphin (black fish) oil, porpoise oil.

The last two members of this group occupy an exceptional position on account of their containing considerable proportions of glycerides of volatile acids.

SEAL OIL

French—*Huile de phoque.* German—*Robbenthran.*

For tables of constants see pp. 491, 492.

Seal oil is the oil obtained from the blubber of the various species of the seal, as *Phoca vitulina*, *Phoca grœnlandica*, *Phoca lagura*, *Phoca caspica*, etc.

The colour of seal oil varies with its quality; it is either white, or yellow, or brown. In commerce we find four brands of seal oil, and besides these, mixtures of seal oils with various fish oils are sold as seal oil (*e.g.* the Swedish "Three Crown" oil). The fatty acids of two specimens of seal oil examined by *Kremel* consisted of—

No.	Liquid Fatty Acids.[1]	Solid Fatty Acids.
	Per cent.	Per cent.
1	85·02	10·23
2	89·25	9·81

[1] Kurbatoff has found linolic acid among the liquid fatty acids of the Caspian seal, cp. p. 318.

Physical and Chemical Constants of Seal Oil.

Specific Gravity.			Solidifying Point.		Hehner Value.		Reichert Value.	
°C.		Observer.	°C.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.
15	0·9155-0·926	Schaedler	Deposits "stearine" at 3	Schaedler	95·45	Kremel	0·07-0·22	Chapman and Rolfe
,,	0·925	Kremel			92·8-94·2	Chapman and Rolfe		
,,	0·9249-0·9263	Chapman and Rolfe	−2 to −3	Jean				
15·5	0·9240-0·929	Allen						
,,	0·9244-0·9261	Thomson and Ballantyne						
99	0·8733	Allen						

Physical and Chemical Constants of Seal Oil—continued.

Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index. Oleo-refractometer.	
Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	"Degrees."	Observer.
189-196	Stoddart, Deering	91-95 [1]	Mills	92	Allen	+8	Jean
178-179	Kremel	125-130	Schaedler			+15	,,
189·3-192·8	Thomson and Ballantyne	127-128	Kremel	Specific Temperat. Reaction.		+ 30 to + 36 at 22 °C.	Pearmain
190·7-196·2	Chapman and Rolfe	142·2-152·4	Thomson and Ballantyne				
		130·6	Lewkowitsch				
		133-141 [2]	Chapman and Rolfe	212-229	Thomson and Ballantyne		

[1] Calculated from bromine value.

[2] Bromine values 69·6-80, corresponding to iodine values 110·5-126·7. Cp. p. 308, footnote.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Saponific. Value.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.
Titer Test. 15·5-15·9	Lewkowitsch	22-33	Chapman and Rolfe	190·4-196	Chapman and Rolfe

The following table contains the proportions of free fatty acids and unsaponifiable matter found by several observers :—

No.	Kind of Seal Oil.	Free Fatty Acids (as Oleic Acid).	Unsaponifiable Matter.	Observer.
		Per cent.	Per cent.	
1	...	1·95	...	Deering
2	...	2·01	...	,,
3	Cold-drawn, pale . .	1·80	0·5	Thomson and Ballantyne[1]
4	Steamed, pale . .	1·46	0·38	,,
5	Tinged (brown) . .	8·29	0·42	,,
6	Norwegian . . .	7·33	0·51	,,
7	Swedish "Three Crowns"	...	1·4	Fahrion[2]
8	Very pale . . .	0·98-1·13	...	Chapman and Rolfe[3]
9	Yellow . . .	1·41	...	,, ,,
10	Light brown . .	4·09	...	,, ,,
11	Dark brown . .	19·95	...	,, ,,

Adulteration with resin oil can be easily detected by determining the proportion of unsaponifiable matter.

WHALE OIL

French—*Huile de baleine.* German—*Walfischthran.*

For tables of constants see pp. 493, 494.

Whale oil is the oil extracted from the blubber of various species of the genus *Balæna*, as *Balæna mysticetus*, Greenland or "Right" whale (Northern whale oil), *Balæna australis* (Southern whale oil), *Balænoptera longimana*, *Balænoptera borealis* (Fin-back oil, Humpback oil). The northern whale oil is the "train oil" proper; but this name has become a generic name, and has been extended to all other "blubber oils" included in this class.

[1] *Jour. Soc. Chem. Ind.* 1891, 236. [2] *Ibid.* 1893, 607.
[3] *Ibid.* 1894, 843.

Physical and Chemical Constants of Whale Oil

Specific Gravity.			Solidifying Point.		Hehner Value.		Reichert Value.		Saponific. Value.		Iodine Value.		Maumené Test.		Refractive Index. Oleo-refractometer.	
°C.		Observer.	°C.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	'Degrees.'	Observer.
15	0·925-0·927	Schaedler	Deposits crystals at +10	Schaedler	93·5	Lewkowitsch	3·7-12·5	Allen	193·1[1]	Deering	49[2]	Mills	91[3]	Allen	+30·5	Jean
15·5	0·9307	Allen	All "stearine" and spermaceti separates at −2	,,			0·7	Lewkowitsch	188·5-224·4	Stoddard, Allen	110·1	Thomson and Ballantyne	85-86[1]	Dobb	+42 to +48	Pearmain
,,	0·9221-0·9225	Schweitzer and Lungwitz					2·04	Lewkowitsch	188·8	Thomson and Ballantyne	127·3-127	Schweitzer and Lungwitz	92[1]	Archbutt		
15·5	0·9193	Thomson and Ballantyne							188·5	Lewkowitsch			61	Jean		
98-99	0·8725	Allen							187·9-194·2	Schweitzer and Lungwitz			Specific Temperature Reaction.			
													157	Thomson and Ballantyne		

[1] Southern whale oil. [2] Calculated from bromine value. [3] Northern whale oil.

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Iodine Value.	
At 100° C. (Water 100° C. = 1.)	Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.
		Titer Test.					
0·8922	Archbutt	22·9-23·9	Lewkowitsch	27	Jean	130·3-132	Schweitzer and Lungwitz
				14-15 16 16·2 18	Schweitzer and Lungwitz		

Whale oil has a yellowish-brown or dark brown colour, and an offensive "fishy" smell. Refined oil, freed from the "stearine" by cooling, possesses a light colour. The physical and chemical properties vary considerably according to the kind of animal from which the oil has been obtained.

The constitution of whale oil is not known. *Fahrion* isolated from one sample palmitic acid. *Allen*, again, found in some whale oils glycerides of volatile fatty acids, whereas other specimens (see table) are practically devoid of them.

The "stearine" deposited on cooling consists of palmitin, and most likely of a small quantity of spermaceti. The amounts of unsaponifiable matter found in whale oils (see following table) point to the presence of the latter.

Description of Oil.	Per cent.	Observer.
Norwegian, yellowish-red	0·65	Fahrion
,, yellowish-brown	1·26	,,
,, brown	1·37	,,
Pale	1·22	Thomson and Ballantyne
,, refined	0·92-3·72	Lewkowitsch

Whale oil is used as a burning oil and for leather-dressing; the pale or water-white brands are employed in soap-making. It is largely adulterated with seal oil and resin oil.

DOLPHIN OIL (BLACK FISH OIL)

French—*Huile de dauphin.* German—*Delphinthran.*

For table of constants see p. 496.

Dolphin oil, from the blubber of the black fish (bottlenose dolphin) *Delphinus globiceps*, forms an intermediate link between whale oil (consisting nearly wholly of glycerides with but a small quantity of spermaceti), and sperm oil (which must be considered, from its chemical composition, a true wax).

This oil is of a pale yellow colour. On standing it deposits spermaceti (cetyl palmitate, p. 15) [*Chevreul*]. It is remarkable for the large amount of glycerides of volatile fatty acids it contains, a characteristic which it shares with porpoise oil.

Larger still is the proportion of glycerides of volatile acids in the *jaw oil*, the liquid oil from the soft blubber contained in the head and jaw of the black fish.

This *jaw oil* has a straw-yellow colour; it is limpid, transparent, and has a not unpleasant smell. It is used for lubricating fine machinery.

Physical and Chemical Constants of Dolphin Oil

Specific Gravity.			Solidifying Point.		Hehner Value.		Reichert Value.		Saponification Value.		Iodine Value.	
At °C.		Observer.	°C.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
					Body Oil.							
15 20	0·9180 0·9175	Schaedler ,,	Deposits spermaceti from 5 to −3	Schaedler	93·07	Moore[1]	5·6	Moore	197·3	Moore	99·5	Moore
					Jaw Oil.							
					66·28	Moore	65·92	Moore	290	Moore	32·8	Moore

[1] *Jour. Soc. Chem. Ind.* 1890, 331.

PORPOISE OIL

French—*Huile de Marsouin.* German—*Meerschweinthran.*

For table of constants see p. 498.

Porpoise oil is obtained by boiling with water the whole tissue of the black porpoise, *Delphinus phocæna.* This oil has been examined first by *Chevreul*, who discovered in it valeric acid, named by him "acide phocénique."

The oil is pale yellow or brown, and consists of the glycerides of valeric, palmitic, stearic, and oleic (and physetoleic?) acids.

The porpoise also yields a *jaw oil* which appears to be very similar to the jaw oil of the black fish. The two "body" oils also resemble one another. Since, however, porpoise oil does not deposit spermaceti, we have described the two oils separately, following *Chevreul's* example.

The jaw oil is easily soluble in alcohol at 70° C., and taking advantage of this it is possible to extract it from a mixture of the body and jaw oils.

Physical and Chemical Constants of Porpoise Oil

Specific Gravity.			Solidifying Point.		Hehner Value.		Reichert Value.		Saponification Value.		Iodine Value.		Maumené Test.	
°C.		Observer.	°C.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.	°C.	Observer.
16	0·937	Chevreul	− 16	Schaedler	...	...	11-12	Allen	216-218·8	Allen	...	...	50	Allen
15·5	0·926	Allen	...	...	...	...	23·45 [1]	Steenbuch [3]						
99 (water 15·5 = 1)	0·8714	,,												
					Jaw Oil, skimmed and strained.									
					72·05	Moore [2]	47·77	Moore	253·7	Moore	49·6	Moore		
					68·41	,,	56·00	,,	272·3	,,	30·9	,,		
							65·8 [1]	Steenbuch						
					Jaw Oil, not skimmed and strained.									
					96·5	Moore	2·08	Moore	143·9	Moore	76·8	Moore		

[1] Reichert-Meissl values 46·9 and 131·6 halved for the sake of comparison.

[2] *Jour. Soc. Chem. Ind.* 1890, 331.

[3] *Zeit. angew. Chem.* 1889, 64.

(2) Terrestrial Animal Oils

Under this heading we shall describe the oils obtained from the feet of oxen, sheep, and horses, and from eggs.

Liquid fats are also obtained from lard and tallow by pressing.

These oils are characterised by a low iodine value, lower than that of the non-drying oils, and a low thermal reaction. They yield solid elaïdins with nitrous acid.

SHEEP'S FOOT OIL

French—*Huile de pieds de mouton.* German—*Hammelklauenoel.*

For tables of constants see p. 500.

This oil is obtained from sheep's trotters in the manner described for neat's foot oil (see p. 504).

It resembles very much neat's foot oil, and is, as a rule, mixed with it.

Physical and Chemical Constants of Sheep's Foot Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index. Oleo-refractometer.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	"Degrees."	Observer.
0·9175	Schaedler	0 to 1·5	Schaedler	194·75 [1]	Lewkowitsch	74-74·4 [1]	Lewkowitsch	49·5	Jean	0 [2]	Jean

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	
°C.	Observer.
Titer Test.	
20·0-21·1 [1]	Lewkowitsch

[1] Specimen prepared in the laboratory.

[2] Sheep's foot oil is the standard oil for Jean's oleo-refractometer.

HORSES' FOOT OIL

French—*Huile de pieds de cheval.* German—*Pferdefussoel.*

For tables of constants see p. 502.

This oil, obtained from horses' feet, is prepared and used like the preceding oil.

A sample rendered in my laboratory and filtered contained certain impurities, so that the oil gave a number of colour reactions which have been considered hitherto as characteristic of marine animal oils (cp. p. 279). The oil also gave a high acetyl value.

Physical and Chemical Constants of Horses' Foot Oil

Specific Gravity.		Saponification Value.		Iodine Value.		Acetyl Value.		Maumené Test.	
At 15° C.	Observer.	Per cent.	Observer.	Per cent.	Observer.		Observer.	°C.	Observer.
0·913 0·9202-0·9205 0·9270	Schaedler Jean Amthor and Zink	195·0-196·8	Lewkowitsch	73·7-73·9 90·3	Lewkowitsch Amthor and Zink	9·1-10·3	Lewkowitsch	38	Jean

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	
°C.	Observer.
Titer Test.	
27·1-28·6	Lewkowitsch

EGG OIL

French—*Huile des Jaunes d'Œufs.* German—*Eieröl.*

Physical and Chemical Constants of Egg Oil

Specific Gravity.			Solidification Point.		Melting Point.		Saponific. Value.		Hehner Value.		Reichert-Meissl Value.		Iodine Value.		Refractive Index.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	At 25° C.	Observer.
15 20 100 (water at 15° = 1)	0·9144 0·9156 0·881	Kitt Paladino and Toso Spaeth	8-10	Paladino and Toso	22-25	Paladino and Toso	190·2 185·2-186·7 184·4	Kitt Spaeth	95·16	Kitt	0·4 0·66	Kitt Spaeth	72·1 81·2-81·6 68·5	Kitt Paladino and Toso Spaeth	1·4713	Spaeth
															Butyro-refractometer.	
															At 25° C.	Observer.
															68·5	Spaeth

Physical and Chemical Constants of the Mixed Fatty Acids

Melting Point.		Saponification Value.		Iodine Value.		Mean Molecular Weight.	
°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.		Observer.
34·5-35 36 36-39[1]	Paladino and Toso Spaeth Kitt	194·9	Kitt	72·6 73·25	Spaeth Kitt	285	Kitt

[1] Capillary tube method.

Egg oil is contained in the yellow of the egg (of chicken). It is extracted from the yolk of hard-boiled eggs either by pressure or by solvents. *Paladino* and *Toso* obtained by the former method 25 to 35 per cent, *Kitt*, using ether as a solvent, 19 per cent only. The ether extracts, besides egg oil, other substances, notably lecithin.

The expressed oil was limpid and of a yellow colour. On cooling it deposited crystals of cholesterol. The extracted oil, freed by filtration from other ether-soluble substances, was semi-solid and of an orange-yellow colour. The specimen examined by *Kitt* contained 0·2 per cent of lecithin, and 1·5 per cent of cholesterol, and had an acid value of only 1·2.

Egg oil gives the elaïdin reaction. The acetyl value 11·9 given by *Kitt* must be accepted with reserve (see p. 164). It is apparently high on account of the cholesterol present.

NEAT'S FOOT OIL

French—*Huile de pieds de bœuf.* German—*Ochsenklauenoel.*

For tables of constants see p. 505.

Neat's foot oil is the oil obtained from the feet of oxen by boiling in water. It is a pale yellow, odourless oil, of bland taste.

The commercial samples, even if unsophisticated, consist mostly of true neat's foot oil mixed with sheep's foot and horses' foot oils. On standing the oil deposits "stearine." Neat's foot oil is valued as a lubricating oil, for the reason that it does not turn rancid easily.

The high price of the oil acts as an incentive to fraud. It is largely adulterated with fish, poppy seed, rape, cotton seed, and mineral oils. These adulterations can be easily detected by determination of the iodine absorption, the proportion of unsaponifiable matter, the thermal reaction, etc.

Lard Oil (see p. 584).

Tallow Oil (see p. 591).

Physical and Chemical Constants of Neat's Foot Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index. Oleo-refractometer.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	"Degrees."	Observer.
15 15 18 99 (water 15·5 = 1)	0·914-0·916 0·9152-0·9165 [1] 0·9142 0·8619	Allen Jean Stilurell Allen	0 to 1·5 10 [1]	Schaedler Jean	194·3 [2]	Lewkowitsch	69·3-70·4 [2]	Lewkowitsch	47-48·5	Jean	−3 to −4 −1 to −3 at 22° C.	Jean Pearmain

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
Titer Test. 26·1 -26·5 [2]	Lewkowitsch	29·8-30·8 [1]	Jean	61·98-63·26 [1]	Jean

[1] American oil. [2] Oil rendered in the laboratory.

II. SOLID FATS

1. Vegetable Fats

The members of this group are solid at the ordinary temperature, presenting, however, a variety of gradations from the soft, buttery masses of, say, cotton seed stearine, to the hard, wax-like Japan wax. As the hardness of the fats increases approximately in direct proportion to the decrease of glycerides of oleic acid (including with it the small quantities of linolic acid, if present), the iodine value seems to indicate the order in which the individual fats should be enumerated in the absence of other chemical characteristics. Palm nut oil and cocoa nut oil, however, have been placed together as undoubtedly constituting, together with mocaya oil, a well-defined group, distinguished by a considerable amount of glycerides of lower fatty acids, and in that respect resembling to some extent butter fat.

The following fats are described: Cotton seed stearine, chaulmoogra oil, carapa oil, laurel oil, mowrah seed oil, shea butter, vegetable tallow, palm oil, macassar oil, sawarri fat, mafura tallow, nutmeg butter, Rambutan tallow, Mkanyi fat, cacao butter, kokum butter, Borneo tallow, dika oil, Mocaya oil, palm nut oil, cocoa nut oil, myrtle wax, ucuhuba fat, Japan wax, Malabar tallow, wild olive fat.

COTTON SEED STEARINE

French—*Margarine de coton, Margarine végétale.*
German—*Baumwollenstearin, Vegetabilisches Margarin.*

For tables of constants see pp. 507, 508.

Cotton seed stearine is the solid fat deposited from cotton seed oil. This "stearine" is obtained on a large scale, especially in America, by cooling cotton seed oil (the fluid part constituting the "winter" oil) and pressing the solid deposit. According to the process of manufacture, the "stearine" will contain larger or smaller proportions of liquid glycerides, therefore the numbers given in the table for the melting point vary considerably. A sample examined by *Hehner* and *Mitchell* contained 3·3 per cent of stearic acid.

Cotton seed stearine is a light yellow fat of buttery consistency. It is used for soap-making, but is chiefly employed in the manufacture of lard and butter substitutes, for which purpose it is specially adapted on account of its neutrality and its physical properties.

Under the name of "cotton seed stearine" there is in commerce a distilled stearic acid (p. 692) with which the neutral cotton seed stearine must not be confounded.

Physical and Chemical Constants of Cotton Seed Stearine

Specific Gravity.			Solidifying Point.		Melting Point.		Helner Value.		Saponific. Value.		Iodine Value.		Maumené Test.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
15	0·923	Schaedler	31-32·5	Allen	40	Allen	95·5	Muter	194·6	Hart	89·8	Allen	48	Hart
,,	0·91884	Crampton												
37·7	0·9115-0·912	Muter	...	...	32·2	Muter	96·3	Hart	194·8-195·1	Lew-kowitsch	93·6	Hart		
40	0·90313	Crampton												
50	0·89671	,,												
99 (water 15·5=1)	0·8684	Allen	...	...	39	Mayer	...	...	...	...	88·7	De Negri and Fabris		
100	0·867	Hart	...	...	30-31	Hart								
,,	0·86463	Crampton	16-22	De Negri and Fabris	26-29	De Negri and Fabris	...	...	...	...	92·7-92·8	Lew-kowitsch		
			Titer Test Method.								99·2-103·8	Schweitzer and Lungwitz		
			16-16·05	Lew-kowitsch										

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
23-21[1]	De Negri and Fabris	27-30	De Negri and Fabris	94·3	De Negri and Fabris
Titer Test.					
34·9-35·1	Lewkowitsch				

CHAULMOOGRA OIL

French—*Beurre de Chaulmougra.* German—*Chaulmugraoel.*

Physical and Chemical Constants of Chaulmoogra Oil

Saponification Value.		Iodine Value.	
Mgrms. KOH.	Observer.	Per cent.	Observer.
204	Lewkowitsch	90·35-90·9	Lewkowitsch

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Iodine Value.	
°C.	Observer.	Per cent.	Observer.
Titer Test.			
39·5-39·6	Lewkowitsch	86	Lewkowitsch

Chaulmoogra oil is a fat of buttery consistency obtained from the seeds of *Gynocardia odorata.* Its chemical constitution is unknown. According to *Allen*[2] this fat contains umbellulic acid. The acid value of a sample examined in my laboratory was 37·4.

[1] This figure cannot possibly be correct.
[2] Thorpe, *Dictionary of Applied Chemistry*, iii. 43.

CARAPA OIL (CRAB WOOD OIL)

French—*Beurre (huile) de Carapa.* German—*Carapafett.*

Physical and Chemical Constants of Carapa Oil

Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
18 36	Schaedler Hannau[1]	23-25 31	Schaedler Hannau	239	Hannau	72·1	Hannau

This fat is expressed from the seed of several species of plants belonging to the genus *Carapa*, as *Carapa guianensis*, *Carapa moluccensis.*

Carapa oil is a product of Brazil, Guiana, West Coast of Africa, India, Moluccas, where it is chiefly used for soap-making, etc.; it is also imported into this country and France for the same purpose.

LAUREL OIL

French—*Beurre de laurier.* German—*Lorbeeroel.*

For tables of constants see p. 510.

Laurel oil[2] is obtained from the berries of the laurel-tree (*Laurus nobilis*, L.) either by pressing, or by boiling the pounded berries with water. It has a green colour, and at the ordinary temperature a buttery consistency; its taste and aromatic odour are peculiar.

Laurel oil is completely soluble in boiling alcohol; on cooling, crystals of trilaurin separate. Trilaurin is stated to be the chief constituent of this oil, but judging from the high iodine value it must contain considerable quantities of olein. *Allen* has found small quantities of volatile acids (acetic). A sample examined by the writer had the acid value 26·3. Laurel oil is only used in veterinary practice. It is sometimes adulterated with other fats (lard) coloured green with copper salts (detected by incinerating, cp. p. 98).

[1] *Annali del Laboratorio delle Gabelle*, 1891-1892, p. 271.

[2] Laurel oil must not be confounded with the oil from the seeds of *Calophyllum inophyllum*, described by Hooper (*Jour. Chem. Soc.* 1889, Abstr. p. 541) under the name of *Laurel nut oil.* According to *Schaedler*, this substance is Poonseed oil (German *Tacahamacfett*). The greenish-yellow colour seems to have been the cause of the misnomer laurel nut oil. Nor must laurel oil be confounded with Indian laurel oil, described p. 365, from the fruits of *Laurus indica.*

Physical and Chemical Constants of Laurel Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Reichert Value.		Iodine Value.	
°C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.
...	...	...	...	...	...	...	...	...	...	...	49	Hübl
15	0·93317	Cloëz	24	Villon	33-36	Villon	198·9	Allen	1·6	Allen	67·8	De Negri and Fabris
98·5 (water 15·5=1)	0·8806	Allen	25	De Negri and Fabris	32-34	De Negri and Fabris	197·5 197·7-198·1	De Negri and Fabris Lewkowitsch	...	...	80·4-80·5	Lewkowitsch.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Iodine Value.	
°C.	Observer.	Per cent.	Observer.
Titer Test.			
14·3-15·1	Lewkowitsch	81·6-82·0	Lewkowitsch

MOWRAH SEED OIL[1] (MAHWAH BUTTER)

French—*Beurre d'Illipé*,[2] *Huile de Mowrah.*
German—*Mahwabutter*, *Illipeoel*,[2] *Bassiaoel.*

For tables of constants see p. 512.

Mowrah seed oil is obtained from the seeds of *Bassia longifolia*, but the commercial fat is a mixture of this fat with that prepared from *Bassia latifolia*.[3]

When in the fresh state the fat is yellow; it is bleached on exposure to the air, becoming white, at the same time turning rancid. The fat has the consistency of lard, possesses a bitter aromatic taste, and a characteristic odour recalling that of cacao beans.

It contains considerable quantities of free fatty acids, the crystals of which can be recognised under the microscope.

Nördlinger found in a sample 28·54 per cent of free fatty acids; the sample examined in the writer's laboratory contained 17·2 per cent. The proportion of glycerol in the sample examined by Valenta was but 3·09 per cent. The fatty acids consist of 63·5 parts of oleic acid and 36·5 solid fatty acids; the chief constituent of the latter is palmitic acid.

Mowrah seed oil is an important article of commerce; it is imported from India into this country and France, and used for candle and soap making.

[1] Valenta, *Dingl. Polyt. Jour.* 251. 461.
[2] It should be noted that Illipé oil is not necessarily identical with Mowrah seed oil.
[3] The fat from *Bassia butyracea* is the commercial Phulwara butter.

Physical and Chemical Constants of Mowrah Seed Oil

Specific Gravity.		Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.	
At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
0·9175	Valenta	17·5-18·5	Valenta	25·3	Valenta	192·3	Valenta	50·1 [1]	De Negri and Fabris
...	...	36 [2]	De Negri and Fabris	42 [2]	De Negri and Fabris	188·4 [2]	De Negri and Fabris	60·4 [2]	De Negri and Fabris
...	...	19-22 [3]	De Negri and Fabris	28-31 [3]	De Negri and Fabris	199·9 [3]	De Negri and Fabris		
...	...	...	...	...	...	192·4 [4]	Lewkowitsch	62 [4]	Lewkowitsch

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
38	Valenta	39·5	Valenta	56·6	Lewkowitsch
40 [2]	De Negri and Fabris	45 [2]	De Negri and Fabris		
39·7-40·3 [4]	Lewkowitsch				

[1] Valenta, *Dingl. Polyt. Jour.* 251. 461. [2] From *Bassia longifolia.* [3] From *Bassia latifolia.* [4] Commercial fat.

SHEA BUTTER (GALAM BUTTER)

French—*Beurre de Cé, Beurre de Shée, Suif de Noungou.*
German—*Sheabutter, Galambutter.*

For tables of constants see p. 514.

This fat is obtained from the seeds of *Bassia Parkii.* It is characterised by its grey or greyish-white colour and a peculiar aromatic odour. It is somewhat viscous, possessing, at the ordinary temperature, the consistency of butter.

Shea butter consists, according to *Stohmann*,[1] of tristearin and triolein, in the proportion of seven parts of the former to three parts of the latter, and contains also 3·5 per cent of a wax-like substance.

The sample examined in my laboratory had the acid value 29·43; its low saponification value points to the presence of a notable amount of an unsaponifiable, or not readily saponifiable substance.

[1] Muspratt's *Chemie*, 4th edition, vol. iii. p. 574.

Physical and Chemical Constants of Shea Butter

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Hehner Value.		Iodine Value.	
°C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.
15	0·9175	Valenta	21-22 rising to 23·5	Schaedler	28-29	Schaedler	192·3	Valenta	94·76	Valenta	56·2-56·9	Lewkowitsch
98-99 (water 15·5 = 1)	0·859	Allen	17-18	Valenta	28	Allen	178·8	Lewkowitsch				
	...	...	...	...	23-43·3	Stohmann						
	...	...	...	...	25·3	Valenta						

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
38	Valenta	39·5	Valenta	56-57·2	Lewkowitsch
Titer Test.					
53·75-53·8	Lewkowitsch	56	Stohmann		

VEGETABLE TALLOW (OF CHINA)

French—*Suif végétal de la Chine.* German—*Chinesischer Talg.*

For tables of constants see p. 516.

Vegetable tallow is the fat obtained from the seeds of the Chinese tallow-tree *Stillingia sebifera* (*Croton sebiferum*). The seeds are coated with the fat, which is removed by steaming.

From the endosperm a brownish-yellow oil (*Ting-jou*) is obtained, used as a burning oil, and also for the preparation of varnishes on account of its drying properties.[1] Therefore vegetable tallow prepared in the laboratory by extracting the seeds with solvents contains some *oil* and is characterised by an iodine number higher than that of the commercial fat (cp. table). The following constants of the oil were ascertained by *Hobein*:—

Specific gravity	0·9458
Saponification value	203·8
Iodine value	145·6

In its pure state this fat leaves no grease-spot on paper. The samples examined in my laboratory possessed an acid value varying from 7·07 to 7·51. *De Negri* and *Fabris* found 2·4, both for commercial fat and fat extracted from the seeds; *De Negri* and *Sburlati*[1] give 2·2 as acid value.

According to *Maskelyne*, vegetable tallow consists of palmitin and olein. A confirmation of this statement may be found in the fact that *Hehner* and *Mitchell*[2] obtained no stearic acid crystals from a specimen absorbing 22·87 per cent of iodine.

The commercial vegetable tallow represents, as an inspection of the numbers recorded in the tables, demonstrates, a harder material than the fat extracted from the seeds by means of solvents (see above).

Very likely the commercial article consists of a mixture of fats obtained from different species or even different families.

Vegetable tallow is imported from China in hard, brittle white cakes weighing about 1 cwt., and is used for candle and soap making.

[1] De Negri and Sburlati, *Jour. Soc. Chem. Ind.* 1897, 339.
[2] *Analyst*, 1896, 328.

[TABLE

Physical and Chemical Constants of Vegetable Tallow

Specific Gravity.		Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.	
At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
0·918	Thomson and Wood	26·7	Thomson and Wood	44·5	Thomson and Wood	200·3 [1]	Lewkowitsch	32·1-32·3 [1]	Lewkowitsch
		24·2-26·2 [1]	Lewkowitsch	43-46 [1]	Lewkowitsch	179 [1]	De Negri and Fabris	45·2 [1]	De Negri and Fabris
		34 [1]	De Negri and Fabris	44 [1]	De Negri and Fabris	178·7-179 [2]	,,	52·2-53 [2]	,,
		27-29 [2]	,,	37-38 [2]	,,	203·6 [1]	Hobein	22·87	Hehner and Mitchell
		35 [1]	Hobein	43-45	Hobein	203·3 [3]	,,	35·5 [1]	Hobein
		32 [3]	,,	39-42	,,	199-202·2 [4]	De Negri and Sburlati	28·5 [3]	,,
		27·2-31·1 [4]	De Negri and Sburlati	36·5-44·1 [4]	De Negri and Sburlati			28·5-37·7 [4]	De Negri and Sburlati

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.		Saponification Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.
Titer Test.							
52·1-53·47 [1]	Lewkowitsch	56-57	Mayer	34·2-34·3 [1]	Lewkowitsch	182·1 [1]	De Negri and Fabris
42 [1]	De Negri and Fabris	47 [1]	De Negri and Fabris	47 [1]	De Negri and Fabris	181·2-182 [2]	,,
34-35 [2]	,,	39-40 [2]	,,	54·1-54·8	,,	207·9 [1]	Hobein
41 [1]	Hobein	51 [1]	Hobein	38·1 [1]	Hobein	206·4 [3]	,,
40 [3]	,,	49 [3]	,,	29·2 [3]	,,	202-208·5 [4]	De Negri and Sburlati
45·2-47·9 [4]	De Negri and Sburlati	53-56·9 [4]	De Negri and Sburlati	30·3-39·5 [4]	De Negri and Sburlati		

[1] Commercial sample.
[2] Extracted from the seeds by means of ether (and carbon bisulphide), *Il Selmi*, 1894, 32. No doubt the fat thus obtained contained some of the endosperm oil.
[3] Prepared from the seeds by steaming.
[4] Ten samples of commercial fat.

PALM OIL

French—*Huile de palme.* German—*Palmoel.*

For tables of constants see p. 518.

Palm oil is obtained from the fleshy part of the fruit of the palm trees *Elæis guineensis* and *Elæis melanococca*, which form vast forests along the West Coast of Africa, extending between Cape Blanco and St. Paul de Loando. The fat is recovered in an exceedingly crude fashion by the natives, either by storing the fruits for some time in holes in the ground, when fermentation of the mass sets in and the oil rises to the surface, or by expressing the oil from the fresh fruits. The former process yields the lower but "harder" qualities, whereas by the latter the finer and "softer" palm oils are obtained. The fruit kernels remain intact in either of these processes (see "Palm Nut Oil").

The consistency of commercial palm oil varies, therefore, from that of butter (Lagos oil) to that of tallow (Congo oil); also the colour varies greatly, ranging, through all shades, from orange-yellow (Lagos) to dark dirty red. Palm oil has a somewhat sweetish taste, and, when fresh, a pleasant odour of violets, which also adheres to the soap made from it. Lower qualities of palm oil possess a disagreeable smell.

Palm oil is characterised by the very large amount of free fatty acids it contains. Even in the fresh state the proportion of fatty acids, calculated as palmitic acid, amounts to 12 per cent, and may, in older samples, reach as much as 100 per cent—in other words, the splitting up of the glycerides may become complete. I have found in a large number of commercial palm oils from 50-70 per cent of free palmitic acid.

The chief constituents of palm oil are palmitic acid, palmitin, and olein. *Hazura* and *Grüssner* have found among the liquid fatty acids small quantities of linolic acid, identified by the sativic acid yielded on oxidation. The solid fatty acids consist, according to *Nördlinger*,[1] of 98 per cent of palmitic acid, 1 per cent of stearic, and 1 per cent of a heptadecylic acid, $C_{17}H_{34}O_2$ (most likely identical with daturic acid, p. 47).

The colouring matter of palm oil is bleached by exposure to air, or by heat, or by chemicals, such as chromic acid, etc. The two latter processes are adopted in practice for preparing bleached palm oil, which is almost colourless. By "chemical" bleaching the odour is destroyed, but it is not affected by heating to a high temperature. The colouring principle and the odour are not destroyed by saponification with alkalis or lime (candle manufacture); acid saponification, however (p. 746), destroys both.

[1] *Jour. Soc. Chem. Ind.* 1892, 445.

Physical and Chemical Constants of Palm Oil

Specific Gravity.			Melting Point.	Hehner Value.		Saponification Value.		Reichert Value.		Iodine Value.		Refractive Index.	
°C.		Observer.	°C.	Per cent.	Observer.	Mgrms. KOH.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
15	0·945	Schaedler	From 27 to 42·5 according to age and origin of the oil.	95·6	Hehner	202-202·5	Valenta	0·5	Medicus and Scherer	51·5	Hübl	1·4510	Thoerner
,,	0·9209-0·9245	Tate		94·2-97	Tate	196·3	Moore			51-52·4	Wilson		
18	0·946	Stilurell				201-202	Thoerner						
50 (water 15·5=1)	0·8930	Allen											
98-99 (water 15·1 – 1)	0·8586	,,											

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Mean Molecular Weight.		Iodine Value.	
°C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.
98-99 (water 15·5=1)	0·8369	Allen	Average 44·13	De Schepper and Geitel	..	..	206·5-207·3	Valenta	273	Tate	53·3	Thoerner
100 (water 100=1)	0·8701	Archbutt	As a rule 44·5-45; rarely 39-41 or 45·5-46·2	..	..	..	204	Thoerner	270	Allen		
..	..	..	..	..	..	..	..	..	263	Williams		
..	..	..	42·5-43	Valenta	47·75	Valenta						
..	..	..	42·7	Hübl	47·8	Hübl						
..	..	..	45·5	Allen	50	Allen						
..	..	..	Highest 45·4-45·5	Lewkowitsch								
..	..	..	Lowest 35·8-35·9	,,								

The colouring principle of palm oil belongs to the class of lipochromes. The colour reactions for palm oil given by older writers are due to this substance. These colour reactions are useless, and in any case unnecessary, since palm oil cannot easily be confounded with other fats or oils. It may, however, be stated that some specimens of palm oil—Lagos oil and Old Calabar oil—give with sulphuric acid a colour reaction similar to that obtained with cod liver oil in chloroformic solution, although the blue is much fainter ; other specimens do not give this blue colour, but turn red at once.

Palm oil is, as a rule, not adulterated with other fats, and the commercial valuation embraces, therefore, the determination of water, of usual impurities (mostly sand, added fraudulently by negroes), and of the solidifying point. The proportion of water and sand together should not exceed 2 per cent ; for any excess allowance has usually to be made by the seller.

The following table, due to *Y. de Schepper* and *Geitel*,[1] gives the proportion of water, impurities, neutral fat, and the solidifying points of the mixed fatty acids of a number of commercial brands of palm oil :—

Kind of Oil.	Water.	Impurities.	Solidifying Point of Fatty Acids.	Neutral Fat.
	Per cent.	Per cent.	°C.	Per cent.
Congo . . .	0·78-0·95	0·35-0·7	45·90	16-23·0
Saltpond[2] . . .	3·5-12·5	0·9-1·7	46·20	15-25
Addah . . .	4·21	0·35	44·15	18·0
Appam . . .	3·60	0·596	45·0	25·0
Winnebah . . .	6·73	1·375	45·6	20·0
Fernando Po . .	2·68	0·85	45·90	28
Brass . . .	3·05	2·00	45·1	35·5
New Calabar . .	3·82	0·86	45·0	40·0
Niger . . .	3·0	0·70	45·0	40·0-47·0
Accra . . .	2·2-5·3	0·60	44·0	53-76
Benin . . .	2·03	0·20	45·0	59-74
Bonny . . .	3·0-6·5	1·2-3·1	44·5	44·0-88·5
Gr. Bassa . . .	2·4-13·1	0·6-3	44·6	41-70·0
Cameroons . .	1·8-2·5	0·2-0·7	44·6	67-83
Cape Labon . .	3·6-6·5	0·7-1·5	41·0	55-69
Cape Palmas . .	9·7	2·70	42·10	67
Half Jack-Jack . .	1·9-4·2	0·7-1·24	39-41·3	55-77·0
Lagos . . .	0·5-1·3	0·3-0·6	45·0	58-68
Loando . . .	1·5-3·0	1·0-1·9	44·5	68-76
Old Calabar . .	1·3-1·6	0·3-0·8	44·5	76-83
Gold Coast . .	1·98	0·50	41·0	69
Sherboro . . .	2·6-7·0	0·3-1·2	42·0	60-74
Gaboon . . .	2·0-2·8	0·3-0·7	44·5	79-93·0

Palm oil is chiefly used in the soap and candle industries. In the latter case its "titer" is of the chief importance (cp. p. 133). On account of its non-drying qualities it is also employed in the tinplate industry, to preserve the surface of the heated iron

[1] *Dingl. Polyt. Jour.* 245. 295.

[2] This is the cheapest hard oil ; "Drewin" is the cheapest soft oil.

sheet from oxidation until the moment of dipping into the bath of melted tin.

For the purposes of the tin industry "palm oil greases" are sold consisting of palm oil adulterated with cotton seed oil and mineral oil, spec. grav. 0·905.

MACASSAR OIL

German—*Macassar Oel*

Physical and Chemical Constants of Macassar Oil

Specific Gravity.		Melting Point.		Hehner Value.		Saponific. Value.		Iodine Value.	
At 15° C.	Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
0·924	Itallie	28	Schaedler	91	Itallie	230	Itallie	53	Itallie
...	...	22	Itallie	...	...	213·4	Schaedler	48·3	Lewko-witsch
...	...	...	...	...	...	221·5	Lewko-witsch		

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
Titer Test.					
51·6-53·2	Lewkowitsch	54-55	Schaedler	49·7-50·7	Lewkowitsch

Macassar oil is the fat from the seeds of *Schleicheria trijuga*.

At the ordinary temperature it is a yellowish-white mass of buttery consistency. It consists chiefly of the glycerides of oleic, lauric, and arachidic acids, and contains also small quantities of acetic and butyric acids. A very small proportion of hydrocyanic acid seems to be characteristic of macassar oil. A sample examined in the writer's laboratory had the acid value 35·43.

SAWARRI FAT [1]

French—*Huile de noix de Souari.* German—*Souaributter.*

Physical and Chemical Constants of Sawarri Fat

Specific Gravity at 40° C. (Water at 15°=1)	Solidifying Point. °C.	Melting Point. °C.	Hehner Value. Per cent.	Saponific. Value. Mgrms. KOH.	Reichert Value. c.c. $\frac{1}{10}$ norm. KOH.	Iodine Value. Per cent.
0·8981	29-23·3	29·5-35·5	96·91	199·51	0·65	49·5

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point. °C.	Melting Point. °C.	Mean Molecular Weight.	Iodine Value. Per cent.
46-47	48·3-50	272·8	51·5

Sawarri fat is the fat contained in the nuts from *Caryocar tomentosum*, imported occasionally into this country as "butter nuts." The fat is colourless, and possesses a pleasant nutty taste. The free fatty acids in the specimen examined amounted to 2·4 per cent calculated as oleic acid.

The solid fatty acids consist chiefly of palmitic acid. The liquid fatty acids contain besides oleic acid—identified by its oxidation product, dihydroxystearic acid—some hydroxy acids that are readily converted into lactones. The acetyl value of the liquid fatty acids was 14·03, determined by the method described page 165.

MAFURA TALLOW [2]

French—*Graisse de Mafouraire.* German—*Mafuratalg.*

For tables of constants see p. 522.

Mafura tallow is contained in the seeds of *Mafureira oleifera* (*Trichilia emetica*), from which the fat is obtained by expression.

The fat has a yellowish colour; it is free from taste, and its odour recalls that of cacao butter.

According to *Villon*, it consists of 55 parts of oleic and 45 parts of palmitic acid.

The high melting point renders this fat especially suitable for the manufacture of soaps and candles.

[1] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1890, 844; *Proceedings Chem. Soc.* 1889, 69.
[2] De Negri and Fabris, *Annali del Laboratoria Chimico delle Gabelle*, 1891-92, 271.

Physical and Chemical Constants of Mafura Tallow

	Solidifying Point.		Melting Point.		Saponific. Value.		Iodine Value.	
	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
I. Prepared in the Laboratory	33·25	De Negri and Fabris	35·41	De Negri and Fabris	200·08	De Negri and Fabris	44·85	De Negri and Fabris
II. Commercial	37·30	De Negri and Fabris	35·5-42	De Negri and Fabris	220·96	De Negri and Fabris	46·14	De Negri and Fabris
	36	Schaedler	42	Schaedler				

Physical and Chemical Constants of the Mixed Fatty Acids

	Solidifying Point.		Melting Point.		Iodine Value.	
	°C.	Observer.	°C.	Observer.	Per cent.	Observer.
I.	47·44	De Negri and Fabris	51·54	De Negri and Fabris	46·92	De Negri and Fabris
II.	48·44	De Negri and Fabris	52·55	De Negri and Fabris	48·19	De Negri and Fabris

NUTMEG BUTTER (MACE BUTTER)

French—*Beurre de muscade.* German—*Muscatbutter.*

For tables of constants see p. 525.

Nutmeg butter is obtained from the seeds of *Myristica officinalis* (s. *moschata*, s. *fragrans*). This fat has the consistency of tallow, is of whitish colour, and possesses the strong taste and odour of nutmegs.

Nutmeg butter varies considerably in its composition (see table below). It contains from 4 to 10 per cent of an ethereal oil (therefore low saponification value); and about 45 per cent of a solid fat—chiefly trimyristin—the rest being a liquid fat containing free acid.

Cold alcohol dissolves the liquid fat, the free acid, and the ethereal oil (unsaponifiable), leaving about 45 per cent undissolved. The undissolved portion yields on crystallisation from ether pure trimyristin, melting point 55° C.

Boiling alcohol, ether, and chloroform dissolve nutmeg butter almost completely.

Corresponding to the varying composition of nutmeg butter, the constants given in the table p. 525 vary within comparatively wide limits. The following table contains a few constants for a number of samples determined by *Dieterich;* the first five samples were prepared by that chemist himself by extracting nutmegs with ether:—

No. of Sample.	Specific Gravity at 15° C.	Melting Point.	Saponific. Value.	Acid Value.	Ether Value by Difference.	Iodine Value.	Solubility in Parts of Boiling Alcohol.
		°C.					
1	...	...	156·8	22·4	134·4	...	...
2	...	...	159·6	22·4	137·2	...	...
3	0·996	51	154·0	22·4	131·6	...	15
4	...	...	156·8	22·4	134·4	...	...
5	...	...	156·8	22·4	134·4	...	...
6	0·945	42	151·2	39·2	112·0	...	12
7	0·957	45	140·0	33·6	106·4	...	12
8	0·966	48	134·0	44·8	89·6	...	10
9	...	38·5-39	178·25	17·25	161·0	45·32	...
10	...	42	173·13	19·60	153·53	42·71	...
11	...	43	172·2	18·67	153·53	40·14	...
12	...	42·5-43	174·54	18·67	155·87	41·38	...
13	...	39	175·93	21·93	154·0	52·04	...
14	...	38·5-39	178·67	22·80	155·87	48·60	...

Spaeth examined a number of fats from various commercial brands; his results are given in the following table:—

Origin.	Melting Point. °C.	Saponific. Value.	Iodine Value.[1]	Reichert-Meissl Value.	Refractive Index. Butyro-refractometer at 40° C. Scale Divisions.
Banda .	25-26	170-173	77·8-80·8	4·1-4·2	76-82
Bombay .	31-31·5	189·4-191·4	50·4-53·5	1-1·1	48-49
Menado .	25·5	169·1	76·9-77·3	...	74-74·5
Penang .	26	171·8-172·4	75·6-76·1	...	84·5-85
Macassar	25-25·5	171·8-172·4	75·6-76·1	...	78·5
Zanzibar .	25·5-26	169·9-170·5	76·2-77	...	77·5

Nutmeg butter must not be confounded with *Ucuhuba fat* (p. 544), the fat obtained from *Myristica becuhyba*.

[1] The iodine numbers are remarkably high.

Physical and Chemical Constants of Nutmeg Butter

Specific Gravity.			Solidifying Point.		Melting Point.		Saponific. Value.		Iodine Value.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15 98-99 (water 15·5 = 1)	0·945-0·996 0·898	Dieterich Allen	... 41-42 Turbid at 33 rising to 41·5-44	... Rüdorff Wimmel	... 47-48 43·5-44 51 42 45 48 38·5-43	... Rüdorff Wimmel Dieterich ,, ,, ,, ,,	154-159·6 153·53-161	Dieterich ,,	31 40·1-52·0	Hübl Dieterich

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.	
°C.	Observer	°C.	Observer
40	Hübl	42·5	Hübl
Titer Test. 35·5-35·95 | Lewkowitsch			

RAMBUTAN TALLOW [1]

German—*Rambutantalg.*

Rambutan tallow is obtained from the seeds of *Nephelium Lappaceum.*

Physical and Chemical Constants of Rambutan Tallow

Specific Gravity.	Solidifying Point.	Melting Point.	Saponific. Value.	Iodine Value.
0·9236	38-39	42-46	193·8	39·4

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.	Saponific. Value.	Mean Molec. Weight.	Iodine Value.
57	58-61	186·4	300·9	41·0

The high mean molecular weight of the mixed fatty acids indicates the presence of fatty acids higher than stearic acid; indeed, arachidic acid was isolated. The proportion of oleic acid in the mixed fatty acids was found to be 45·5 per cent. A small quantity of stearic acid was obtained, but palmitic acid is stated to be absent.

MKANYI FAT

German—*Mkányifett.*

For tables of constants see p. 527.

This fat forms about 67 per cent of the seeds of the East African *Guttifera — Stearodendron Stuhlmanni*, Engl. (called Mkányi by the natives of Uluguru).

The fat as prepared by the natives is of yellowish-white colour. The acid value of a specimen of the native product was found = 23·33. According to *Heise*,[2] who examined this fat, Mkanyi fat consists chiefly of the mixed glyceride oleodistearin of the formula $C_3H_5(OC_{18}H_{35}O)_2$ $(OC_{18}H_{33}O)$, melting at 44°-44·5° C. (cp., however, p. 3).

[1] Baczewski, *Jour. Soc. Chem. Ind.* 1895, 1049.

[2] Heise, *Arbeiten aus dem kaiserlichen Gesundheitsamte*, 1896, 540.

Physical and Chemical Constants of Mkanyi Fat[1]

Specific Gravity.		Solidifying Point.	Melting Point. °C.	Saponific. Value. Mgrms. KOH.	Hehner Value. Per Cent.	Iodine Value.	Reichert-Meissl Value. c.c. $\frac{1}{10}$ norm. KOH.
At °C. 40 98 (water 15° = 1)	0·8926 0·85606	38	40-41	190·5	95·65	38·63	1·21

Physical and Chemical Constants of the Mixed Fatty Acids[1]

Solidifying Point. °C.	Melting Point. °C.
57·5	59

CACAO[2] BUTTER—(COCOA BUTTER)

French—*Beurre de Cacao.* German—*Cacaobutter.*

For tables of constants see pp. 530, 531.

Cacao butter is expressed from the cacao beans, the seeds of the cacao-tree, *Theobroma Cacao.* The proportion of fat in the beans varies from 36·8 per cent in Caracas beans to 50·9 per cent in Tabasco beans.

The fat has a yellowish-white colour, turning white on keeping. It possesses an agreeable taste and pleasant odour like chocolate. At the ordinary temperature it is somewhat brittle.

Cacao butter consists chiefly of the glycerides of stearic, palmitic, lauric acids (*Traub*,[3] however, could not detect any lauric acid), and, further, of small quantities of the glycerides of arachidic,[4] linolic,[5] formic, acetic, and butyric acids. Theobromic acid, $C_{64}H_{128}O_2$, stated by *Kingzett*[6] to occur in the fat, is, according to *Graf*,[7] absent, no higher acid than arachidic having been found by him. A specimen of cacao butter examined by *Hehner* and *Mitchell*[8] contained 39·9 to 40·6 per cent of stearic acid.

The acid value of commercial samples of cacao butter was found by *Dieterich* from 1·0 to 2·3; 1 grm. of the freshly expressed fat required 0·06 to 0·25 c.c. decinormal alkali for neutralisation of the free fatty acids. The same observer contradicts the statement made by

[1] Heise, *Arbeiten aus dem kaiserlichen Gesundheitsamte*, 1896, 540.

[2] I prefer the spelling "cacao" instead of "cocoa," in order to avoid confounding this fat with cocoa nut oil or kokum butter.

[3] Wagner's *Jahresbericht*, 1883, 1159.

[4] Specht and Gössmann, *Liebig's Annalen*, 90. 126.

[5] Benedikt and Hazura, *Monatshefte*, 1889, 353.

[6] *Jour. Chem. Soc.* 1878, 38.

[7] *Arch. Pharm.* 1888, 830.

[8] *Analyst*, 1896, 328.

several chemists that cacao butter does not readily turn rancid, cacao butter not behaving differently to any other fat in that respect. Thus a sample of cacao butter, requiring in the fresh state 0·06 c.c. of decinormal alkali, took, after keeping for six months in bottles closed by parchment, 0·22 c.c. of alkali. The proportion of free acids increasing to double the amount during the customary operation of dehydrating and filtering in the hot water funnel, care should be taken that the fat is heated as little as possible. In some Dutch cacao butters *Filsinger* finds acid values as high as 56.

Cacao butter dissolves in five parts of boiling absolute alcohol; it is, however, insoluble in 90 per cent alcohol.

Cacao butter is often adulterated with tallow, almond, arachis, sesamé (hazelnut) oils, cocoa nut oil,[1] "copraol,"[2] beeswax, stearic acid, and paraffin wax. For the detection of most of these adulterants the quantitative reactions will suffice. *Paraffin wax* and *beeswax* lower the **saponification value,** and are indicated by a large amount of unsaponifiable matter. *Cocoa nut oil*, on the other hand, increases the saponification value considerably, and reduces the *Hehner* and iodine values. A high **acid value** would indicate *stearic acid*. The presence of the vegetable oils, almond, arachis, sesamé (hazelnut), is easily recognised by the increased **iodine value** and the lowering of the **melting point** of the mixed fatty acids. In the case of suspected adulteration with *tallow* recourse must be had to the following two tests :—

1. **Ether test,** recommended by *Björklund*.[3]—Place about 3 grms. of the sample in a test-tube, add twice the weight of ether, at the temperature of 18° C., close the test-tube with a cork, and effect solution, if possible, by shaking. If *wax* be present the solution will be turbid and refuse to become clear on warming. If, however, the fat dissolves to a clear solution, immerse the tube in water of 0° C., note the number of minutes that the liquid takes to become milky, or to deposit white flocks, and observe the temperature at which the solution becomes again clear when removed from the water. The following table gives the observations made on pure cacao butter and on samples mixed with tallow :—

	Turbidity at 0° C. after Minutes.	Clear Solution at °C.
Pure cacao butter	10-15	19-20
Cacao butter + 5 per cent of beef tallow .	8	22
Cacao butter + 10 per cent of beef tallow .	7	25

[1] Especially the neutral cocoa nut oil: "lactine" (*Hamel-Roos*). Some commercial cacao butters consist wholly of lactine.

[2] Fancy name for a fat prepared from palm nut oil.

[3] *Zeit. analyt. Chemie*, 3. 233.

According to *Kremel*,[1] the ether solution need only remain clear for three minutes. According to the German Pharmacopœia, a solution of one part of cacao butter in two parts of ether should remain clear for a whole day, if kept at a temperature of 12° to 15° C. *Dieterich*, however, thinks that twelve hours should be deemed sufficient, genuine cacao butter having given deposits after twelve hours. It may, however, be mentioned that *dika oil* would pass this test.

Björklund's test has been modified by *Filsinger*,[2] who melts 2 grms. of the sample in a graduated test-tube, and agitates with 6 c.c. of a mixture consisting of four parts of ether (specific gravity 0·725) and one part of alcohol (specific gravity 0·810). A clear solution will result if the sample be pure, and remain so even on cooling to 0° C.

2. **Aniline test,** proposed by *Hager*.[3]—Warm about 1 grm. of the sample with 2-8 grms. of aniline until solution ensues, and allow to stand for one hour at 15° C., or for one and a half to two hours at 17° to 20° C. If the sample be pure cacao butter an oily layer will be found floating on the top of the aniline, not solidifying before the lapse of many hours. If, however, the cacao butter has been adulterated with *tallow*, *stearic acid*, or a small quantity of *paraffin wax*, granular particles will be observed in the oily layer, which, on being agitated gently, adhere to the wall. In the presence of *beeswax*, or of large quantities of *paraffin wax*, the fatty layer solidifies, whereas in the presence of large quantities of *stearic acid* the whole contents of the test-tube solidify to a crystalline mass without forming two layers.

[1] *Pharm. Post.* 1889, 5. [2] *Zeit. analyt. Chemie*, 1880, 247.
[3] *Ibid.* 1880, 246.

[TABLE

Physical and Chemical Constants of Cacao Butter

Specific Gravity.			Solidifying Point.		Melting Point.		Hehner Value.		Saponific. Value.		Reichert Value.		Iodine Value.		Refractive Index.		
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	At °C.		Observer.
15	0·950-0·952 (fresh)	Hager	20	Hager	32-34	Hager	94·59	Bensemann	192-202	Filsinger	1·6	Allen	34	Hübl	60	1·4496	Thoerner
,,	0·945-0·946 (old)	,,	25-26	Herbst	30-33	Herbst	..	..	193·55	De Negri & Fabris	..	..	34-37·5	Filsinger	40	1·4565 to 1·4578[1]	Strohl
,,	0·964-0·976	Dieterich	..	..	25-26	Bensemann	..	..	198-200	Thoerner	..	..	32-37·7	Dieterich			
50 (water 15·5 = 1)	0·8920	Allen	..	..	28-29 ,, 32·1-33·6	Filsinger	..	..	..	..	..	..	36·62	De Negri & Fabris	Butyro-refractometer.		
98 (water 15·5 = 1)	0·8577	,,	..	..	30-32	Dieterich	..	..	..	..	..	..	32·8-41·7[1]	Strohl			
	..	..	..	..	30-34	,,									At 40° C.		Observer.
			27·3	Rüdorff	33·5	Rüdorff	..	..	..	..	..	..	33·8 36·5	Beckurts			
			23-21·5	De Negri & Fabris	28-30	De Negri & Fabris									46-47·8		Strohl
			23	Thoerner	32-33	Thoerner	..	..	..	..	..	..	34	Thoerner	46-46·5		Mansfeld

[1] Forty commercial samples. There seemed to exist this proportionality between iodine value and refractive index, that the lower the iodine value the lower was the refractive index.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Saponific. Value.		Iodine Value.		Refractive Index.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
51	Hübl	52	Hübl	190	Thoerner	39·1	De Negri & Fabris	1·422	Thoerner
..	..	48-49 / 51-52	Bensemann			32·6	Thoerner		
..	..	49-50 / 52-53	Bensemann						
47-45	De Negri & Fabris	48-50	De Negri & Fabris						
46-47	Thoerner	49-50	Thoerner						
Titer Test.									
48-48·27	Lewkowitsch								

It is evident from the description given that it is necessary to make comparative tests with a specimen of genuine cacao butter side by side with the suspected sample. For the detection of *beeswax* and *paraffin wax* preference should be given to the quantitative reactions previously described.

Cacao butter is a by-product in the manufacture of chocolate, and therefore obtainable in large quantities. It is used in pharmacy and in the preparation of perfumes.

KOKUM BUTTER, GOA BUTTER, MANGOSTEEN OIL

French—*Beurre de Cocum.* German—*Kokumbutter.*

For tables of constants see p. 532.

This fat is obtained in the East Indies from the seeds of the Guttifera, *Garcinia indica, Choisy* (*Mangosteena indica*).

Heise[1] states that this fat consists chiefly of oleodistearin (like Mkanyi fat) cp. chap. i. p. 3, footnote.

The fatty acids of kokum butter are oleic and stearic acids, with small quantities of (probably) lauric acid. A specimen examined by *Heise* contained 10·5 per cent of free fatty acids.

[1] *Arbeiten aus dem kaiserlichen Gesundheitsamte*, 1896, 13. 302.

Physical and Chemical Constants of Kokum Butter

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Hehner Value.		Reichert-Meissl Value.		Iodine Value.		Refractive Index at 25° C.
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	
40 98	0·8952 0·8574	Heise ,,	33·3 27·5 37·6-37·9	Redwood Flückiger & Hanbury Heise [1]	36·7 42·5-45 41-42	Redwood Flückiger & Hanbury Heise [1]	191·3	Heise	95·59	Heise	1·54	Heise	33·1	Heise	1·4628

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point. °C.	Melting Point. °C.	Mean Molecular Weight.
59·4	60-61	282

[1] The melting point varied according to whether the melted fat was allowed to solidify rapidly at 0° C., or kept at the ordinary temperature; in the former case the melting point was 32°-33° C., in the latter it rose to 40° C. after 24 hours' standing (cp. chap. i. p. 4).

BORNEO TALLOW[1]

French—*Suif végétale de Borneo.* German—*Borneotalg.*

Borneo tallow is obtained from the fruits of a number of plants belonging to the family of *Dipterocarpus*, as *Shorea stenoptera*, *Hopea aspera*, etc.

Borneo tallow has a light green colour, changing to yellow, then white on prolonged exposure to the air. In its consistency at ordinary temperature, and in its taste, it resembles cacao butter. It has a crystalline granular structure, and is covered with fine white needles of stearic acid, the quantity of which amounted, in the case of the sample examined by *Geitel*, to 9·5-10 per cent.

Borneo tallow begins to melt at 35°-36° C., and is completely liquid at 42° C. The solidifying point of the free fatty acids is 53·5°-54° C.; they consist of 66 per cent of stearic and 34 per cent of oleic acids. The probable iodine value of the fat, calculated (by the writer) from the last given figure, would be about 31. I therefore place Borneo tallow next to kokum butter.

DIKA OIL (OBA OIL)

French—*Beurre de Dika.* German—*Dikafett.*

Physical and Chemical Constants of Dika Oil

Specific Gravity.		Solidifying Point.		Melting Point.		Iodine Value.	
At °C.	Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.
0·820	Schaedler	...	...	30-31	Hamel-Roos	30·9-31·3	Dieterich
?	...	...	...	29	Dieterich		
...	...	34·8	Heckel	41·6	Heckel		

This fat is obtained from the seeds of *Irvingia Gabonensis*,[2] a tree indigenous to the West Coast of Africa.

Dika oil has an orange-yellow colour in the solid state; when melted it is yellowish-grey. It has a characteristic smell, which becomes more distinct on warming.

According to *Oudemans*,[3] this fat consists of laurin and myristin only, to the exclusion of olein. The same statement has been re-

[1] Geitel, *Jour. Soc. Chem. Ind.* 1888, 391.
[2] Heckel, 2° *Mémoire des Annales du Musée et de l'Institut Colonial de Marseille.*
[3] *Jour. prakt. Chemie*, 81. 356.

peated by *Heckel*, on the ground that he could not obtain from the fatty acids an ether-soluble lead salt. This, however, is not definite proof (p. 192). In any case, it cannot hold good for the specimen examined by *Dieterich*, he having found 30·9-31·3 as the iodine absorption of the fat, corresponding to about 34 per cent of olein.

Dika oil easily becomes rancid; the acid value of a specimen examined by *Dieterich* was 19·6.

Dika oil behaves like cacao butter in *Björklund's* ether test for the latter.

The fat from *Irvingia Oliveri* (indigenous to Cochin China), named Caÿ-Caÿ by the Annamites, is, according to *Heckel*, almost identical with Dika oil.

MOCAYA OIL [1]

Mocaya oil is obtained from the seeds of *Acrocomia sclerocarpa* (*Cocos sclerocarpa*), a palm-tree occurring in Paraguay and forming there vast forests.

This oil is very similar to cocoa nut oil; it is white, of buttery consistency, and resembles also in its odour cocoa nut oil. It is soluble in alcohol and the ordinary solvents for fats.

Physical and Chemical Constants of Mocaya Oil

Solidifying Point. °C.	Melting Point. °C.	Saponific. Value.	Reichert-Meissl Value. c.c. $\frac{n}{10}$ KOH.	Iodine Value. Per cent.
22	24-29	240·6	7·0	24·63

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point. °C.	Melting Point. °C.	Saponific. Value. Mgrms. KOH.
22-20	23-25	254
		Saponific. Value of the Non-volatile Acids. 244·8

[1] De Negri and G. Fabris, *Giorn. farmac.* 1896, No. 12; *Chem. Rev.* 1897, 82.

PALM NUT OIL

French—*Huile de palmiste.* German—*Palmkernoel, Kernoel.*

For tables of constants see p. 536.

Palm nut oil is obtained from the kernels of the palm-tree fruit. The kernels are imported to Europe, and the fat is obtained from them either by expression or by extraction with solvents. The percentage of oil in the kernels varies a good deal with their origin.[1] The colour of the palm nut oil is white; the darker oils, formerly met with owing to faulty manufacture, have disappeared from the market. It possesses a pleasant smell and an agreeable nutty taste.

When fresh, the oil is neutral, but on keeping it easily turns rancid with liberation of free fatty acids. The following table gives the proportions found in various samples of palm nut oil:—

Free Fatty Acids in Palm Nut Oil

Kind of Oil.	No. of Samples.	Free Fatty Acids as Oleic Acid.	Observer.
		Per cent.	
...	2	13·26-13·39	Salkowski
Expressed oil .	27	3·30-17·65	Nördlinger
Extracted oil .	10	4·17-11·42	,,

The chemical composition of palm nut oil is the following, according to *Oudemans*[2]:—

Glyceride.	Per cent.
Triolein	26·6
Stearin, Palmitin, Myristin	33·0
Laurin, Caprin, Caprylin, Caproin	44·4

[1] In the following table, due to Nördlinger (*Jour. Soc. Chem. Ind.* 1895, 585), details are given.

Origin of Palm Kernels.	Proportion of Fat. Per cent.	Origin of Palm Kernels.	Proportion of Fat. Per cent.
Sierra Leone . . .	48·6	Togo District, French .	49·3
Island of Sherboro . .	46·7	Lagos	50·4
Liberia	49·4	Benin	49·8
Grand Bassa . . .	50·2	Niger	50·5
Half Jack	50·8	Brass	52·5
Apollonia	47·2	Calabar	50·9
Dixcove	48·2	Bonny	51·0
Cape Coast Castle . .	50·2	Opobo	52·3
Winnebah	46·1	Cameroons	49·0
Quitta	48·4	Congo	47·4
Togo District, German .	52·1	Loanda	50·9

[2] *Jour. prakt. Chemie*, 11. 393.

Physical and Chemical Constants of Palm Nut Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Hehner Value.		Saponific. Value.		Reichert Value.		Iodine Value.		Refractive Index.	
°C.		Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
15	0·9520	Schaedler	20·5	Schaedler	23-28	Valenta	91·1	Lewkowitsch	247·6	Valenta	2·4	Allen	10·3-17·5	Valenta	1·4431	Thoerner
40 (water at 15·5 = 1)	0·9119	Allen			27-28	Schaedler			246-250	Thoerner			13·4-13·6	Morawski and Demski		
99 (water at 15·5 = 1)	0·8731	,,			25-26	Thoerner							13-14	Thoerner	Butyro-refractometer.	
															At 40° C.	Observer.
															36·5	Beckurts and Seiler

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Saponific. Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
Titer Test.											
20·0-20·5	Lewkowitsch	25-28·5	Valenta	258-265	Valenta	211	Valenta	12·07	Morawski and Demski	1·4310	Thoerner
22·5-24·5	,,	20·7	Thoerner	264	Thoerner			12	Thoerner		
23·5-24·5	,,										
24·6-25·5	,,										

Valenta [1] has examined the fatty acids from palm nut oil. On passing a current of steam through the acids a small quantity volatilised, the distillate consisting of *caproic* acid and most likely also of *caprylic* acid. After drying the acids that remained behind and distilling them, at a pressure of 100 to 160 mm., six fractions were obtained, the examination of which led to the results recorded in the table :—

Fraction No.	Boiling Point.	Melting Point.	Saponif. Value.	Iodine Value.	Yield.	Saturated Fatty Acids.	Oleic Acid.	Approximate Composition of Fatty Acids.
	°C.	°C.			Per cent.	Per cent.	Per cent.	
1	135-190	..	..	0	4	100	0	Caprylic, capric
2	190-200	31·5	310	2·6	10	97·2	2·8	Capric, oleic
3	200-205	37·5	275	3·4	58	96·3	3·7	Lauric, capric, oleic
4	205-225	32·5	264	7·8		91·5	8·5	,, ,, ,,
5	225-245	31·5	251	16·7	15	81·7	18·5	Lauric, myristic, oleic
6	245-270	35·0	219	41·3	5	54·6	45·8	Myristic, palmitic, oleic
7	Residue	..	..	..	8	..	..	

The chief constituent of palm nut oil is therefore lauric acid. From the iodine value we calculate the proportion of olein as 12 to 20 per cent. Palm nut oil is very nearly related in its chemical composition to cocoa nut oil. It is remarkable, like the latter, for the high saponification value, and the notable amount of glycerides of volatile fatty acids (cp. "Cocoa Nut Oil," p. 538). Like cocoa nut oil, it requires strong caustic soda for saponification, and yields a hard white soap, which is only thrown out in the "salting out" process by the addition of a large amount of salt.[2]

Palm nut oil is chiefly used for soap-making. For its employment in the manufacture of vegetable butter, see "Cocoa Nut Oil" (p. 541).

By subjecting palm nut oil to hydraulic pressure a hard fat is obtained, and the liquid "*palm nut oleine.*" A sample of the latter, examined by the writer, had the titer test 16·8° to 17° C.

COCOA NUT OIL

French—*Huile de coco, Beurre de coco.* German—*Cocosoel, Cocosnussoel*

For tables of constants see pp. 539, 540.

Cocoa nut oil is the fat obtained from the kernels of the cocoa nut, especially those from the two species *Cocos nucifera* and *Cocos butyracea.*

In commerce three qualities of oil are distinguished : (1) *Cochin oil,*

[1] *Zeit. f. angew. Chemie*, 1889, 335.

[2] Cp. Lewkowitsch, *Jour. Soc. Dyers and Colourists*, 1894, March ; *Jour. Soc. Chem. Ind.* 1894, 258.

the finest and whitest quality, prepared in Cochin (Malabar);[1] (2) *Ceylon oil*, chiefly imported from Ceylon, where the fat is expressed or boiled out on a large scale; (3) *Coprah oil*, the fat from the *coprah*, *i.e.* the kernels, shipped in enormous quantities to Europe, where the oil is either expressed or extracted in a similar way to palm nut oil.

In order to reduce its bulk the *coprah* is dried before shipping, hence the commercial terms "sun-dried" and "kiln-dried" coprah.

By expressing the kernels in the cold an oil is obtained of the solidifying point 13°-12° C., and the melting point 20° C. This cold-pressed oil, however, is not a commercial product, being used where it is produced as a substitute for butter fat.

Cocoa nut oil is, in our climate, at the ordinary temperature a solid white fat possessing a bland taste, and, when fresh, a peculiar though not unpleasant odour. It turns, however, easily rancid, acquiring at the same time a disagreeable flavour and an acrid taste. Coprah oil is richer in free fatty acids than Ceylon oil. The writer has found in a great number of samples of Coprah oil free fatty acids to the extent of 25 per cent, Ceylon oil as a rule only containing from 5 to 10 per cent of free acids calculated as oleic acid.

Cocoa nut oil resembles palm nut oil in its chemical composition, containing, like the latter, large proportions of trimyristin and trilaurin, smaller quantities of tripalmitin and triolein, and also the glycerides of the volatile caproic, caprylic, and capric acids. It is practically free from hydroxy acids[2] (*Lewkowitsch*).

This composition explains the very high saponification and the high Reichert values of both fats. The two constants are so characteristic of them, that both oils are easily distinguished thereby from all other fats with the exception of butter fat.

Cocoa nut oil is soluble in alcohol to a considerable extent, one volume of oil dissolving in two volumes of 90 per cent alcohol at 60° C.

In consequence of its abnormal chemical composition, the behaviour of cocoa nut oil is different from that of other oils and fats, excepting only palm nut oil, in that it is not easily saponified by weak caustic lyes. It requires alkaline lyes of high strength for saponification, and is so easily converted into soap by them that it is quite sufficient to stir the oil and caustic alkali well together and allow the mixture to stand. After some time saponification will take place with liberation of heat. (Soap-making by the cold process.) The soap thus formed is very hard, and combines with a very large amount of water without becoming soft. Cocoa nut oil soap has further the remarkable property of requiring very large quantities of salt to throw it out of its aqueous solution.

Cocoa nut oil is chiefly used for soap-making and in the candle manufacture (night-lights); for the latter purpose the fat is subjected to hydraulic pressure, when a soft fat ("cocoa nut oleine") and a

[1] There are also the commercial brands: Cochin Australia, Cochin Mauritius.

[2] Unpublished experiments.

Physical and Chemical Constants of Cocoa Nut Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Hehner Value.		Reichert Value.		Iodine Value.		Refractive Index.	
°C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
18	0·9250	Stilurell	20·5-16	Allen	20-28	Allen	257·3-268·4	Valenta	83·75	Jean Lewkowitsch	3·7	Reichert	8·9	Hübl	1·441	Thoerner
40 (water 15·5=1)	0·9115	Allen	..	..	..	..	..	..	88·6-90·5		..	..	8·97-9·35	Wilson	Butyro-refractometer.	
99 (water 15·5=1)	0·8736	,,	19·5-15·7	Valenta	23·5-24·1	Valenta	250·3 washed oil.	Moore	..	..	..	..	8·8·6	De Negri and Fabris		
..	..	..	..	..	26·2-26·4	Filsinger	246·2	,,	..	..	3·5-3·7	Allen, Moore, Muter	9·9·5	Thoerner	At 40° C.	Observer.
..	..	..	16-14	De Negri and Fabris	24-27	De Negri and Fabris	253·4-262	De Negri and Fabris			Reichert-Meissl Value.				33·5	Beckurts and Seiler
..	..	..	16-14	De Negri and Fabris	23-26	De Negri and Fabris									35·5	Mansfeld
..	..	..	20-16	De Negri and Fabris	25-28	De Negri and Fabris	255-260	Thoerner			7·5	Thoerner				
			22-23	Thoerner	23-24	Thoerner										

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Saponific. Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
At 98°-99° C. (Water 15·5 = 1)	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60 °C.	Observer.
0·8354	Allen	..	..	..	..	258	Thoerner	196-204	Alder Wright	8·39-8·79	Morawski and Demski	1·4295	Thoerner
..	..	20·4	Hübl	24·6	Hübl	..	..	201	Williams	9·3	Williams		
..	..	19·5-15·7	Valenta	24-25	Valenta	..	..	211[1]	Lewkowitsch	8·62-8·92	De Negri and Fabris		
..	..	18-16	De Negri and Fabris	25-27	De Negri and Fabris	..	..	..	..	8·5-9	Thoerner		
		20	Thoerner	24-25	Thoerner								
		Titer Test.								Iodine Value of the Liquid Fatty Acids.			
		21·2-22·55	Lewkowitsch							54·0	Wallenstein and Finck		
		21·9-24·7	,,										
		23·0-23·6	,,										
		23·3-23·9	,,										
		23·9-25·0	,,										
		24·8-25·2 (Cochin)	,,										

[1] Ceylon Oil.

hard fat ("cocoa nut stearine") are obtained. *Allen*[1] has examined these two products with the following result:—

	Specific Gravity. (Water at 15·1 = 1.)			Solidifying Point.	Melting Point.	Reichert Value.
	At 15·5° C.	At 60° C.	At 89·5° C.	°C.	°C.	c.c. $\frac{1}{10}$ norm. KOH
Cocoa nut oleine.	0·9262	...	0·8710	4, rising to 8	...	5·6
Cocoa nut stearine	Solid	0·8959	0·8696	21·5, rising to 26·0	28·5	3·1

Cocoa nut oil is further used as an ingredient in margarine manufacture (cp. "Butter Fat," p. 636).

During recent years "vegetable butter" has been manufactured by *Schlick's* process from cocoa nut oil by treatment with alcohol and animal charcoal, whereby chiefly the free acids are removed.[2] This product, sold under various names as "Mannheim cocoa nut butter," "Vegetable butter," "Lactine," "Vegetaline," "Nucoline," "Laureol," is therefore practically *neutral* cocoa nut oil. *Fresenius* gives the following analysis:—

	Per cent.
Fat	99·979
Water	0·020
Ash	0·001

The colour of this product is perfectly white; it has the consistency of butter, and possesses a sweet, neutral, agreeable flavour, and is said to be free from any tendency to turn rancid.[3] Lower qualities, however are yellowish and have a granular structure. They also are neutral, and are either tasteless or possess a faint nutty taste (*Ambühl*). A few constants of this product are given in the following table. The Reichert, saponification, and iodine numbers are, of course, identical with those stated for the ordinary cocoa nut oil.

Fat

Specific Gravity.		Solidifying Point.		Melting Point.		Deviation in Oleo-refractometer.	
At 35° C.	Observer.	°C.	Observer.	°C.	Observer.	'Degrees.'	Observer.
0·9124	Herz[4]	19·5	Fresenius	26·5	Fresenius	−59	Jean
...	...	...	...	24-25	Ambühl		

[1] *Commerc. Org. Analysis*, ii. 137.

[2] Another process consists in treating cocoa nut oil with magnesia (*Jeserich*) or lime (Ruffin).

[3] Jean, *Jour. Soc. Chem. Ind.* 1891, 275.

[4] Butter fat, 0·9121; Margarine, 0·9017.

Fatty Acids

Solidifying Point.		Melting Point.	
°C.	Observer.	°C.	Observer.
19·9	Fresenius	25·25	Fresenius
20	Herz	25	Herz

Cocoa nut oil is not adulterated with other fats. Its admixture with palm nut oil cannot be detected, owing to the great similarity of these two fats. As they are about the same price, and as the uses they are put to are identical, an examination of cocoa nut oil for palm nut oil, and *vice versa*, is of little practical importance.

MYRTLE WAX

French—*Cire de Myrica*. German—*Myricawachs*.

For tables of constants see p. 543.

Myrtle wax is obtained by boiling the berries of various species of *Myrica* (as *Myrica cerifera*, *M. carolinensis*, *M. caracassana*, *M. cordifolia*, *M. lacinata*) with water. It has a green colour, due to chlorophyll; on exposure to the air the uppermost layers are changed to a whitish mass.

Myrtle wax consists of the glycerides of stearic, palmitic, and myristic acids, and a small quantity of oleic acid. It is therefore not a true wax but a glyceride. A sample examined by *Allen* yielded 13·38 per cent of glycerol. The acid values of two specimens of myrtle wax were 3 and 4·4 (*Deering*).

Myrtle wax is used like beeswax.

Physical and Chemical Constants of Myrtle Wax

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0·995	Allen	39-43	Allen	40-44	Allen	205·7-211·7	Allen	10·7 [1]	Mills
98-99 (water 15·5=1)	0·875	,,								

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Mean Molecular Weight.	
°C.	Observer.	°C.	Observer.		Observer.
46	Allen	47·5	Allen	243	Allen

[1] Calculated from bromine value 6·34.

UCUHUBA FAT

French—*Graisse d'Ucuhuba.* German—*Ucuhubafett.*

For tables of constants see p. 545.

Ucuhuba fat is the fat from the nuts of *Myristica becuhyba* s. *officinalis.*

The crude fat is yellowish-brown, and possesses an aromatic odour (due to a small quantity of an ethereal oil), recalling that of cacao.

This fat consists of myristin and olein (10·5 per cent of the latter; other glycerides are absent), and small quantities of an ethereal oil, of a resinous substance, and of a wax-like compound. The odour of the resinous substance resembles that of Peru balsam; it is soluble in ether, hot alcohol, petroleum ether, and chloroform.

The sample examined by *Valenta* contained 8·8 per cent of free fatty acids.

The fat gives with sulphuric acid a beautiful red colouration (*Peckolt*).

Ucuhuba fat must not be confounded with the fat from the "oil nuts," the seeds of *Myristica surinamensis.* The latter fat melts at 45° C., according to *Reimer* and *Will*,[1] and appears to have a similar chemical composition, consisting of almost pure myristin and a caoutchouc-like (resinous) substance.

[1] *Berichte*, 1888, 2011.

Physical and Chemical Constants of Ucuhuba Fat

Solidifying Point.		Melting Point.		Hehner Value.		Saponific. Value.		Iodine Value.	
°C.	Observer.	°C.	Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.
...	...	39	Valenta[1]	93·4	Valenta	219-220	Valenta	9·5	Valenta
32-32·5	Nördlinger	42·5-43	Nördlinger[2]						

Physical and Chemical Constants of the Mixed Fatty Acids

Melting Point.	
°C.	Observer.
46	Valenta
42·5-43	Nördlinger

[1] *Jour. Soc. Chem. Ind.* 1889, 202.

[2] *Berichte,* 1888, 2617.

JAPAN WAX

French—*Cire de Japon.* German—*Japanwachs, Sumachwachs, Japantalg.*

For tables of constants see pp. 547, 548.

The name of Japan wax (like that of myrtle wax) is misleading, as it is a true fat consisting of glycerides, and not a wax.

Japan wax is prepared in Japan and China from the berries of several sumach trees, viz. *Rhus succedanea*, *R. acuminata*, *R. venicifera*, *R. sylvestris*; it is imported to this country in small slabs.

Japan wax is a pale yellow, hard substance, of conchoidal, somewhat lustrous fracture. It possesses a wax-like consistency, and can be easily kneaded between the fingers. Its odour recalls that of tallow and beeswax at the same time.

On keeping, Japan wax turns yellower, becoming coated with a white powder consisting of microscopical prismatic needles. Also neutral Japan wax exhibits a crystalline structure under the microscope.

The numbers for the specific gravity given in the table vary considerably; this is no doubt due to the samples having been derived from different sources.

Kleinstück[1] has determined the specific gravity of several samples of Japan wax at different temperatures, and states that its density is equal to that of water at 16°-18° C.; below 16 C°. it is heavier, and above 18° C. lighter than water. Japan wax which has been freshly melted has a higher specific gravity than the normal one, the density only becoming normal again after keeping for some time. This phenomenon is due to the coëfficient of expansion of Japan wax being higher than that of water, as shown in the following table given by *Kleinstück*:—

Specific Gravity of Japan Wax compared with that of Water at 4° C.

Temperature. °C.	Japan Wax.		Water.
	Kept for some time.	Freshly melted.	
4	...	...	1·00000
6·5	...	1·00237	0·99995
7·2	1·00737	...	0·99991
17·0	...	0·99123	0·99884
17·5	0·99846	...	0·99875
23·0	...	0·98747	0·99762
26·5	0·98615	0·98683	0·99674

[1] *Jour. Soc. Chem. Ind.* 1890, 1072.

Physical and Chemical Constants of Japan Wax

Specific Gravity.			Solidifying Point.		Melting Point.		Saponific. Value.		Iodine Value	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0·977-0·978	Hager	50·8	Rüdorff	50·4-51	Rüdorff	222·4	Becke	4·2	Hübl
,,	0·963-0·964 (very old)	,,	53	Allen	56	Allen	220	Hübl	4·9-6·6	Lewkowitsch
,,	0·975	Dieterich	40·5-41 rising to 45·5-46	Schaedler	53·5-54·5	Schaedler	222	Valenta	2·4-3·7[1]	Mills
,,	0·970-0·980	Schaedler		...	(cp. p. 548)		214-221·3	Allen		
15·5	0·984-0·993	Allen					221·6	Henriques		
60 (water 15·5 = 1)	0·9018	,,								
98-99 (water 15·5 = 1)	0·8755	,,								
Bleached Japan Wax.										
15	1·000-1·006	Schaedler								

[1] Calculated from bromine value.

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Mean Mol. Weight.	
At 98-99° C. (Water 15·5=1.)	Observer.	°C.	Observer.	°C.	Observer.		Observer.
0·848	Allen	53·0-56·5	Allen	56-57	Allen	265·3 257·6	Allen Harris[1]
		Titer Test.					
		58·8-59·4	Lew-kowitsch				

The melting points recorded above also vary considerably. The normal melting point of a specimen of Japan wax being 53·5°-54·5° C., it was found after melting to have fallen to 42° C.

Japan wax is insoluble in cold alcohol, but dissolves readily in boiling alcohol, separating out on cooling almost completely as a granular, crystalline mass. It dissolves easily, like all other fats, in ether, benzene, and petroleum ether.

Japan wax is almost completely saponifiable (*Allen* and *Thomson* found 1·14 per cent of unsaponifiable matter only[1]), and consists chiefly of palmitin and free palmitic acid. Besides these constituents, it also contains small quantities of stearin,[2] arachin, and, according to *Allen*, 8·4 per cent of soluble fatty acids, calculated as caprylic acid.

The amount of free fatty acids in commercial samples naturally varies, as shown in the following table :—

Free Fatty Acids. Per cent.	Observer.
9·13	Hübl
3·87	Nördlinger
8·96	Allen
9·03	,,
12·72	,,
9·40	Harris[1]

The proportion of glycerol has been found by *Allen* for three samples from 11·59 to 14·7 per cent. These high values—obtained by the permanganate method (p. 208)—seemed to speak in favour of *Berthelot's* statement that Japan wax contains dipalmitin. *Benedikt*, however, has been unable to detect diglycerides on boiling with acetic anhydride (p. 190).

Commercial Japan wax contains from 0·02-0·08 per cent of ash.

Japan wax is easily distinguished from true waxes by its yield-

[1] Determined in the writer's laboratory ; the fatty acids had been previously freed from unsaponifiable matter. The Japan wax examined contained 1·1 per cent of the latter.

[2] This requires further investigation, as Hehner and Mitchell's method of determining tearic acid in fats and oils breaks down, curiously enough, in the case of Japan wax.

ing glycerol. Its detection in beeswax, for the adulteration of which it is sometimes used, will be described pp. 660, 666.

On account of its physical characteristics adulteration with other fats is easily detected. The presence of tallow will be indicated by the low melting point and the high iodine absorption of the sample.

According to *Stohmann*,[1] commercial Japan wax is frequently adulterated with from 15 to 30 per cent of water. *La Wall*[2] found a number of commercial samples adulterated with starch to the extent of 20 to 25 per cent. On treating the adulterated wax with a solvent (p. 89) the wax only is dissolved. A more rapid method to detect starch is to moisten a freshly cut surface with iodine solution.

MALABAR TALLOW (PINEY TALLOW)[3]

French—*Suif de Piney.*
German—*Malabartalg, Vateriafett, Pineytalg, Pflanzentalg.*

Physical and Chemical Constants of Malabar Tallow

Specific Gravity.			Solidifying Point.		Melting Point.		Saponific. Value.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.
9·4	0·9102	Dal Sie	30·5	Vierthaler and Bottura	36·5	Vierthaler and Bottura	191·9	Höhnel and Wolfbauer
15	0·915	Höhnel and Wolfbauer			30 42	Dal Sie Höhnel and Wolfbauer		

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.	
°C.	Observer.	°C.	Observer.
54·8	Höhnel and Wolfbauer	56·6	Höhner and Wolfbauer

This fat is obtained from the seeds of *Vateria indica.*

In the fresh state it has a greenish-yellow colour; on exposure to the air it is rapidly bleached. Its consistency approaches that of mutton tallow.

[1] Muspratt's *Chemie*, 4th edition, vol. iii. p. 571. [2] *Jour. Soc. Chem. Ind.* 1897, 247.
[3] Wagner's *Jahresbericht*, 1884, 1186.

The sample of Malabar tallow examined by *Höhnel* and *Wolfbauer* consisted of 19 per cent of free fatty acids and 81 per cent of glycerides. The solid fatty acids melted at 63·8° C.

WILD OLIVE FAT

The seeds of a wild olive of the *Simaruba* variety (found native in San Salvador) yield a solid yellow fat, which is used for soap-making.

The fat melts at 30° C.; it yields over 90 per cent of solid white fatty acids, melting at 48°-49° C.

These fatty acids are stated to consist of equal parts of saturated and unsaturated fatty acids; the former melted at 54°-55° C., and were fractionated by means of the barium salts into three portions, melting at 58°-59° C., 44° C., and 38° C.

2. Animal Fats

The fats here described vary in their hardness, like the vegetable fats, in inverse proportion to the amount of olein they contain, or, in other words, to the amount of iodine they absorb. Butter fat, in a similar fashion to cocoa nut and palm nut oils, occupies a singular position owing to its high proportion of volatile acids. In a system based on similarity of chemical composition butter fat would be classed with those two vegetable oils, but it is more convenient, and will remain so until our knowledge of the subject is much more extended than it is at present, to retain a subdivision into vegetable and animal fats.

The liquid fatty acids were until recently considered to consist of oleic acid only, but it is proved now that some animal fats contain less saturated acids (linolic?), notably so the American lards (cp. chap. x. p. 232). A few of the fats possess distinct drying properties (cp. chap. x. p. 232).

The constants of a number of lesser known fats are collated in the following table, due to *Amthor* and *Zink*:—

[Table

Kind of Fat.		Specific Gravity at 15° C.		Solidifying Point.		Melting Point.		Saponification Value. Mgrms. KOH.		Hehner Value.	Reichert Value.	Iodine Value. Per cent.		Remarks.
		Fat.	Fatty Acids.	Fat. °C.	Fatty Acids. °C.	Fat. °C.	Fatty Acids. °C.	Fat.	Fatty Acids.	Per cent.	$\frac{1}{10}$ c.c. normal KOH.	Fat.	Fatty Acids.	
	German.													
Blackcock . .	Auerhahn .	0·9296	0·9374	...	25-28	...	30-33	201·6	199·3	...	2·10	121·1	120	Possesses drying properties.
Wild duck .	Wildente .	...	...	15-20	30-31	...	36-40	198·5	...	...	1·30	84·6	...	
Domestic duck	Hausente .	...	...	22-24	...	36-39	...	...	...	...	...	58·5	...	
Starling . .	Staar . .	...	...	15-18	30·31	30-35	38-39	209·2	...	...	...	83·7	79·4	
Pigeon . . .	Taube . .	...	...	...	33-34	...	38-39	...	...	...	...	82·3	...	
Turkey . .	Truthahn .	0·9220	0·9385	...	31-32	...	38-39	200·5	210·1	...	...	81·15	70·7	
Fox	Fuchs . .	0·9412	0·9492	24-26	36-37	35-40	41-43	191·7	205·7	...	1·30	79·7	65·4	
Badger. . .	Dachs . .	0·9226	0·9230	17-19	28-30	30-35	34-26	193·1	193·7	96	0·36	71·3	73	
Pine marten .	Edelmarder	0·9345	...	24-27	35-37	33-40	39-43	204	...	93	1·10	70·2	53(?)	
Chicken . .	Haushuhn .	0·9241	0·9283	21-27	32-34	33-40	38-40	193·5	200·8	...	1·00	66·7	64·6	
Polecat . .	Iltis . . .	...	...	...	26-27	...	34-40	...	...	...	...	62·8	60·6	
Dog. . . .	Hund . .	0·9229	0·9278	21-23	34·5-35·5	37·5-40	39-40·5	195·4	199·15	95·65	0·57	58·5	50·15	
Wild cat . .	Wildkatze .	0·9304	0·9366	26-27	36-37	37-38	40-41	199·9	203·8	...	2·5	57·8	58·8	
Domestic cat .	Hauskatze .	0·9304	0·9251	24-26	35-36	39-40	40-41	190·7	...	96	0·90	54·5	54·8	
Elk	Elch . . .	0·9625	0·9584	37-38	48-50	49-52	53-55	195·1	201·4	...	0·78	35·0	27·8	
Roebuck . .	Reh . . .	0·9659	0·9622	39-41	49-50	52-54	62-64	199·0	200·5	95·8	0·99	32·1	27·9	
Fallow buck .	Damhirsch.	0·9615	0·9524	40	47-48	52-53	50-53	195·6	201·4	...	1·70	26·4	28·2	
Chamois . .	Gemse . .	0·9697	0·9546	42-43	51-52	54-56	57-58	203·3	206·5	...	1·80	25·0	24·4	

HORSE FAT

French—*Graisse de cheval.* German—*Pferdefett.*

For tables of constants see pp. 553, 554.

Fresh horse fat is of a yellowish colour, and has a buttery consistency. On standing it separates into a solid and liquid portion.

It is neutral when fresh; older samples become rancid, and absorb oxygen (cp. p. 12).

In a sample of kidney fat *Hehner* and *Mitchell* could not detect any stearic acid.

In consequence of the increasing consumption of horse meat, horse fat has become a commercial article. It is used by the poorer classes on the Continent as an edible fat in place of lard, and serves, no doubt, as an adulterant for more expensive fats.

The following constants for horse fat from various parts of the body have been published by various observers:—

Horse Fat from	Consistency.	Colour.	Specific Gravity.		Solidifying Point. °C.	Melting Point. °C.	Solidifying Point of Fatty Acids. °C.	Melting Point of Fatty Acids. °C.	Hehner Value.	Reichert Value.	Saponific. Value.	Acid Value.	Iodine Value of		Observer.
			At °C.										Fat.	Fatty Acids.	
Kidneys . .	Salve-like, soft	Golden yellow	15	0·9320	22	39	30-30·5	36-37	95·47	0·33	198·7	1·73	81·09	83·88	Amthor and Zink
,,	..	..	..	..	..	..	..	..	..	..	..	..	85·4	..	Hehner and Mitchell
,,	..	..	17·5	0·9212	48-47	53-54	..	..	..	..	187·6	..	82·6	84·0	Frühling
,,	..	..	50	0·8987	..	..	..	..	..	..	..	..	..	..	,,
Neck . .	Like fresh hard butter	Deep orange-yellow	15	0·9330	30	34-45	32-33	41-42	95·42	0·22	199·5	2·44	74·84	74·41	Amthor and Zink
Leaf . .	Butterlike	Golden yellow	15	0·9319	20	36-37	31-32·5	39-40·5	94·78	0·38	197·8	1·84	81·6	83·37	,,
Back . .	..	..	17·5 50	0·9159 0·8963	45-43	52-53	..	..	..	..	182·8	..	79·9	81·4	Frühling
Heart . .	.	..	17·5 50	0·9167 0·8948	34-32	40-41	..	..	..	..	184·7	..	77·4	78·3	,,

Physical and Chemical Constants of Horse Fat

Specific Gravity.			Melting Point.		Hehner Value.		Saponification Value.		Reichert-Meissl Value.		Iodine Value.		Refractive Index. Butyro-refractometer	
At °C.		Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	At 40° C.	Observer.
15	0·9189	Filsinger	20	Lenz	96-97·8	Kalmann	197·1	Filsinger	1·64-2·14	Kalmann	86·1	Kalmann	53·7	Mansfeld
			41·8-43·2 [1]	Kalmann	...	...	195·1-196·8	Kalmann	...	...	84	Filsinger		
98-99	0·861	Allen		...	...	...	...	...	...	...	71·4-72·4	Lewkowitsch		

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Saponific. Value.		Iodine Value.	
°C.	Observer.	°C.	Observer	Mgrms. KOH.	Observer.	Per cent.	Observer.
37·3-37·7	Kalmann	37·5-39·5	Kalmann	202·6-202·7	Kalmann	83·9-87·1	Kalmann
33·6-33·7	Lewkowitsch						

[1] Capillary tube method.

HORSE MARROW FAT[1]

French—*Moëlle de cheval.* German—*Pferdemarkfett.*

Physical and Chemical Constants of Horse Marrow Fat

Specific Gravity.	Solidifying Point.	Melting Point.	Saponific. Value.	Reichert Value.	Iodine Value.
At 15° C.	°C.	°C.	Mgrms. KOH.	c.c. $\frac{1}{10}$ norm. KOH.	Per cent.
0·9204-0·9221	24-20[2]	35-39[2]	199·7-200	1·0	77·6-80·6

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.	Solidifying Point.	Melting Point.	Saponification Value.	Iodine Value.
At 15° C.	°C.	°C.	Mgrms. KOH.	Per cent.
0·9182-0·9289	36-34[2]	42-44[2]	210·8-217·6	71·8-72·2

Horse marrow fat is pale yellow. A specimen of freshly rendered fat had the acid value 1·0, and a sample three months old 0·8.

HARE FAT

French—*Graisse de lièvre.* German—*Hasenfett.*

For tables of constants see p. 556.

The fat obtained from several hares is, according to *Amthor* and *Zink*,[3] pale yellow to orange-yellow, very soft, and separates on standing into a thick yellow oil and a white crystalline precipitate. Even in the fresh state it has a disagreeable rancid smell, which becomes more unpleasant on standing.

Exposed in a thin layer—spread on a glass plate—hare fat dries in about 8 days to a tolerably viscid varnish, becoming solid after 4 more days. The iodine number after 38 days' exposure was 19·4.

Hare fat would thus appear to be a drying fat. Hare fat contains linolic acid (chap. ix. p. 318).

The acid value of the specimen examined by Amthor and Zink was, in the fresh state, 2·73, and 8 after 6 months.

[1] Zink, *Forschungsberichte über Lebensmittel, etc.*, 1896, 441.
[2] Capillary tube method.
[3] *Zeit. f. analyt. Chemie*, 1897, 8.

Physical and Chemical Constants of Hare Fat

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Hehner Value.		Reichert Value.		Iodine Value.		Refractive Index.	
															Butyro-refracto-meter.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mrgms. KOH.	Observer.	Per cent.	Observer.	cc. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	At 40 °C.	Observer.
15	0·9349	Amthor and Zink	17-23[1]	A. and Z.	35-40[1]	A. and Z.	200·9	A. and Z.	95·2	A. and Z.	1·59	A. and Z.	102·2	A. and Z.	49	Drumel.
100	0·861	Drumel	28-30	Drumel	44-46	Drumel			95·5	Drumel	Reichert-Meissl Value.					
											2·64	Drumel				

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Refractive Index.	
										Butyro-refractometer.	
At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At 40 °C.	Observer.
0·9361	Amthor and Zink	36-40[1]	A. and Z.	44-47[1]	A. and Z.	209·0	A. and Z.	93·3	A. and Z.	36	Drumel
		39-41	Drumel	48-50	Drumel						

[1] Capillary tube method.

RABBIT FAT

French—*Graisse de lapin.* German—*Kaninchenfett.*

For tables of constants see p. 558.

This fat is of a dirty yellow colour, separating on standing into a liquid and a solid portion.

The fat from the wild rabbit differs very notably from that of the tame rabbit in the iodine value. On exposure to the atmosphere the fat from the wild animal dries after 7 days to a moderately solid varnish, becoming solid after 6 more days. After 50 days' exposure the iodine number was only 26. The fat from the tame animal does not exhibit drying properties.

The acid values of the wild rabbit fat and tame rabbit fat were 7·2 and 6·2 respectively.

Physical and Chemical Constants of Rabbit Fat

Source.	Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Hehner Value.		Reichert Value.		Iodine Value.		Refractive Index.	
	At °C.		Observer.	°C.	Observer.	°C.	Observer.	M'ms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	Butyro-refractometer. At 40° C.	Observer.
Wild Rabbit	15	0·9393	Amthor and Zink [1]	17-22 [2]	A. and Z.	35-38 [2]	A. and Z.	199·3	A. and Z.	..	..	0·7	A. and Z.	99·8	A. and Z.		
Tame Rabbit	15	0·9342	,,	22-24 [2]	,,	40-42 [2]	,,	202·6	,,	..	..	2·8	,,	67·6	,,		
												Reichert-Meissl Value.					
	100	0·861	Drumel [3]	28-30	Drumel	44-46	Drumel	..	..	95·5	Drumel	2·64	Drumel	..	..	49	Drumel

Physical and Chemical Constants of the Mixed Fatty Acids

Source.	Specific Gravity.		Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Refractive Index.	
	At °C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Butyro-refractometer. At 40° C.	Observer.
Wild Rabbit .	0·9246	Amthor and Zink	35-36 [2]	A. and Z.	39-41 [2]	A. and Z.	209·5	A. and Z.	101·1	A. and Z.		
Tame Rabbit .	0·9264	,,	37-39 [2]	,,	40-42 [2]	,,	218·1	,,	64·4	,,		
			39-41	Drumel	48-50	Drumel					36	Drumel

[1] *Zeit. f. analyt. Chemie*, 1897, 9.

[2] Capillary tube method.

[3] *Bulletin de l'Assoc. Belge*, 1896 (9), 323.

As a rule, the fat of domesticated animals is richer in olein than that of wild animals, but in this case as well as in that of the wild goose the reverse obtains.

GOOSE FAT

French—*Graisse d'oie.* German—*Gänsefett.*

For tables of constants see pp. 560, 561.

Goose fat is a semi-pellucid, pale yellow fat of granular consistency. It consists of olein, palmitin, stearin, and small quantities of caprin.

The proportion of soluble fatty acids varies, according to *Young*, from 0·7 to 3·5 per cent, calculated as oleic acid.

There are added in the table some constants of the fat from the wild goose; from the iodine value it would follow that the wild animal's fat is richer in olein than that of the domesticated goose.

Physical and Chemical Constants of Goose Fat

	Specific Gravity.			Solidifying Point.		Melting Point.		Hehner Value.	
	At °C.		Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.
Domesticated goose	37·8 (water at 37·8 = 1)	0·909	Young	18 rising to 22	Schaedler	25-26	Schaedler	95·88	Bensemann
,,	15	0·9229-0·9300	Rözsényi	18·1-18·4	Rözsényi	33-34	Bensemann	92·4-95·7	Young
,,	...	...	...	...	...	27·5-31·7	Rözsényi	94·5-95·3	Rözsényi
,,	15	0·9274	Amthor and Zink	18-20	Amthor and Zink	32-34	Amthor and Zink	...	...
Wild goose . .	...	...	...	18-20	,,				
Wild goose, 2 years in captivity	15	0·9158	,,						

Physical and Chemical Constants of Goose Fat—continued

	Saponification Value.		Reichert Value.		Iodine Value.		Refractive Index. Butyro-refractometer.	
	Mgrms. KOH.	Observer.	1/10 c.c. norm. KOH.	Observer.	Per cent.	Observer.	At 40° C.	Observer.
Domesticated goose	192·6	Valenta	0·98	Amthor and Zink	71·5	Erban and Spitzer	50-50·5	Rözsényi
,,	184-198	Young			58·7-66·4	Rözsényi		
,,	191·2-193	Rözsényi	Reichert-Meissl Value.					
,,	193·1	Amthor and Zink			67·6	Amthor and Zink		
Wild goose . .	...	...			99·6	,,		
Wild goose, 2 years in captivity	196	Amthor and Zink	0·2-0·3	Rözsényi	67·0	,,		

Physical and Chemical Constants of the Mixed Fatty Acids

	Specific Gravity.		Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.	
	At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
Domesticated goose .	...	...	...	...	37-38 and 40-41	Bensemann				
,, .	...	...	...	...	36·6-49·2	Rözsényi				
,, .	0·9257	Amthor and Zink	31-32	Amthor and Zink	38-40	Amthor and Zink	202·4	Amthor and Zink	65·3	Amthor and Zink
Wild goose . .	...	...	33-34	,,	34-40	,,				
Wild goose, 2 years in captivity . .	0·9251	Amthor and Zink	32	,,	36-38	,,	196·4	,,	65·1	,,

Human Fat

French—*Graisse d'homme.* German—*Menschenfett.*

Human fat has been examined by *Chevreul* and also by *Heintz;* but its examination by modern methods of fat analysis has only been undertaken recently by *Mitchell.*[1]

Physical and Chemical Constants of Human Fat

Specific Gravity.	Solidifying Point.	Melting Point.	Saponification Value.	Iodine Value.	Reichert Value.	Thermal Test.
At 25° C. (Water at 25° C. = 1.)	°C.	°C.	Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ norm. KOH.	Heat of Bromination.
0·9033	15	17·5	195	61·5	0·3	11·3° C.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.	Iodine Value.
°C.	°C.	Per cent.
30·5	35·5	64
		Iodine Value of the Liquid Fatty Acids. 92·1

The specimen examined was of pale yellow colour; its consistency was somewhat less than that of butter. On crystallisation from ether there was only a slight deposit of crystals, melting at 51·5° C.; under the microscope these crystals somewhat resembled those frequently obtained from flare lards.

A closer examination into the nature of the fatty acids, using Twitchell's modification of Jean's method (p. 202), led to the following results:—

	Per cent.	Iodine Value.	Melting Point.	Mean Molec. Weight.
			°C.	
Solid acids .	50·2	37	35·5	278
Liquid acids .	49·8 (by difference)	92	below 15	

No definite conclusions can be drawn from these numbers, chiefly because the "solid acids" contain too high a proportion of liquid acids.

[1] *Analyst*, 1896, 172.

LARD

French—*Saindoux.* German—*Schweinefett.*

For tables of constants see pp. 564-566.

Lard is the fat rendered from the leaf of the pig, *i.e.* the fat from the kidneys and the bowels. This is the fat sold as home-rendered lard. There are, however, enormous quantities of lard imported by the large American packing-houses (in Chicago and elsewhere) that does not represent lard as defined here. In the retail trade we find the following brands of American lard:—(1) The best quality "bladder lard," which should be or approaches lard proper; and (2) "Keg lard," containing also the fat from other parts of the animal. According to *Wiley*,[1] the following kinds of lard are known in the American packing-trade:—

(*a*) *Neutral Lard.*—This consists of the fat from the leaf of the slaughtered animal, rendered in a perfectly fresh state at a temperature from 40°-50° C. This lard is all but neutral, and is used almost exclusively for "oleomargarine."

(*b*) *Leaf Lard.*—The residue not rendered for neutral lard yields this fat on being subjected to steam heat under pressure. Formerly this was the only kind of lard recognised by the Chicago Board of Trade, and was then prepared from the whole leaf. "Bladder lard" is most likely "leaf lard."

(*c*) *Choice Lard, Choice Kettle-rendered Lard.*—This kind of lard is obtained from the remaining portions of the leaf (after the fat for oleomargarine (see *a*) has been rendered), together with the fat cut from the backs. It takes its name from the process, being rendered in steam-jacketed open kettles. According to the regulations of the Chicago Board of Trade, choice lard is defined as lard made from leaf and trimmings only, either steam or kettle rendered; the manner of rendering must be branded on each tierce.

(*d*) *Prime Steam Lard.*—This is defined thus: Standard prime steam lard is the product of the trimmings and other fat parts of hogs, rendered in tanks by the direct application of steam, etc. This lard is passed solely on inspection, and as the inspector has no authority enabling him to supervise rendering establishments, in order to secure a proper control, we may take it that prime steam lard consists of the fat from any part of the hog, either from the whole animal or from portions of it.

A lower quality still is made from "*guts*" only.

Lard possesses a granular texture and a salve-like consistency. It has a pure white colour and an agreeable taste.

[1] Lard and Lard Adulterations, U.S. Department of Agriculture, Bulletin No. 13, Part iv.

Physical and Chemical Constants of Lard

Specific Gravity.			Solidifying Point.		Melting Point.		Hehner Value.	
°C.		Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.
15	0·931-0·932	Hager	27·1-29·9	Goske	40·5	Buff	96·15	West Knights
,,	0·934-0·938	Dieterich			41·5-42	Wimmel	95·8	Bensemann
40	0·8985	Allen			42-48	Koenigs	93-95	Wiley
(water at 15·5 = 1)					45-46	Bensemann		
50	0·8818	Saussure			36-45·5	Dieterich		
,,	0·890	Bockairy						
,,	0·89159-0·90038	Fairley and Cooke						
(water at 50 = 1)								
69	0·8811	Saussure						
90	0·894-0·897	Dieterich						
94	0·8628	Saussure						
98-99	0·8608	Allen						
(water at 15·1 = 1)								
100	0·861	Koenigs						
(water at 15 = 1)								
100	0·8610-0·8614	Gladding						
100	0·8589-0·8641 [1]	Dennstedt & Voigtländer						
(water at 15° C. = 1)	(American)							
		Fat from Wild Boar						
15	0·9424	Amthor and Zink	22-23	Amthor and Zink	40-44	Amthor and Zink		

[1] Exceptionally 0·8700 in one case.

Physical and Chemical Constants of Lard—continued.

Saponification Value.		Reichert Value.		Iodine Value.		Maumené Test.		Refractive Index.	
Mgrms. KOH.	Observer.	$\frac{1}{10}$ c.c. norm. KOH.	Observer.	Per cent.	Observer.			At 60° C.	Observer.
195·8	Köttstorfer			59	Hübl	(See Table, p. 576.)		1·4539	Thoerner.
195·3-196·6	Valenta			57·1-60	Wilson				
				49·9-63·8	Dieterich			Oleo-refractometer.	
				56·9-59	Engler and Rupp				
				62·4 (American)	Schweitzer and Lungwitz			"Degrees."	Observer.
				60·4-70·4 (American)	Raumer			−12·5	Jean
				59-68·4 (American)	Dennstedt and Voigtländer		Butyro-refractometer.		
				55 (European)	,,		At °C.	At 40° C.	Observer.
				(Cp. also pp. 572-575.)			40	48·6-51·2	Mansfeld
							,,	44·8-53	Dennstedt and Voigtländer
							25	56·8-58·5	Spaeth
			Fat from	*Wild Boar*					
195·1	Amthor and Zink.	0·68	Amthor and Zink.	76·6	Amthor and Zink.				

Physical and Chemical Constants of the Mixed Fatty Acids

	Specific Gravity.			Solidifying Point.		Melting Point.		Mean Molecular Weight.		Iodine Value.		Thermal Test. Heat of Bromination.		Refractive Index.	
	°C.		Observer.	°C.	Observer.	°C.	Observer.		Observer.	Per cent.	Observer.	°C.	Observer.	At 60 °C.	Observer.
	99° (water 15·5=1)	0·8445	Allen	34 39 39 41·45-42 (Titer test)	Mayer Allen Terreil Lewko-witsch	35 44 43 43-44 and 46-47	Mayer Allen Terreil Bense-mann	278	Allen	64·2	Williams	10·4-11	Hehner and Mitchell	1·4395	Thoerner
										Iodine Value of the Liquid Fatty Acids.				Oleo-refractometer.	
										89·4-90·7 (European) 93-96 (European) 103-105 (American) 96·9-103·2 (American)	Dieterich Wallen-stein and Finck v. Raumer			'Degrees.'	Observer.
														−30	Jean
										Fatty Acids.					
Wild boar	15	0·9333	Amthor and Zink	32·5-33·5	Amthor and Zink	39-40	Amthor and Zink	275·5[1]	Amthor and Zink	81·2	Amthor and Zink				

[1] Calculated from saponific. value 203·6.

Lard consists of the glycerides of palmitic, stearic, and oleic acids, and smaller quantities of linolic acid. The proportion of stearic acid in a number of commercial lards determined by *Hehner* and *Mitchell's* method,[1] varied between 6 and 16 per cent. The statement made by *Fahrion*, viz. that lard contained linolic acid (in contradiction of *Benedikt* and *Hazura's* experiments) is confirmed by the fact that the liquid fatty acids of lards, especially of American lards, have iodine values varying from 93-106. *Twitchell* calculated the composition of the mixed fatty acids from a specimen of American lard as follows:—

Linolic acid	10·06 per cent.
Oleic acid	49·39 ,,
Solid acids, by difference . .	48·55 ,,

The analytical differences between the lards from the different parts of the hog are summarised in the following tables. As there are important differences between American and European lards, no doubt due to the mode of fattening, the writer will differentiate as far as possible between European and American lards.

European Lards

Fat from	Spec. Grav. at 100° C. (Water 15=1.)	Melting Point of Fat.	Melting Point of Fatty Acids.	Iodine Value of		Free Fatty Acids.		Observer.	Remarks.
				Fat.	Fatty Acids.	c.c. norm. KOH per 100 Grms.	Calculated to Oleic Acid.		
		°C.	°C.				Per cent.		
Back .	0·8607	33·8	40	60·58	61·90	0·54	0·152	Spaeth	Mean results from examination of fats from 8 animals.
Kidney.	0·8590	43·2	43·2	52·60	54·20	0·58	0·163		
Leaf. .	0·8588	44·5	42·9	53·10	54·40	1·28	0·360		

[1] *Analyst*, 1896, 326.

[TABLE

American Lards

Fat from	Specific Gravity at 100° C. (Water at 15° C=1.)	Iodine Value.	Maumené Test at 40° C.	Melting Point: Bensemann's Method.		Refractive Index.	Observer.
				Drop formed at °C.	Melted to a clear drop.	Butyro-refractometer at 40° C.	
						"Degrees."	
Head	0·8637	66·2	33	24	44·8	52·6	Dennstedt and Voigtländer
	0·8629	66·6	32	24	44·8	52·5	
	0·8631	65·0	34	24	45·0	52·0	
Back	0·8611	61·5	37	28·5	48·5	52·4	
	0·8621	65·0	35	28·5	48·5	51·8	
	0·8616	65·1	38	31·5	46·0	51·9	
Leaf	0·8637	62·2	..	26	45	51·4	
	0·8615	59·0	..	29	44	50·2	
	0·8700	63·0	30	28·5	44·5	52·0	
Foot	0·8589	68·8	..	24	40	44·8	
Ham	0·8641	68·4	38	26	45	51·9	
	0·8615	66·6	..	26	44	51·9	
	0·8628	68·3	..	26	44·5	53·0	
Ham (German)	0·8597	55·0	30	32	46	49·2	

As a corollary to these tables, I add the following table, due to *Hehner* and *Mitchell*,[1] setting out the percentages of stearic acid in lards taken from various parts of a pig (Somersetshire, six months old) :—

Fat from	Melting Point. °C.	Iodine Absorption.	Stearic Acid.	
			Per cent.	Melting Point. °C.
Head	34·8	67·7	8·67-9·47	67·8-66·2
Ham	34·6	61·6	8·74-9·02	67·5-67·3
Breast	36·8	64·2	11·84-10·9	67·2-66·8
Flare	40·0	52·8	15·7-14·4	66·5-67·2
Back	35·6	67·9	8·59-9·2	67-66·5

Pure lard may be said to be almost free from unsaponifiable matter, *Allen* and *Thomson* having obtained 0·23 per cent only.

Freshly-rendered lard is almost neutral; determinations made by several chemists gave the following numbers :—

Free Fatty Acids as Oleic Acid.	No. of Samples.	Observer.
Per cent.		
0·280-0·420	?	Dieterich
0·350-1·000	12	Wiley
0·098-0·564	24	Spaeth

[1] *Analyst*, 1896, 326.

The increase of acidity on exposure to air in loosely-corked flasks is numerically shown in the following table, together with the alterations of the iodine number (*Spaeth*) :—

No.	Free Fatty Acids, c.c. norm. KOH per 100 grms.			Iodine Values.		
	Freshly rendered.	After one year.	After three years.	Freshly rendered.	After one year.	After three years.
1	0·6	6·4	32·0	63·25	53·80	39·26
2	0·45	2·75	23·0	61·15	55·45	39·37
3	0·75	7·80	31·6	62·90	51·85	39·56
4	0·80	11·60	50·0	62·95	48·80	29·41
5	1·25	6·70	36·0	57·25	49·40	26·51
6	0·35	6·00	30·0	55·88	47·80	31·19
7	0·45	8·40	23·0	60·10	51·04	41·08
8	0·55	21·20	41·3	55·80	37·50	22·97
9	1·45	1·80	10·0	52·30	52·20	40·91
10	0·55	9·60	30·0	57·08	46·70	33·69
11	1·60	15·40	46·0	51·75	36·71	21·56
12	0·65	9·60	33·0	63·61	49·00	38·04
13	0·60	4·20	18·0	52·35	46·85	36·48
14	0·50	7·60	32·0	60·95	52·72	36·03

The free fatty acids were separated by washing the lards with hot water into soluble and insoluble acids. Their relative proportions were measured by the amounts of normal alkali required to saturate the free acids. The following table gives the details :—

No.	Free Fatty Acids after three years' exposure.	Soluble Fatty Acids.	Insoluble Fatty Acids.[1]
	c.c. normal Alkali per 100 grms.	c.c. normal Alkali per 100 grms.	c.c. normal Alkali per 100 grms.
1	32·0	4·5	27·5
2	23·0	4·7	18·3
3	31·6	4·2	27·4
4	50·0	8·1	41·9
5	36·0	6·6	29·4
6	30·0	4·0	26·0
7	23·0	3·4	29·6
8	41·3	7·4	33·9
9	10·0	1·9	8·1
10	30·0	3·9	26·1
11	46·0	7·1	38·9
12	33·0	4·1	28·9
13	18·0	2·1	15·9
14	32·0	4·4	27·6

[1] Evidently found by difference.

Lard, like butter and olive oil, is adulterated on the largest scale, with beef fat, cotton seed oil, etc., and in America adulteration has become an openly acknowledged practice, nay, it has even been claimed that the addition of cotton seed oil constitutes an improvement in the manufacture. Thus the American brand "refined lard" was found to be a mixture of lard with cotton seed oil and a sufficient quantity of beef stearine, etc., to obtain the consistency possessed by pure lard.

Owing to the interference of the law in this and other countries, the name "refined lard" has been abandoned, and has been replaced by such terms as "compound lard" or "lard compound." Some of these artificial preparations do not even contain any lard at all, being judiciously prepared mixtures of beef stearine and cotton seed oil or cotton seed stearine.

Water which was often used as an adulterant is, at any rate in American lards, not common, no doubt because it is too easily detected. The same holds good of other adulterants that will be mentioned under tallow (p. 596). Adulterations of this kind, as perhaps also the addition of arachis oil (*Wiley*), may be practised on a small scale, but are of little importance commercially.

According to *Hehner*,[1] however, cotton seed oil is now but rarely met with in lard, although the iodine value has increased, and it appears, therefore, that other vegetable oils, perhaps arachis, sesamé, and especially maize oil, are being substituted for cotton seed oil.

We shall consider here chiefly the sophistication with vegetable oils, notably cotton seed oil (cotton seed stearine), and beef stearine. With regard to the latter it should be mentioned that the admixture of 5 per cent beef stearine, as a "stiffener," is openly advocated by the trade as a necessary operation.

Artificial lard, that is, a product prepared from vegetable oils (cotton seed oil, arachis oil, etc.) and beef stearine, solidifies, according to *Langfurth*, to a coarsely crystalline mass, exhibiting a more or less polished surface, whereas genuine lard, whether crude or refined, shows a finely crystalline texture and a dull wrinkled surface. This observation has been re-stated by *Soltsien*.[2] But very little importance should be allowed to indications of this kind.

The following physical and chemical constants may be used in the detection of adulterants in lard :—

Specific Gravity.—The determination of the specific gravity can only be considered as a useful corroboration of other tests, since some of the usual adulterants have nearly the same specific gravity as pure lard.

Cotton seed oil, however, raises the specific gravity, as also does arachis oil. Therefore a sample having a higher specific gravity than 0·861 at 100° C. may be considered suspicious. *Langfurth* recommends to wrap about 1000 grms. of the lard under examination in strong linen and slowly press at the ordinary temperature, when the filtered

[1] *Jour. Soc. Chem. Ind.* 1889, 123. [2] *Pharm. Ztg.* 1894, 350.

oil should be examined. Pure lard oil has a specific gravity of 0·912-0·914 at 18° C., whereas, in the case of artificial lards, the expressed oil, if amounting to 30-40 per cent, will have a specific gravity of 0·916-0·918 at 18° C. The same proposal has been repeated by *Wainwright*.[1]

The following table contains some specific gravities, reference to which will be found useful :—

Specific Gravity of Lard, Lard Adulterants, and Adulterated Lards

Kind of Fat.	Specific Gravity at °C.			Observer.
	37·8° (100° F.) (Water 37·8=1.)	99° (Water 15·5=1.)	100° (Water 40=1.)	
Pure lard . . .	0·905-0·907	0·860-0·861	0·85997-0·86191	Allen, Pattinson, Crampton
Lard stearine . .	..	..	0·8575-0·85792	Crampton
Cotton seed oil . .	..	0·868-0·8725	0·8672	Pattinson, Allen
,, . .	..	..	0·86681-0·86774	Leone and Longi
Cotton seed stearine	0·911-0·912	..	0·86463	Allen, Crampton
Beef stearine . .	..	0·8570	0·85444-0·85888	Pattinson, Crampton
Arachis oil . .	..	0·8673	..	Allen
Cocoa nut oil . .	0·910-0·916	0·8736	..	,,
Armour's compound lard . . .	..	..	0·86121-0·86222	Crampton
Fairbanks' ,, ,,	..	..	0·86289	,,

Fairley and *Cooke*[2] have prepared the following mixtures of lard and cotton seed oil, and determined the specific gravities at 50° C. :—

	I. Lard, 0·90038 ; Cotton Seed Oil, 0·90879.	II. Lard, 0·89159 ; Cotton Seed Oil, 0·89992.
Lard with 10 per cent of cotton seed oil .	0·90116	0·89246
,, 20 ,, ,, ,, .	0·90209	0·89328
,, 30 ,, ,, ,, .	0·90302	0·89421
,, 50 ,, ,, ,, .	0·90494	0·89617
,, 75 ,, ,, ,, .	0·90736	0·89850

Melting Point.—Although the melting point of the fat is not of itself of great importance, many adulterated lards having the same melting points as pure lard, still its determination should never be neglected. In the case of unadulterated pig's fat it is possible to ascertain from what part of the body the fat has been rendered ; as will be seen by a glance at the following table :—

[1] *Jour. Soc. Chem. Ind.* 1896, 620. [2] *Ibid.* 1890, 1162.

Melting Points of Lards from different parts of Hogs—American and European

Source.	Fat from	Melting Point. °C.	Observer.[1]
American .	Foot	35·1	Wiley
	Head	35·5	,,
	Back		
	Kidney		
	Leaf		
	Leg	42·5	,,
	Ham	44·5	,,
European .	Back	33·8	Spaeth
	Kidney	43·2	,,
	Leaf	44	,,

Goske[2] takes the solidifying point of the lard in a manner identical with that employed in *Dalican's* titer test. The following table contains his numbers :—

Fat.		Solidifying Point. °C.
Home-rendered lard	European .	27·10-28·62
,, ,, .	,, .	26·64-29·34
,, ,, .	,, .	29·10-29·95
Pure steam lard .	American .	24·10-26·00
,, ,, .	,, .	25·05-25·5
,, ,, .	,, .	26·40-27·06
,, ,, .	,, .	24·9
,, ,, .	,, .	23·67-26·18
Adulterated lard .	. . .	30·50
,, ,, .	. . .	29·73-29·80
,, ,, .	. . .	29·90-30·15
,, ,, .	. . .	31·95-33·00
,, ,, .	. . .	35·90-36·58
,, ,, .	. . .	35·50-35·75

In this table account is only taken of adulteration with tallow, the presence of which is masked by addition of lard oil.

The solidifying point of the fatty acids would not be of much use in the case of adulteration with cotton seed oil; maize oil and other vegetable oils, however, if present in not too small quantities, may thus be indicated. *Fresenius*[3] believes that positive results may be obtained with the help of his "Thermo-table."

Iodine Value.—Pure lard should not absorb more than 63 per cent, and not less than 46 per cent of iodine. A sample, the iodine value of which falls outside of this range, must be considered as adulterated or at best as inferior lard (see table, p. 573). Of course, the converse does not follow that a sample having a normal absorption must be pure, as the combinations of fats of low (tallow, cocoa nut oil) and high absorptions (cotton seed, arachis, maize oils) enable the

[1] Cp. also Dennstedt and Voigtländer's table, p. 568. [2] *Jour. Soc. Chem. Ind.* 1893, 470. [3] *Chem. Ztg.* 1896, 130. 151.

adulterator to prepare a variety of mixtures which will satisfy the limits laid down above. *Therefore a normal iodine absorption cannot be considered of itself as a final test.* Thus in the case of artificial lards made from steam lard, tallow stearine, and lard oil, to the exclusion of vegetable oils, the iodine value will as a rule be about correct. The following table, due to *Goske*, gives the iodine values of several artificial lards calculated from those of its components, assuming the following iodine numbers for the latter: beef stearine, 20; steam lard, 65; mutton tallow, 40; lard oil, 85.

Fat No.	Beef Stearine.	Steam Lard.	Mutton Tallow.	Lard Oil.	Calculated Iodine Value.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1	10	90	...	...	60·5
2	15	85	...	...	58·25
3	...	70	30	...	57·50
4	25	45	...	30	59·75
5	35	25	40	...	57·27

The influence of exposure on the iodine value of lard may be gathered from the table, p. 569.

As will be seen from the following table, it is possible, if adulterations with foreign fats be excluded, to ascertain by means of the iodine value from what part of the animal the lard has been derived :—

Source.	Fat from	Iodine Value.	Observer.
American .	Head	85·03	Wiley
		66·2-70·4	v. Raumer
		65·0-66·6	Dennstedt and Voigtländer
		63	Dupont
	Foot	77·28	Wiley
		69·5-69·6	v. Raumer
		65	Dupont
	Back	63·6-66·7	v. Raumer
		61·5-65·1	Dennstedt and Voigtländer
		61	Dupont
	Leaf	58	Dupont
		53·1	Spaeth
		52·55	Wiley
		60·4-66·7	v. Raumer
		59-63	Dennstedt and Voigtländer
	Ham	67·7-69·0	v. Raumer
		66·6-68·4	Dennstedt and Voigtländer
	Gut lard	60	Dupont
European .	Back	53·0-58·5	v. Raumer
		61·7	,,
	Leaf	50·4	v. Raumer
	Ham	55·0	Dennstedt and Voigtländer

Steam lard, consisting as it does of the mixed fats from all or at least various parts of the animal, may therefore in some cases have a normal value, say up to 63, in other cases it may absorb more iodine. *Wiley* has found the iodine value of steam lards to vary from 60·34 to 66·37.

Whereas, considering the very wide limits between 46 and 63, which some chemists even wish to see extended in an upward direction, the iodine value of the **fat** affords but indefinite information; by far more certain results are furnished by the determination of the iodine value of the **liquid fatty** acids. In the present state of our knowledge this is the only *reliable* method for ascertaining admixture of vegetable oils and fats with lard. From the general table given above we gather that in the case of European lards the iodine values of the liquid fatty acids vary between 90 and 96, and in the case of American lards between 97 and 106; therefore the highest limits permissible should be 96 for European lards, and 106 for American lards. If, therefore, the iodine value of the liquid fatty acids of a sample be found to lie above these limits, adulteration with a vegetable oil is proved; if much below these limits, admixture with cocoa nut oil or palm kernel oil must be assumed.

In order to emphasise this point, I give here the following table:—

Fat or Oil.	Iodine Value of		Observer.
	Fat.	Liquid Fatty Acids.	
Lard, "Western Steam Lard"	65·4	104·5	Wallenstein and Finck[1]
,, Berlin	52·7	96·6	,,
,, Vienna	60·9	95·2	,,
,, Hungarian	60·4	96·2	,,
,, Roumanian	59·5	96·0	,,
,, Bavarian (5 samples)	52·2-61·2	92·8-96·6	v. Raumer[2]
Beef tallow, Australian	38·3	92-2	Wallenstein and Finck
,, Berlin	45·2	92·4	,,
,, Hungarian	38·6	92·7	,,
Cotton seed oil, American, white	108·0	147·5	,,
,, ,, ,, yellow	107·8	147·3	,,
,, ,, Egyptian, bleached	106·5	146·8	,,
,, ,, ,, yellow	108·0	148·2	,,
,, ,, Peruvian	106·8	147·8	,,
Niger Seed oil	133·5	147·5	,,
Maize oil	122·0	140·7	,,
Arachis oil	98·9	128·5	,,
Rape oil	101·1	120·7	,,
Cocoa nut oil	8·0	54·0	,,

[1] *Jour. Soc. Chem. Ind.* 1894, 79. [2] *Zeits. f. angew. Chemie*, 1897, 210.

The following table, due to *v. Raumer*,[1] gives a comparison of iodine values of lards from various parts of the hog (American), and of their liquid fatty acids :—

American Lards (*v. Raumer*)

Fat from	Iodine Value of	
	Fat.	Liquid Fatty Acids.
Head I. . . .	70·0-70·4	102·4
,, II. . . .	66·2-66·4	97·8-97·6
,, III. . . .	68·2-68·4	101·2
Back I.	64·6-64·9	101·6-101·0
,, II. . . .	63·6-63·6	102·8-102·3
,, III. . . .	66·7-66·5	101·1-100·6
Leaf I.	66·4-66·7	103·0-102·6
,, II. . . .	62·7-62·9	97·8-97·8
,, III. . . .	60·7-60·4	96·9
Foot	69·5-69·6	98·6-98·3
Ham I. . . .	67·9-67·9	101·6-101·0
,, II. . . .	67·9-67·7	99·9-100·2
,, III. . . .	68·7-69·0	103·0-103·2

If, *e.g.*, tallow were mixed with so much cotton seed oil as is required to produce a fat of the consistency of lard—33 per cent—the iodine value of the liquid fatty acids would be 113·7-114·1 (*v. Raumer*).

It must, however, be understood that if the iodine value of a sample under examination is found within the permissible limits, the lard cannot be reported yet as unadulterated.

For on the one hand the proportion of any admixed vegetable oil may have been compensated by cocoa nut oil (the taste of the desired product permitting) or to some smaller extent by beef tallow.

The test will, therefore, have to be supplemented in suspected cases by special tests for cocoa nut oil and tallow (see below). With regard to methods for the approximate quantitative determination of vegetable oils, see " Edible Fats," chap. xii. p. 683.

Thermal Tests.—As a preliminary test the rise of temperature on treating with concentrated sulphuric acid or with bromine will be found to furnish useful results in a short time ; this holds especially good of the second method.

Maumené Test.—The rise of temperature found on mixing the sample with sulphuric acid has been recommended for the detection and even approximate estimation of cotton seed oil in lard by *Hehner*, *Ambühl*, *Wiley*, and *Engler* and *Rupp*, whereas *Williams* failed to obtain decisive results.

The rise of temperature obtained by different experimenters has been stated so differently, that the safest plan will be to make comparative tests with pure specimens of lard and cotton seed oil before examining the sample. It need hardly be said that the sample must be thoroughly dry before testing. The following table contains a few values given by the observers named :—

[1] *Zeits. f. angew. Chemie*, 1897, 210.

Fat.	Observer.	Rise of Temp. °C.	Method Employed.
Lard	Hehner	24-27·5	50 grms. of fat; 10 c.c. conc. H_2SO_4
Cotton seed oil	,,	70	,, ,, ,,
Lard	Ambühl	13-15	,, ,, ,, initial temp. 40° C.
Cotton seed oil	,,	50-52	,, ,, ,, ,, ,, ,,
"American" lard	,,	30-35	,, ,, ,, ,, ,, ,,
Lard	Wiley	41·5	,, ,, ,, ,, ,, 35° C.
Cotton seed oil	,,	85·4	,, ,, ,, ,, ,, ,,
Steam lard	,,	38·8-42·1	,, ,, ,, ,, ,, ,,
"Oleostearine"	,,	20·8	,, ,, ,, ,, ,, ,,
Lard stearine	,,	37·7	,, ,, ,, ,, ,, ,,
Artificial lards	,,	42·1-58·9	,, ,, ,, ,, ,, ,,
,, ,,	,,	51·3-68·8	,, ,, ,, ,, ,, ,,
Lard	Engler and Rupp	31-32	,, ,, ,, ,, ,, not stated
Cotton seed oil	,,	81	,, ,, ,, ,, ,, ,,
Lard with 10 per cent of cotton seed oil	,,	34	,, ,, ,, ,, ,, ,,
,, ,, 20 ,,	,,	40-42	,, ,, ,, ,, ,, ,,
,, ,, 50 ,,	,,	58	,, ,, ,, ,, ,, ,,
Lard	Schweitzer and Lungwitz	35	,, ,, ,,[1] ,, ,, 35° C.
Lard oil		45·3	,, ,, ,, ,, ,, ,,
"Oleostearine"	,,	31·9	,, ,, ,, ,, ,, 45° C.
Cotton seed oil	,,	61·5	,, ,, ,, ,, ,, 35° C.
Armour's compounded lard	,,	58·0	,, ,, ,, ,, ,, ,,
Tallow	,,	31·6	,, ,, ,, ,, ,, 45° C.

[1] Acid of 100 per cent H_2SO_4, prepared by mixing fuming acid with conc. commercial acid.

In order to obtain more decisive results the liquid portion obtained by expression may be examined as well (*Langfurth*).

Heat of Bromination.—The following numbers were obtained by *Hehner* and *Mitchell*;[1] the iodine values calculated from the temperatures observed are collated with those actually found by experiments with Hübl's solution :—

Fat.	I. Heat of Bromination. Rise of Temperature.	II. Iodine Value. Experiment.	III. Iodine Value calculated from I.
	°C.	Per cent.	Per cent.
Lard No. 1	10·6	57·15	58·3
,, 2	10·4	57·13	57·2
,, 3	11·2	63·11	61·6
,, 4	11·2	61·49	61·6
,, 5	11·8	54·69	64·9
,, 6	11·8	63·96	64·9
,, 7	10·2	57·15	56·1
,, 8	10·4	57·80	57·2
,, 9	9·0	50·38	49·5
,, 10	11·0	58·84	60·5
Lard +10 per cent cotton seed oil .	11·6	64·13	63·8

Refractometric Examination.—*Amagat* and *Jean* state that adulterations with tallow, cocoa nut oil, and cotton seed oil are easily recognised by means of the oleo-refractometer. Although not absolutely reliable, and, indeed, in some cases valueless, as in that of lard mixed with 10 per cent of beef tallow, this method may be employed in conjunction with others as a preliminary or as a corroborative test in doubtful cases. The numbers recorded in the following table may therefore be found useful :—

[1] *Jour. Soc. Chem. Ind.* 1897, 88.

[TABLE

Kind of Fat or Oil.	"Degrees" in the Oleo-refractometer.	
	Fat.	Fatty Acids.
Lard, pure	−12·5	−30
Steam lard	−13	−30
Lard stearine	−10 to −11	
Beef tallow	−16 ; −17	−40
,, stearine	−34	
Veal ,,	−19	
Cotton seed oil	+20	+10
,, stearine	+25	+20
Sesamé oil	...	−18
Arachis oil	−15	
Lard with 10 per cent of beef tallow	−12	
,, ,, 20 ,, ,, ,,	−13	
,, ,, 50 ,, ,, ,,	−14	−33
,, ,, 5 ,, cotton seed oil	−10	
,, ,, 10 ,, ,, ,,	− 8	
,, ,, 15 ,, ,, ,,	− 7	
,, ,, 20 ,, ,, ,,	− 6	
,, ,, 25 ,, ,, ,,	− 5	
,, ,, 30 ,, ,, ,,	− 4	
,, ,, 40 ,, ,, ,,	− 0	
,, ,, 50 ,, ,, ,,	− 3	
,, ,, 5 ,, ,, stearine	−11	
,, ,, 10 ,, ,, ,,	− 7	
,, ,, 20 ,, ,, ,,	− 4	
,, ,, 30 ,, ,, ,,	− 3	
,, ,, 40 ,, ,, ,,	− 2	
,, ,, 50 ,, ,, ,,	+ 1	
Lard with 20 per cent of arachis oil	− 8	−23
,, ,, 20 ,, sesamé ,,	...	−20
,, 40 per cent ; beef tallow 40 per cent ; cotton seed oil 20 per cent	...	−24
Steam lard 60 per cent ; beef tallow 15 per cent ; arachis oil 25 per cent	− 8	
Lard 60 per cent ; mutton tallow 25 per cent ; arachis oil 15 per cent	−13	−22
Cocoa nut oil	−54	

From the following table, due to *Dupont*,[1] it will be seen that the American lards show less deviation than the European lards, and if judged solely by the standard of European lards, they might be rashly condemned as containing cotton seed oil :—

American Lard.	Oleo-refractometer "Degrees."	Iodine value.
From leaf	−11·5	58
,, back	−5	61
,, intestines	−7	62
,, head	−7	63
,, foot	−4	65
Gut lard	−11	60
Rancid lard	−7	63
Sour lard	−6·5	64

[1] *Jour. Soc. Chem. Ind.* 1895, 828.

The difference between European and American lards is not quite so distinctly shown in the refractometric constants as in the iodine absorption. A glance at the following table proves this :—

Refractive Indices determined by means of the Butyro-refractometer.

Kind of Fat.	European.		American.	
	Scale Divisions at 40° C.	Observer.	Scale Divisions at 40° C.	Observer.
Lard from head . .	...	...	52-52·6	Dennstedt & Voigtländer
,, ,, back . .	50·2-50·4	Mansfeld	51·8-52·4	,,
,, ,, leaf . .	51·2	,,	50·2-52	,,
,, ,, outer part of leaf . . .	50·7	,,		
,, ,, belly . .	50·4	,,		
,, ,, intestines .	49·0	,,		
,, ,, foot . .	...	...	44·8	,,
,, ,, ham . .	...	...	51·9-53	,,
Beef tallow . . .	49·0			
Horse fat . . .	53·7			
Cocoa nut oil . .	35·5			
Cotton seed oil . .	61			

The influence of rancidity on the refractometric constant is illustrated by the numbers given in the following table ; they are collated with the Reichert-Meissl values (*Spaeth*) :—

Deviation in the Butyro-refractometer calculated for 25° C.		Reichert-Meissl Values.
After 1 year.	After 3 years.	After 3 years.
59·35	62·60	...
60·21	62·30	4·3
60·49	62·45	9·36
57·71	58·75	1·32
60·35	62·70	...
61·35	63·10	...
58·14	63·1	3·74

Whereas adulteration with vegetable oils and fats can be detected with certainty, the recognition of beef tallow, oleomargarine, and beef stearine, presents considerable difficulties, the more so as small quantities down to 5 per cent repay the cost entailed in the mixing.

I shall indicate in the following lines special methods for the detection of the more important adulterants.

Seed Oils.—The phospho-molybdic acid test (p. 316) has been recommended by several observers as indicating presence of vegetable oils in lard with certainty. The writer has, however, shown[1] that, on the one hand, a slightly rancid lard also reduces the reagent, and, on the other hand, that an admixture of less than 15 per cent of cotton seed oil with pure lard cannot be thus detected. This test can therefore only be admitted as a preliminary one. The writer's experiments have since been confirmed by *Samelson* and *Tennille*. The surest proof for the presence of seed oils is obtained by the determination of the iodine value of the liquid fatty acids (see above). If the presence of a vegetable oil has been indicated by an abnormally high iodine value, one of the following four oils should be specially looked for :—Arachis oil, sesamé oil, cotton seed oil (cotton seed stearine), maize oil.

Arachis Oil.—Renard's test should give a positive result.

Sesamé Oil.—This would be detected readily by Baudouin's reaction.

Cotton Seed Oil.—The *nitric acid test* (p. 381) will afford very valuable corroboration of the results obtained by the iodine test, but it should be borne in mind that some lards undoubtedly give the brown colouration with nitric acid. Further corroboration will be given by *Becchi's* test if a positive reaction has been obtained (p. 382). It should, however, be remembered that even a brown colouration is not always absolute proof of presence of cotton seed oil, since *Wesson*[2] has obtained a brownish deposit due to silver sulphide with a sample of fresh hog's fat. His observation has been confirmed by *Mariani*, and, further, by *Bevan*,[3] who has found that lard exposed to the air for some time gave a strong reaction with silver nitrate. In the latter case, undoubtedly, a body of an aldehydic nature had been formed.

The following modifications of the silver nitrate test have been proposed with a view to the examination of adulterated lards :—

Pattinson[4] dissolves in a test-tube 40 drops of the melted lard in 10 c.c. of ether, and adds 2 c.c. of an alcoholic solution of silver nitrate (1 part of silver nitrate to 100 of alcohol). He allows the test-tube to stand for five to six hours in a place protected from light. If cotton seed oil is present, the silver is reduced, and the solution assumes a maroon colour, the depth of the colour depending on the proportion of cotton seed oil the sample contains.

Hehner omits the colza oil, using the silver nitrate reagent only (No. I. p. 382). He adds one volume of the silver solution to two volumes of the oil and heats for fifteen minutes.

Wesson[5] prepares his reagent by dissolving 2 grms. of silver nitrate in a mixture of 200 c.c. of 95 per cent alcohol and 40 c.c. of ether, and before using it he exposes it to sunlight for some time, and decants the clear liquid from the deposit. 5 c.c. of the reagent are shaken with 10 grms. of the melted lard in a cylindrical vessel of 60

[1] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1894, 619.
[2] *Jour. Chem. Soc.* 1894, Abstr. ii. 75.
[3] *Analyst*, 1894, 88.
[4] *Jour. Soc. Chem. Ind.* 1889, 30.
[5] *Jour. Chem. Soc.* 1894, Abstr. ii. 75.

c.c. capacity, and placed in a water-bath for fifteen minutes. Lard containing much cotton seed oil gives a mirror, the liquid at the same time assuming a dark greenish colour. In presence of small quantities of cotton seed oil the fat is said to become red, some metallic silver being deposited. Pure lard becomes only slightly darker and of a purple tint, with little or no separation of silver. Presence of cotton seed oil is only proved if metallic silver has separated.[1]

The test becomes safer if both the sample and the liquid portion, obtained from it on expressing the fat after it has been allowed to solidify by cooling slowly to 25°-30° C., are examined (*Goske*).

As has been stated already, cotton seed oil heated to 240° C. does not reduce silver nitrate. For the detection in lard of cotton seed oil which has been thus treated, *Crook*[2] recommends the following process :—

Ten grains—0·648 grm.—of the sample are placed in a cup-shaped porcelain capsule of about half an ounce capacity. A small disc of white filter paper (previously soaked in hydrochloric acid, washed, and dried) is just moistened with a 12 per cent solution of silver nitrate, and placed in the concave side of a watch-glass, which is then inverted over the capsule containing the sample. The capsule is then slowly heated in an oil-bath to 115° C., when the source of heat is immediately withdrawn. In presence of even less than 1 per cent of heated cotton seed oil, a very marked colouration appears on the disc, varying from a light brown to a nearly black. If the sample be pure and fresh no colouration is observed. In the writer's hands this method has proved to be worthless.

For other colour reactions for cotton seed oil, as *Hirschsohn's* and *Labiche's* test, cp. p. 384.

Cotton seed stearine can be detected by the increased specific gravity and the colour reactions for cotton seed oil. *Allen* recognises it by the adulterated lard remaining fluid for some time at a comparatively low temperature after having been melted, and when allowed to cool remaining softer than the original sample.

As lard gives a liquid product with **sulphur chloride**, soluble in carbon bisulphide, cotton seed oil may also be detected qualitatively by means of that reagent (*B. Warren*, *Jones*[3]). In the presence of cotton seed oil a hard mass partly insoluble in carbon bisulphide is produced.

I have tried this method and found it very useful indeed. My observations are given in the following table :—

[1] Schweitzer and Lungwitz (*Jour. Soc. Chem. Ind.* 1894, 615) recommend *Millian's* test (p. 383) as thoroughly reliable for the detection of cotton seed oil in lard, repeating *Millian's* statement that admixture with cotton seed oil down to 1 per cent is shown by the mirror-like precipitate of metallic silver.

[2] *Analyst*, 1893, 221.

[3] *Ibid.* 1888, 170.

Mixtures of Lard and Cotton Seed Oil

5 grms. of fat dissolved in 2 c.c. CS_2, added 2 c.c. S_2Cl_2, and placed on the water-bath

Lard. Per cent.	Cotton Seed Oil. Per cent.		Solubility of Product in Carbon-Bisulphide.
100	0	No reaction	Completely soluble
90	10	Thickens after 35 minutes	,, ,,
80	20	,, ,, 30 ,,	52 per cent ,,
70	30	,, ,, 26 ,,	39·6 ,, ,,
60	40	,, ,, 18 ,,	34·8 ,, ,,
50	50	Solid after 10 ,,	37·4 ,, ,,
40	60	,, ,, 8 ,,	30·6 ,, ,,
30	70	,, ,, 7 ,,	32·6 ,, ,,
20	80	,, ,, 6 ,,	30·0 ,, ,,
10	90	,, ,, 4 ,,	28·4 ,, ,,
0	100	,, ,, 3 ,,	24 ,, ,,

It will be best to test the sample side by side with pure lard, or better still, with mixtures of lard and cotton seed prepared in a similar fashion to that illustrated by the table.

Maize Oil.—If arachis and sesamé oils are absent a too high iodine value can then be due only to cotton seed oil or maize oil. The solidifying point of the mixed fatty acids would in this case lead to a decision if only one oil be present. If both are present this method breaks down.

Cocoa nut oil or palm kernel oil will be recognised by the high saponification value, and especially by the definite Reichert value of the sample. The search for cocoa nut oil may become necessary under the conditions pointed out above, *i.e.* if the iodine value of the lard or of the mixed fatty acids is abnormally low.

The detection of **tallow** and **beef stearine** is a difficult problem, and, at the present state of our knowledge, can only be solved successfully by strict comparison with samples of pure lard and of lard mixed with known proportions of the adulterant suspected. This problem is rendered all the more difficult as American steam lard behaves very differently from European home-rendered lard (*Goske*).

Beef stearine, when present in quantities of at least 10 per cent, may be detected, according to *Leopold Mayer*, by melting a somewhat large quantity in a capacious beaker and allowing it to stand at a temperature of 31° to 32° C. for 36 hours. Pure lard crystallises homogeneously from the bottom of the vessel upwards, whereas presence of beef stearine is said to be indicated by the appearance of crystals resembling cauliflower. This test will only have the value of a preliminary one.

Belfield dissolves the sample in ether, and examines the crystals from the ethereal solution under the microscope. Forty drops of the

melted lard are dissolved in 10 c.c. of ether in a test-tube and allowed to cool (*Pattinson*[1]). Should no crystals form, the cork is removed from the tube and a loose plug of cotton-wool substituted, when crystals will be obtained by the spontaneous evaporation of the ether. If the crystals have been formed too rapidly it is best to redissolve them by addition of more ether. Some of the crystals are then placed on an object-glass and examined microscopically. Crystals from pure lard usually form oblong plates, occasionally radiated, and have oblique terminals, whereas those from beef tallow form curved tufts somewhat of the shape of an "*f*." The difference in the shape of the crystals[2] is caused by the larger proportion of stearin in beef stearine. This has been proved experimentally by *Hehner* and *Mitchell*.[3]

Goske,[4] who uses this method, employs 1 grm. of lard, and allows the solution to crystallise at from 12°-13° C. (at 4° C. or below but rarely good crystals are obtained). Lard adulterated with beef stearine crystallises in small needles grouped in tufts radiating from centres. Lard stearine remaining in solution, plates are never observed in presence of beef stearine. *Goske* stated at first that 5 per cent of beef fat, or 15 per cent of mutton fat (which does not crystallise so well), may be safely detected. But later he admits that the question becomes complicated if for beef stearine oleomargarine is substituted. Besides, German home-rendered lard does not yield the crystalline plates, crystallising as it does in needles which are not readily discernible from those yielded by beef stearine under the same conditions. *Hehner*, however, rejected this method, as the stearine crystals from hog's caul-fat have the same appearance as beef stearine crystals. *Wallenstein*[5] considers this objection as irrelevant, since caul-fat alone is hardly brought into the market. He recommends in such cases to subject the crystals to a grinding action by pressing down the cover glass (which *Stock*, however, deprecates), when the oblique terminals are said to become distinctly visible.

Stock[6] compares the crystals obtained from an ethereal solution with those from two standard sets of mixtures, the first consisting of pure lard melting at 34°-35° C., with 5, 10, 15, and 20 per cent of beef stearine melting at 56° C.; the second of pure lard, of melting point 39°-40° C., with 5, 10, 15, and 20 per cent of beef fat melting at 50° C. *Stock* proceeds as follows:—The melting point of the sample is determined first by the capillary tube method. Suppose the melting point be found at 34° C., 3 c.c. of the melted fat are run into a graduated stoppered cylinder of 25 c.c. capacity, 21 c.c. of ether are added, and the fat dissolved at 20°-25° C. 3 c.c. of each of the first set of mixtures are treated in exactly the same way. The five cylinders are cooled down to 13° C., and allowed to remain at that temperature—particularly during the last hours—for twenty-four hours.

[1] *Jour. Soc. Chem. Ind.* 1888, 30.
[2] For photographs of characteristic crystals refer to *Lard and Lard Adulterations*, etc.
[3] *Analyst*, 1896, 328.
[4] *Jour. Soc. Chem. Ind.* 1893, 469.
[5] *Chem. Zeit.* 1894, 1189.
[6] *Analyst*, 1894, 2.

An approximate estimate as to the amount of the adulterant is arrived at by reading off the apparent volume of deposited crystals. The ether is then poured off as far as possible, and 10 c.c. of fresh ether at 13° C. are added in each case. The cylinders are again shaken, cooled as before, and the proportion of crystals read off. Finally, the contents of the cylinders are emptied into weighed shallow beakers, the ether drained off carefully, the mass allowed to dry for fifteen minutes at 10° C., and weighed. The weight obtained for the sample under examination is compared with the weight of crystals obtained from whichever of the standards comes nearest to it.

The second set of mixtures is used for samples with a higher melting point.

The actual presence of beef fat must then be proved by microscopical examination, using a 1-inch objective and the C eyepiece.

No sample of pure lard melting below 39° C. yielded more than 0·011 grm. of crystals under the above-stated conditions. A sample of the melting point 45·8° C. gave, however, 0·146 grm. of crystals.[1]

In the present state of our knowledge, *Stock's* modification of *Belfield's* method must be considered the best. Unfortunately, the form of crystals obtained from softer lards differs from those obtained from harder ones. According to *Hehner* and *Mitchell*[2] the former yield nothing but broad plates with pronounced chisel-shaped ends, whereas from the latter bunches of more pointed, though still chisel-edged, needles crystallise. On being repeatedly recrystallised from ether they become more and more needle-like, approaching the form of beef stearine crystals, until they become undistinguishable from them.

It may, therefore, be hoped that the direct determination of stearic acid will lead to practical results, for lards contain (see above p. 567) from 6-16 per cent of stearic acid, whereas beef stearine gave 50·19 per cent. More decisive results still will be obtained if the determination of stearic acid be carried out with the solid acids, freed from the liquid acids, so that the combination of the stearic acid and iodine tests should lead to decisive results.[3]

For the preparation of **lard oil** (French—*Huile de graisse;* German—*Schmalzoel*) "*prime steam lard*" is subjected to pressure in hydraulic presses. The press-cakes are **lard stearine** used for making "compound lard," and possess, therefore, a higher value than lard itself.

The expressed oil, *lard oil*, is used as an edible oil, and also as a high-class burning and lubricating oil. According to the pressure and the temperature employed, the solidifying point of lard oil will

[1] Gladding recently described his *modus operandi*, *Jour. Soc. Chem. Ind.* 1896, 560.

[2] *Analyst*, 1896, 328.

[3] A curious method to detect and determine the quantity of beef fat in lard is proposed by Balló, viz. to measure the amount of air enclosed in the melted fat; pure lard on solidifying is stated not to enclose any air, whereas pure beef fat encloses air (100 grms. about 6·5 to 8·8 c.c.) Balló is of the opinion that even 3 per cent of beef fat may be thus detected (*Jour. Soc. Chem. Ind.* 1897, 764).

vary, so that some specimens will deposit stearine at the ordinary temperature, or even solidify completely at 10°-12° C., whereas others do not deposit any crystals unless cooled to the freezing point.

The specific gravity of a sample examined by *Allen* was 0·915 at 15·5° C. According to the same author, the density of pure lard oil should not exceed 0·916 (0·920 according to *Schweitzer* and *Lungwitz*). If heavier, it is presumably adulterated with fish oil or a vegetable oil.

Long[1] gives the following table for the specific gravity of lard oil :—

C.	Specific Gravity.
18	0·9137
20	0·9122
25	0·9088
30	0·9053
35	0·9019

The iodine value of lard oil will, of course, vary considerably with the temperature and pressure employed in preparing it. Thus *Schweitzer* and *Lungwitz* find for several specimens from 67 to 79, whereas *Dupont* gives 80-82.

In the elaïdin test, in *Maumené's* test, and with nitric acid, lard oil behaves very much like olive oil.

Pure lard oil should be free from fatty acids. Adulterants, such as mineral oils or vegetable oils, may be detected by the quantitative reactions, and possibly also by colour reactions (cp. Cotton seed oil, Sesamé oil).

[1] *Amer. Chem. Jour.* 1888.

BEEF MARROW FAT

French—*Moëlle de bœuf.* German—*Rindermarkfett.*

Physical and Chemical Constants of Beef Marrow Fat

Specific Gravity.		Solidifying Point.		Melting Point.		Saponific. Value.		Reichert Value.		Iodine Value.	
At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.
0·9311-0·938	Zink	31-29	Zink	37-45	Zink	199·6 195·8-198·1	Lewkowitsch Zink	1·1	Zink	55·4 39·2-50·9	Lewkowitsch Zink

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Saponific. Value.		Iodine Value.	
At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
0·9300-0·9399	Zink	37·9-38 40-39	Lewkowitsch Zink	44-46	Zink	204·5	Zink	55·5	Lewkowitsch

Beef marrow fat is the fat from the marrow bones of cattle.

Medullic acid, stated by *Eylerts* to occur in beef marrow, is, according to *Thümmel*,[1] a mixture of palmitic and stearic acids.

A specimen of freshly rendered marrow fat had the acid value 1·6, and a specimen eight months old 1·9 (*Zink*).

Beef marrow fat is used in pharmacy, and for making pomades.

BONE FAT

French—*Suif d'os.* German—*Knochenfett.*

For tables of constants see p. 588.

Bone fat, if prepared from fresh bones by boiling, has a white to yellowish colour, and a faint odour and taste. Its consistency is that of butter. It does not readily turn rancid, and is for that reason a valuable lubricant.

Bone fat, as found in commerce, is usually recovered from old, partially putrid bones by either boiling with water or by extracting with solvents, such as petroleum ether.

The fat obtained by the latter process is dark brownish, and has a most unpleasant smell, which is very difficult to remove. It contains large quantities of free fatty acids, and the following impurities: Lime soap,[2] cholesterol, calcium lactate, calcium butyrate, hydrocarbons from the petroleum ether, and colouring substances.

Pure bone fat prepared by boiling with water is slightly brownish, and contains, besides neutral fat and free fatty acids, but small quantities of impurities.

The extracted fat is therefore far more difficult to bleach than the boiled out fat.

It should be borne in mind that in small manure works, where kitchen refuse is worked up, the kitchen grease is usually added to the bone fat.

Bone fat is chiefly used for candle-making and soap-making; its valuation is made like that of tallow (p. 596).

[1] *Berichte*, 1890, Ref. 493. [2] Cp. p. 749.

Physical and Chemical Constants of Bone Fat[1]

Specific Gravity.		Solidifying Point.		Melting Point.		Saponific. Value.		Iodine Value.	
At 15·5° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
0·914-0·916	Allen	15° rising to 17°	Schaedler	21-22	Schaedler	190·9	Valenta	46·3-49·6	Wilson
...	...	...	...	...	...	...	...	48-55·8	Valenta

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.		Saponific. Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.
28	Hübl	30	Hübl	57·4[2]	Morawski and Demski	200	Valenta
...	...	...	...	55·7-57·3[3]			

[1] Prepared by boiling out fresh bones. [2] Crude fat. [3] Refined fat.

Valenta[1] gives the following analyses of a number of bone fats :—

Bone Fat.	No.	Water.	Fatty Acids.	Free Fatty Acids.	Melting Point of Fatty Acids.	Saponific. Value of Fatty Acids.	Iodine Value of Fatty Acids.	Ash.	Remarks.
		Per cent.	Per cent.	Per cent.	°C.			Per cent.	
Extracted .	1	6·31	89·8	25·8	41·5	206	52·1	1·35	Very impure, nearly black, smell unpleasant.
,, .	2	2·20	93·7	...	42·3	204·5	50·9	1·85	Brown.
,, .	3	2·55	91·5	18·7	41·7	205	51·3	2·01	...
,, .	4	...	...	...	42·0	205	48	...	Fatty acids obtained from No. 1 by distillation.
,, .	5	17·0	93·5	26·5	41·5	200	51·3	1·3	Rather dark.
,, .	6	1·33	...	24·6	41·5	206·1	55·8	0·11	...
,, .	7	...	92·9	18·4	41·8	205·8	52·8	...	Very dark.
,, .	8	...	92·3	20·1	42·0	205	...	...	...
Boiled out	9	...	...	...	45·1	201	44·3	...	Fatty acids from marrow bones prepared in laboratory.
,, .	10	...	...	...	33·5	208·1	75	...	Fatty acids from horse marrow bones, prepared in laboratory.
,, .	11	2·05	90·4	14·8	41·5	207	53·5	...	...
,, .	12	3·08	90·7	21·9	41·7	206	52·8	...	...

[1] *Zeit. f. chem. Industrie*, 1887, 265 ; *Jour. Soc. Chem. Ind.* 1888, 219.

Troicky,[1] differing from *Valenta*, considers that bone fat extracted with petroleum ether is superior to boiled out fat, because containing less water and ash, and more solid fatty acids. But this is an erroneous opinion, for the fat extracted with solvents has a dark colour, unpleasant smell, and is richer in oleic acid. *Troicky's* analyses are given below :—

No.	Description of Bone Fat.	Water.	Ash.	Fatty Acids.	Saponification Value.	Iodine Value.	Solidifying Point of Fatty Acids.	Oleic Acid.	Stearic Acid.
		Per cent.	Per cent.	Per cent.			°C.	Per cent.	Per cent.
1	Boiled out . . .	1·20	0·31	93·20	187·0	57·2	39·0	59·18	34·02
2	,, . .	0·47	0·94	94·40	194·3	56·0	40·2	58·69	35·71
3	Extracted . .	0·58	0·56	94·12	193·8	52·0	40·9	54·34	39·78
4	Boiled out, Russian	0·84	2·40	86·10	172·0	50·3	42·65	48·08	38·02
5	Extracted, ,, .	0·78	1·25	91·30	188·7	51·5	40·75	52·20	39·10
6	,, . .	0·85	1·76	91·00	181·0	54·8	40·0	55·36	35·64
7	,, . .	1·82	1·52	92·40	185·6	55·8	40·1	57·24	35·16
8	,, . .	0·91	1·06	92·85	187·0	55·2	40·9	56·90	35·95
9	Boiled out, from horse bones	1·52	1·82	91·50	184·0	62·7	36·1	63·69	27·81

[1] *Chem. Zeit.* 1890, Rep. 239.

Tallow

In commerce a distinction is made between *beef tallow* and *mutton tallow*. The former is obtained from bulls, oxen, cows, and calves; the latter from rams, sheep, and goats.

The quality—especially the hardness—of the tallow depends on the breed and the age of the animal, and to some extent on the food. The fat from the male beast is generally harder than that obtained from the female. Animals fed on grass yield a harder fat than those fed with oilcakes, etc.

The raw fat is delivered with the adhering tissue, etc., to the tallow-melters, and is rendered at a temperature of about 100° C. or above.

The fats from different parts of the carcass, although of unequal value, are not kept separate, unless the fat be intended for the manufacture of oleomargarine. In that case the more valuable kidney fat ("suet") and bowel fat ("midgerum fat") [French, *suif en branches* or *en rames*; German, *Rohkern*] is dealt with separately and not mixed with the caul- (or kell-) fat [French, *dégraisse*; German, *Rohausschnitt*].

In the preparation of the raw material for oleomargarine, butterine, etc., for which beef tallow only (and not mutton tallow[1]) is suitable, the "suet" and "midgerum" fat is rendered at a temperature not exceeding 60°-65° C., and poured off the impurities that have settled out. This product is named "premier jus." It is allowed to cool down to 35° C. and subjected to pressure, when a liquid part (prima-margarine, oleomargarine[2]) and a solid part (pressed tallow, tallow stearine) are obtained in about equal proportions. The latter is used for candle-making.

In a similar manner the caul-fat is sometimes resolved into two portions, when second qualities of "premier jus" and of pressed tallow are obtained. The latter is employed in soap-making.

If tallow be pressed at a lower temperature **tallow oil** (French, *huile de suif*; German, *Talgoel*) is obtained, which is, as a rule, liquid at the ordinary temperature. Tallow oil is mostly used in admixture with mineral oils as lubricating oil. Its solidifying and melting points naturally vary according to the conditions under which it has been expressed.

Commercial brands of tallow are therefore—

(1) Rendered tallow, which contains all the fat from the carcass.

(2) Pressed tallow.

(3) "Premier jus." The tallows supplied from foreign countries, such as Australian (beef and mutton), South American, North American, Russian, are, of course, tallows of the first kind.

Tallow is sold according to its titer (titre), *i.e.* the solidifying point of the fatty acids as determined by *Dalican's* method (p. 133).

Dalican has given the following solidifying points for tallows (cp. also p. 594).

[1] On the Continent, however, also mutton tallow is used.

[2] In the U.S.A. the term "margarine oil" is used, oleomargarine denoting there the butter-substitute "margarine" of this country.

Kind of Tallow.	Titer Test. °C.
Town tallow, Paris	43·5
,, ,, Florence	44
,, ,, Vienna	44·5
Beef tallow, ordinary	44
,, ,, suet	45·5
Mutton tallow, ordinary	46
,, ,, suet	48
Russian tallow	43·5
,, ,, Odessa	44·5
,, ,, ,,	45
North American tallow	43·5
South American tallow, beef	44·5
,, ,, ,, mutton	45
Bone fat	42·5

The numbers recorded in the subjoined table, due to *De Schepper* and *Geitel*, give melting points of tallows and some fats used for its adulteration :—

Kind.	Titer Test. °C.
Various kinds of tallows	40-46
Margarine	38-44
Pressed tallow	50·5
Mutton tallows	46·1
Beef tallows	44·5
Suif d'épluchures[1]	40·7-42·3
Bone fat[2]	40·3
Cotton seed oil	34
Cocoa nut oil	23
Stearine grease	44

BEEF TALLOW

French—*Suif de bœuf.* German—*Rindertalg.*

For tables of constants see pp. 593, 594.

Beef tallow, when fresh, is almost white, free from any disagreeable odour, and almost tasteless. Foreign tallow is greyish-white to yellow (Russian), and marked by a more or less rancid flavour.

One part of tallow dissolves in forty parts of alcohol of 0·821 specific gravity.

Tallow consists nearly exclusively of the glycerides of palmitic, stearic, and oleic acids. The amount of olein may be calculated from the iodine value. Thus a tallow absorbing 40 per cent of iodine will contain 46 per cent of olein.

The proportions of palmitin, stearin, and olein vary in the fats rendered from different parts of the same beast. *Leopold Mayer* has examined the fats obtained from different parts of the body of a Hungarian ox, three years old, with the following result :—

[1] This fat has a green colour, and emits on drying the odour of sulphurous acid. It is most likely a mixture of a low class tallow and sulphocarbon (olive) oil.

[2] Containing 4·5 per cent of ash, partly in the form of soap.

Tallow from	Fat.				Fatty Acids.				
	Solidifying Point (Pohl's method).	Melting Point (Pohl's method).	Saponification Value.	Hehner Value.	Solidifying Point (Pohl's method).	Melting Point (Pohl's method).	Saponific. Value.	'Stearic Acid,'[1] Solidifying Point 54·8° C.	Oleic Acid, Solidifying Point 5·4° C.
	°C.	°C.			°C.	°C.		Per cent.	Per cent.
Intestines .	35·0	50·0	196·2	95·7	44·6	47·5	201·6	51·7	48·3
Lungs . .	38·0	49·3	196·4	95·4	44·4	47·3	204·1	51·1	48·9
Caul . .	34·5	49·6	193·0	95·8	43·8	47·1	203·0	49·0	51·0
Heart . .	36·0	49·5	196·2	96·0	43·4	46·4	200·3	47·5	52·5
Neck . .	31·0	47·1	196·8	95·9	40·4	43·9	203·6	38·2	61·8
Groins . .	35·0	42·5	198·3	95·4	38·6	41·1	199·6	33·4	66·8

[1] In the commercial sense of the term.

Physical and Chemical Constants of Beef Tallow

Specific Gravity.			Solidifying Point.		Melting Point.		Hehner Value.		Saponification Value.		Reichert Value.	Iodine Value.		Thermal Test. Heat of Bromination.		Refractive Index.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Per cent.	Observer.	°C.	Observer.	At 60° C.	Observer.
15	0·943-0·952	Dieterich	37	Chateau	45-46; 42-43, not below 40	Wolkenhaar	95·6	Bensemann	195·7-200	Filsinger	0·25	40	Hübl	6·1[3]	Archbutt	1·4510	Thoerner
15	0·952-0·953	Hager	..	..	47·6-48·5	Dieterich	95·4-96	L. Mayer	193·2-198	Köttstorfer		43·3-44	Wilson	6·7-7·2[4]	,,		
50 (water 15·5 = 1)	0·8950	Allen	35-27 Temperature rises a few degrees without, however, remaining constant	Rüdorff	43·5-45	Rüdorff				Deering		35·4-36·4	Filsinger			Butyro-refractometer.	
98 (water 15·5 = 1)	0·8626	,,								L. Mayer		35·6-38·9	Dieterich				
100 (water 15 = 1)	0·860-0·861	Wolkenhaar										45·2[1]	Wallenstein & Finck			At 40° C.	Observer.
100 (water 15 = 1)	0·860	Koenigs										38·3[2] 38-40	,, Thoerner			49	Mansfeld

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Saponific. Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
At 100° C. (water at 100 = 1)	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
0·8698	Archbutt	Titer Test.		43-44 and 46-47	Bensemann	197·2	Lewkowitsch	270-285	A. Wright	41·3	Williams	1·4375	Thoerner.
				45	Hübl	201·6	Thoerner	284·5	Lewkowitsch	25·9-32·8	Demski and Morawski	Oleo-refractometer.	
		43·5-45	Dalican							Iodine Value of the Liquid Fatty Acids.			
		44·5	De Schepper and Geitel									"Degrees."	Observer.
		43	Hübl							92·4[1]	Wallenstein and Finck	−40	Jean
		Cp. p. 327.	Lewkowitsch							92·2[2]	,,		

[1] Australian. [2] Berlin town tallow. [3] American beef. [4] Home-refined.

The ratio of stearin to palmitin in tallow is about 1 : 1. In oleomargarine palmitin predominates, consequently the proportion of stearin in tallow stearine must be larger.

According to *Wallenstein*[1] a sample of tallow stearine had the following composition :—

Olein	21·4 per cent.
Stearin	65·4 ,, ,,
Palmitin . . .	13·2 ,, ,,

The ratio of stearic acid to palmitic acid is therefore 100 : 20·2.

More definite information as to the amount of stearic acid and its proportion to palmitic acid is obtained by *Hehner* and *Mitchell's* method of determining stearic acid (chap. vi. p. 198). The following table[2] contains some of their results :—

	Iodine Number.	Stearic Acid in Fatty Acids.
		Per cent.
Beef stearine . .	2·0	50·19-51·05
Oleomargarine .	46·50	21·26-23·6
Margarine I. . .	...	24·8
,, II. . .	41·19	11·72

The amount of free fatty acids in tallow naturally varies considerably. *Deering* has stated the results of his examination in the following table :—

Free Fatty Acids in Beef Tallow

Kind of Tallow.	No. of Sample.	Acid Value.	Calculated as Oleic Acid. Per cent.	Remarks.
Russian	5	5·1–24·6	0·55–12·3	Old
,, ...	2	10·1–12·4	5·05– 6·2	Fresher
,, P.Y.C. . .	3	4·4–10·4	2·2 – 5·2	Old
,, P.Y.C. . .	3	4·4– 4·7	2·2 – 2·35	Fresh
Australian . . .	4	3·5–30·47	1·75–15·2	...
Town tallow . . .	2	9·0–14·2	4·5 – 7·1	...
,, ,, . . .	1	50	25	Six years old

Examination of Tallow

Water and **non-fatty** substances are determined in the usual manner. The *non-fatty* substances in genuine tallow are fragments of tissue and calcium phosphate.

Soft fat is sometimes hardened by addition of lime, the lime soap producing a firmer consistency. On extracting the fat with ether or

[1] *Jour. Soc. Chem. Ind.* 1893, 54. [2] *Analyst*, 1896, 328.

chloroform the lime soap remains undissolved, and the lime may then be determined quantitatively.

The extracted, filtered, and dried fat serves for the double purpose of estimating the commercial value of the tallow and detecting adulterants if present.

Valuation of Tallow.—The value of tallow is determined by the solidifying point of its fatty acids; the higher this is the more valuable the fat. The titer test of tallow intended for candle-making should not be below 44° C. Tallows of a lower titer are employed for soap-making.

A large amount of **free fatty acids** depreciates the value considerably, as the fatty acids obtained from such tallow in the lime saponification process turn out dark, and the soap made from it has an inferior colour ("foxy"). Of course, rancid tallow should not be used for lubricating purposes. The amount of free fatty acids is estimated according to the directions given above (p. 148), adopting 275 as the mean molecular weight of the tallow fatty acids (cp. also "Candles," p. 749).

Detection of Adulteration.—Tallow is adulterated with *resin*, *resin oil*, *paraffin wax*,[1] *palm nut oil*, *cocoa nut oil*, *distilled grease stearine*, *cotton seed oil*, and *cotton seed stearine*; also goat's tallow must, under certain conditions, be considered an adulterant.

Resin, resin oil, and paraffin wax are easily detected by the methods described in chap. vii.

Presence of cocoa nut or palm nut oil would be detected by a *low* **solidifying point** of the fatty acids, a *high* **saponification value** (tallow 196, cocoa nut oil 257·3-268·4, palm nut oil 247·6), and a *low* **iodine value** (tallow 36-40, cocoa nut oil 8-9, palm nut oil 10-17).

The different solubilities of cocoa nut and palm nut soaps on the one hand, and of tallow soap on the other, in concentrated solutions of common salt or caustic alkalis, have been made use of by *Lant Carpenter* and by *Roediger* for the detection of cocoa nut and palm nut oils in tallow.

Lant Carpenter dissolved 10 grms. of the fatty acids of the sample in 39-40 c.c. of normal caustic soda, boiled, and brought the soap solution to 50 grms. by evaporation or by addition of water, as the case may be. A saturated solution of common salt was then run in from a burette until the soap was thrown up. I have tested this method, but found it very unsatisfactory, as yielding erratic results.

Roediger saponifies 150 grms. of the sample with caustic lye, and throws the soap up by a measured quantity of caustic soda of 1·35 spec. grav. Saponification of tallow by means of aqueous alkalis requiring a good deal of practice, and therefore likely to lead to very disappointing results in the hands of an inexperienced operator, I cannot recommend *Roediger's* method.

If at all necessary to use such a method, the writer proposes to combine the two methods in the following manner:—10 grms. of the

[1] In Germany paraffin oil is used by the custom-house officers for "denaturing" tallow if caustic soda be objected to.

fatty acids of the sample are dissolved in 40 c.c. of normal caustic soda, boiled, and brought up to 75 grms. by addition of water, when caustic soda of spec. grav. 1·35 is run in from a burette, with constant stirring, until the soap is thrown up. The following table gives some results I have obtained by this method :—

10 Grms. of Fatty Acids from	Brought up to 75 Grms. Required Caustic Soda 1·35. c.c.
Tallow	8·6 ; 9·9
Cocoa nut oil	40·4 ; 39·0
Palm nut oil	27·8
50 parts of tallow and 50 parts of cocoa nut oil	22·0
50 parts of tallow and 50 parts of palm nut oil	20·1 ; 19·7

It is evident that the quantitative reactions in conjunction with the solidifying points give far more reliable and characteristic results.

Distilled grease stearine has been employed, according to *L. Mayer*,[1] for the adulteration of tallow. This "stearine" is obtained by distilling "recovered grease," and expressing the solid portion of it; it consists chiefly of stearic acid (p. 691), isooleic acid, and smaller quantities of cholesterol and isocholesterol.[2] Its detection is therefore easy. In the first instance, a tallow thus adulterated would have a peculiar smell and possess a high acid value. The best method, however, is to saponify the tallow, extract the soap with ether, and test the residue obtained on evaporating the solvent for cholesterol and isocholesterol (p. 84). A rapid process would be to test the sample with acetic anhydride and concentrated sulphuric acid, when a green fluorescence[3] would point to the presence of isocholesterol and, inferentially, to distilled grease stearine.

The fatty acids obtained from tallow thus adulterated turn yellow after a few days, and exhibit the peculiar smell characteristic of wool fat and its derivates.

A high acid value may also be due to admixture with stearic acid from cotton seed mucilage; in that case, of course, no isocholesterol reaction will be obtained.

Cotton seed oil and **cotton seed stearine** would be indicated by a high iodine value. Their detection is, however, easily and with certainty effected, according to *Mayer*, by melting the sample and allowing the fat to crystallise at a temperature of 35° C. After 18 hours' standing the liquid portion is removed by squeezing through a cloth and then examined. The determination of the "titer test" and of the iodine absorption will afford sufficient evidence of the adulteration. In presence of cotton seed oil or cotton seed stearine the solidifying point will be below 39° C., and the iodine value far above 55, the normal value for tallow oleine (cp. also "Detection of Cotton Seed Oil in Lard").

[1] *Dingl. Polyt. Jour.* 247. 305.
[2] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1892, 142.
[3] *Ibid.* 1892, 144.

Goat's tallow, sold in commerce as mutton tallow, would also be considered an adulterant by a candle-maker; although it has a high melting point, and consequently a large proportion of stearin, it is not suitable for candles, on account of its fatty acids not crystallising well, but solidifying into an amorphous mass, from which it is difficult to remove the imprisoned oleic acid. The candles prepared in the ordinary way from goat's tallow are of low quality, not possessing the metallic ring of first-class candles, and easily becoming discoloured on account of the oleic acid they retain. The detection of goat's tallow is difficult; the surest indication would be given by the smell of the sample (*Chevreul's* "acide hircique").

A mixture of 70 parts of goat's tallow and 30 parts of cotton seed oil has been sold, according to *Mayer*, as beef tallow. Neither the solidifying point of the fatty acids nor the iodine value of this fat reveal the fraud. Recourse must therefore be had to the determination of the iodine value of the liquid fatty acids. The nitric acid and *Becchi's* test given for cotton seed oil (see p. 382) (or *Mayer's* device of allowing the fat to crystallise at 35° C.) would not give equally certain results.

MUTTON TALLOW

French—*Suif de Mouton.* German—*Hammeltalg.*

For tables of constants see pp. 599, 600.

Mutton tallow very much resembles beef tallow, indeed, it is frequently sold mixed with the latter. It is, however, as a rule, harder than beef tallow, and consequently its solidifying and melting points, as well as those of its fatty acids, are higher. It is also more liable to turn rancid, and cannot for this reason be used in the manufacture of superior butter-substitutes or best soaps.

Deering[1] has found for four samples of Australian mutton acid values varying from 1·7 to 14·3, corresponding to 0·85 to 7·15 per cent of free fatty acids.

The fat rendered from various parts of two sheep gave, according to *Moser*[2] the following results:—

Fat from	Fat.			Fatty Acids.	
	Solidifying Point.	Melting Point.	Saponific. Value.	Solidifying Point.	Melting Point.
	°C.	°C.		°C.	°C.
Kidneys . .	40·7-40·9	54·0-55·0	194·8-195·2	51·9-51·9	56·2-56·5
Caul and intestines	39·2-39·7	52·0-52·9	194·6-194·8	50·4-50·6	54·9-55·8
Adipose tissue .	34·1-34·9	49·5-49·6	194·2-194·4	43·7-46·2	50·7-51·1

[1] *Jour. Soc. Chem. Ind.* 1884, 541.
[2] *Bericht der Thätigkeit der Versuchsstation. Wien*, 1882, 1883.

Physical and Chemical Constants of Mutton Tallow

Specific Gravity.			Solidifying Point.		Melting Point		Hehner Value.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.
15	0·937-0·940	Hager	...	...	50-51	Bensemann	95·54	Bensemann
,,	0·937-0·953	Dieterich	...	...	47-49	Dieterich	...	...
100	0·860	Koenigs	36-32	Rüdorf	46·5-47·4	Rüdorf	...	...
,,	0·858	Thoerner	rising several degrees		44-45	Thoerner		
			40-41	Thoerner				

Physical and Chemical Constants of Mutton Tallow—continued

Saponification Value.		Iodine Value.		Thermal Test. Heat of Bromination.		Refractive Index.	
Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	At 60° C.	Observer.
192-195·2	Thoerner	35·2-46·2	Wilson	8·1 [1]	Hehner and Mitchell	1·4501	Thoerner
...	...	34·8-37·7	Dieterich				
...	...	32·7	Thoerner	7·6 [2]	,, ,,		
		43-44	,,	7·55 [3]	Archbutt		
		38·6	Wallenstein and Finck	8·9 [4]	,,		
		48-61·3	Hehner and Mitchell				

[1] From kidney. [2] From flare. [3] Australian mutton. [4] Home refined.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Refractive Index.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
...	...	49-50 and 53-54	Bensemann	210	Thoerner	34·8	Thoerner	1·4374	Thoerner
41	Thoerner	49	Thoerner			Iodine Value of the Liquid Fatty Acids.			
39	,,	46-47	,,						
Titer Test.						92·7	Wallenstein and Finck		
45-46 also 43·2	Dalican								
46·1	Schepper and Geitel								
See p. 327.	Lewkowitsch								

Very instructive is also the information contained in the following table, due to *Hehner* and *Mitchell*;[1] the different specimens of fat were taken from a Scotch sheep eighteen months old :—

Fat from	Iodine Value.	Melting Point of Fatty Acids.	Stearic Acid.
	Per cent.	°C.	Per cent.
Kidneys . .	48·16	45·6	26·2-27·7
Back . .	61·3	41·4	24·8
Neck . .	48·6	42·2	16·4
Breast . .	58·2	33·8	About 1
Ham . .	50·6	40·8	No deposit after two days

BUTTER FAT

French—*Beurre de vache* German—*Butterfett.*

For tables of constants see pp. 602, 603.

Butter fat or milk fat is the fat of cow's milk.[2]

Normal cow butter, not melted and not salted, has, according to *Koenig*, the following composition :—

Fat	87·0 per cent
Casein	0·5 ,,
Milk sugar	0·3 ,,
Ash	0·3 ,,
Water	11·7 ,,

The percentage composition of butters varies, however, to a considerable extent, the proportion of fat, on the one hand, rising in some cases to 95 per cent, whereas, on the other hand, the water may reach as high a figure as 35 per cent.

[1] *Analyst*, 1896, 327.

[2] The following constants of the milk fats from other animals have been published :—

Milk Fat from	Specific Gravity.		Solidifying Point.	Melting Point.	Saponific. Value.	Hehner Value.	Reichert-Meissl Value.	Iodine Value.	Refractive Index.	Observer.
	At 15° C.	At 100°C.								
Goat . .	0·9312	0·8669	24·31	27·38·5	221·6	86·5-87·3	23·1-25·4	30·4-34·6	1·4596	Solberg
,, . .	..	..	31	36·5	..	..	28·6	..	..	Pizzi
Sheep .	..	..	..	29-30	..	..	32·9	..	..	,,
Mare . .	..	..	..	..	..	..	11·2	..	..	,,
Ass . .	..	..	..	..	..	..	13·1	..	..	,,
Buffalo .	..	..	29	38	..	..	26·2	..	..	,,
Reindeer .	0·9428	0·8640	34-39	37-42	219·2	86-89	31·4	25·1	1·4647	Solberg
Gamboose	..	..	..	..	220·4-231·7	86·9-87·5	34·7-35	32-35	..	H. D. Richmond
Woman .	..	..	..	30-31	..	..	Volatile fatty acids 1·4 per cent	..	..	Laves

Physical and Chemical Constants of Butter Fat

Specific Gravity.			Solidifying Point.		Melting Point.[1]		Hehner Valu e		Saponification Value.	
°C.		Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.
15	0·936-0·940	Hager	19-20	Wimmel	31-31·5	Hehner	87·5	Hehner	227	Köttstorfer,
,,	0·9275	Winter Blyth	..	..	29·5-34·7	Bell	86·45-89·8	Bell	(221·5-233·4)	Valenta,
,,	0·926	Casamajor	..	..	29·4-33·3	Cameron				Moore,
37·8 (100° F.)	0·911-0·913	Bell	20-23	Thoerner	28-33	Thoerner				Allen, etc.
40 (water at 15·5=1)	0·9041	Allen							225-230	Thoerner
100 (water at 15=1)	0·865-0·868	Koenigs								
100 (water at 15·5=1)	0·867-0·870	Allen								
100 (water at 100=1)	0·901-0·904	Wolkenhaar								
,,	0·9094-0·9140	Bell								
,,	0·9105-0·9138	Muter								
,,	0·9099-0·9132	Allen								

[1] According to Meyer (*Milch. Zeit.* 1892, 49) the melting point of cow butter is lowered by food consisting of easily digestible carbohydrates, but raised by straw, oil cakes, or sour fodder.

Physical and Chemical Constants of Butter Fat—continued

Reichert Value.		Iodine Value.		Thermal Test. Heat of Bromination.		Refractive Index.	
c.c. $\frac{n}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	At 60° C.	Observer.
						1·445-1·448	Thoerner
14 (12·5-15·2)	Reichert, Moore, Allen, etc.	26·0-35·1 19·1 [1] 25·7-37·9 [2] 28-32	Hübl Moore Woll Thoerner	6·6-7·0	Hehner and Mitchell	Oleo-refractometer.	
						"Degrees."	Observer.
						−29 to −31 −25 to −31	Jean Pearmain
Reichert-Meissl Value.						Butyro-refractometer.		
20·63-33·15	Cp. p. 633.					At °C.	Scale Divisions.	Observer.
						25	52·5	Skalweit
						35	44·8-47	Besana
						40	41-42	Mansfeld
						40	40·5	Beckurts and Seiler
						40	40·5-44	Delaite

[1] Very old sample.

[2] 56 samples, mean 33·32.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.[1]		Saponification Value.		Iodine Value.		Heat of Bromination.		Refractive Index.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	At 60° C.	Observer.
35·8	Hübl	38	Hübl	210-220	Thoerner	28-31	Thoerner	6·2	Hehner and Mitchell	1·437-1·439	Thoerner
37·5-38	Paris Municipal Laboratory	41-43 and 43-45	Bensemann								
33-35	Thoerner	38-40	Thoerner								

[1] Butter from cows fed on cotton seed cakes have a considerably (by 8° to 9° C.) higher melting point. (Lupton, *Jour. Amer. Chem. Soc.* 1891, 134.) Cp. footnote p. 634.

The composition of a good English butter is, according to *Bell*, the following :—

Fat	90·27 per cent
Curd	1·15 ,,
Salt	1·03 ,,
Water	7·55 ,,

Vieth has published from a large number of analyses of butters the following numbers :—

Origin of Butter.	Fat.	Curd.	Salt.	Water.
	Per cent.	Per cent.	Per cent.	Per cent.
English . .	86·85	0·59	1·02	11·54
French . .	84·77	1·38	0·09	13·76
,, salted .	84·34	1·60	2·01	12·05
Kiel. . .	85·24	1·17	1·35	12·24
Danish . .	83·41	1·30	1·87	13·42
Swedish . .	83·89	1·33	2·03	13·75

The curd and the water in butter render it liable to become easily rancid. This occurs, according to *Stockmeyer*, with special facility in the case of all butters containing more than 2 per cent of curd. Butter is therefore usually preserved by mixing with it a small quantity of salt. The same object is accomplished by keeping butter in a melted state for some time until it has become quite clear, and separating it from the curd and water.[1]

Pure butter fat consists chiefly of triglycerides of fatty acids ; it contains besides minute quantities of a colouring principle, lecithin,[2] cholesterol, phytosterol, and a lipochrome. The following acids have been identified hitherto : Acetic, *butyric*, *caproic*, *caprylic*, *capric*, lauric, myristic, *palmitic*, *stearic*, arachidic, and *oleic*. The quantity of stearic acid seems to be very small (*Hehner* and *Mitchell*). *Wachtel*, and also *Bondzyński* and *Rufi*, state that also hydroxy acids occur in butter fat ; but this stood greatly in need of confirmation. (The great discrepancy in the values found by these observers is explained by the writer's comments on *Benedikt's* acetyl values (cp. 165).) Experiments made by the writer (unpublished) prove that butter practically contains no hydroxy acids.

Wanklyn,[3] has put forward the opinion that the solid fatty acids of butter fat consist chiefly of a hypothetical acid of the composition $C_{16}H_{30}O_2$, named by him aldepalmitic acid ; this opinion is absolutely unsubstantiated by experiments, and need not be referred to further.

[1] The flavour of butter suffers, however, considerably, according to *Vieth*, by this treatment.

[2] According to *Wrampelmeyer*, the proportion of lecithin, calculated from the phosphoric acid found, is 0·017 per cent. *Schmidt*, however, gives the figures 0·15-0·17 per cent.

[3] *Jour. Soc. Chem. Ind.* 1891, 212.

The extraordinarily high proportion of glycerides of soluble fatty acids in butter fat—when contrasted with other fats—is characteristic; the chief components, however, appear to be, besides small quantities of stearin: palmitin and olein. Stearin and palmitin are often comprised in the name "margarin."

J. Bell[1] is of the opinion that butter fat most likely contains mixed glycerides, *i.e.* glycerides in the molecule of which the glycerol is combined with three different acid radicles, forming a tri-acid compound of the composition

$$C_3H_5\begin{cases}O\,.\,C_4H_7O\\O\,.\,C_{16}H_{31}O\\O\,.\,C_{18}H_{33}O\end{cases}$$

The following facts agree with this opinion: If ordinary animal fat is melted and mixed with—say 10 per cent of—butyrin, the latter compound may be entirely removed by digestion with alcohol, the animal fat being recovered practically in its original condition. If, on the contrary, butter fat is treated with hot alcohol, from 2 to 3 per cent only of its weight passes into the alcohol. The fat thus dissolved does not consist, as might be supposed, of butyrin or caproin, but of a fat which is liquid at 15·5° C., and yields, on saponification, from 13 to 14 per cent of soluble fatty acids, and from 79 to 80 per cent of insoluble fatty acids. The latter have a higher melting point than the mixed insoluble acids obtained from the original butter fat; this tends to disprove the opinion that the low melting point of the extracted fat might be due to an increased proportion of oleic acid in its molecule. These results agree closely with a compound of the above-given formula, which *Bell* has named oleo-palmito-butyrate of glycerol.

Bell's theory is confirmed by the experiments of *A. W. Blyth* and *Robertson*,[2] who state that they isolated from butter fat a crystalline glyceride, to which they ascribe the formula

$$C_3H_5\begin{cases}O\,.\,C_4H_7O\\O\,.\,C_{16}H_{31}O\\O\,.\,C_{18}H_{35}O\end{cases}$$

The fact that *Hehner* and *Mitchell* have found but small quantities of stearic acid agrees better with *Bell's* formula. The proportion of the several fatty acids in a sample of butter fat examined by *Bell* is stated as follows:—

Butyric acid	6·13 per cent
Caproic, caprylic, and capric acids .	2·09 ,, ,,
Palmitic, stearic, and myristic acids .	49·46 ,, ,,
Oleic acid	36·10 ,, ,,
Glycerol	12·54 ,, ,,
	106·32

[1] *The Chemistry of Foods*, ii. 44. [2] *Jour. Chem. Soc.* 1889, Proceed. 5.

The fatty acid soluble in water at 15·5° C. was considered to be butyric acid. The second group—caproic, caprylic, and capric acids—comprises the acids soluble in hot water; their mean molecular weight was calculated as 136 from the analysis of their mixed barium salts. Oleic acid was regarded as the product obtained on decomposing the ether soluble lead salts of the insoluble fatty acids; the mixed palmitic, stearic, and myristic acids were estimated by difference.

According to *Duclaux*,[1] butter fat contains from 2 to 2·26 per cent of caproic, and from 3·38 to 3·65 per cent of butyric acid. From the analyses of twenty-eight butter fats, *Viollette*,[2] somewhat arbitrarily, assumes the proportion in which butyric acid stands to caproic in butter fat to be 1·645. Thus he is enabled to calculate severally the proportions of butyric, caproic, solid volatile, and insoluble fatty acids by proceeding in the following way: 50 grms. of butter are saponified and the volatile acids removed, as in *Reichert's* distillation process. The solid volatile acids are separated by filtration, and their quantity determined after drying; the amount of the fixed (insoluble) fatty acids is arrived at in the same way. The total quantity of the soluble acids is ascertained by titration with decinormal alkali, and calculated to butyric acid. If A represents this quantity of butyric acid, then the true quantities of butyric and caproic acids B and C are found with the help of the following equations:—

$$B = A \times 0{\cdot}68469$$
$$C = A \times 0{\cdot}41565$$

In the subjoined table *Viollette's* results are reproduced:—

Fatty Acids.	Superior Qualities of Butter.			Inferior Qualities of Butter.				
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Butyric acid. .	6·07	5·33	5·50	5·05	4·62	4·80	4·76	4·37
Caproic acid. .	3·66	3·23	3·34	3·06	2·80	2·92	2·89	2·65
Solid volatile acids	2·85	3·00	2·80	3·00	2·90	2·40	3·00	2·95
Non-volatile acids	82·28	82·63	82·87	83·20	84·32	84·31	83·83	84·62
Total . .	94·76	94·19	94·41	94·31	94·64	94·43	94·48	94·59

By ascertaining finally the mean molecular weights of the solid volatile and of the non-volatile acids, *Viollette* obtained all the data necessary for calculating the percentage composition of the butter fats. This is given in the following table:—

[1] *Compt. rend.* 102. 1022. [2] *Jour. Soc. Chem. Ind.* 1890, 1157.

Glycerides.	Superior Qualities of Butter.			Inferior Qualities of Butter.				
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Butyrin . . .	6·94	6·09	6·28	5·76	5·28	5·49	5·45	5·00
Caproin . . .	4·06	3·58	3·70	3·39	3·09	3·23	3·10	2·94
Glycerides of solid volatile acids . . .	3·06	3·22	2·96	3·16	3·06	2·53	3·16	3·15
Glycerides of non-volatile acids . . .	85·98	86·62	86·60	86·93	88·10	88·10	87·60	88·42
Difference . . .	0·04	0·49	0·46	0·76	0·47	0·65	0·69	0·49
	100	100	100	100	100	100	100	100

I subjoin a table showing the composition of butter fat as calculated by me from *Bell's* results, and as given by the other chemists named :—

Glycerides.	J. Bell.	W. Blyth.	Spallanzani.[1]
	Per cent.	Per cent.	Per cent.
Butyrin . . .	7·012	7·7	5·080
Caproin . . .	2·280	0·1	1·020
Caprylin and caprin .			0·307
Olein	37·730	42·2	93·593
Palmitin, stearin, etc. .	52·978[2]	50·0	
	100	100	100

The composition of a butter fat may be calculated approximately in the following manner :—

Let the *Hehner* value be 87·5, and the mean molecular weight of the insoluble fatty acids 270. The molecular weight of the corresponding glycerides would then be $3 \times 270 + 38 = 848$, containing $3 \times 270 = 810$ parts of fatty acids. Hence—

$$810 : 848 = 87{\cdot}5 : x \; ; \; x = 91{\cdot}605 \text{ per cent.}$$

The proportion of mixed palmitin, stearin, and olein (including myristin and arachin) amounts therefore to 91·605 per cent.

Further, let the iodine value of the butter fat be 31·0 ; the corresponding amount of olein calculated by the formula

$$O = 1{\cdot}1601 \, I$$

will then be 35·96. Assuming that the proportion of volatile acids make up the difference, the composition of the sample would be—

[1] *Le Staz. Sperim. Agr. Italian.* vol. iv. 417. [2] By difference.

Palmitin and stearin . . .	55·64 per cent
Olein	35·96 ,, ,,
Butyrin, caproin, etc. . . .	8·40 ,, ,,
	100

A further insight into the nature of the volatile acids may be gained from the *Reichert-Meissl* value. Let the mean *Reichert-Meissl* value of butter be 28·78, or, in other words, the volatile acids obtained from 5 grms. of butter fat are neutralised by 28·78 c.c. of decinormal potash. The volatile acids from 100 grms. would then require 57·56 c.c. of normal potash. Since $3 \times 56{\cdot}1$ grms. of KOH correspond to 92 parts of glycerol, $C_3H_8O_3$, or 38 parts of C_3H_2, the alkali used will correspond to

$$\frac{38 \times 57{\cdot}56 \times 56{\cdot}1}{3 \times 56{\cdot}1} = 0{\cdot}729\ C_3H_2.$$

On subtracting the last number from 8·40 (the amount found above for the glycerides of the volatile acids), we obtain 7·673 as the percentage of volatile acids in the sample.

These 7·673 grms. volatile acids require, as found by titration, 57·56 c.c. of normal potash, hence their mean molecular weight—

$$M = \frac{7{\cdot}673 \times 1000}{57{\cdot}56} = 133{\cdot}3.$$

According to theory we have the following molecular weights :—

Acid.	Formula.	Molecular Weight.
Butyric . .	$C_4H_8O_2$	88
Caproic . .	$C_6H_{12}O_2$	116
Caprylic . .	$C_8H_{16}O_2$	144
Capric . .	$C_{10}H_{20}O_2$	172

We may therefore safely conclude that *W. Blyth's* numbers for butyrin on the one hand, and for caproin, caprylin, and caprin, on the other hand, require a correction, allowing a larger proportion for the latter glycerides.

Butter fat contains even in the fresh state small quantities of free fatty acids (cp. below, "Determination of Free Fatty Acids").

The microscopic appearance of fresh butter shows that it consists of a mass of transparent minute globules of fat, each being distinct. In stale butter, however, crystals have been found by *Hassal ;* therefore the presence of crystals cannot be adduced as a proof of adulteration with other fats, as has been asserted by several chemists. The crystals are best observed, according to *Mylius*,[1] under the polarisation-micro-

[1] *Berichte*, 1879, 270.

scope with crossed nicols, the crystals alone appearing illuminated in the otherwise dark field.

On exposure to air, especially to sunlight, butter loses its yellow colour, whilst acquiring the colour and also the odour of tallow. According to *Duclaux*, the weight of butter increases thereby, reaching an increment of 1·3 per cent.[1]

Melted butter fat does not solidify homogeneously throughout its mass, a kind of crystallisation being noticeable. The portions adhering to the sides of the containing vessel, and consequently solidifying first, have a composition somewhat different from that of the innermost portions, which remain liquid for a longer period. In the case of melted butter fat the solidification takes place with separation of an oil, "butter oil." The latter may also be prepared by melting butter, allowing to cool to 20° C., and subjecting it to pressure. According to *Blyth* and *Robertson*, butter fat consists of 45·5 per cent of butter oil and 54·5 per cent of solid fat.

Adulteration of Butter

The substances that are fraudulently admixed with butter are of various kinds.

Gross adulterants, easily detected, however, are the following: *starch, potato pulp, ground white cheese, a.o.* Also *borax*,[2] *alum, sodium silicate* have been discovered in butter, added with the view of preserving it, and of allowing at the same time the fraudulent incorporation of large quantities of *water*.

Other sophistications may be looked for in the form of colouring matters, such as annatto, curcuma, saffron, azo-colours, etc.

The most important and most common adulteration of butter however, is the admixture of foreign animal or vegetable fats, as lard, tallow, goose fat, cotton seed stearine, cocoa nut and palm nut oils, and, most of all, "margarine" or "oleomargarine."

The frauds are being perpetrated on such extensive lines that legislation has stepped in to protect the genuine article. In this country no butter-substitute, however small the proportion of foreign fat, may be sold without bearing a distinct acknowledgment as to its true nature.[3]

[1] On the change in the composition of butter on long keeping, cp. *Chem. Zeit.* 1895, 846.

[2] In Italy the addition of 2 grms. of borax per 1000 grms. of butter is allowed.

[3] In Germany, Soxhlet has proposed the enactment of a law, that to every hundredweight of a butter-substitute 0·5 grm. of phenolphthalein must be added, so as to make the detection of any admixture with genuine butter an easy operation. F. Hart, however, has shown (*Chem. Zeit.* 1893, 1908) that phenolphthalein acts injuriously on the organism. Later on it was proposed that "margarine" be mixed with a "latent" colouring matter, viz. dimethylamidoazobenzene, so that detection of margarine or of butter adulterated with margarine should be within the reach of everybody, by testing it with dilute acid, when margarine or butter adulterated with margarine would turn red. According to the latest German Margarine Act the manufacturer of margarine is bound to admix with the fats and oils employed 10 per cent of sesamé oil, the recognition of which is easy by the Baudouin colour reaction (p. 390).

Whereas gross adulteration with substances of a non-fatty nature are easily recognised, the detection of foreign fats has caused great difficulty for a long time, until we got the excellent methods of *Köttstorfer*, *Hehner*, and *Reichert*.

Unfortunately the adulterator has kept pace with the progress of analytical methods, and has succeeded with great ingenuity in preparing mixtures that possess the same saponification and Hehner values as genuine butter. Thus a judiciously prepared mixture of oleomargarine and cocoa nut oil could not be recognised as an artificial article if subjected to the first two tests only. The *Reichert* value, however, affords a very valuable means of detecting adulteration of this kind, but it should be borne in mind that an admixture of 10 per cent of "margarine" cannot be revealed with certainty.[1] The fear which the writer expressed in the first edition of this work that the artificial butter industry may succeed in providing means to prepare butter-substitutes having a correct *Reichert* value has been realised, since butyric acid, tributyrin, and also amyl acetate are being sold (in 40 per cent alcoholic solution) for that purpose.

In order to pronounce on the genuineness of a sample of butter it will therefore be required to determine the *Reichert* value in the first instance, and then the saponification value and specific gravity. On account of its rapidity optical analysis will serve as a sorting test. These will as a rule suffice, and other tests are therefore rarely applied.

The literature bearing on the examination of butter is an extraordinarily voluminous one, and still grows. The list of methods detailed below cannot therefore lay claim to completeness, although no important and really valuable method will be found missing. A large number of insignificant modifications of known methods and a host of valueless proposals have been deliberately omitted.

For further information reference must be made to special works on butter.[2]

The examination of butter divides itself naturally into two parts: the first embraces the estimation of not-fats (water, curd, etc.); the second deals with the examination of the butter fat itself.

1. Examination of Butter

1. **Water** is determined by drying the sample at 100°-120° C. The Society of Bavarian Analytical Chemists recommends drying the butter at a 100° C. for six hours, with occasional stirring (cp. also p. 88).[3]

[1] I wish to lay stress on this point, as many chemists who propose new methods entirely overlook the fact that it does not involve the slightest difficulty to distinguish pure butter from "margarine," or, in short, from any other fat.

[2] Sell, *Arbeiten aus dem Kaiserl. Reichsgesundheitamt*, 1886; Duclos, *Le Lait. Étude chimique et microbiologique*, Paris, 1887; Girard and Bevans, *La Margarine*, Paris, 1888; Besana, *Sui Metodi a distinguere il burro artificiale dal burro naturale*, Lodi, 1888; Zune, *Traité général d'analyse des beurres*, 2 vols., Paris et Bruxelles, 1892.

[3] For Crismer's method of determining the amount of water by the critical temperature the reader is referred to the *Bullet. de l'Assoc. Belge des Chim.* 1896 (9), 359; *Analyst*, 1896, 241.

In cases where scientific accuracy is not the chief object, as for market control and police regulation purposes, the amount of water may be determined rapidly by *Birnbaum's* method as modified by *Wimmel*[1] in the following manner: 10 grms. of butter are shaken up with 30 c.c. of ether, saturated with water, in a tube corked at one end and provided with a stop-cock at the other, through which the separated aqueous liquid is run off into a second narrow graduated tube, containing 5 c.c. of saturated brine and a minute quantity of acetic acid, so as to produce a distinct red colour with litmus. The increase of volume, due to the water in the butter, is then read off. The results are stated to be but slightly below those obtained by gravimetric analysis.

The proportion of water in a butter should not exceed 16 per cent. *J. Bell* has found in the analysis of 113 genuine English butters values varying from the minimum of 4·15 to the maximum of 20·75 per cent, the majority of samples, however, containing from 11-14 per cent. The following table gives a few values culled from analyses by *Vieth* and *H. D. Richmond*,[2] and arranged by the writer according to their amount of water :—

Kind of Butter.	Number of Samples examined.	Samples containing per cent of Water.			Observer.
		From 11-14.	From 10-15.	Above 16.	
		Per cent.	Per cent.	Per cent.	
English and foreign . .	560	83·8	94·2	0·9	Vieth
English . . .	143	70·7	85·4	0·7	H. D. Richmond
Foreign . . .	417	88·3	97·2	1·0	,,
French . . .	451	...	...	8·6	,,
,,	48	...	...	0·0	,,

2. **Solids not-fat** are best determined in the sample of butter previously employed for the estimation of water, by exhausting the dried butter with ether, chloroform, carbon bisulphide, or petroleum ether, and weighing the residue after drying.

If a fresh quantity of butter be taken for this assay errors may easily arise from the fact that butter is not a homogeneous product, different parts containing varying amounts of butter milk. *Spaeth*[3] has shown that errors due to this cause may amount to several per cents. For the convenient estimation of water and solids not-fat he recommends the drying of the accurately weighed sample in a glass trough, filled one-third with fragments of pumice, and placed inside a weighing bottle, the lid and bottom of which are perforated with holes. After drying, the weighing bottle and contents are transferred to a Soxhlet extractor. The residue left in the glass trough is then dried and weighed.

[1] *Jour. Soc. Chem. Ind.* 1893, 630. [2] *Analyst*, 1894, 17.
[3] *Zeitsch. angew. Chem.* 1893, 513.

In the case of pure butter the solids not-fat consist of *casein*, *milk-sugar*, and *inorganic salts*. By exhausting the dried residue with water, to which a trace of acetic acid has been added, milk-sugar and the bulk of the inorganic salts are removed, leaving casein behind; its weight is ascertained after drying. The minute quantity of salts retained in the casein and found on incineration is deducted.

Koenig suggests to determine the proportion of nitrogen by *Kjehldahl's* process and multiplying by 6·25. The percentages of casein (curd) recorded by *Koenig* for 302 samples of butter vary from 0·19 to 4·78 per cent.

The amount of inorganic salts, chiefly common salt, is found by igniting the ether-insoluble residue from 10 grms. of butter, taking care, however, not to heat the ash to too high a temperature lest sodium chloride should volatilise. The proportion of the latter is determined by titration with standard silver solution, using potassium chromate as an indicator.

With greater accuracy, however, sodium chloride is determined by warming in a porcelain dish 10 grms. of butter with an equal amount of stearic acid and 50 c.c. of water, acidulated with a few drops of nitric acid, and stirring the melted mass. After cooling, the cake is taken off, rinsed well, the aqueous liquid filtered, and the chloride precipitated as silver chloride.

The proportion of sodium chloride in the 113 samples examined by *J. Bell* was found lying between 0·4 and 9·20, the majority yielding from 2 to 7 per cent, in one case only 15·08 per cent. The amount of salt added to butter varies, of course, in different countries and localities. An excessive amount of ash will naturally invite further examination.

Milk-sugar is not determined direct, but found by difference.

The proportion of *fat* is likewise found by difference; it can, of course, be determined direct by evaporating the ether-extract and weighing the residue (p. 90).

Fraudulently added substances of a non-fatty nature, as *starch*, etc., are detected as described page 88.

3. **Colouring Matters.**—Summer butter is yellow, winter butter is almost white[1]; the latter is therefore, as a rule, coloured artificially before being placed on the market. The naturally yellow butter is rapidly bleached when exposed to light and air.

Experiments by *Soxhlet* have demonstrated the fact that a layer of butter ½ cm. thick loses its colour in sunlight within eight hours. The butter thus becomes white, and resembles tallow in appearance.

Foreign colouring matters are detected by shaking the melted

[1] In this connection it may be interesting to note that in some Swiss farms having an abundant growth of *Leontodon* and *Ranunculus*, the cows gave butter of such intense yellow colour that suspicion was aroused; the butter obtained after the second grazing was very much paler.

butter with alcohol. In presence of foreign colouring matters the alcoholic layer becomes tinted, whereas natural butter leaves the alcohol colourless.

Moore [1] and *Martin* [2] recommend the use of a mixture of alcohol and carbon bisulphide. According to *Martin*, 5 grms. of butter are shaken up with 25 c.c. of a mixture consisting of 15 parts of methyl alcohol, or ordinary alcohol, and 2 parts of carbon bisulphide. Two layers are formed, the lower one consisting of the fat dissolved in carbon bisulphide, the upper alcoholic layer containing the colouring matter.

Stebbins,[3] however, has pointed out that the small quantity of fat retained by the alcoholic layer may interfere with the subsequent examination, and that carrotin, the colouring matter from carrot juice, is more easily soluble in carbon bisulphide than in alcohol. He substitutes, therefore, the following process: Melt 50 grms. of the sample in a narrow beaker on the water-bath, stir into the melted mass 5 to 10 grms. of finely-powdered fuller's earth, agitate thoroughly for two or three minutes, and allow to settle out completely whilst warm. Drain off the bulk of the fat, add 20 c.c. of benzene, stir well, allow to deposit, and decant the solution through a filter. Repeat this process until the fat is removed entirely, and wash the precipitate on the filter with benzene. Test the filtrates for carrotin. Dry the precipitate on the water-bath, and boil out three times with about 20 c.c. of 94 per cent alcohol. Evaporate the alcoholic extracts in a tared dish, dry at 100° C., and weigh the residue.

The residue obtained by the one or the other method is then examined by means of special reactions for the colouring matter present.

In the Paris Municipal Laboratory curcuma, annatto, and saffron are tested for in the manner described below. The first two colouring matters are at present chiefly used in France. A preparation for colouring butter is sold there under the name of "jaune gras" (fat yellow), made by digesting annatto with sesamé oil. With a view of imparting to it an orange-yellow or straw-yellow hue curcuma is added. Five drops of the filtered mixture are said to suffice for one kilo of butter.

Curcuma is indicated by the appearance of a brownish yellow coloration on adding a few drops of ammonia, and a reddish brown coloration on adding hydrochloric acid.

Annatto is identified by a reddish brown residue, dissolving in concentrated sulphuric acid with production of a blue colour.

In the presence of *saffron* an orange-coloured precipitate is obtained on dropping lead acetate into the aqueous solution of the residue.

Leeds [4] dissolves 100 grms. of butter in 300 c.c. of pure petroleum ether of 0·638 specific gravity in a separating funnel, draws off the curd

[1] *Analyst*, 11. 163.
[2] *Ibid.* 12. 70.
[3] *Jour. Amer. Chem. Soc.* 1887, 41.
[4] *Analyst*, 1887, 150.

and water, and washes several times with water, using about 100 c.c. The solution of butter fat is then kept at 0° C. for about twelve to fifteen hours, when the bulk of the solid glycerides will crystallise out. The liquid fat is poured off and shaken with 50 c.c. of decinormal alkali, whereby the colouring matters are removed from the ethereal solution. The aqueous layer is drawn off and very carefully neutralised with hydrochloric acid, until just acid to litmus. The colouring matters, containing a minute quantity of fatty acids, are thus precipitated; the precipitate is transferred to a tared filter, washed with cold water, dried, and weighed.

For the discrimination of the several colouring matters the precipitate is dissolved in alcohol, and two or three drops of the solution tested with an equal quantity of the reagents as given in the following table:—

[TABLE

Reactions of Colouring Matters

Colouring Matters.	Concentrated H_2SO_4	Concentrated HNO_3	$H_2SO_4+HNO_3$	Concentrated HCl.
Annatto	Indigo blue, changing to violet	Blue, becoming colourless on standing	Same	No change, or only slight dirty yellow and brown
Annatto + decolourised butter	Blue, becoming green, and slowly changing to violet	Blue, then green and bleached	Decolourised	No change, or only slight dirty yellow
Turmeric [1]	Pure violet	Violet	Violet	Violet, changing to original colour on evaporation of HCl
Turmeric + decolourised butter	Violet to purple	Violet to reddish violet	Same	Very fine violet
Saffron.	Violet to cobalt blue, changing to reddish brown	Light blue, changing to light reddish brown	Same	Yellow, changing to dirty yellow
Saffron + decolourised butter.	Dark blue, changing quickly to reddish brown	Blue, through green to brown	Blue, quickly changing to purple	Yellow, becoming dirty yellow
Carrot.	Umber brown	Decolourised	Do. with NO_2 fumes and odour of burnt sugar	No change
Carrot + decolourised butter	Reddish brown to purple, similar to turmeric	Yellow, and decolourised	Same	Slightly brown
Marigold	Dark olive green, permanent	Blue, changing instantly to dirty yellow green	Green	Green to yellowish green
Safflower	Light brown	Partially decolourised	Decolourised	No change
Aniline yellow	Yellow	Yellow	Yellow	Yellow
Martius yellow	Pale yellow	Yellow, reddish precipitate. Magenta at margin	Yellow	Yellow, precipitate treated with NH_3 and ignited deflagrates
Victoria yellow	Partially decolourised	Same	Same	Same, colour returns on neutralising with NH_3

According to *Leffmann*,[2] methylorange is extensively used in the U.S.A., especially for oleomargarine. The colouring matter is ex-

[1] Ammonia gave with turmeric reddish brown, returning to original colour on driving off NH_3.

[2] Second annual report of the Dairy and Food Commissioner of Pennsylvania.

tracted as described above and tested with dilute acid, when the well-known red tint will appear.

Butter colours are similarly treated, using, of course, smaller quantities of the samples. About 5 grms. are dissolved in 20-25 c.c. petroleum ether, and treated with 10 c.c. of a 4 per cent solution of potash.[1]

4. **Preservatives.**—*Borax* will have been discovered by examining the ether-insoluble portion (see p. 89).

Salicylic acid is sometimes used to preserve butter.[2] According to the directions of the Paris Municipal Laboratory it is detected by repeatedly exhausting 20 grms. of butter with a solution of sodium bicarbonate, whereby the acid is converted into easily soluble sodium salicylate. The aqueous liquid is acidulated with dilute sulphuric acid, extracted with ether and a little mercurous nitrate added to the residue left after evaporating off the ether, when a precipitate, nearly insoluble in water, is obtained. This is filtered off, washed and decomposed by dilute sulphuric acid, free salicylic acid resulting again. It is redissolved in ether, the solvent evaporated off, and the residue warmed to 80°-100° C., until nearly dry. In order to remove any other acid present, the residue is extracted with neutralised petroleum ether, the ethereal liquid diluted with an equal volume of 95 per cent alcohol, and titrated with decinormal alkali, using phenolphthalein as an indicator. 1 c.c. of decinormal alkali corresponds to 0·0138 grm. of salicylic acid.

For further identification the salicylic acid may be liberated again by a corresponding amount of standardised hydrochloric acid and tested with a drop of very dilute iron perchloride solution, when a violet coloration should be obtained.

Formalin (formaldehyde) is best detected by *Hehner's* method in the form given it by *Richmond* and *Boseley*:[3] Add to the aqueous liquor obtained when butter is melted a drop of milk, and pour the mixture carefully on the surface of concentrated sulphuric acid contained in a test-tube. In the presence of formalin a blue ring will appear at the zone of contact of the two liquids. A trace of ferric chloride renders the reaction far more distinct.

2. Examination of Butter Fat

Free Fatty Acids.—Fresh butter contains a small quantity of free fatty (butyric) acid; according to *Duclaux*, from 0·005 to 0·0100

[1] The following formulæ for butter colours have been taken by *Leffmann* from a *Druggists' Circular*:—

Extract of Annatto 10 ounces.	Annatto seed, bruised 10 parts.
Turmeric . . 5 ,,	Turmeric . . . 3 ,,
Logwood chips . 2½ ,,	Ammonium carbonate 1 ,,
Cotton seed oil . 1 gallon	Cotton seed oil . . 75 ,,
	Lard . . . . 10 ,,

[2] *Jour. Soc. Chem. Ind.* 1887, 670.

[3] *Analyst*, 1895, 155; 1896, 92, 94, 157.

grm. per 1000 grms. The quantity of free acids, however, increases rapidly on keeping, due perhaps to the action of microbes on the nitrogenous matter of the butter.[1] The butter becomes thereby "rancid." *Butter fat*, however, offering no suitable nourishment to microbes, does not decompose so rapidly, although formation of free fatty acids gradually sets in.

Butter containing as little as 0·02 to 0·03 grm. of free fatty acids per 1000 grms. has a "rancid" taste; in the case of old butter the free acids may amount to 1·5 grms.

Butter can therefore be examined for its state of freshness by titrating the amount of free fatty acids. The acidity may be expressed by its *acid value* (p. 148), or in terms of oleic acid, or, as is usually done in Germany, by "degrees of acidity," *i.e.* the number of c.c. of normal alkali required for 100 grms. The table given page 150 affords an easy comparison between the various modes of expressing the results of titration.

The "rancidity" of butter is, however, not necessarily in proportion to the amount of free fatty acids, rancidity not being synonymous with acidity (cp. chap. i. p. 11).

It is usually assumed that, on butter becoming rancid, the glycerides of the volatile fatty acids are split up first, decomposition gradually proceeding to the higher glycerides. *Bondzyński* and *Rufi*[2] are of the opinion that the rancidity of old butter is due to a high proportion of free *insoluble* acids, and not to the soluble or volatile acids. The method, however, they employed (p. 196) being open to objections, their opinion must be accepted with due reserve, all the more as it is in conflict with the well-established fact that marked rancidity is a safe indication of genuine butter as opposed to old artificial butter (which is, of course, free from glycerides of volatile acids). Nevertheless, *Spaeth's* experiments on lard would seem to lend support to their statement.

TESTS FOR FOREIGN FATS

Preliminary Tests

A reliable preliminary test for the discrimination of margarine from genuine butter is, according to *Hehner*,[3] to heat the fat with a quantity of alcoholic potash insufficient for complete saponification. The formation of *ethyl butyrate*, easily recognised by its pleasant smell (recalling that of pine-apples), will indicate the presence of butter.

[1] The following notes, taken from the opening address of Prof. H. M. Ward at the Toronto Meeting of the Brit. Assoc. 1897, may be of interest:—"Some years ago Storch found that the peculiar aroma of a good butter was due to a bacterium which he isolated, and Wiegmann has now two forms, or races, one of which develops an exquisite flavour and aroma, but the butter keeps badly, while the other develops less aroma, while the butter keeps better. According to Conn's publication, this subject has been advanced considerably in America, for they have isolated and distributed to numerous dairies pure cultures of a particular butter-bacillus which develops the famous 'June flavour' hitherto only met with in the butter of certain districts during a short season of the year."

[2] *Jour. Soc. Chem. Ind.* 1890, 422. [3] *Analyst*, 1884, 76.

A number of margarines examined by the writer failed to give the odour of the butyrate; this appeared, however, on adding a small quantity of genuine butter.

A large number of tests, based on the **behaviour with solvents**, have been proposed for the same purpose. They should, however, not be solely relied upon; at best they can only point to possible adulteration with another fat.

Thus *Hoorn*[1] dissolves 1 grm. of the sample to be tested in 7 c.c. of petroleum ether, and allows it to stand in a closely-corked bottle at 10°-15° C. for several hours. Pure butter fat remains dissolved, whereas tallow and lard are said to separate out.

Münzel[2] dissolves 1 grm. of the sample in 12·5 c.c. of absolute alcohol (spec. grav. 0·797) in a test-tube by warming on the water-bath, and then closes it with a tightly-fitting cork provided with a thermometer reaching into the liquid. The contents of the test-tube are then allowed to cool, and the temperature is noted at which solidification takes place. The following observations are recorded by *Münzel*:—

Fat.	Temperature at which Solidification sets in. °C.
Genuine butter	34
,, ,, +10 per cent of horse fat	37
,, ,, +20 ,, ,, ,,	40
,, ,, +30 ,, ,, ,,	44
,, ,, +10 ,, tallow	40
,, ,, +20 ,, ,,	43
,, ,, +30 ,, ,,	46
,, ,, +10 ,, lard	38
,, ,, +20 ,, ,,	41
,, ,, +30 ,, ,,	43
Margarine	56
Genuine butter +25 per cent of oleomargarine	40
,, ,, +50 ,, ,,	48

Horsely, *Ballard*, *Husson*, and *Filsinger* have tried to make use of the different solubilities of butter and butter-substitutes in ether or in ether-alcohol. *E. Scheffer*[3] employs for the same purpose a mixture of forty parts (by volume) of rectified fusel-oil and sixty parts (by volume) of ether of specific gravity 0·725. The different solubilities of the fatty acids in alcohol and benzene suggest another analytical method (cp. *Dubois* and *Padé*, p. 328).

According to *Bockairy*,[4] foreign fat in butter may be detected by the following method: 15 c.c. of the filtered fat are dissolved, in a graduated cylinder, in 15 c.c. of toluene, and 40 c.c. of alcohol of 96·7° Gay-Lussac are added. The mixture is warmed to 50° C. and agitated, when a butter substitute will give a turbidity, whereas butter, even when containing a little foreign fat, yields a clear solution. When kept for thirty minutes at a temperature of 40° C., the

[1] *Zeitsch. analyt. Chem.* 1872, 334.
[2] *Ibid.* 1882, 436.
[3] *Jour. Soc. Chem.* 1887, 148.
[4] *Ibid.* 1888, 350; and *Bull. Soc. Chem.* 49. 331.

solution will be clear or only slightly turbid in the case of pure butter, whereas adulterated butter will cause at first turbidity and then separation of an oily liquid. If the latter exceeds 3 c.c. the butter must be considered adulterated. *Violette* considers this process unreliable.

Valenta's test—behaviour with glacial acetic acid—has been employed by *Allen*[1] for the examination of butter in the following manner: 3 c.c. of the melted fat are poured into a small test-tube, an exactly equal measure of glacial acetic acid is added, and the contents of the tube heated until complete solution takes place on agitation. The liquid is then allowed to cool spontaneously whilst stirred with a thermometer, and the temperature observed at which it becomes turbid. The turbidity temperatures for genuine butter were found from 56°-61·5° C., whereas those for "butterine" were 98°-100° C.

Jean does not regard the turbidity as a criterion, but estimates the volume of acetic acid dissolved by the fat. For his method compare p. 273.

I subjoin some of his results in the following table:—

Fat.	Acetic Acid dissolved. Per cent.
Pure butter	63·33[2]
,, ,, with 10 per cent of cocoa nut oil .	66·66
,, ,, ,, 15 ,, ,, ,, .	90
,, ,, ,, 28 ,, ,, ,, .	96

Carbolic acid, recommended first by *Crook*,[3] has been found suitable by *Lenz*, although his results do not completely agree with those stated by *Crook*. The test is made as follows: Melt 0·648 grm. (10 grains) of the filtered fat in a graduated test-tube in a water-bath at a temperature of about 66° C., and agitate with 1·5 c.c. of liquid carbolic acid—prepared from 373 grms. of crystallised phenol and 56·7 grms. of water. Keep the mixture in the warm water until it has become transparent, and allow to stand for some time at the ordinary temperature. In the case of genuine butter a clear solution results, whereas in the presence of foreign fats, such as tallow or lard, two layers, separated by a well-defined border line, will be noticed.

The following table gives the results obtained by *Crook* and *Lenz*:—

Fat.	Volume of the Lower Layer in per cents.	
	Crook.	Lenz.
Beef tallow	49·7	
Mutton tallow . . .	44·0	39·1
Lard	49·6	37·0

[1] *Commerc. Org. Analys.* ii. 154. [2] Cp. also footnote p. 273.
[3] *Zeitsch. analyt. Chem.* 19, 369.

After somewhat prolonged cooling crystals are distinctly noticeable in the upper layer. According to *Lenz*, no separation into two layers takes place in the case of genuine butter mixed with 5 per cent of lard; after twenty-four hours, however, crystalline deposits appear, differing, though, from those yielded by genuine butter under the same conditions.

Recently *cumene* has been suggested by *Erdélyi*[1] for the detection of foreign fats. A solution of pure butter in cumene, when cooled to 0° C., remains perfectly clear for at least one hour—in most cases very much longer—whilst in presence of foreign fats a more or less pronounced turbidity is developed after 1-1¼ hours' standing. The details given by the author, however, are, in the writer's opinion, not such as to recommend the method as a reliable one.

Physical Methods

(*a*) *Specific Gravity*

It has been pointed out already that, as a rule, the determination of the specific gravity, in conjunction with that of the *Reichert* and of the saponification values, furnish sufficient evidence of the purity or otherwise of a butter fat. The specific gravity of butter fat is higher than that of the majority of fats that might come within the scope of the adulterator.

The determination of the specific gravity at the ordinary temperature, recommended by *A. W. Blyth*[2] and *Casamajor*,[3] has been almost abandoned, and, as a rule, temperatures are preferred at which the butter fat is in a melted state. The methods that are employed have been fully explained, pages 123 *et seq.*

The specific gravity is a very valuable criterion, for the reason that it is almost constant for genuine butters. Small deviations from the normal values appear, according to *Adolf Mayer*, to follow the rule that a high *Reichert value* conditions a high specific gravity.

J. Bell, who first proposed the specific gravity as a critical test, chose the temperature of 100° F. = 37·8° C. The apparatus used was an ordinary pear-shaped specific gravity bottle. In the examination of the large number of samples, reference to which has been made repeatedly, he has found that the experimental values vary within the very narrow limits of 0·911 and 0·913. The corresponding values obtained for other fats are recorded in the subjoined table:—

[1] *Jour. Soc. Chem. Ind.* 1893, 184. [2] *Analyst*, 1880, 76.
[3] *Chem. Centralblatt*, 1882, 252.

Kind of Fat.	Specific Gravity at 100° F. = 37·8° C. J. Bell.
Genuine butter fat (113 samples)	0·911-0·913
Mutton suet	0·90283
Beef suet	0·90372
Fine lard	0·90384
Oleomargarine	0·90384
,,	0·90234
,,	0·90315
,,	0·90379
,,	0·90136

Due regard, however, must be had to the fact that cocoa nut and palm nut oils, if present, could not be thus detected. *Moore* has pointed out that owing to the somewhat higher specific gravity of cocoa nut oil—0·9167 at 37·8° C.—a judiciously prepared mixture of the same with oleomargarine might be incorporated with butter without being detected by an abnormal number for the density. This qualifies *Viollette's*[1] statement that by means of a density determination alone butters may be rapidly sorted into three classes, viz. those undoubtedly adulterated with margarine, those doubtful, and those that may be considered practically pure. The same holds good of other vegetable oils, such as *arachis*, *sesamé*, and *poppy seed oils*.

Skalweit, having found that the differences in the specific gravities of butter and fats likely to be used as adulterants are greatest at 35° C., prefers this temperature. His observations are given in the following table :—

Specific Gravities

Temperature.	Lard.	Margarine.	"Butterine."	Butter Fat.
°C.				
35	0·9019	0·9017	0·9019	0·9121
50	0·8923	0·8921	0·8923	0·9017
60	0·8859	0·8857	0·8858	0·8948
70	0·8795	0·8793	0·8793	0·8879
80	0·8731	0·8729	0·8728	0·8810
90	0·8668	0·8665	0·8663	0·8741
100	0·8605	0·8601	0·8598	0·8672

Other chemists, notably *Koenigs*, have taken the specific gravity at 100° C. (water of 15° C. = 1); the results recorded by the different observers agree in a satisfactory manner :—

[1] *Jour. Soc. Chem. Ind.* 1894, 54.

Specific Gravities at 100° C., *Water at* 15° C. = 1

Fat.	Koenigs.	Sell.	Allen.
			At 99° C., water 15·5 = 1.
Genuine butter	0·866-0·868	0·866-0·868	0·867-0·870
Beef tallow	...	0·859-0·8605	
Lard	...	0·860-0·8605	
Oleomargarine	...	0·859-0·860	0·8585-0·8625
Adulterated butter . . .	0·859-0·865		
3 parts of genuine, 1 part of artificial butter	...	0·865	
1 part of genuine, 1 part of artificial butter	...	0·863-0·864	

The lower limit for the specific gravity of pure butter fat should therefore be 0·866 at 100° C., compared with water of 15° C.

The specific gravities at 100° C., referring to water of 100° C. as unit, are tabulated here—

Specific Gravities at 100° C., *Water at* 100° C. = 1

Fat.	J. Bell.	Muter.	Allen.
Genuine butter fat .	0·9094-0·9140	0·9105-0·9138	0·9099-0·9132
Oleomargarine . .	0·4014-0·9038	0·903-0·906	0·902-0·905

Viollette[1] being of the opinion that, by means of density determination alone, butters may be rapidly sorted into (*a*) undoubtedly adulterated, (*b*) doubtful, (*c*) practically pure butters, proposes to determine the weight *in vacuo* of 1 c.c., measured at 100° C. He has found that—

1 c.c. of	At 100° C. weighs *in vacuo*. Grms.
Genuine butter	0·86328-0·86425
Margarine	0·85766-0·85865

Adolf Mayer has drawn attention to the necessity of taking the barometric pressure into account, when hydrometers are used at 100° C. (cp. p. 127), the specific gravity differing by 0·0001 for a variation of 2 mm. in the pressure. Therefore for a difference of 40 mm. in the atmospheric pressure, which occurs frequently, a correction of 0·002 would have to be made, which is not to be neglected, considering that the difference between genuine and artificial butter amounted to only 0·007 in his method.

[1] *Jour. Soc. Chem. Ind.* 1894, 54.

Instead of determining the specific gravity by weighing a definite volume, according to the formula $d = \frac{m}{V}$ (where m denotes the weight, V the volume, and d the density), *Zaloziecki* proposes to measure the volume of the fatty acids derived from a known weight of butter. Evidently this is no new constant, as, from the formula given, it follows that $V = \frac{m}{d}$, and no further information is gained than that afforded by the specific gravity number of the fat. The volume of the fatty acids is referred to the weight of fat, and it becomes therefore simply a question whether the method proposed by *Zaloziecki* is more expeditious than the simple weighing of the original fat in a picnometer. There can be no doubt that *Zaloziecki's* method is more cumbersome, and for this reason, and for the more cogent one that a serious source of error is introduced by the solubility of the volatile fatty acid, the method cannot be recommended. For further information as to the details of the method the reader is referred to the original paper,[1] the results only being given here :—

Fat.	Volume of Fatty Acids from 10 grms. of Fat at 80° C. c.c.
Best butter A	10·70-10·75
,, ,, B	10·80-10·80
Commercial butter A	10·85
,, ,, B	10·80
Rancid butter	10·95
Cocoa nut oil	10·90-10·95
Beef tallow old	11·70
,, ,, fresh	11·50
Mutton tallow	11·60
Lard	11·50
Margarine	11·60
Oleomargarine	11·35
Olive oil	11·25

(*b*) *Refractometric Examination*

The refractometric examination proposed at first by *Alexander Müller* and *Skalweit* has received powerful assistance by the construction of special apparatus, viz. *Amagat* and *Jean's* oleo-refractometer and *Zeiss's* butyro-refractometer.

We shall consider here only the two last-mentioned apparatuses, *Abbe's* refractometer, which has been made use of by *Skalweit*, having been superseded by them (for butter analysis at any rate) on account of their handiness and rapidity in the manipulation entailed.

Thoerner's observations obtained with *Pulfrich's* refractometer have been given above (p. 263).

[1] *Chem. Revue*, 1897, 119.

For the examination in the oleo-refractometer (description of the instrument p. 119) the sample is prepared, according to *Jean*,[1] in the following manner: Melt from 25 to 30 grms. of butter in a porcelain dish at a temperature not exceeding 50° C., stir well with a pinch or two of gypsum, and allow to settle out at about the same temperature. Then decant the supernatant fat through a hot water funnel plugged with cotton wool, and pour it whilst warm into the prism of the apparatus. Stir with the thermometer until the fat has cooled to 45° C., and observe the deviation. [Ether must not be used for the preparation of the butter fat, as minute traces of the solvent, which is very difficult to get rid of entirely, seriously influence the result.] Genuine butter gives a deviation of 30° to the left. A large number of French and Belgian pure butters showed deviations from −29° to −31°. *Pearmain*[2] finds for 15 samples the maximum −34 and the minimum −25. For the sake of comparison we add some observations made by *Jean* and *Pearmain* on other fats (cp. also p. 264).

No.	Kind of Fat.	Degrees.	Observer.
1	Margarine (Mouriès) . . .	−14	Jean
2	"Crême Mouriès"	−15	,,
3	Oleomargarine	−17	,,
4	Pure butter with 10 % of No. 3 .	−28	,,
5	,, ,, 20 % ,, .	−26	,,
6	,, ,, 30 % ,, .	−25	,,
7	,, ,, 50 % ,, .	−23	,,
8	Cotton stearine	−20	,,
9	"Vegetaline" (cocoa nut butter) .	−59	,,
10	Margarine	−13 to −18	Pearmain
11	Lard	− 8 to −14	,,
12	Tallow	−15 to −18	,,

Admixtures of *vegetable oils* are recognised more easily still, yielding as they do a marked deviation to the *right*.

The value of the refractometric method is demonstrated by *Jean* by the following example:—A pure butter giving a deviation of −30° showed, after having had admixed 5 per cent of arachis or linseed oil, −20° only, thus distinctly indicating an adulteration, whereas, if *Reichert's* process be resorted to, adulteration could not be pronounced upon with certainty.

Lobry de Bruyn, however, has shown that in the case of Dutch butters deviations from −25° to −30° are frequently met with, and that even deviations of 21-26 were observed in the case of butters having the normal amount of volatile fatty acids and possessing good taste.[3] This serious objection to the employment of the oleo-refractometer has to some extent been deprived of its force by *Jean's* explanation

[1] Jean, *Chimie analytique des matières grasses*, Paris, 1892, p. 465.

[2] *Analyst*, 1895, 135.

[3] The same fact, viz. that butters with abnormal refraction gave normal *Reichert* values, has been observed by Fischer, *Chem. Zeit.* 1895, 284.

that abnormal values were only found if the cows had been fed with linseed cakes, minute quantities of linseed oil passing into the milk, and consequently into the butter. In such cases, as *Jean* himself is forced to acknowledge, the indications of the oleo-refractometer must be supplemented by chemical methods (*Reichert's* process, etc.) The chief use of the apparatus would then consist, according to the same author, in admitting of a rapid examination for the purposes of market control, all the samples with the deviation of -30° being allowed to pass, whereas doubtful specimens would have to be referred to the chemist for further examination. But even this restricted use of the oleo-refractometer may become illusory if we bear in mind that mixtures of margarine (deviation -11°) and of cocoa nut butter (deviation -52°) may be prepared showing the correct deviation of -30°. For this reason the indications of the oleo-refractometer must be checked by other methods in every case.

The same critical remarks apply to *Zeiss's* butyro-refractometer, which has been recommended by *Wollny*, and also by *Mansfeld*[1] and *Hefelmann*[2] on account of the great ease with which a large number of samples can be dealt with in a short time (20 samples in one hour).

The instrument is shown in Fig. 44. The following notes concerning its use have been compiled from the printed directions supplied with the butyro-refractometer by its well-known maker.[3]

Place the instrument upon a table, where diffuse daylight or any form of artificial light can be readily admitted for illumination. Supply through nozzle D a stream of water of a constant temperature. Then open the prism casing by giving to pin F about half a turn to the right, until it meets with a stop, and turn the half B (held in position by H) of the casing aside. The prism surfaces must now be cleaned with the greatest care, which is best done by applying soft linen moistened with a little alcohol or ether. Now melt the sample of butter in a spoon, and pour the clear fat through a filter, allowing the first two or three drops to fall on the surface of the prism contained in casing B. For this purpose the apparatus should be raised with the left hand, so as to place the prism surface in a horizontal position. Then press B against A, and bring F back into its original position by turning it in the opposite direction.

While looking into the telescope, give the mirror J such a position as to render the critical line which separates the bright left part of the field from the dark right part distinctly visible. It will be first necessary to ascertain whether the space between the prism surfaces is filled uniformly with butter, failing which the critical line will not be distinct. For this purpose examine the rectangular image of the

[1] *Forschungsberichte über Lebensmittel und ihre Beziehungen zur Hygiene, etc.*, Jahrgang i. Heft. 3.

[2] *Pharm. Centralhalle*, 1894, No. 33.

[3] Carl Zeiss, Optische Werkstätte, Jena.

prism surface about 1 cm. above the telescope with a lens. Finally adjust the movable part of the telescope, so that the scale becomes clearly visible.

The critical line, somewhat hazy at first, approaches after about one minute a fixed position and quickly attains its greatest distinctness. This point being reached, note the appearance of the critical line (*i.e.* whether colourless or coloured, and in the latter case of what colour), and then also note the position of the critical line on

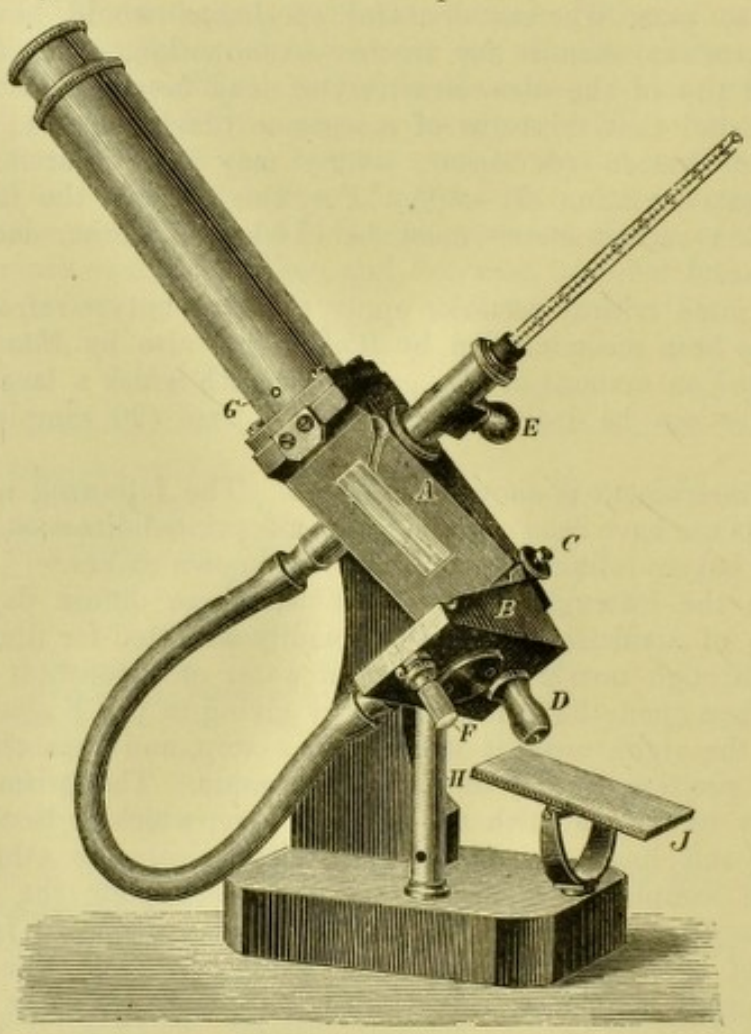


Fig. 44.

the centesimal scale, which admits of tenths being conveniently estimated. The reading of the thermometer is then taken. The adjustment of the instrument should be tested periodically by means of a *standard fluid* supplied with the instrument, the critical line of which must occupy a definite position in the scale. By the aid of a watch-key inserted in G the position of the objective can be altered at will.

The scale divisions may be converted into refractive indices by reference to the following table :—

Table of Refractive Indices

Scale Division.	n_D.	Difference.
0	1·4220	
10	1·4300	8·0
20	1·4377	7·7
30	1·4452	7·5
40	1·4524	7·2
50	1·4593	6·9
60	1·4659	6·6
70	1·4723	6·4
80	1·4783	6·0
90	1·4840	5·7
100	1·4895	5·5

The results obtained by *Wollny* in the examination of a large number of butter and butter-substitutes are given in the subjoined table :—

No.	Kind of Fat.	Temp.	Scale Division.	Refractive Index n_D.
		°C.		
1	Genuine butters . .	25	49·5-54·0	1·4590-1·4620
2	Margarine . . .	25	58·6-66·4	1·4650-1·4700
3	Mixtures of 1 and 2 .	25	54·0-64·8	1·4620-1·4690

All samples giving higher values than 54·0 scale divisions for the critical line will, according to *Wollny*, be found adulterated when tested by chemical methods. As a practical limit 52·5 (at 25° C.) is recommended, so that all samples exceeding that number should be further examined.

Besides the variability of the position of the critical line, also its *appearance* forms a means of comparison. This mode of differentiation is due to the peculiar construction of the double prism, which shows differences of dispersive power by different appearances of the critical line. The prisms are so constructed that the critical line of pure butter is colourless, while margarine and other artificial butters, which have greater dispersive powers than natural butter, show a blue critical line. This distinction, however, is unfortunately not applicable to each case, and the appearance of a blue fringe can only be looked upon as a useful indication in cases of suspected adulteration.

In calculating the position of the critical line for other temperatures than 25° C., a correction of 0·55 scale divisions for 1° C. should be made. The following table compiled in this manner

gives the practical limits for pure butters at the corresponding temperatures :—

Temperature. °C.	Scale Division.
25	52·5
26	51·9
27	51·4
28	50·8
29	50·3
30	49·8
31	49·2
32	48·6
33	48·1
34	47·5
35	47·0
36	46·4
37	45·9
38	45·3
39	44·8
40	44·2
41	43·7
42	43·1
43	42·6
44	42·0
45	41·5

Delaite,[1] however, has shown that calculation to the standard temperature from any other temperature does not give results identical with those observed at the standard temperature.

It is therefore necessary to make the observations at a temperature to be agreed upon. 40° C. seems to be a suitable temperature.

Other physical methods have been proposed, but they are of minor importance ; although the difference in the constants for pure butter fat and other fats are distinct enough, such methods break down when applied to the detection of small quantities of foreign fats in butter.

(*c*) *Critical Temperature of Dissolution*

Crismer's numbers, obtained with absolute alcohol[2] in the open tube, are given below.[3] Old and rancid samples of butter, or fresh butters badly prepared from sour cream, give lower figures. On neutralising, however, the free fatty acids and washing the fat, the normal critical temperature is obtained.

[1] *Bullet. de l'Assoc. Belge des Chimistes*, 1894 (5), 145 ; *Analyst*, 1895, 95.

[2] *Ibid.* 1886 (10), 312 ; *Analyst*, 1897, 72.

[3] Cp. also Asbóth, *Chem. Ztg.* 1896, 686. This chemist employed alcohol of spec. grav. 0·8332 (90 per cent by volume).

Critical Temperatures

	With Alcohol, 0·7967 Specific Gravity (containing 0·9 per cent of water), at 15·5° C. in Open Tube.						With Alcohol 0·8195 (8·85 per cent of water), at 15·5° C. in Sealed Tube.	Difference.
Butter	*a*	*b*	*c*	*d*	*e*	*f*		
1	54·8	54·8	54·8	54·6	54·3	53·8	100·5	45·7
2	54·5	54·5	54·5	54·2	...	...	100·5	46
3	57	57	57	...	...	...	103	46
4	54	54	...	...	...	...	100·5	46
5	50	50	...	...	...	...	105·5	45·5
6	56	...	...	...	...	...	102·5	46
7	56·5	52·2	...	...	...	...	102·5	46
8	52	52·4	56·5	52·4	51·2	...	98·2	45·7
Margarine and Mixtures								
1	78	78	...	...	...	...	124	46
2	72·2	72·2	...	...	...	...	118	45·8
3	72·5	...	...	...	...	...	118	45·5
4	78	...	...	...	...	...	123·8	45·8
5	69	...	...	...	...	...	115	46·0
6	63·8	...	...	...	...	...	109	45·2
Maize oil	70·5	...	...	...	...	...	...	...

It is curious to note that in the case of a rancid butter the number of c.c. of $\frac{n}{20}$ KOH required to neutralise 2 c.c. of butter fat (dissolved in 20 c.c. of absolute alcohol), when added to the figure representing the critical temperature of the acid butter, gives approximately the critical temperature of the neutralised butter.[1]

No. of Samples.	*a* Mean Critical Temperature of Acid Butter. °C.	*b* No. of $\frac{n}{20}$ normal Alkali required for 2 c.c. c.c.	*c* Critical Temperature of Neutralised Butter. °C.	*d* Difference. *c* − *a*.
3 at 80-90° C.	88·5	7·5	96·4	7·9
14 at 90-96° C.	93·5	4·8	98·2	4·7
69 at 96-102° C.	99·12	1·2	101·7	2·6
17 at 102-106° C.	103·9	1·0		

Crismer further points out that there is a certain relation between the *Reichert-Meissl* value of a butter and the critical temperature, the sum of the *Reichert-Meissl* value and the critical temperature corrected for neutralised butter being the constants: 129 for alcohol of 0·8195 spec. gravity, and 83·5 for absolute alcohol. There is also a certain relation between the critical temperature and the *Hehner* values, as evidenced by the following table:—

[1] *Bullet. de l'Assoc. Belge des Chimistes*, 1897 (10), 453; *Analyst*, 1897, 158.

Critical Temperature for		Hehner Value.
Alcohol 0·8195 with 9 per cent of water.	Absolute Alcohol.	Per cent.
°C.	°C.	
Below 100	54	86-88
100-108	54-62	88-90·5
108-118	62-72	90-93·3
118-124	72-78	93-95·5

The variation of this constant for genuine butters is, however, too great to admit of its employment for the detection of small quantities of foreign fats.

(d) Viscosimetrical Examination

This was proposed by *Killing*[1] and *Wender*,[2] but as this method is greatly inferior to others, as regards the chief problem of butter analysis, the reader must be referred to the references given below.

The Calorimetrical Method (*Jour. Soc. Chem. Ind.* 1896, 560), the Electrical Conductivity, and the Cryoscopic Method[3] need only be mentioned in passing.

Chemical Methods. Quantitative Reactions

The most valuable indices in the chemical examination of butter are furnished by the *Hehner* value, the *Reichert* (*Meissl*) value, and the *Köttstorfer* or *saponification* value. The methods for their determination have been fully described in chap. v. pp. 151 - 161. With a special view to shortening the time required for the analysis, "new processes," in reality, however, nothing but modifications and combinations of the well-known methods, are being continually proposed. Most of these proposals hardly deserve the name of "method."

For the sake of completeness we describe several modifications, omitting, however, a host of others.

Perkins[4] combines *Hehner's*, *Reichert's*, and *Köttstorfer's* processes in the following manner :—

Saponify 1 to 2 grms. of butter fat, liberate the fatty acids by means of a solution of oxalic acid, saturated in the cold, taking care to avoid a large excess, and wash the fatty acids on a filter at first with cold, and finally with hot water. Concentrate the filtrate to exactly 200 c.c., distil 100 c.c. off, and examine the distillate, as in *Reichert's* process. Thus the number of mgrms. of KOH required for saturating the volatile fatty acids of 1 grm. of butter fat is found.

[1] *Jour. Soc. Chem. Ind.* 1895, 198. [2] *Jour. Amer. Chem. Soc.* 1895, 719.
[3] Garelli and Carcano, *Staz. Speriment. Agrar.* 1893, 77.
[4] *Jour. Amer. Chem. Soc.* 1889, 144.

Determine the insoluble fatty acids according to *Hehner* by weighing, dissolve them in 100 c.c. of alcohol, and titrate with decinormal potash. *Perkins* found in this manner that the fatty acids in 1 grm. of butter fat required for the saturation of the

Volatile fatty acids . . .	44·2	mgrms. of KOH
Fixed fatty acids . . .	180·0	,, ,,
Or the total of . .	224·2	,, ,,

The last number is, of course, the saponification value found in a somewhat roundabout fashion.

Morse and *Burton's*[1] method is based on the fact that the ratio between the quantities of alkali requisite for the neutralisation of the soluble fatty acids on the one hand, and of the insoluble fatty acids on the other, is constant for any given fat.

These relative quantities are given in the following table :—

Kind of Fat.	Per cent KOH required for	
	Insoluble Acids.	Soluble Acids.
Butter fat	86·57	13·17
Cocoa nut oil, not washed . . .	91·85	8·17
,, ,, ,, washed with hot water .	92·43	7·42
,, ,, ,, ,, ,, dilute CO_3Na_2 .	92·33	7·45
Cotton seed oil	92·05	7·76
Oleomargarine	95·40	4·57
Lard	95·96	3·82
Beef tallow	96·72	3·40

The following four standard solutions are required :—

1. Hydrochloric acid, 1 c.c. of which is equivalent to 20 mgrms. KOH.

2. Hydrochloric acid, 1 c.c. of which is equivalent to 2 mgrms. KOH.

3. Alcoholic potash (prepared with 95 per cent alcohol) approximately corresponding to acid No. 1. Before each experiment its strength must be accurately found by titrating with the acid.

4. Alcoholic potash, corresponding to acid No. 2.

The analysis is carried out as follows :—

Place from 1 to 2 grms. of the dry and filtered fat—the exact quantity need not be known—in an Erlenmeyer flask of 250 c.c. capacity, and saponify with that amount of the strong potash solution which exactly equals 40 c.c. of the strong standard hydrochloric acid. Then add phenolphthalein, and titrate back the excess of alkali by the standard hydrochloric acid. This gives the *saponification value*. Evaporate off the alcohol on the water-bath, and exactly

[1] *Jour. Soc. Chem. Ind.* 1888. 697.

liberate the fatty acids by adding just enough of the weaker standard acid; this quantity is, of course, the difference between 40 c.c. and the number of c.c. used for neutralising the excess of alkali after saponification. Next fit the flask with a condensing arrangement, consisting of a glass tube about 400 mm. long and 5 mm. in diameter, having its upper end bent downwards, and attached to a small U-tube containing water. This is designed to prevent the escape of volatile acids during the heating of the flask, which is continued until its contents become clear. Then filter the solution, to which is added the liquid from the U-tube, through thick paper, well wetted, and wash the insoluble fatty acids until the filtrate measures 1000 c.c. Next dissolve the insoluble acids in 50 per cent alcohol, and titrate with the strong potash solution; finally titrate the soluble acids with the weak potash solution.

The ratio only between the two amounts of alkali being required, it is neither necessary to weigh the fat nor to know the absolute strength of the standard alkalis.

The *Leffmann-Beam* process of saponification having been adopted by several laboratories affiliated to dairies, it may be described here.[1] Mix 20 c.c. of a solution of 100 grms. of caustic soda in an equal weight of water with 180 c.c. of pure concentrated glycerin. Weigh 5 grms. of the filtered fat into an Erlenmeyer flask, add 20 c.c. of the alkali solution, and heat over a naked flame for two or three minutes until the water is driven off and the liquid becomes clear.

Reichert-Meissl Value

From the analyses of several thousand butters the fact has been deduced that this value is by no means so constant as *Reichert's* researches have led to believe, the quantity of volatile acids being influenced to a greater or smaller extent by the nature of the food, the seasons, the period of lactation, the rancidity, the method employed in melting the butter, and so on.

In the following table there are collated the *Reichert-Meissl* values found by a number of chemists, the *Reichert* values (for 2·5 grms.) having been multiplied by 2·2 so as to admit of a comparison with the *Reichert-Meissl* values, although this procedure is, strictly speaking, not altogether correct. But as the limits allowed for variations of butters are greater than any error involved by the employment of a not strictly accurate factor, the table will be found useful for practical purposes.

[1] Cp. *Analyst*, 1896, 251.

[TABLE

Reichert-Meissl Values of Butter Fat

Observer.	Number of Samples.	c.c. Decinormal Potash.	Remarks.
Reichert	?	30·8	Approximate deviation, ±0·9 German butters
Meissl	?	27·0-31·5	
Reichardt	?	27·6-29·4	
Sendtner	?	24-32·8	
Thoerner	?	22-32	
Nilson	797	22·9-41·0	Swedish butters
Corbetta	178	26·1-31·4	Italian butters
Spallanzani	?	20·63	Minima for Italian butters
Spallanzani and Pizzi	?	19·8	
Vigna	?	20·68	
Maissen and Rossi	?	21·56	
Besana	114	21·80	
Longi	?	22·55	
Sartori	?	23·59	
Spallanzani and Pizzi	?	30·14	Maximum for Italian butters
Cornwall and Wallace	?	27·36	American butters
Ambühl	?	28·10-31·10	Swiss butters
Jean	?	29·26	French butters
Muter	?	31·9	English butters
Vieth	28	26·1-30·6	French butters
Vieth	39	26·9-30·8	,, ,, year following
Vieth	22	26·9-29·4	Swedish butters
Vieth	3	27·3-29·1	Holstein butters
Vieth	3	28·8-29·9	,, ,, year following
Vieth	7	27·6-29·2	English butters
Mansfeld	88	24·42-33·15	Austrian butters

These results prove that the *Reichert-Meissl* values of butter vary considerably in different countries. The minimum value adopted in this country, in France, and in Germany is 24, in Sweden 23, and in Italy 20. However, there are well-authenticated cases of genuine butters, prepared under direct supervision of chemical experts, proving that even these minima are sometimes too high. Thus *Vieth*[1] has found for butter prepared by himself from the milk of one particular English farm values ranging from 20·4-21·4. Similar cases having been stated by *Morse*,[2] *Falk* and *Leonhardt*,[3] *Samelson*,[4] *Karsch*,[5] the adopted minimum will have to be modified according to circumstances. This should apply especially, according to *Cornwall* and *Wallace*, to butter fat obtained from *one* cow only. In butters made from the milk of a large number of cows exceptional values are naturally obliterated.

As to the causes influencing the amount of volatile acids the nature of the food may tend to reduce their quantity. Thus *Spallan-*

[1] *Jour. Chem. Soc.* 1891, 507.
[2] *Jour. Analyt. and Applied Chem.* 1893, 1.
[3] *Zeit. angew. Chemie*, 1890, 728.
[4] *Chem. Ztg.* 1895, 1626. The butter gave the following constants: Reichert-Meissl value, 21·6, Hehner value, 89·2, saponification value, 216·0, iodine value, 42·5.
[5] 19·6-22·8, *Chem. Ztg.* 1897, Ref. 19.

zani and *Pizzi*[1] state (in the case of Italian butters) that when cows are out to grass butter is rich in volatile acids, and poorer in volatile acids when stall-fed and on a poor ration. It has further been shown that cows fed with cotton seed cakes yield butters of higher melting point with a corresponding decrease of about 1 per cent of volatile fatty acids.[2] It has been mentioned already that butter from cows fed with linseed cakes behaves abnormally in the refractometric examination. *Schrodt* and *Henzold*, however, deny the influence of the food. The variation of the *Reichert-Meissl* with the seasons is clearly brought out by the following numbers, due to *Vieth*:[3]—

London-made Butter.	Reichert-Meissl Value.
From July 30 to November 12, 1889 . . .	25·8-27·1
From March 25 to June 24, 1890 . . .	27·2-30·0

This agrees with *Swaving's* experience, that in the beginning of the grazing season the volatile acids increase, remaining at a high figure until the close of that season.

Greater fluctuations are caused by the periods of lactation. According to *Nilson*, the *Reichert-Meissl* value decreases from 33·44 in the first month to 25·42 in the fourteenth month of lactation; according to *Vieth*, Holstein butter, made at a time when most of the cows were nearing the end of the period of lactation, gave numbers as low as 21·7; also *Spallanzani* and *Pizzi* find higher *Reichert-Meissl* values in the early stages of lactation than in the later ones. [*Swaving*,[4] indeed, goes so far as to consider 14 as the permissible minimum. This, however, is unquestionably far too low.] Similar depressions occur during the rut-time and illness of the cows.

Samples of butter sent to the chemical laboratory for examination arriving in most instances in a rancid state, the influence of rancidity on the *Reichert-Meissl* value has engaged the attention of several chemists. *C. Virchow* and *Schweissinger* state that highly rancid butters give lower numbers; this has been confirmed by *Corbetta* and *Cornwall*. The decrease due to this cause is, however, comparatively small, for *Corbetta* found, after two and a half months, a loss of 1·7 c.c., and *Cornwall* of 1·6 c.c. only after eight months.

The method employed in melting the butter fat may also bear on the result. *Planchon* states that a sample of butter containing 3·92 per cent of volatile acids (in terms of butyric acid) gave, after warming to 50° C. for two hours, 4·17, and after fourteen hours' warming 4·80 per cent. The butter fat should, therefore, be prepared by melting the butter rapidly at a lower temperature. Nor should the precaution be neglected to obtain a proper average from the sample

[1] *Le Staz. Speriment. Agr. Ital.* 38. 257.

[2] *Revue internat. de falsific.* 1889, 200. Stein (*Jour. Chem. Soc.* 1895, Abstr. ii. 299) states that the substance in cotton seed oil giving the Becchi reaction passes into milk and even butter, when cows are fed with cotton seed cake; not so the substance giving Baudouin's reaction, when the cows are fed on sesamé cake. Cp. footnote p. 603.

[3] *Jour. Chem. Soc.* 1891, 508.

[4] *Landw. Versuchsstat.* 1891, 127.

supplied. *Medicus* and *Scheerer* state that they have found differences amounting to 4 c.c. between samples taken from the interior and the sides of the containing vessel (cp. p. 609).

The literature contains—owing, no doubt, to the importance of butter analysis—a great number of suggestions, some of which verge on the ridiculous. There are also innumerable suggestions as to improvements of the undoubtedly excellent *Reichert* process; most of them, unfortunately, are the reverse of improvements. As an example of a superfluous method may be given *Kreis's* modification of *Reichert's* process, since it has met with greater attention than it actually deserves. *Kreis* employs for saponification instead of alcoholic potash concentrated sulphuric acid, but whereas on a large scale saponification is effected with 3 or 4 per cent of acid, *Kreis* uses no less than 10 c.c. for 5 grms. of butter fat. However, the experience of several chemists, including the writer, has proved that invariably sulphurous acid is liberated, which, of course, must vitiate the results unless the sulphurous acid is removed or otherwise rendered innocuous. The ingenuity of several analysts has been exercised to eliminate the error due to the presence of SO_2; others again have tried to exactly define the strength of the acid required so as to avoid formation of SO_2. In short, minutiæ of a most aggravating character are gone into just in order to squeeze out, as it were, results in agreement with those furnished by *Reichert's* distillation process, which, after all, must be used as a standard to gauge the correctness or otherwise of the new method.

Both *Reichert* and *Meissl*, being under the impression that their values were fairly constant, thought that the quantity of a foreign fat added to the butter could be calculated by their method. The following formula was supposed to give the amount of real butter fat in the sample:—

$$B = \frac{100(n - C)}{28{\cdot}78 - C},$$

where n is the *Reichert-Meissl* value of the sample, and C the corresponding value for the admixed fat. 28·78 is taken as representing the number for pure butter fat. *Meissl* is of opinion that, on an average, C may be assumed to equal 3, which is, no doubt, too high for the majority of fats. Since, however, the *Reichert-Meissl* value is by no means constant, as has been demonstrated in the table given above, a calculation of this kind is inadmissible (*Sendtner*[1]).

Excellent as *Reichert's* method is, a sophistication with 20 per cent of a foreign fat in the case of excellent butter, or of 10 per cent in the case of butter of ordinary quality, cannot be detected with certainty. Still, it must be considered the best method hitherto designed for the detection of frauds, no other method allowing a rapid

[1] *Repert. der analyt. Chemie*, 3. 345.

discrimination between genuine butter and a judiciously prepared mixture of margarine and cocoa nut oil. The following table demonstrates this clearly :—

Reichert-Meissl Values

Kind of Fat.	c.c. Decinormal Potash.	Observer.
Cocoa nut oil	7·0-7·8	Reichert, Moore, Allen, Muter
"Margarine"	2·6	Muter
"Oleomargarine"	0·8-0·9	Jean
Butter fat with 10 per cent of cocoa nut oil	26·8	,,
,, ,, 20 ,, ,, ,,	24·13	,,
,, ,, 25 ,, ,, ,,	24	Muter
,, ,, 50 ,, ,, ,,	18	,,
,, ,, 75 ,, ,, ,,	12	,,
50 parts of butter fat, 22·5 parts of cocoa nut oil, and 27·5 parts of oleomargarine	17·4	Moore

Only in those cases where solely oleomargarine is the adulterant, and it exceeds 10 per cent, the determination of the saponification value may lead to results in a shorter time; this value will then be found low. As a rule it is advisable to combine the determination of the saponification number with that of the *Reichert-Meissl* value. Where butyric acid, butyrin, or amyl acetate have been added to conceal fraud, a high saponification value in conjunction with a normal *Reichert-Meissl* value may reveal it.

If there be reason to suspect that butter oil, containing more volatile acids than butter fat, has been added to a sample, it will be best to resolve the fat into an oily and a solid part (p. 609), or to extract with alcohol and examine each portion separately by the *Reichert-Meissl* process.

In those cases where the *Reichert-Meissl* value just reaches the limit of 24 the analyst is confronted with the uncertainty as to whether the butter is adulterated or not.[1] Additional assistance may be found in such cases in the determination of the specific gravity, the saponification value, and also in the employment of the oleo-refractometer or butyro-refractometer. In the following table some of the *Reichert-Meissl* values given above are tabulated side by side with the deviations in the oleo-refractometer :—

[1] Muter states (*Analyst*, 1891, 90) that there is in the London market much *cheap* butter that shows exactly 26 in the *Reichert-Meissl* test.

Oleo-refractometer

No.	Fat.	Reichert-Meissl Value.	Deviation.	Observer.
1	Genuine butter	29·26	−30	Jean
	,, ,, ...	31·9	−34	Muter [1]
2	Cocoa nut oil	7·8	−59	Jean
	,, ,, ...	7·7	−54	Muter
3	Genuine butter with 10 per cent of cocoa nut oil	26·8	−33	Jean
4	,, ,, ,, 15 ,, ,, ,,	...	−34	,,
5	,, ,, ,, 20 ,, ,, ,,	24·13	−36	,,
6	,, ,, ,, 25 ,, ,, ,,	26·4	−39	Muter
7	,, ,, ,, 50 ,, ,, ,,	19·8	−44	,,
8	,, ,, ,, 75 ,, ,, ,,	13·2	−49	,,
9	Margarine	2·8	− 8·5	,,
10	Genuine butter with 25 per cent of margarine	24	−27	,,
11	,, ,, ,, 50 ,, ,,	17·1	−22	,,
12	,, ,, ,, 75 ,, ,,	9·9	−15	,,
13	Margarine with 50 per cent of cocoa nut oil .	6·1	−32	,,
14	50 per cent genuine butter with 25 per cent of margarine and 25 per cent of cocoa nut oil .	19·3	−33	,,
15	25 per cent genuine butter with 50 per cent of margarine and 25 per cent of cocoa nut oil .	12·3	−27	,,

Similar observations with the butyro-refractometer are recorded in the following table, due to *Mansfeld* :—

[1] The Reichert values given by *Muter* have been multiplied by 2·2 for the sake of better comparison.

[TABLE

Butyro-refractometer

No.	Fat.	Scale Divisions at 40° C.	Reichert-Meissl Value.	Remarks.
1	Butter . .	41·6	31·5	Genuine
2	,, . .	42·3	30·8	,,
3	,, . .	43·6	29·8	,,
4	,, . .	44·2	28·7	,,
5	,, . .	44·2	28·6	,,
6	,, . .	41·6	28·6	,,
7	,, . .	43·0	28·2	,,
8	,, . .	44·0	28·1	,,
9	,, . .	43·5	27·9	,,
10	,, . .	44·1	27·1	,,
11	,, . .	42·5	27·0	,,
12	,, . .	44·4	26·8	,,
13	,, . .	43·3	26·7	,,
14	,, . .	43·7	26·7	,,
15	,, . .	42·1	26·4	,,
16	,, . .	43·2	26·3	,,
17	,, . .	43·1	26·2	,,
18	,, . .	44·0	25·4	,,
19	,, . .	43·1	...	,,
20	,, . .	42·3	...	,,
21	,, . .	43·0	...	,,
22	,, . .	41·6	24·4	Suspected on account of low Reichert - Meissl value
23	,, . .	42·4	24·3	
24	,, . .	42·5	23·9	
25	,, . .	45·1	22·6	Contains 18 % of foreign fat
26	,, . .	46·1	7·2	,, 76 % ,,
27	,, . .	47·1	6·5	,, 78 % ,,
28	,, . .	48·6	3·7	,, 89 % ,,
29	Butter substitute	49·2	3·1	,, 91 % ,,
30	Melted butter .	49·0	3·0	,, 91·5 % ,,
31	Artificial butter	48·6	2·3	,, 94 % ,,
32	Oleomargarine .	48·6	1·2	

The inspection of the figures in the table headed oleo-refractometer proves that 10 to 15 per cent of cocoa nut oil—Nos. 3 and 4—cannot be detected by either method. A commercial butter thus adulterated would, in the present state of our knowledge, have to be considered genuine.[1] Even values, like those given in No. 5, would not justify the analyst in condemning a butter, although he may declare it suspicious. In the case, however, of values like No. 6 being obtained, adulteration may be taken as proved because of the abnormal deviation conjointly with a *Reichert-Meissl* value just reaching the limit. In all other cases the distillation process alone leads to unmistakable results.

Muter suggests that there may exist a relation between *Reichert-Meissl* value and deviation in the oleo-refractometer, as shown in the following table :—

[1] It is to be hoped that the determination of stearic acid in the insoluble acids according to Hehner and Mitchell's method may lead to unmistakable results.

	Reichert-Meissl Value.	Deviation.
Pure butter .	32	−36
,, .	30·5	−35
,, .	29·0	−34
,, .	27·5	−33
,, .	26	−32
,, .	24·5	−31
? .	23	−30
? .	21·5	−29

Saponification Value

Köttstorfer[1] found that 1 grm. of butter fat required from 221·5 to 232·4 mgrms. KOH; the mean saponification value of butter may therefore be taken as 227.

There are, however, exceptions. The saponification number 216 for a genuine butter has been recorded already (p. 633, footnote 4).

The following table gives the results of the examination of 185 butters (Silesian), due to *Seyda* and *Woy*:—

Saponification Number.	Per cent of the Samples examined.
221-223	4
223-225	7
225-226	7
226-228	15
228-230	21
230-233	28
Above 233	18

The saponification value of oleomargarine being about 195·5, it would appear that the proportion of it in a sample may be calculated from the formula

$$X = 100 \cdot \frac{227 - n}{227 - 195{\cdot}5} = 3{\cdot}17(227 - n).$$

If, however, the usual variations in the saponification value be allowed for, errors amounting to as much as 10 per cent and even more may occur. Moreover, *Moore* has shown that, owing to the exceptionally high saponification value of cocoa nut (and palm nut) oil, it would be an easy matter to prepare mixtures of this oil and margarine having exactly the saponification value of genuine butter fat.

[1] *Zeitsch. analyt. Chem.* 1879, 199.

Hehner Value

Hehner's[1] experiments demonstrated the fact that the proportion of insoluble acids in butters varies from 86·5 to 87·5 per cent, reaching sometimes 88 per cent; therefore 87·5 was taken by him as the mean value.

In some butters, however, containing considerable quantities of lauric acid, which can only be washed out with difficulty, too high values may be found, unless *Fleischmann* and *Vieth's* device (p. 160) be adopted. The limits for the *Hehner* value obtained by other experimenters are given in the subjoined table:—

Hehner Values of Butter

Observer.	Per cent Insoluble Acids.	
	Lower Limit.	Upper Limit.
J. Bell	85·5	87·9
Fleischmann and Vieth .	85·79	89·73
West-Knight . . .	...	88·08

Butter having a *Hehner* value exceeding 90 must, according to *Fleischmann* and *Vieth*, be considered adulterated; butters yielding 88-90 per cent are suspicious, whereas 88 or less would point to genuine butter. The same chemists state that the *Hehner* value is not influenced by rancidity, whereas *J. Bell* has demonstrated by experiments that the amount of the insoluble acids increases on keeping, as shown in the following table:—

Analysis of Samples of Butter after keeping (J. Bell).

Original Butter.		Time Kept.	After Keeping.	
Specific Gravity at 37·8° C. (=100° F.)	Hehner Value.		Specific Gravity at 37·8° C. (=100° F.)	Hehner Value.
0·91228	87·30	12 weeks	0·91074	88·97
0·91158	87·80	7 „	0·90919	90·00
0·91389	85·50	7 „	0·91357	85·72
0·91178	87·40	6 „	0·91100	87·97
0·91106	87·72	8 „	0·91061	88·40
0·91148	87·65	6 „	0·91133	88·00

[1] *Zeitsch. analyt. Chem.* 1877, 145.

It should, however, be borne in mind that a high state of rancidity is in itself a guarantee for the purity of butter.

Moore has pointed out that mixtures can be prepared from oleomargarine and cocoa nut oil giving the same *Hehner* value as pure butter. Thus a mixture consisting of 50 parts of butter fat, 27·5 parts of oleomargarine, and 22·5 parts of cocoa nut oil, yields 89·5 per cent of insoluble acids.

It is therefore evident that the *Hehner* value alone cannot be considered a criterion of the purity of a sample of butter.

Iodine Value

The iodine absorption is of but little value in the examination of butter. This is shown in the first instance by the great variations found by different observers [1] as set out in the following table :—

Iodine Values of Butter Fat

Observer.	Per cent.	
	Minimum.	Maximum.
Hübl . .	26	35·1
Moore . .	19·5	38
Woll [2] . .	25·7	37·9
Williams [3] .	32·25	38·91
Zenoni [4] . .	22·8	35·8

On the other hand mixtures may be prepared with the greatest ease from cocoa nut oil (iodine value 8·9) and animal fats, the iodine absorptions of which coincide with those tabulated above.

STAG FAT [5]

French—*Graisse de cerf.* German—*Hirschtalg.*

For tables of constants see p. 642.

The specimen examined by *Amthor* and *Zink* [6] had the acid value 3·5 in the fresh state, and 5·9 after one year.

[1] The abnormal butter referred to, p. 633, footnote 4, had the iodine value 42·5.
[2] *Zeitsch. analyt. Chem.* 1888, 532. [3] *Analyst*, 1889, 104.
[4] *Il Selmi*, 1894, 28 ; 46.
[5] The constants of fats from animals closely related to the stag have been given above (p. 551). [6] *Zeitsch. f. analyt. Chemie*, 1897, 4.

Physical and Chemical Constants of Stag Fat

Specific Gravity.		Solidifying Point.		Melting Point.		Saponific. Value.		Reichert Value.		Iodine Value.		Refractive Index. Butyro-refracto-meter.	
At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	$\frac{1}{10}$ c.c. norm. KOH.	Observer.	Per cent.	Observer.	At 40° C.	Observer.
0·9670	Amthor & Zink	39-40 48	Amthor & Zink Beckurts [1] & Oelze	51-52 49-49·5	Amthor & Zink Beckurts & Oelze	199·9	Amthor & Zink	1·66	Amthor & Zink	25·7 20·5	Amthor & Zink Beckurts & Oelze	44·5	Beckurts & Oelze

[1] *Arch. Pharm.* 1895 (233), 429.

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.	
At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
0·9685	Amthor & Zink	46-48	Amthor & Zink	50-52 49·5	Amthor & Zink Beckurts & Oelze	201·3	Amthor & Zink	23·6	Amthor & Zink

B. WAXES

I. LIQUID WAXES

Only two representatives of this class are known, viz. sperm oil and Arctic sperm oil. They are in many respects, as regards origin, smell, and taste, and some colour reactions, very similar to blubber oils; so much so, that some writers class them with the latter oils. On account of their different chemical composition, I have separated them from the other blubber oils, disregarding the fact that amongst the members of the blubber oil group we notice a gradual transition from the nearly pure glycerides (seal oil), through some intermediate members (dolphin oil) containing considerable proportions of waxes, to the true liquid waxes. The general characteristics of this class have been given already (p. 277).

SPERM OIL

French—*Huile de cachalot; Huile de spermaceti.* German—*Walratoel.*

For tables of constants see below, and p. 644.

Sperm oil is the liquid portion of the blubber from the sperm whale, or cachelot, *Physeter macrocephalus.* The fresh blubber separates on standing in the cold into two portions, a solid (spermaceti; cp. p. 669) and a liquid one (sperm oil). The latter is separated by filtration or expression.

Sperm oil is a pale yellow, thin oil, almost free from odour. Its chemical constitution assigns to it a place amongst the waxes, consisting as it does wholly of compound ethers (esters) of fatty acids and monovalent alcohols.

Contrary to *Hoffstätter's* statement, the absence of glycerides has been proved by *Allen* and by the writer. Possibly *Hoffstätter*[1] has examined an oil mixed with porpoise oil, since he has found valeric as well as glycerol.

The fatty acids of sperm oil, a few characteristic constants of which are given p. 644, appear to belong to the oleic series, as shown by their iodine value, and by their property of yielding elaïdin with nitrous acid. The nature of the acids is as yet unknown. *Hoffstätter's*[2] earlier statement that the acid is physetoleic acid stands in need of confirmation.

Physical and Chemical Constants of Alcohols (Unsaponifiable Matter)

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
23-23·4	Lewkowitsch	25·5-27·5	Lewkowitsch	64·6-65·8	Lewkowitsch

[1] *Liebig's Annalen*, 91. 177. [2] *Ibid.*

Physical and Chemical Constants of Sperm Oil

Specific Gravity.			Saponific. Value.		Iodine Value.		Reichert Value.		Fatty Acids.		Alcohols.		Maumené Test.		Refractive Index. Oleo-refractometer.	
°C.		Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.	°C.	Observer.	Degrees.	Observer.
15·5	0·875-0·844	Allen	123·4-147·4	Deering, Stoddart, Allen	84	Archbutt	1·3	Allen	60-64	Allen	39-41·5	Allen	51	Archbutt	−12 to −17·5	Jean
,,	0·8808	Thomson and Ballantyne														
99 (water at 15·5=1)	0·833	Allen	..	..	81·3	Thomson and Ballantyne	..	..	..	..	41	Lewkowitsch	45-47	Allen		
													Specific Temp. Reaction.			
			132·5	Thomson and Ballantyne	86·5[1]	McIlhiney	..	..	..	..	37·41	Thomson and Ballantyne	100	Thomson and Ballantyne		

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Mean Molecular Weight.		Iodine Value.	
At 15·5	Observer.	°C.	Observer.	°C.	Observer.		Observer.	Per cent.	Observer.
		Titer Test.							
0·899	Allen	11·1-11·9	Lewkowitsch	13·3	Williams	281-294 305	Allen Williams	88·1 83·2-85·6	Williams Lewkowitsch

[1] Calculated from bromine addition value 54·54 (bromine substitution value being 1·04).

The alcohols of sperm oil are also unknown. The writer[1] has tried to resolve the mixed alcohols into their several constituents by fractional distillation of both the alcohols themselves and of their acetates, but hitherto these experiments have not led to any definite result—except this, that neither dodecatyl nor pentadecyl alcohol is present, and that the sperm oil alcohols belong for the most part, if not wholly, to the ethylene series, the higher members of which have been hitherto unknown.

This will be readily seen from the following table, giving the saponification values of the acetates of the five fractions into which the total acetates had been resolved, and the iodine values of the corresponding alcohols themselves. For the sake of comparison the theoretical numbers are given for alcohols, the presence of which might be naturally expected.

Alcohols from Sperm Oil.	Saponific. Value of Acetate.	Iodine Value of Alcohol.
1st fraction . . .	190·2	46·48
2nd ,, . . .	183·8	63·30
3rd ,, . . .	180·7	69·80
4th ,, . . .	174·4	81·80
5th ,, . . .	161·4	84·90
Alcohol $C_{16}H_{32}O$ (unknown)	199	106·6
,, $C_{18}H_{36}O$ (unknown)	180	94·8
,, $C_{20}H_{40}O$ (unknown)	166	85·8

On heating[2] the alcohols with soda lime, the bulk was converted into fatty acids, only 4-6 per cent of unchanged alcohol being recovered; the crude fatty acid had the acid value 181·7, and the melting point 38°-40° C.

The writer is still engaged on a research into the nature of the sperm oil constituents.

Commercial sperm oil contains but small quantities of free fatty acids. The following table records a few numbers :—

No.	Sperm Oil.	Free Fatty Acids, as Oleic Acid. Per cent.	Observer.
1	Best quality, cold bagged .	0·29	Deering
2	Second, "hot pressed" . .	0·42	,,
3	Intermediate quality . .	0·15	,,
4	Oil of good quality . .	0·42	,,
5	Oil of doubtful quality . .	0·11	,,
6	,, ,, ,, . .	0·41	,,
7	Oil of bad quality . . .	0·42	,,
8	,, ,, . . .	2·64	Thomson and Ballantyne

[1] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1892, 134.

[2] *Ibid.* 1896, 41.

Sperm oil is a valuable lubricating oil for spindles and light machinery, on account of its high viscosity and slight tendency to become rancid and, consequently, to gum the bearings. Its comparatively high price suggests adulterations with fatty oils or hydrocarbon oils. Its characteristic properties, however, render the detection of all adulterants an easy task, with the exception of Arctic sperm oil, the physical and chemical characters of which are almost identical with those of sperm oil.

The **specific gravity** of sperm oil being very low, a high density would point to the presence of fatty oils. Mineral oils of the same specific gravity could, of course, not be detected by the determination of this constant. However, a mixture of fatty oils with hydrocarbon oils, to meet the specific gravity test, would require oils of so low a specific gravity that the flash point of the resulting oil would be very low indeed.

The *low* **saponification value** furnishes a ready means of detecting added fatty oils, such as rape oil, blubber oils, etc. As, however, a judiciously added quantity of mineral oil may compensate the increase of the saponification value due to this cause, an apparently normal oil may result in the end. In fact, *Lobry de Bruyn*[1] has shown that oils occur in commerce consisting of a mixture of sperm, blubber, and mineral oils. The saponification value alone cannot, therefore, be considered as finally proving the purity of the sample.

Certainty can only be attained by examining, on the one hand, the unsaponifiable matter as detailed above (pp. 224-233); and, on the other hand, by estimating the amount of glycerol (cp. p. 207). The proportion of the latter multiplied by 10 will approximately yield the percentage of fatty oils.

The **viscosity** of sperm oil is very characteristic; it is lower than that of any other non-drying fatty oil, and it does not vary so much as that of other oils with an increase of temperature (cp. tables, p. 268). *Allen* recommends the observations to be made at the following three temperatures: 15·5° C., 50° C., 100° C.

Colour reactions are hardly required in the examination of sperm oil. Any of the liver oils, which might have been used as an adulterant (*Allen*), would be detected by the sulphuric acid test in which liver oils give a violet colouration, changing to red, whereas sperm oil yields a brown colour, changing to dark brown. Besides, liver oils would be readily detected by the high iodine value, Maumené's test, and the presence of glycerol in the sample.

[1] *Jour. Soc. Chem. Ind.* 1894, 426.

ARCTIC SPERM OIL (BOTTLENOSE OIL)

French—*Huile de l'hyperoodon.* German—*Döglingthran.*

For tables of constants see below; and p. 648.

Arctic sperm oil is the oil obtained chiefly from the bottlenose whale, *Hyperöodon rostratus.* It is, as a rule, darker in colour than sperm oil, which it so closely simulates that, notwithstanding the slight differences to be found in the tables (solidifying points of fatty acids), they might be declared identical as far as chemical examination goes. In the elaïdin test Arctic sperm oil yields a very much softer elaïdin than sperm oil. According to the table of constants the refractometer would appear to furnish a ready means of distinguishing Arctic sperm oil from sperm oil, but the refractometric constants require confirmation.

In commerce, however, these two oils are readily distinguished by their taste. Arctic sperm oil is lower in price on account of its more pronounced tendency to "gum."

Scharling, writing in the year 1848, states that Arctic sperm oil is the dodecatyl ether of doeglic acid. It hardly needs pointing out that this statement requires confirmation. The writer is engaged on an inquiry into the nature of the constituents of this oil.

The amount of free fatty acids in two samples of Arctic sperm oil, examined by *Deering*, and *Thomson* and *Ballantyne*, was found 0·42 and 1·97 per cent respectively.

Physical and Chemical Constants of Alcohols (Unsaponifiable Matter)

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
21·7-22·0	Lewkowitsch	23·5-26·5	Lewkowitsch	64·8-65·2	Lewkowitsch

[TABLE

Physical and Chemical Constants of Arctic Sperm Oil

Specific Gravity.			Saponification Value.		Iodine Value.		Reichert Value.		Fatty Acids.		Alcohols.		Maumené Test.		Refractive Index. Oleo-refractometer.	
At °C.		Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.	°C.	Observer.	Degrees.	Observer.
15·5	0·8808	Allen	126	Deering, Allen	77·4 [1]	Mills and Akitt	1·4	Allen	61-65	Allen	37·41	Allen	42	Archbutt	+50	Pearmain
,,	0·8799	Thomson and Ballantyne	123-134	Archbutt	80·4	Archbutt					36·32	Thomson and Ballantyne	41-47	Allen		
98·99 (water 15·5 = 1)	0·8274	Allen	130·4	Thomson and Ballantyne	82·1	Thomson and Ballantyne					31·7	Lewkowitsch	Specific Temp. Reaction.			
			133-135·9	Lewkowitsch							34·11-34·9	,,	93	Thomson and Ballantyne		

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
Titer Test.					
8·3-8·6	Lewkowitsch	10·3-10·8	Lewkowitsch	82·2-83·3	Lewkowitsch

[1] Calculated from bromine value.

II. SOLID WAXES

1. VEGETABLE WAXES

Vegetable waxes, the exudations of plant leaves, seem to be widely spread over the vegetable kingdom, though mostly occurring in small quantities. With the exception of carnaüba wax (which has been exhaustively examined), the nature of these waxes (opium wax (p. 15), palm wax, ocuba wax, getah wax, ocotilla wax, cotton seed wax, etc.) has been but little studied.

CARNAÜBA WAX

French—*Cire de carnauba.* German—*Carnaubawachs, Cearawachs.*

For table of constants see p. 650.

Carnaüba wax is a vegetable wax exuded by the leaves of *Corypha cerifera* (*Copernicia cerifera*), a palm indigenous to tropical South America, especially to the province of Ceara, Brazil.

The crude wax, as obtained from the plant, is dirty greenish, or yellowish, very hard, and so brittle that it can be readily powdered.

Carnaüba wax dissolves completely in ether and boiling alcohol; on cooling, a crystalline mass, of melting point 105° C., is deposited from the alcoholic solution. On ignition, carnaüba wax yields 0·43 per cent of ash.

Carnaüba wax consists chiefly of myricyl cerotate, and small quantities of free cerotic acid and myricyl alcohol; the latter is easily removable by cold ethyl alcohol. *Stürcke*,[1] who has carried out a very complete research into the chemistry of carnaüba wax, maintains that free cerotic acid is absent. The definite acid value, however, found by independent observers, undoubtedly points to its presence. According to *Stürcke*, the constituents of carnaüba wax are the following:—

(1) A hydrocarbon, melting point 59°-59·5° C.
(2) An alcohol of the composition $C_{26}H_{54}O$ (ceryl alcohol), melting point 76° C.
(3) Myricyl alcohol, $C_{30}H_{62}O$, melting point 90° C.[2]
(4) A dihydric alcohol $C_{25}H_{52}O_2$ (cp. p. 76), melting point 103·5°-103·8° C.
(5) An acid $C_{24}H_{48}O_2$ (carnaübic acid), melting point 72·5° C.
(6) Cerotic acid, $C_{26}H_{52}O_2$.
(7) An hydroxy acid $C_{21}H_{42}O_2 = C_{19}H_{38}\begin{matrix}CH_2OH\\COOH\end{matrix}$, or its lactone

$$C_{19}H_{38}\begin{matrix}CH_2\\CO\end{matrix}O.$$

[1] *Liebig's Annalen*, 223. 283.

[2] Gascard (*Jour. Soc. Chem. Ind.* 1893, 955) assigns to it the formula $C_{31}H_{64}O$.

Physical and Chemical Constants of Carnaüba Wax

Specific Gravity.			Solidifying Point.		Melting Point.		Acid Value.		Saponific. Value.		Ether Value.		Iodine Value.		Unsaponifiable.	
°C.		Observer.	°C.	Observer.	°C.	Observer.		Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	Per cent.	Observer.
15	0·999	Maskelyne	..	..	84·1	Mills and Akitt	..	..	93·1	Becker	..	..	..	..	54·87	Allen and Thomson
[1] ,,	0·990	Husemann-Hilger	..	..	85	Allen	4	Hübl	79	Hübl	75	Hübl	13·5	Lewkowitsch	55	Stürcke
90 (water 15·5 = 1)	0·8500	Allen	..	..	84	Wiesner	..	..	94·5-95	Valenta						
98	0·8422	,,	80-81	Stürcke	83-83·5	Stürcke	4·8	Allen	80-84	Allen	76	Allen				
					85-86 [1]	,,	3·4	Henriques	78·4	Henriques [3]						
			86-87	Schaedler	90-91 [2]	Schaedler	7·0	,,	83·4	,,						

[1] Recently purified.

[2] Old specimen.

[3] By saponification in the cold.

Carnaüba wax is not readily saponified by alcoholic potash; this may explain the unsatisfactory agreement between the saponification numbers given above.

Carnaüba wax is employed in the manufacture of candles and of some wax varnishes.[1]

Valenta has examined the melting points of the following mixtures of carnaüba wax with stearic acid, cerasin, and paraffin wax :—

Proportion of Carnaüba Wax.	Melting Point of Mixtures of Carnaüba Wax with		
	Stearic Acid of Melting Point 58·5° C.	Cerasin of Melting Point 72·7° C.	Paraffin Wax of Melting Point 60·5° C.
Per cent.	°C.	°C.	°C.
5	69·75	79·10	73·90
10	73·75	80·56	79·20
15	74·55	81·60	81·10
20	75·20	82·53	81·50
25	75·80	82·95	81·70

The table shows that the addition of 5 per cent of carnaüba wax to the substances named causes a considerable increase in their melting point; further additions, however, do not cause a proportional increase.

Stearic acid in carnaüba wax would be detected by the high acid value of the sample; cerasin and paraffin wax by the high percentage of unsaponifiable matter.

2. ANIMAL WAXES

The animal waxes contain but small quantities of unsaturated acids and alcohols. The components of beeswax, spermaceti, and insect wax are well known; their acids and alcohols belong chiefly to the saturated (aliphatic) series. Wool wax, however, has an exceptional chemical composition; some of its alcohols are derivatives of the aromatic series, and its fatty acids are characterised by the facility with which they become dehydrated. Wool wax is also remarkable for the great difficulty with which it is saponified even by alcoholic caustic potash.

WOOL WAX[2] (WOOL GREASE)

French—*Suint.* German—*Wollfett, Wollschweissfett.*

For tables of constants see pp. 653, 654.

The term wool wax has been proposed by the writer for the neutral portion of the raw wool fat, the fatty matter excreted by sheep, and obtained from the wool by extraction with volatile solvents, or in the process of washing the wool with dilute sodium

[1] *Jour. Soc. Chem. Ind.* 1894, 744. [2] Lewkowitsch, *ibid.* 1892, 135; 1896, 14.

carbonate. The raw wool fat contains besides potassium salts of volatile fatty acids, naturally free fatty acids and free alcohols; and if recovered by washing the wool it is contaminated with fatty acids derived from soap. The raw wool fat will be dealt with in chap. xii.; here, we only consider the neutral portion as obtained after removing the free fatty acids from the raw product. In this state it still contains free alcohols. The constants given pp. 653, 654 refer, therefore, to the neutral esters *plus* free alcohols. There is also added a table No. IV. containing a few chemical constants of the neutral esters only.

Wool wax is a pale yellow, translucent substance, having a slight but not unpleasant smell (whereas the raw wool grease is characterised by its peculiar disagreeable smell, recalling that of sheep). Its consistency is that of a thin ointment.

Wool wax is sparingly soluble in alcohol, but dissolves readily in chloroform and ether and ethyl acetate. Although insoluble in water, it possesses the remarkable property of absorbing large quantities of water, forming an emulsion with it that has the appearance of a perfectly homogeneous mass. Thus wool wax can be mixed with as much as 80 per cent of water. A mixture of neutral wax and water, containing about 22-25 per cent of the latter, is sold in commerce under the name "lanoline" (p. 689).

Wool wax cannot be wholly saponified by aqueous caustic alkalis; even prolonged boiling with alcoholic potash under ordinary pressure does not effect complete saponification. Sodium alcoholate (or absolute alcohol and metallic sodium) or alcoholic potash under pressure, however, effect complete saponification (cp. chap. ii. p. 22).

Glycerides do not occur in wool wax.

The chemical composition of wool fat is as yet unknown. It is evidently a very complex mixture of ethers; amongst the alcohols, cholesterol and isocholesterol occur to a large extent. *Lewkowitsch* was the first to show that the statement previously accepted, viz. that neutral wool wax is a mixture of cholesteryl (and isocholesteryl) oleates and stearates, is erroneous. The low iodine value of both the fatty acids and the alcohols precludes this altogether. Nor is the presence of ceryl cerotate, asserted by *Buisine*, to be accepted without further proof, as ceryl alcohol occurs in raw wool fat in the free state. An inquiry into the nature of the components (on which the writer is still engaged) has shown that the mean molecular weight of the alcohols (239), in conjunction with the low iodine value (36), points to the presence of lower saturated alcohols, cholesterol and isocholesterol having the molec. weight 372, and the iodine absorption 68·3. The fatty acids, as is shown by their very low iodine absorption, cannot consist to any great extent of oleic acid. They consist of hydroxy acids,[1] easily giving off the elements of water at temperatures little above 100° C., with formation of inner anhydrides or lactones, and assimilating considerable quantities of acetic anhydride, forming acetylated acids.

[1] *Jour. Soc. Chem. Ind.* 1892, 136; 1896, 14.

I. *Physical and Chemical Constants of Wool Wax* (i.e. *Esters and Free Alcohols*)

Specific Gravity.			Solidifying Point.		Melting Point.		Saponific. Value.		Iodine Value.		Fatty Acids.		Alcohols.	
°C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.	Per cent.	Observer.
15	0·973	Schaedler	..	..	39-42·5	Stöckhardt	98·3	Allen	25·9-26·8[1]	Lewko-witsch	59·8	Lewko-witsch	43·6	Lewko-witsch
98·5 (water 15·5=1)	0·9017	Allen	..	..	36-41	Benedikt	102·4[1]	Lewko-witsch	25·8-28·9[1]	,,			51·84[2]	,,
			30-30·2[1]	Lewko-witsch	31-35 }[1] 39-41 }	Lewko-witsch			17·1-17·6[2]	,,				

II. *Physical and Chemical Constants of the Mixed Fatty Acids*

Solidifying Point.	Melting Point.	Mean Molecular Weight.	Iodine Value.	Observer.
°C. 40	°C. 41·8	327·5	Per cent. 17	Lewkowitsch.

[1] From raw wool fat.

[2] Prepared from "lanoline."

III. *Physical and Chemical Constants of the Mixed Alcohols*

Solidifying Point. °C.	Melting Point. °C.	Mean Molecular Weight.	Iodine Value.	Observer.
28 [1]	33·5 [1]	239 [1]	36 [1] 26·4 [2]	Lewkowitsch ,,

IV. *Chemical Constants of the Neutral Esters*

Saponification Value.		Fatty Acids.		Alcohols.	
Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.
96·9	Lewkowitsch	56·66	Lewkowitsch	47·55	Lewkowitsch

Marchetti [3] states that he has isolated an alcohol of the formula $C_{12}H_{24}O$—termed lanolin alcohol. Since, however, two other alcohols described by *Darmstädter* and *Lifschütz*,[4] and supposed to form a homologous series with lanolin alcohol, have been shown to be lactones (see above), the existence of this alcohol becomes doubtful.

The following fatty acids have been isolated by *Darmstädter* and *Lifschütz* [5] from wool wax:—

(1) Lanoceric acid, $C_{30}H_{60}O_4$ (p. 66).
(2) Lanolpalmic acid, $C_{16}H_{32}O_3$ (p. 63).
(3) Myristic acid.
(4) Carnaübic acid.
(5) An oily acid.
(6) A volatile acid, presumably caproic acid.

The alcohols were resolved by absolute alcohol into four fractions, in which hitherto cholesterol and the saturated alcohol carnaübyl alcohol have been identified.

From the researches of *G. de Sanctis* [6] it would follow that cerotic and palmitic acids must be added to the wool wax fatty acids.

On account of its property of forming an emulsion with water and being easily absorbed by the skin, wool wax is used as a basis for ointments and cosmetics.

For wool fat, cp. xii. p. 686.

[1] From raw wool fat.
[2] From lanoline.
[3] *Gazz. Chimica*, 1895, 22.
[4] *Berichte*, 1895, 3133.
[5] *Ibid.* 1896, 618; 2890; *Jour. Soc. Chem. Ind.* 1896, 548; 1897, 150.
[6] *Chem. Ztg.* 1895, 651.

BEESWAX [1]

French—*Cire des abeilles.* German—*Bienenwachs.*

For table of constants see p. 656.

The wax as obtained from the honeycombs is, as a rule, of a yellow or yellowish colour. There are, however, some commercial waxes, mostly of non-European origin, having a greenish, reddish, or brown colour.

Yellow wax has the pleasant smell of honey, and is almost tasteless. At low temperatures it is brittle, and of fine granular fracture.

By repeated melting in water, or by exposure to sunlight, in the shape of granules, or strips, or ribbons, *white wax* is obtained.[2] This is of a pure white or slightly yellowish colour, odourless, and tasteless. It has a higher specific gravity than yellow wax, and is more brittle. It is transparent at the edges; its fracture is smooth, and no longer granular.

In practice it is customary to mix with the yellow wax previous to air-bleaching 3 to 5 per cent of tallow, or a small quantity of oil of turpentine, so as to accelerate the process, and to obtain a pure white product; these additions also prevent the wax from becoming too brittle. Yellow wax may also be decolourised by treatment with animal char or with chemicals, such as potassium permanganate, potassium bichromate and sulphuric acid, and hydrogen peroxide (*Buisine*).

Wax is not greasy to the touch, but if dropped on paper in the melted state it causes a permanent transparent spot.

A regular constituent of wax is pollen, so that wax when in admixture with other substances may be detected by microscopic examination.

Considered chemically, wax[3] is chiefly a mixture of crude *cerotic acid*[4] (cp. p. 50) and *myricin* (myricyl palmitate). In smaller quantities there occur also melissic acid, $C_{30}H_{60}O_2$, or $C_{31}H_{62}O_2$, in the free state; and, according to *Schwalb*, *myricyl alcohol*,[5] $C_{30}H_{62}O$, or $C_{31}H_{64}O$, and small quantities of *ceryl alcohol* and of another alcohol of unknown composition. Small quantities of unsaturated fatty acids and *hydrocarbons* have also been found. *Schwalb* has isolated the two hydrocarbons — *heptacosane*, $C_{27}H_{56}$, melting point 60·5° C., and *hentriacontane*, $C_{31}H_{64}$, melting point 67° C. (cp. below, p. 665).

The ratio of free (cerotic) acid to myricin has been found by *Hübl* and *Hehner* in a number of well-agreeing experiments as 14 : 86.

[1] The bibliography of beeswax, arranged chronologically, and of waxes used in adulterating it, will be found *Jour. Soc. Chem. Ind.* 1892, 756.

[2] Cp. also Ramboe, *Jour. Soc. Chem. Ind.* 1897, 150.

[3] Brodie, *Liebig's Annalen*, 67. 180; 71. 144. Schalfejeff, *Berichte*, 9. 278; 1688. Nafzger, *Liebig's Annalen*, 224. 225; Schwalb, *ibid.* 235. 106. Marie, *Jour. Soc. Chem. Ind.* 1894, 207; 1895, 599; 1896, 362.

[4] Containing about 30-40 per cent of homologous acids (Marie).

[5] According to Gascard (*Jour. Soc. Chem. Ind.* 1893, 955), the myricyl alcohol from beeswax is identical with that from carnaüba wax, and has the formula $C_{31}H_{64}O$.

Physical and Chemical Constants of Beeswax

Specific Gravity.			Solidifying Point.		Melting Point.		Acid Value.		Saponification Value.	
°C.		Observer.	°C.	Observer.	°C.	Observer.		Observer.	Mgrms. KOH.	Observer.
15	0·965-0·975	Hager	60·5 [1]	Allen	62-62·5 [1]	Schaedler	20	Hübl	95	Hübl
,,	0·965-0·969	Wagner	62 [5]	,,	64 [1]	Lepage	18·6 [2]	Dieterich	90·4-91·4 [2]	Dieterich
,,	0·956-0·964	Röttger	61·5 [6]	,,	61·5-62 [1]	Payen	16·8-20·6 [1]	,,	87·8-96·2 [1]	,,
,,	0·958-0·960	,,	60·5-62·8 [3]	Camilla	63 [1]	Allen	19·02-20·6 [1]	Buisine	97·107	Becker
,,	0·962-0·966 [1]	Dieterich			63-64 [2]	Schaedler	19·04-20·9 [3]	Camilla		
,,	0·962-0·963 [1]	Hardy			65 [2]	Barfoed	20·9-21·2 [4]	,,		
,,	0·960-0·963 [1]	Schaedler			69-70 [2]	Lepage				
,,	0·973 [2]	,,			63·5 [5]	Allen				
,,	0·965-0·969	,,			63·0 [6]	Allen				
,,	0·964-0·968 [2]	Dieterich			63-64·4 [3]	Camilla				
15	0·959-0·966 [3]	Camilla			62·5-63·6 [4]	,,				
,,	0·959 [4]	,,								
80 (water 15·5 = 1)	0·8356 [1]	Allen								
98	0·8221 [1]	,,								
98-99	0·827 [5]	,,								
,,	0·818	,,								

Physical and Chemical Constants of Beeswax—continued

Ether Value.		Reichert-Meissl Value.		Iodine Value.		Unsaponifiable.		Refractive Index. Butyro-refractometer.	
	Observer.	$\frac{1}{10}$ c.c. norm. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.	At 62° C.	Observer.
75	Hübl	0·34-0·41 [3]	Camilla	8·3-11	Buisine	55·25	Schwalb	29·5-30 [1]	Kremel
71·8-72·8 [2]	Dieterich	0·54 [4]	,,	7·9-8·9	Guyer [7]	52·38	Allen and Thomson	28-28·5 [2]	,,
71·8-75·6 [1]	,,								
72·2-75·3 [3]	Camilla								
74·8-76·1 [4]	,,								

[1] Yellow wax. [2] White wax. [3] Italian waxes not Ligurian. [4] Ligurian wax from *Apis Ligustica Spinola*. [5] Chemically bleached.
[6] Air-bleached. [7] Eleven samples of pure English waxes (*Jour. Pharm.* 1897, 308).

The proportion of hydrocarbons in wax is, according to *Schwalb*, 5 to 6 per cent. *A.* and *P. Buisine*, however, have found from 12·7 to 13·0 per cent. They further disagree with him by stating that the hydrocarbons belong partly to the ethylene series. *Mangold*[1] has confirmed *Buisine's* results.

Beeswax is almost insoluble in cold alcohol, but boiling alcohol dissolves from it the bulk of the cerotic acid and a small quantity of myricin. The alcoholic solution reddens blue litmus paper feebly; a solution of phenolphthalein, made just pink by a trace of alkali, is instantly decolourised by it. On cooling, the cerotic acid separates out in the form of thin needles so completely that the alcoholic solution does not become turbid on mixing with water, a slight opalescence only appearing.

Warm ether dissolves beeswax with facility; on cooling, however, a portion separates out.

Nothing is extracted by treatment with sodium carbonate or dilute alkali. By alcoholic caustic alkali wax is completely hydrolysed (saponified).

By distilling beeswax with lime an oil is obtained—beeswax oil.[2]

Beeswax is very frequently adulterated. *Water* and *mineral matters* (such an ochre, gypsum, etc.), also *flour* and *starch*, are easily detected. Fraudulent admixture with *tallow*, *stearic acid*, *Japan wax*, *carnaüba wax*, *resin*, *paraffin wax*, and *cerasin* may be detected by the methods described below.

Examination of Beeswax for Adulterants

As a preliminary test *Long*[3] recommends the microscopic examination of the wax, first dissolving the sample in chloroform, and placing a few drops on an object glass. When the solvent has evaporated partly so that a solid particle is seen, the cover is placed on the wax and the crystals examined after a little time. In the case of pure wax characteristic tufts of crystals are noticed, having the shape of dumb-bells, the spheres of which consist of curved needles. In presence of about 20 per cent of paraffin wax, tallow, or stearic acid, the microscopic appearance is changed completely, paraffin wax seemingly preventing the formation of crystals, whereas in the case of fats and fatty acids the crystals characteristic of the latter are noticeable.

Robineaud[4] extracts 1 grm. of the sample with 50 c.c. of cold ether; if less than 0·5 grm. remain undissolved, the wax under examination must be considered as adulterated with paraffin wax, tallow, Japan wax, stearic acid, or resin. *Vogel*, again, agitates one part of the finely divided sample with six or eight parts of chloroform; the undissolved portion should not amount to less than 75 per cent.

The surest and quickest means, however, of judging of the purity

[1] *Jour. Soc. Chem. Ind.* 1891, 861.
[2] *Liebig's Annalen*, 2. (1832) 255; *Jour. Soc. Chem. Ind.* 1895, 1050.
[3] *Chem. Zeit.* 9. 1504. [4] *Dingl. Polyt. Jour.* 163. (1862) 80.

of a sample (with certain restrictions) is furnished by applying *Köttstorfer's* process, in the form recommended specially for the examination of beeswax by *Hübl*, *Hehner*, and *Benedikt* and *Mangold*. This method gives at the same time a clue to the nature of the adulterants. The *melting point* and the *specific gravity* of the sample are employed as corroborative tests.

In most cases these determinations will be deemed sufficient; but in special cases it may be necessary to estimate also the iodine absorption, the volume of hydrogen obtained on heating the sample with potash-lime, and the proportion of hydrocarbons (*A.* and *P. Buisine*).[1]

If the exact analysis of a yellow wax be required the sample should first be boiled with water and dried, otherwise it may possibly retain small quantities of honey (which, on becoming acid, will affect the acid value) or water—as a rule, from 0·5 to 0·7 per cent.

Specific Gravity.—This constant may be determined by *Dieterich's* method, as described p. 129. The limits given by this chemist are for pure yellow wax 0·962 to 0·966 at 15° C., and for pure white wax 0·964 to 0·968; *Röttger*, however, admits for both yellow and white wax as limits 0·956 to 0·964.

On account of the difficulties attached to the correct determination of the specific gravity at 15° C., *Allen* prefers to take it at 100° C.

The **melting point** of pure wax has been given in the foregoing table; the influence of chemicals (used in bleaching) on this constant will be shown in *Buisine's* table (see below).

Saponification Process.—*Köttstorfer's* process was employed first for the examination of beeswax by *Becker*.[2] He saponified 2 grms. of the melted and filtered sample in a flask of 150 c.c. capacity with 25 c.c. of normal to half-normal potash under a pressure of 5 cm. of mercury. A glance at the numbers given by him for various wax-like substances shows that mixtures having the normal saponification value may be easily prepared.

Substance.	Saponification Value.
Beeswax	97-107
Paraffin wax, cerasin	0·0
Japan wax	224·4
Carnaüba wax	93·1
Spermaceti	108·1
Tallow	196·5
Resin	194·3

Consequently the saponification value alone does not prove the purity of the sample.

Hübl recommends, therefore, the determination of both the acid value and the ether value of the sample. The ether value (p. 154) gives the number of mgrms. of KOH used for the saponification of myricin. The sum of the acid and the ether values is the *saponification value*. The following is *Hübl's* process:—

[1] *Jour. Soc. Chem. Ind.* 1891, 52. [2] *Zeitsch. f. analyt. Chem.* 19. 241.

Warm 3 to 4 grms. of the sample with 20 c.c. of 95 per cent alcohol in a flask until the wax is melted, distribute the wax by shaking, and titrate with half-normal alcoholic potash, using phenolphthalein as an indicator, taking care that the wax remains in a melted state during the operation. Then add 20 c.c. of standard alkali, heat for forty-five minutes on the water-bath, and titrate back the excess of alkali with half-normal acid.

Of course the saponification value can be also determined in another quantity. The ether value is then obtained by difference (p. 154).

The acid value for a number of samples of yellow wax was found by *Hübl* from 19 to 21, in most cases 20, and the ether value from 73 to 76, in most cases 75. The higher and lower values occur, according to *Hübl*, as a rule, together, so that the ratio of acid value to ether value only varies between 3·6 and 3·8, and the mean 3·7 may be accepted as expressing that ratio.

The following table, compiled from *Hübl's* results and supplemented by those of other observers, gives the numbers for beeswax and substances that may be employed as adulterants :[1]—

Substance.	1 Acid Value.[2]	2 Ether Value.	3 Saponification Value.	4 Ratio of 1 : 2. "Ratio number"	5 Observer.
Beeswax, yellow .	20	75	95	3·75	Hübl
,, ,, .	20·6	76·5	97·1	3·72	Henriques[3]
,, ,, .	20·4	73·9	94·3	3·58	,,
,, ,, .	20·6	73·6	94·2	3·6	,,
,, white .	22·4	76·1	98·5	3·41	,,
,, chemically bleached	24	71	95	2·96	Allen
,, ,, .	28·4	76·6	105	2·71	Henriques[3]
Carnaüba wax . .	4	75	79	19	Hübl
,, ,, . .	4-8	76	80-84	9·5-19·5	Allen
Japan wax . .	20	200	220	10	Hübl
,, ,, . .	20	195	215	9·75	Allen
Chinese wax . .	Traces	63	63	...	,,
Spermaceti . .	,,	128	128	...	,,
Myrtle wax . .	3	205	208	68·3	,,
Tallow . . .	4	191	195	48	Hübl
Tallow and stearine .	10	185	195	18·5	Allen
Stearic acid . .	195	0	195	...	Hübl
,, commercial	200	0	200	...	Allen
Resin . . .	110	1·6	112	0·015	Hübl
,, . . .	180	10	190	0·0556	Allen
,, Austrian . .	130-146	16·4-21·1	146·8-167·1	0·126-0·144	Schmidt and Erban
,, American . .	154·1-164·6	29·5-30·0	183·6-194	0·191-0·182	Lewkowitsch
Galipot . . .	138	36·1	174·6	0·261	,,
Paraffin wax, cerasin[4]	0	0	0	...	...

[1] Cp. also *Jour. Soc. Chem. Ind.* 1894, 745.

[2] See note 2, p. 660.

[3] By saponification in the cold.

[4] Commercial paraffins or cerasins, however, may have a definite acid value.

If wax consisted of cerotic acid and myricin only, the saponification value should be 90·9, assuming 20 as the acid value. The fact that the number 95 and more has been found proves, in agreement with the above-mentioned researches, that wax must necessarily contain other substances.

Hübl has drawn from his values, recorded in the foregoing table, the following conclusions:—

If the saponification value of a sample of wax be found below 92, the ratio being at the same time that of pure wax, *paraffin wax* or *cerasin* must be present.

If the ratio is greater than 3·8, an admixture with *Japan wax*, *carnaüba wax* or *tallow* may be suspected. If the acid value is at the same time less than 20, *Japan wax* is absent.

If, however, the ratio is less than 3·8, *stearic acid* or *resin* is present.

Hübl's results have been confirmed for yellow wax by *Allen*, *Dieterich*, and *Röttger*. Still, *Mangold*,[1] on examining a large number of undoubtedly genuine waxes, has found a few the ratio of which showed larger[2] deviations. Thus an Hungarian wax gave—

Acid Value.[2]	Saponification Value.	Ratio.
23	90·6	2·89

White wax, especially chemically bleached wax, frequently exhibits greater deviations from *Hübl's* numbers. Thus *Allen* has found the ratio number 2·96, *Henriques* 2·71 (see table above), and *Buchner*[3] 3·10.

A. and *P. Buisine* have thoroughly studied the changes yellow wax undergoes on being bleached by various methods. They find the changes in the acid and saponification values very remarkable (cp. also the last table). Thus—

	Melting Point.	Acid Value.	Saponification Value.	Iodine Value.	1 Grm. yields Hydrogen.	Hydrocarbons.
	°C.				c.c.	Per cent.
Pure yellow waxes	63-64	19-21	91-95	10-11	52·5-55	13-14
Air-bleached waxes, with 3-5 per cent of tallow added	63·5-64	21-23	105-115	6-7	53·5-57	11-12
Pure yellow wax	63·5	20·17	93·5	10·9	53	13·5
Same wax air-bleached, with 5 per cent of oil of turpentine added . . .	63·5	20·2	100·4	6·8	54·9	12·4
Same wax, bleached by hydrogen peroxide	63·5	19·87	98·4	6·3	56·1	12·5
Pure yellow wax	63	20·40	95·1	11·2	54·5	14·3
Same wax, decolourised by animal char.	63	19·71	93·2	11·4	53·6	13·3
,, ,, permanganate	63·7	22·63	103·3	2·6	..	..
,, ,, ,,	63·5	21·96	99·2	5·8	55·5	13·3
,, ,, bichromate .	63·2	21·86	98·9	7·9	51	13·2
,, ,, ,, .	64	23·43	107·7	1·1	53·6	11·8

[1] *Jour. Soc. Chem. Ind.* 1891, 860.

[2] A lower acid value, and therefore a higher ratio number, has been given by Weinwurm (*Chem. Zeit.* 1897, 519) for a genuine Silesian wax—

Acid Value.	Ether Value.	Saponific. Value.	Ratio Number.
17·8	74·5	92·3	4·2

Acid values of 25-26 have been observed by the same chemist, due to the artificial combs containing stearic acid.

[3] *Jour. Soc. Chem. Ind.* 1888, 871.

Hehner,[1] before *Hübl*, employed the same method, but expresses the results in a somewhat different form by calculating from the amounts of alkali used the percentages of "cerotic" acid and myricin, assuming that 1 c.c. of normal KOH neutralises 0·410 grm. of free acid, and saponifies 0·676 grm. of myricin. The following are his results :—

Kind of Wax.	Cerotic Acid.	Myricin.	Total.
	Per cent.	Per cent.	Per cent.
Wax from Hertfordshire . .	14·35	88·55	102·90
,, ,, . .	14·86	85·95	100·81
,, Surrey . . .	13·22	86·02	99·24
,, Lincolnshire . .	13·56	88·16	101·72
,, Buckinghamshire .	14·64	87·10	101·74
,, Hertfordshire . .	15·02	88·83	103·85
,, New Forest . .	14·92	89·87	104·79
,, Lincolnshire . .	15·49	92·08	107·57
,, Buckinghamshire .	15·71	89·02	104·73
Commercial waxes, 8 samples .	13·12 to 15·91	86·73 to 89·58	99·85 to 105·49
Wax from America . . .	15·16	88·09	103·25
,, Madagascar .	13·56	88·11	101·67
,, Mauritius . .	13·04	88·28	101·32
,, ,, . .	12·17	95·68	107·85
,, ,, . .	13·72	96·02	109·74
,, Jamaica . . .	13·49	85·12	98·61
,, ,, . .	14·30	85·78	100·08
,, Mogadore . .	13·44	89·00	102·44
,, Melbourne . .	13·92	89·24	103·16
,, ,, . .	13·18	87·47	100·65
,, Sydney . . .	13·06	92·79	105·85
,, ,, . . .	13·16	88·62	101·78

The figures given in the last column mostly exceed 100, reaching almost 110 ; this agrees with *Hübl's* result referred to above, that wax requires more alkali for saponification than the amount found by calculation for a mixture of pure cerotic acid and myricin. Calculating from *Hehner's* results the ratio of acid and ether values, according to *Hübl*, the number 3·59 is obtained, in satisfactory agreement with *Hübl's* number 3·75.

Benedikt and Mangold's Process.[2]—Excellent as the *Hübl-Hehner* method is, it has the drawback that some kinds of wax are not readily saponified by alcoholic potash. Boiling for half an hour suffices but rarely, in most cases it being necessary to heat on the water-bath until the alcohol has nearly completely evaporated off.[3] If a wax contains cerasin the saponification values obtained are nearly always too low. In fact, the method requires a great deal of practice, so much so, that *Benedikt* and *Mangold* have had repeatedly to pronounce commercial samples of wax pure which had been returned as adulterated by less experienced operators. To avoid these inaccuracies, *Benedikt* and *Mangold* have recommended the following modifications :—

[1] *Analyst*, 1883, 16. [2] *Jour. Soc. Chem. Ind.* 1891, 861.

[3] Weinwurm (*l.c.*) completely evaporates the alcohol, and states that he thereby easily effects complete saponification.

The acid number is ascertained by titration with half-normal caustic soda; it is, however, advisable to use for the test 7 to 10 grms. of the sample.

Instead of the saponification value the "total acid number" is determined, *i.e.* the number of mgrms. of caustic potash required to neutralise the mixture of fatty acids and alcohols obtained after decomposing the previously saponified wax with dilute hydrochloric acid. This mixture, termed conveniently "decomposed wax," is obtained by adding 20 grms. of the previously melted wax to a boiling solution of 20 grms. of potassium hydrate in 15 c.c. of water contained in a porcelain dish of 350 to 500 c.c. capacity. The mixture is heated and stirred vigorously for ten minutes, then diluted with 200 c.c. of water, heated again and acidified with 40 c.c. of hydrochloric acid slightly diluted with water. It is then boiled until the fatty layer is quite clear, and allowed to cool. The cake of "decomposed wax" is boiled first with water containing some hydrochloric acid, and subsequently twice with water alone. It is then allowed to solidify, taken off, pressed between filter paper, melted in a drying oven, and filtered on to a watch-glass. The solidified mass is conveniently broken up into fragments.

6 to 8 grms. of the "decomposed wax" are then treated with neutralised alcohol, heated on the water-bath, and titrated with caustic potash, using phenolphthalein as indicator. Even in presence of large quantities of cerasin the saponification has been found to be complete.

The total acid value thus obtained is, of course, a little lower than the saponification value (the "decomposed wax" having assimilated the elements of water in the process of saponification).

Let s be the acid value, S the total acid number, and a the ether value, then $a + s$ expresses, of course, the saponification value, and we have further

$$a = \frac{56100\,(S - s)}{56100 - 18\,S},$$

hence

$$S = \frac{56100\,(a + s)}{56100 + 18a}.$$

Thus, assuming $s = 20$, the saponification values $(a + s)$ and the total acid values S will have the following corresponding values :—

		Calculated.		Calculated	
a	$a+s$	S	S	a	$a+s$
69	89	87·07	87	68·91	88·91
70	90	88·02	88	69·96	89·96
71	91	88·97	89	71·02	91·02
72	92	89·92	90	72·08	92·08
73	93	90·87	91	73·14	93·14
74	94	91·82	92	74·19	94·19
75	95	92·77	93	75·25	95·25
76	96	93·72	94	76·30	96·30
77	97	94·67	95	77·36	97·36
78	98	95·61	96	78·41	98·41

Reasoning as follows, I arrive at a simpler formula for the calculation :—

Let the amount of myricin in 1 grm. of wax be x grms., requiring a grms. of KOH for saponification; in the decomposed wax these x grms. are represented by $\frac{M}{M+18}\,x$ grms. only, or, since M, the molecular weight of myricin, is 676, by $0{\cdot}974\,x$ grms. As these $0{\cdot}974\,x$ grms. require $S-s$ mgrms. of KOH, and consequently x require $\frac{S-s}{0{\cdot}974}$, we have

$$a=\frac{S-s}{0{\cdot}974},$$

hence

$$S=0{\cdot}974\,a+s,$$

which leads to results almost identical with those given in the table.

Henriques' Process of Saponification in the Cold.—Henriques reverts to the direct determination of the saponification value, recommending to effect this in the cold, the acid value being determined at the same time. His directions are—

Dissolve 3 grms. of beeswax in 25 c.c. of petroleum ether by warming, and titrate with half-normal alcoholic soda, phenolphthalein being the indicator. This gives the acid value. Then warm again if necessary, add 25 c.c. of normal alcoholic soda, and allow to stand in the cold for 24 hours, when complete saponification takes place. By titrating back the excess of alkali the saponification value is obtained.

If the ratio number (see above) be calculated not from the ether and acid values, but from the total acid and the acid values, then we find for a normal wax, having the saponification value 95, the ratio number from the proportion—

$$S-s:s=72{\cdot}77:20=3{\cdot}64.$$

The ratio number is not, however, as constant as has been assumed by *Hübl*. Thus a sample of wax, having the acid value 18 and the saponification value 90 (corresponding to the total acid value 88), may yet be pure, a large number of yellow waxes from various sources having given numbers lying between 88 and 93 for S.

The examination of wax by determining the ratio number only is not sufficient, as it is easy to prepare mixtures having a normal ratio number without any wax whatever, as the following table shows for a mixture of 37·5 parts of Japan wax, 6·5 parts of stearic acid, and 56 parts of cerasin or paraffin wax :—

	Acid Value.	Ether Value.	Parts in 100.	Conditioning:	
				Acid Value.	Ether Value.
Japan wax . .	20	200	37·5	7·5	75
Stearic acid . .	195	0	6·5	12·7	0
Cerasin, paraffin wax .	0	0	56·0	0	0
Mixture . .				20·2	75

The ratio number of this mixture would be 3·71. It is evident that indefinite quantities of the above mixture, or of a similarly prepared one, might be admixed with wax without being detected by this method.

It will thus be seen that further examination is required, and for this purpose the following determinations are recommended: The iodine value, which should be for pure wax, according to the table p. 656, from 8 to 11, the volume of hydrogen gas liberated on heating the sample with potash-lime (p. 215). 1 grm. of pure wax should yield from 53·5 to 57·5 c.c. of hydrogen, corresponding to 52·5 respectively 56·5 per cent of myricyl alcohol. The estimation of hydrocarbons will also furnish valuable information as to the genuineness of the sample (cp. below, detection of paraffin wax and cerasin).

In doubtful cases the sample of wax should be examined by the methods detailed below.

Estimation of Cerasin and Paraffin Wax in Beeswax

The examination of beeswax by the saponification process will reveal the presence of cerasin and paraffin wax down to 10 or 8 per cent with certainty if no other adulterant is present (see above). If the admixture sinks below 5 per cent or even below 8 per cent, the deviations from the normal acid and saponification values become so small, that adulteration cannot be considered as established beyond doubt,[1] and the sample can, at best, only be looked upon as suspicious. It should be borne in mind, though, that, considering the difference of prices, 5 per cent and even less of cerasin will repay the cost of adulteration.[1]

If from the results obtained by the **saponification process** there is reason to assume the presence of considerable quantities of paraffin wax or cerasin, the amount of the adulterant may be calculated approximately with the help of the following formula:—

$$P = 100 - \frac{100K}{95}$$

where K is the saponification value of the sample, 95 being the

[1] Cp., however, p. 666, footnote 7.

number for pure wax. It would not be quite correct to substitute for K the total acid number, S, and for 95 the corresponding number, 92·77, given in the table p. 662, as wax assimilates 2·33 per cent of water on saponification. The error, however, amounts to only 0·7 per cent, and may therefore be neglected, the more so as the saponification value of the beeswax in the sample is unknown. Still, correct values may be found by the use of the following formula :—

$$P = 100 - \frac{100\,w\,S}{92{\cdot}77 - S(1-w)} = 100 - \frac{97{\cdot}72\,S}{92{\cdot}77 - 0{\cdot}0228\,S}$$

where

$$w = \frac{100}{102{\cdot}33} = 0{\cdot}9772.$$

The determination of the **specific gravity** will also reveal the presence of large proportions of cerasin and paraffin wax, and may therefore be used as a preliminary test. Strictly quantitative results cannot be expected, as the specific gravities of commercial beeswax, paraffin wax, and cerasin fluctuate too much. The following two tables cannot therefore be taken as of general application :—

Specific Gravity of Mixtures of Beeswax and Paraffin Wax (Wagner) [1]

Beeswax.	Paraffin.	Specific Gravity.
Per cent.	Per cent.	
0	100	0·871
25	75	0·893
50	50	0·920
75	25	0·942
80	20	0·948
100	0	0·969

Specific Gravity of Mixtures of Beeswax and Cerasin (Dieterich) [2]

Yellow Wax.	Yellow Cerasin.	Spec. Grav. of Mixture.	White Wax.	White Cerasin.	Spec. Grav. of Mixture.
Per cent.	Per cent.		Per cent.	Per cent.	
100	0	0·963	100	0	0·973
90	10	0·961	90	10	0·968
80	20	0·9575	80	20	0·962
70	30	0·953	70	30	0·956
60	40	0·950	60	40	0·954
50	50	0·944	50	50	0·946
40	60	0·937	40	60	0·938
30	70	0·933	30	70	0·934
20	80	0·931	20	80	0·932
10	90	0·929	10	90	0·930
0	100	0·922	0	100	0·918

[1] *Zeitsch. f. analyt. Chem.* 5. 280. [2] Wagner's *Jahresbericht*, 1882, 1028.

Boiling with concentrated sulphuric acid in order to decompose the wax and leave behind the unchanged hydrocarbon (as recommended by *Dullo*,[1] *Liès-Bodart*,[2] *Hager*,[3] and others) yields such erratic results that this method cannot be recommended. The same applies to *Buchner's*[4] method (boiling with alcoholic potash) and *Hager's*[5] process (boiling with sodium carbonate and subsequently mixing with benzene).

The proportion of paraffin wax or cerasin in beeswax is most accurately determined by the process described by *A.* and *P. Buisine* (p. 215). The **liberated hydrogen** may be measured at the same time and calculated to myricyl alcohol. In case the latter is not required, the apparatus for receiving and measuring the gas need not be employed.

2 to 10 grms. of the sample are heated with potash-lime to 250° C., and the residue is powdered and extracted in a Soxhlet extractor with dry ether or dry petroleum ether. The extract is filtered if necessary, the solvent evaporated off, and the residue dried and weighed. As the proportion of hydrocarbons in genuine yellow wax varies from 12 to 14·5 per cent, adulteration with 2 to 3 per cent of foreign hydrocarbons can be easily detected.

The admixed hydrocarbons, expressed in percentage C, can be calculated by the following formula given by *Mangold*,[6] where p is the percentage of hydrocarbons found by analysis, and 13·5 represents the mean percentage of hydrocarbons in pure beeswax—

$$C = \frac{100p - 1350}{86{\cdot}5}.$$

The hydrocarbons from pure beeswax have a melting point of 49·5° to 51° C., and absorb from 22 to 22·5 per cent of iodine.[7]

Determination of Glycerides in Beeswax

Presence of glycerides will in most cases be proved by the saponification process; still, as has been pointed out above, judiciously prepared mixtures of glycerides, stearic acid, and paraffin wax or cerasin will give the acid and saponification values of pure wax. Adulteration with a glyceride (tallow, Japan wax, etc.) would be proved by the detection of glycerol in the saponified product. If the

[1] *Zeitsch. f. analyt. Chem.* 2. 510. [2] *Ibid.* 5. 252. [3] *Ibid.* 9. 419.
[4] *Dingl. Polyt. Jour.* 231. 272. [5] *Zeitsch. f. analyt. Chem.* 19. 241.
[6] *Jour. Soc. Chem. Ind.* 1891, 860.

[7] Weinwurm (*l.c.*) states that 3 per cent of added cerasin or paraffin wax can be detected qualitatively by the following process, which is based on the fact that a hot aqueous glycerin solution dissolves the unsaponifiable matter of beeswax, whereas cerasin and paraffin wax are insoluble:—Saponify 5 grms. of the sample with 25 c.c. half normal alcoholic alkali, evaporate off the alcohol, add 20 c.c. of glycerin, heat in the water-bath until solution is effected, and then run in 100 c.c. of boiling water. Pure beeswax gives a more or less clear, transparent, or translucent mass, through which ordinary print can be read easily. If 5 per cent of hydrocarbons were admixed the solution is cloudy, and the print is no longer legible; and in the case of 8 per cent a precipitate is obtained. Adulteration up to 3 per cent is said to be detected by repeating the experiment with a fresh quantity of the sample to which 3 per cent of cerasin has been previously added.

glycerol be determined quantitatively (p. 208) the proportion of neutral fat is found approximately by multiplying the percentage of glycerol by 10. For the determination of amounts below 10 per cent about 20 grms. of the sample should be taken.

This is the best method, and should be employed to the exclusion of all others.[1]

Detection of Stearic Acid in Beeswax

On treating the sample with boiling alcohol any stearic acid present will be dissolved together with cerotic acid, but will not separate out so completely as the latter on cooling. Stearic acid may therefore be detected by the following process suggested by *Fehling*,[2] and recommended (lately) by *Röttger*:[3] 1 grm. of the sample is boiled for a few minutes with 10 c.c. of 80 per cent alcohol; after cooling, the alcoholic solution is filtered and the filtrate mixed with water. In the case of a pure wax the liquid is perfectly clear, or is but slightly opalescent, but in the case of adulteration with stearic acid it loses its transparency, and flocks of stearic acid separate and rise to the top. This reaction is plainly perceptible even if the adulteration amounts to as little as 1 per cent of stearic acid. It should be borne in mind that resin also, if present, will be dissolved, giving an emulsion with water. An adulterated sample will, as a rule, show a high acid value, provided no compensating substance (see above) has been added. (Of course, resin will also cause an increase of the acid value.) The percentage of stearic acid, A, is found by the following formula, where s is the acid value of the sample, assuming 20 and 195 as the acid values of pure wax and stearic acid respectively:—

$$A = \frac{100(s-20)}{175}.$$

Jean[4] heats 3 to 4 grms. of the sample with 60 c.c. of 96 per cent alcohol to boiling, allows the solution to cool, and titrates with half-normal alkali, using phenolphthalein as indicator. The alkali used is calculated to stearic acid. In presence of resin this process is obviously useless.

Detection of Carnaüba Wax in Beeswax

Carnaüba wax in beeswax will lower the acid value, the ether value remaining unchanged. The specific gravity and melting point of the sample will, however, be higher, provided no compensating substance has been added. *Allen*[5] recommends the following somewhat tedious process: Warm the sample with alcohol and neutralise

[1] This method has been re-stated by Dugowski, *Chem. Ztg.* 1897, Rep. 11.
[2] *Dingl. Polyt. Jour.* 147. 227.
[3] *Jour. Soc. Chem. Ind.* 1890, 771.
[4] *Jour. Soc. Chem. Ind.* 1891, 728.
[5] *Commerc. Org. Analys.* ii. 187.

carefully with alcoholic potash, using phenolphthalein as indicator. Saponify the separated neutral wax with alcoholic potash and precipitate with lead acetate. Then exhaust the precipitate with petroleum ether and decompose the undissolved lead soap with hot hydrochloric acid. Pure beeswax yields palmitic acid of melting point 62° C., while from carnaüba wax, cerotic acid, melting-point 79° C., is obtained.

Bearing in mind the rule that a mixture of fatty acids has a melting point lower than calculation would indicate, *Allen's* method can only be of little use. This is clearly brought out by determinations of the melting points of mixtures of pure palmitic and cerotic acids made by the writer. The numbers obtained are given in the following table :—

Melting Points of Mixtures of Palmitic and Cerotic Acids (Lewkowitsch)

Palmitic Acid. Per cent.	Cerotic Acid. Per cent.	Melting Point. °C.
100	0	60
90	10	56·0
85	15	56·5
75	25	60·5
60	40	65·5
50	50	68·6
40	60	70·0
0	100	78·5

Detection of Wool Fat or Wool Wax in Beeswax.

Admixture of this adulterant will be best recognised by testing for cholesterol or isocholesterol.

Detection and Determination of Resin Acids

Resin renders beeswax more viscous, and imparts to it a resinous smell and taste ; it may be detected with certainty by the *Liebermann-Storch* reaction (p. 226).

Donath's[1] test, recommended by *E. Schmidt*,[2] and by *Röttger*,[3] is carried out as follows : 5 grms. of the sample are boiled with four or five times as much nitric acid (1·32 to 1·33 specific gravity) for *one* minute. The mixture is then diluted with an equal volume of water, and made strongly alkaline with ammonia. If the wax is pure the liquid poured off from the solidified wax will be yellow, but if adulterated with resin, it will be coloured more or less reddish-brown. By this method, according to *Röttger*, as little as 1 per cent of resin

[1] Wagner's *Jahresb.* 1872, 408. [2] *Berichte*, 10. 835.
[3] *Jour. Soc. Chem. Ind.* 1891, 575.

may be detected. It can be made still more accurate if an alcoholic extract be used, obtained by boiling the sample with 15 parts of 50 per cent alcohol, and filtering when cold.

By employing alcohol of the given strength stearic acid, if present, is not extracted.

The last method may yield quantitative results if the alcohol be evaporated and the residue weighed.

A better method to estimate resin acids quantitatively is afforded by employing *Twitchell's* process (p. 244). The sample is saponified with alcoholic potash, and the saponified mass extracted with petroleum ether to remove the alcohols and other unsaponifiable substances. The undissolved soap is then decomposed and the mixed fatty and resin acids examined.[1]

SPERMACETI (CETIN)

French—*Blanc de Baleine.* German—*Walrat.*

For table of constants see p. 671.

Spermaceti (cetin) occurs chiefly in the head cavities, and (held in solution by sperm oil) in the blubber of the sperm whale, *Physeter macrocephalus* (cp. p. 643); it has been also found in other cetacea, and constitutes the solid portion of dolphin oil (p. 495).

Spermaceti forms lustrous, white, translucent masses with a broad, leafy crystalline structure; it is so brittle that it can be rubbed to powder; it is almost without taste and odour. In the melted state it gives a grease-spot on paper.

Spermaceti is insoluble in cold alcohol of 90 per cent, but very sparingly soluble in alcohol of 96 per cent. It dissolves, however, easily in boiling alcohol (1 part in 40 parts); on cooling, the greater part separates again in a crystalline condition.

Spermaceti consists chiefly of cetin,[2] *i.e.* cetyl palmitate, to which adhere minute quantities of other ethers of a similar constitution, as also glycerides of lauric, myristic, and stearic acids.[3] By crystallisation from alcohol these substances are removed, pure cetin separating out. Spermaceti thus purified gives therefore no acroleïn on dry distillation, which impure commercial samples will yield.

Spermaceti is free from acids, its acid value is therefore *nil*; nor does it absorb any iodine when pure. The writer has found, on examining commercial samples, iodine absorptions of from 3·52 to 4·09, no doubt due to small quantities of sperm oil adhering to them. If other iodine-absorbing impurities (tallow) are absent, the proportion of sperm oil may be calculated, adopting 82·5 as iodine value of the latter.

[1] A rapid method proposed by Buchner (*Jour. Soc. Chem. Ind.* 1895, 1070) yields but approximate results; it cannot therefore be recommended.

[2] The requirements of the U.S.P. appear to correspond rather with the values for cetin than those for spermaceti, cp. L. Kebler, *Jour. Soc. Chem. Ind.* 1896, 206.

[3] Heintz, *Liebig's Annalen*, 92. 291.

Spermaceti is readily saponified by boiling with alcoholic potash; on diluting the alcoholic solution with water cetyl alcohol is precipitated.

Spermaceti is not easily adulterated, as any foreign substance causes it to lose its physical characters, such as transparency and crystalline structure.

A definite acid value of the sample would indicate the presence of *stearic acid* or *beeswax*, a high iodine value that of *tallow*. These substances would also be pointed out by an abnormal saponification value. They may be detected, as also *paraffin wax*, by the methods described under "Beeswax."

A rapid process for the detection of *stearic acid*[1] is to melt the sample in a porcelain basin, and to stir it well with a few c.c. of ammonia. After cooling, the solidified cake is removed and the aqueous solution acidified, when stearic acid separates. The presence of even 1 per cent of stearic acid may be thus ascertained.

[1] *Les Corps gras industriels*, 13. 207.

Physical and Chemical Constants of Spermaceti

Specific Gravity.			Solidifying Point.		Melting Point.		Saponific. Value.		Alcohols.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0·960	Dieterich	43·4-44·2	Rüdorff	43·5-44·1	Rüdorff	108·1	Becker	51·48	Allen
,,	0·943	Schaedler	48	Allen	49	Allen	128	Allen		
,,	0·905-0·945	Kebler	42-47	Kebler	45	Barfoed	125·8-134·6	Kebler		
60 (water at 15·1 = 1)	0·8358	Allen					130·6-131·4	Henriques		
98-99 (water 15·5 = 1)	0·8086-0·812	Allen								

INSECT WAX (CHINESE WAX)

French—*Cire d'insectes.* German—*Insektenwachs, Chinesisches Wachs.*

Physical and Chemical Constants of Insect Wax

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.
15	0·926	Gehe						
15	0·970	Allen	80·5-81	Allen	80·5-81	Allen	63	Allen
99 (water 15·5=1)	0·810	„			81·5-83	Hen-riques	93	Hen-riques
							80·5	„

Insect wax is the secretion of an insect, *Coccus ceriferus*, Fabr., or *Coccus pela*, Westwood, deposited on the twigs of the Chinese ash, *Fraxinus chinensis.*

This wax has a white colour with a trace of yellow ; it is odourless and tasteless, has a lustrous appearance and a crystalline structure. It resembles spermaceti in appearance, it is, however, more fibrous and considerably harder, so much so that it can almost be powdered.

Insect wax is very slightly soluble in alcohol and ether, and very easily soluble in benzene, from which it can be obtained in a crystalline state. It consists chiefly of ceryl cerotate, $C_{26}H_{53} . C_{26}H_{51}O_2$, which is readily obtained from the wax by repeated crystallisation from petroleum ether (boiling point 115-135° C.) The theoretical saponification value of ceryl cerotate is 73·7, but owing to the separation of potassium cerotate during titration low results for the saponification value were found by several observers. A commercial sample of Chinese wax examined by the writer absorbed 1·4 per cent of iodine.

Insect wax is used in China and Japan for making candles, for polishing furniture and leather, and as a sizing for paper and cotton goods. On account of its extensive use where it is produced it is not exported to Europe.[1]

[1] *Jour. Soc. Chem. Ind.* 1897, 685.

CHAPTER XII

TECHNICAL AND COMMERCIAL ANALYSIS OF THE RAW MATERIAL AND PRODUCTS OF THE FAT AND OIL INDUSTRIES

A. OLEAGINOUS SEEDS AND OIL CAKES

THE primary operations in the fat and oil industries are the preparation of the fats and oils themselves.

The animal oils and fats are obtained in a very simple manner by boiling out with steam (or less advantageously with water, over open fire) those parts of the animals which contain the oil or fat. The preparation of cod liver oil, the boiling of blubber, and the rendering of lard and tallow would fall under this head, but the residual parts hardly reaches the analyst's laboratory.

The manufacture of seed oils forms the basis of important industries, and the determination of the proportion of oil in oleaginous seeds or oil-cakes is, therefore, a frequently practised operation.

For such estimations a quantity of not less than 100 grms. should be used.

The sample is prepared for analysis by disintegrating it in a suitable manner, say by means of a cake-mill or a coffee-grinder,[1] and exhausting it with ether or petroleum ether or carbon tetrachloride,[2] using any one of the extracting apparatus described, pp. 90-92.

If ether is employed it is necessary to dry the material prior to extraction, moist seeds or cakes being apt to yield to the ether non-fatty substances also. The ether should also have been purified previously; this is best done by washing it with water in order to remove any alcohol, then drying by shaking with calcium chloride, and distilling off; finally, the ether is distilled off over metallic sodium in order to get rid of the last traces of water and alcohol.

The drying of seeds or cakes which contain drying oils, such as linseed and linseed cake, requires some care, the drying oils easily becoming insoluble if the material has been dried at too high a temperature, or for too long a period. This fact is clearly brought

[1] With regard to errors caused by deviating from these directions, cp. *Jour. Soc. Chem. Ind.* 1895, 447.

[2] Bilteryst, *Bull. de l'Assoc. Belge*, 1897 (10), 406.

out by some experiments recorded in the following table due to *Klopsch*:[1]—

Linseed Cake.	Oil. Per cent.
Dried 3 hours at 94°-96° C. gave . .	8·97
Dried 6 hours at 100° C. gave . . .	8·55
Dried 12 hours at 94°-96° C. gave . .	7·89

The powdered cake should therefore be dried in a water-oven for three hours.

Baessler[2] maintains that correct results are only obtained if the cake has been dried either *in vacuo* over sulphuric acid or in a current of dry hydrogen. Contact with moist air should also be guarded against by attaching a calcium chloride tube to the extraction apparatus. For hydrogen coal gas may be conveniently substituted (*Wrampelmeyer*).[3]

If the cakes have been dried at too high a temperature, brown resinous extracts are obtained. An analysis can therefore only be looked upon as correct if the extract has the appearance of a fresh, clear oil.

If petroleum ether or carbon tetrachloride be used as solvent, the drying of the material may be omitted (*Nördlinger*, *Bilteryst*).

In special cases the examination of the extracted oil may be required; the microscopical examination of the meal may in such cases greatly assist the chemical tests.

A large number of analyses of seeds and oil-cakes have been published by various observers. We select the results given by *Nördlinger*[4] as throwing some light on the proportion of neutral oil to free fatty acids.

The total fat was obtained by extraction with petroleum ether, and the free fatty acids were titrated with alkali and calculated to oleic acid.

Seeds.	100 parts contain		Free Fatty Acids in Total Fat.
	Free Fatty Acids.	Total Fat.	
			Per cent.
Rape (*Brassica rapa*) . . .	0·42	37·75	1·10
Cabbage (*Brassica campestris*) . .	0·32	41·22	0·77
Poppy (*Papaver somniferum*) . .	3·20	46·90	6·66
Earthnut (*Arachis hypogæa*)—			
(*a*) Seed	1·91	46·09	4·15
(*b*) Husks	1·91	4·43	43·10
Sesamé (*Sesamum orientale*) . .	2·21	51·59	4·59
Castor (*Ricinus communis*) . . .	1·21	46·32	2·52
Palm nut (*Elæis guineensis*) with 6 per cent husks	4·19	49·16	8·53
Coprah (*Cocos nucifera*) . . .	2·98	67·40	4·42

[1] *Zeitsch. analyt. Chem.* 1888, 452. [2] *Jour. Chem. Soc.* 1889, Abstr. 322.

[3] A special contrivance for this operation has been described by Aitken, *Jour. Soc. Chem. Ind.* 1894, 669.

[4] *Jour. Soc. Chem. Ind.* 1890, 422.

Cakes.	Number of Samples.	100 parts contain		Free Fatty Acids in Total Fat.
		Free Fatty Acids.	Total Fat.	
				Per cent.
Rape . . .	6	0·93	8·81	10·55
Poppy seed . .	10	5·66	9·63	58·89
Earthnut (Arachis)	20	1·42	7·65	18·62
Sesamé . .	15	6·15	15·44	40·29
Palm nut . .	38	1·47	10·39	14·28
Cocoa nut . .	5	1·31	13·11	10·51
Linseed . .	2	0·75	8·81	9·75
Castor . .	10	1·27	6·53	20·07

The ratio of total fat to fatty acids is, according to *Nördlinger*, the same in the exhausted meals as in the extracted oils.

This does not hold good of the oils obtained by pressing, the "first expressed" oils ("salad oils") containing far less free fatty acids than the total fat in the seeds. Consequently more fatty acids remain in the seeds. The oils from a second and third pressing are richer in fatty acids, but still the greater portion thereof remains behind in the cakes.

The following example will illustrate this :—

100 Kg. of Poppy Seed yielded	Oil. Per cent.	Containing Free Fatty Acids. Per cent.
When extracted with solvents .	46·9	6·82
When expressed—(*a*) Salad oil .	39·0	1·92
(*b*) Commercial oil	2·5	15·37
There remained in the cakes . .	5·4	38·32

The test for free fatty acids, in conjunction with the microscopical examination, serves, therefore, to distinguish "extracted" meal from "pressed" meal. Further, by testing the oils for free acids, "extracted" and "pressed" oils can be distinguished.

The examination of a number of linseed cakes by *Dyer* and *Gilbard*[1] has shown that the oil extracted from freshly made linseed cakes contained no free fatty acid ; on the other hand, the proportion of free acids increased when the cakes had "heated" or become mouldy in storing. In a further paper[2] these chemists give a large number of determinations of free fatty acids in linseed cakes ; in 116 freshly made cakes the oil contained only about 3 per cent of free fatty acids. As a general rule impure cakes show a higher

[1] *Jour. Soc. Chem. Ind.* 1893, 8. [2] *Ibid.* 1896, 288 ; *Analyst*, 1895, 241.

acidity than pure cakes, and when high acidity is found in pure cakes it is probably due to bad condition, such as that produced by "heating" or mouldiness. The reader must be referred to the original paper for the analyses of linseed, rape, arachis (ground nut), and niger seed cakes; here we can only quote figures relating to uncrushed seeds.[1]

Uncrushed Seeds.	Moisture. Per cent.	Oil. Per cent.	Fatty Acids in 100 parts of Oil.
Linseed (13 samples) . .	6·3	39·7	1·30
Cotton seed (6 samples) .	9·8	21·3	7·4 { 3·6 lowest 12·6 highest
Rape seed (4 samples) .	5·8	39·5	0·81 { 0·15 lowest 1·15 highest
Ravison rape (6 samples)	7·7	25·4	0·90 { 0·50 lowest 1·87 highest
Jambo rape (2 samples) .	7·1	25·7	2·4
Niger seed	7·3	38·0	0·9
Sunflower seed	6·2	29·2	1·9

B. FATS AND OILS

The individual natural fats and oils have been dealt with at length in the preceding chapter, and the analytical methods employed for their identification and for the detection of adulterations have been fully described.

1. Synthetical Fats

The supply of natural fats and oils being well-nigh inexhaustible, the artificial preparation of fats has no practical importance, except in the case of *acetin*, the triglyceride of acetic acid.

ACETINE

Acetine is used as a solvent (possessing certain advantages over other solvents, such as alcohol, etc.) for indulin and other colouring matters employed by the calico printer as a steam colour.

Commercial "acetine" consists of a mixture of diacetin and triacetin and smaller quantities of acetic acid and water; it is prepared by heating together glycerin and glacial acetic acid (p. 3).

The proportions of diacetin and triacetin are found by determining on the one hand the combined acetic acid, and on the other hand the glycerol by *Benedikt* and *Cantor's* method (see p. 806). One operates as follows:—

An accurately weighed quantity of the sample is titrated with half-normal aqueous potash, using phenolphthalein as indicator. An

[1] With regard to the iodine of oil extracted from linseed cake, cp. Ketel and Antusch, and also Mastbaum, *Jour. Soc. Chem. Ind.* 1896, 150. 471.

accurately measured quantity of caustic soda of 1·1 specific gravity, the strength of which is ascertained by titrating with half-normal hydrochloric acid, is then run into the neutral solution, and the latter boiled for half an hour, whereby the diacetin and triacetin are hydrolysed, the acetic acid combining with the caustic soda. After titrating back the excess of caustic soda with half-normal hydrochloric acid, the number of c.c. of half-normal caustic soda used for one grm. of substance is found.

A fresh quantity—about 1·5 to 2 grms.—of the sample is then weighed off accurately and the glycerol determined as described p. 806.

Suppose we have found 1 grm. of the sample required 2 c.c. of half-normal caustic soda for saturation, then the sample contains $\frac{2 \times 3^1}{2} = 3$ per cent of free acetic acid. Let the number of c.c. of half-normal caustic soda required to neutralise the combined acetic acid in *one* grm. be 20 c.c., and the percentage of glycerol found be 33·3 per cent. It is convenient to calculate the combined acetic acid to C_2H_2O (42), as the sum of the percentages of C_2H_2O and of glycerol equals the sum of the diacetin and triacetin in the sample. The proportion of combined C_2H_2O is $20 \times 2{\cdot}1 = 42$ per cent. Let x and y be the percentages of diacetin and triacetin respectively, then we have

$$x + y = 42 + 33{\cdot}3 = 75{\cdot}3.$$

One molecule of diacetin, or 176 parts, contains 92 parts of glycerol; one molecule of triacetin, or 218 parts, also contains 92 parts of glycerol; hence

$$\frac{92x}{176} + \frac{92y}{218} = 33{\cdot}3.$$

From these equations we find $x = 60{\cdot}12$ and $y = 15{\cdot}18$. The sample has, therefore, the following composition :—

Diacetin	60·12 per cent.
Triacetin	15·18 ,, ,,
Acetic acid	3·00 ,, ,,
Water (by difference) . . .	21·70 ,, ,,
	100·00

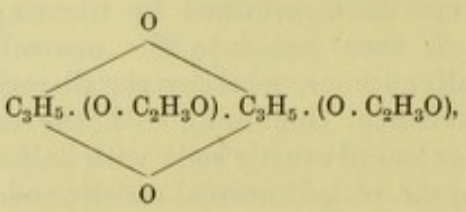
According to recent researches of *Geitel*,[2] the chemical change occurring on heating glycerol and acetic acid is not so simple as stated above. *Geitel* proved that there are always formed triacetin, diacetin, and monoacetin in variable quantities depending on the special conditions of each experiment, whilst a certain amount of glycerol remains unattacked. Besides, the several acetines react with glycerol to form products of condensation, such as monoacetyl-diglycerol

$$C_3H_5 . (OH)_2 - O - C_3H_5 . (O . C_2H_3O) . OH,$$

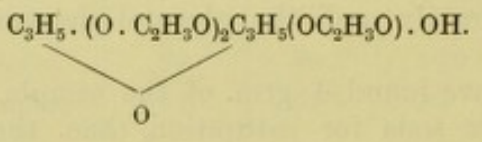
[1] Acetic acid, $C_2H_4O_2 = 60$.

[2] *Jour. f. prakt. Chemie*, 1897 (55), 428.

and diacetylglycid



and triacetyldiglycerol



2. Edible Fats and Oils

Mention has been made in the preceding chapter of a number of "manufactured" fats, obtained from the natural products by cooling or pressing, such as cotton seed stearine, tallow stearine, lard stearine, tallow oil, lard oil, etc.

Under this head those fats and oils, and their substitutes, that serve as food-stuffs will be considered.

The animal fats used for this purpose are butter, suet, and lard (goose fat); they are largely substituted by artificial mixtures, conveniently termed *edible fats.*

(*a*) *Edible Fats*

From a sanitary point of view, no objection can be raised against the substitution of the cheaper animal or vegetable fats for the more expensive animal fats, as long as these substitutes are sold under their proper name, and are not used for fraudulent purposes. It is rather to be desired that the industry of fat substitutes should extend further, yielding, as it does, cheap palatable food stuffs, and thereby tending to exclude from consumption the unwholesome fat from diseased animals, etc.

The edible fats may be conveniently subdivided into butter substitutes and lard substitutes.

The **butter substitutes**—"oleomargarine,"[1] "margarine" (older names, partly suppressed by legislation, are: "butterine," "Dutch butter," "Wiener Sparbutter," "Kunstbutter")—are, as a rule, if not forbidden by law, coloured yellow with annatto, methylorange, etc. (for the examination of the colouring matter cp. "Butter Fat," p. 615). The fatty raw material chiefly used is oleomargarine (p. 591), or certain portions of lard, or lard oil (p. 584), with which varying quantities of vegetable oils, chiefly cotton seed oil, are

[1] Cp. footnote 2, chap. xi. p. 591.

admixed. Some manufacturers also add milk, or genuine butter in small quantities, or butyric acid, etc.

The manufacture (and, consequently, the examination) of butter substitutes is affected by legislation as enacted in different countries.[1] In this country (and in the United States) mixing of margarine (oleomargarine) with butter is not forbidden, as according to the Margarine Act any "butter" containing even the smallest proportion of foreign fat is looked upon as "margarine" ("oleomargarine"); whereas in France mixing is permitted, provided the article so prepared is sold with proper declaration as to its composition. In Germany, on the contrary, mixing of margarine with butter is forbidden, and in the manufacture of the former no more than 100 parts of milk or a corresponding quantity of cream may be used for 100 parts of foreign fats;[2] and in Denmark the proportion of butter fat allowed in margarine has been reduced from 50 per cent to 12 per cent.

According to the latest German Margarine Act, margarine must, in order to render its detection in butter easy, contain 10 parts of sesamé oil for 100 parts of fat, the proposal to add the "latent" colouring matter dimethylamidoazobenzene (cp. footnote, p. 609) having been rejected.

The examination of margarine (oleomargarine), especially the methods for distinguishing it from true butter fat, have been exhaustively dealt with in the preceding chapter (p. 616). It may suffice, therefore, to give a table, containing some physical and chemical constants of fat from margarine; further a table, due to *Wallenstein*,[3] containing the analyses of the fat of a number of margarines from various sources, and finally the analyses of a few German margarines.

[1] A. Lavalle, *Die Margarine Gesetzgebung*, Bremen, 1896.

[2] The German margarines may, therefore, not contain more than 3·5 per cent of butter fat in the melted fat; or, in other words, their *Reichert-Meissl* value must not exceed 2, provided cocoa nut oil or palm nut oil is absent.

[3] *Jour. Soc. Chem. Ind.* 1893, 54.

[TABLE

Specific Gravity.			Hehner Value.		Reichert Value.		Saponific. Value.		Iodine Value.	
At °C.		Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0·924-0·930	Hager	95·56	Cornwall	0·4-0·6	Cornwall	195-197·4	Cornwall	55·3	Hübl
100	0·859	Koenigs	...	..	0·99	Sell	192-200	Thörner	50	Moore
,,	0·859-0·860	Sell	...	...	...	...	...	...	46 48-64	Zenoni Thörner

Source.	No.	Melting Point (Pohl's Method).	Melting Point of Fatty Acids.	Solidifying Point of Fatty Acids.	Free Fatty Acids		Iodine Value.	Saponification Value of the total Fatty Acids.	Triolein.	Tripalmitin.	Tristearin.	Ratio of Palmitin to Stearin.
					Before Drying.	After Drying at 70° C.						
		°C.	°C.	°C.	Per cent.	Per cent.	Per cent.		Per cent.	Per cent.	Per cent.	
American Margarines.	1	26·0	45·0	42·5	1·26	1·55	44·3	205·7	51·4	34·6	14·0	100 : 40·5
	2	17·3	43·7	41·0	0·85	1·22	47·0	201·8	54·5	15·6	39·9	100 : 255·7
	3	25·0	44·0	42·4	0·56	1·00	43·8	204·8	50·8	30·2	19·0	100 : 62·9
	4	27·0	44·2	41·5	0·99	1·29	44·3	205·3	51·3	32·7	16·0	100 : 48·9
	5	25·0	43·8	42·0	0·70	1·04	45·0	205·8	52·2	35·1	12·7	100 : 36·2
	6	25·5	44·5	42·0	0·85	1·20	44·6	206·4	51·7	38·0	10·3	100 : 27·1
Austro-Hungarian Margarines.	7	25·0	42·9	41·5	1·35	1·60	45·8	206·0	53·1	36·1	10·8	100 : 29·9
	8	26·0	43·0	41·0	0·85	1·01	47·2	205·7	54·8	34·6	10·6	100 : 30·6
	9[1]	23·25	42·0	40·0	1·56	1·83	47·6	206·4	55·2	38·0	6·8	100 : 17·9
	10	26·5	44·0	41·7	0·85	1·24	45·5	205·4	52·8	33·2	14·0	100 : 42·2
	11	25·25	43·5	42·0	1·42	1·74	44·1	204·9	51·1	30·7	18·2	100 : 59·3
	12	24·0	43·8	41·25	1·28	1·69	46·5	205·5	53·9	33·7	12·4	100 : 36·8
	13	25·5	43·5	41·75	1·28	1·68	45·1	205·8	52·1	35·1	12·8	100 : 36·5
	14	25·5	44·25	42·0	1·35	1·58	44·0	205·5	51·1	33·7	15·2	100 : 45·1
	15[1]	24·75	43·7	42·2	1·30	1·59	44·4	206·8	51·5	40·0	8·5	100 : 21·2
	16	23·0	43·7	42·2	1·40	1·66	44·2	205·5	51·2	33·7	15·1	100 : 44·8

[1] Inferior quality.

Composition of a few German Margarines [1]

	Water.	Fat.	Not-Fat.	Ash.	NaCl.	Hehner Value.	Reichert Value. c.c. $\frac{1}{10}$ norm. KOH.	Butyro-refractometer. Deviation at 45° C.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.		"Degrees."
Margarine F . . .	8·8	88·78	2·33	1·58	1·53	94·5	0·33	..
,, FF . . .	8·5	88·81	2·69	1·76	1·74	94	0·44	43° 21′
,, "Brillant"	8·6	88·9	2·4	1·6	1·5	94·7	1·43	..

The determination of stearic acid in a sample may lead to valuable results in the examination of butter substitutes, as evidenced by the following numbers, hitherto published by *Hehner* and *Mitchell*:—

Fat.	Containing Stearic Acid. Per cent.
Oleomargarine	21·3-23·6
Margarine I.	24·8
,, II.	11-72

How far admixture with vegetable oils (especially inferior oils, as sunflower oil [2]) constitutes an adulteration of oleomargarine must be left to the analyst to decide in each individual case.

Vegetable butter ("*lactine*," "*vegetaline*") has been described page 541. Latterly "vegaline" is being offered as a butter substitute. Judging from its price it must be cotton seed stearine.

Leffmann states that he found in (American) oleomargarines paraffin wax. The determination of unsaponifiable matter should, therefore, not be considered unnecessary.

The **lard substitutes** consist chiefly of mixtures of lard-, beef-,[3] and cotton seed stearine with the following vegetable oils and fats:—cotton seed, maize, arachis, sesamé, and cocoa nut or palm kernel oils. Their examination has been described fully under "Lard" (p. 580). Only in rare instances it will be required to determine quantitatively the proportion of the ingredients of a lard substitute. In special cases it may be necessary to test for unsaponifiable matter, since even patents are taken for lard substitutes containing large proportions of mineral oil.

If there be reason to assume that the sample under examination is lard adulterated with cotton seed oil, the latter may be calculated approximately from the iodine value of the liquid acids of the sample in the following manner:[4] — Let J be the iodine value of the liquid fatty acids of the sample, 94 the corresponding value for lard, and

[1] Partheil, *Apoth. Zeitung*, 12. 220, 221.
[2] Jolles, *Jour. Soc. Chem. Ind.* 1893, 935.
[3] On the Continent also mutton stearine.
[4] Asbóth, *Jour. Soc. Chem. Ind.* 1890, 418.

136 for cotton seed oil, then x, the proportion of the mixed cotton seed oil fatty acids among the liquid fatty acids, is found by means of the equation

$$x : 100 = J - 94 : 136 - 94,$$

hence

$$x = \frac{100\,J - 9400}{42}.$$

Let, further, A be the percentage of the liquid fatty acids of the sample, and 70 that of cotton seed oil, then C, the proportion of cotton seed oil in the sample, will be

$$C = \frac{A}{70}x = \frac{A(100\,J - 9400)}{70 \times 42} = \frac{10A(J - 94)}{294}.$$

Wallenstein and *Finck*[1] calculate approximately the proportion of liquid glycerides in a lard substitute from the iodine value i of the fat, the iodine value J of its liquid fatty acids, and the Hehner value h by the following formula :—

$$L = \frac{10000i}{hJ},$$

provided cocoa nut oil be absent.

I consider it useful to indicate step by step how this formula can be derived. i and J are determined quantitatively ; also h may be determined, but considering the assumption that cocoa nut oil (palm nut oil) is absent, or, in other words, that both the liquid fatty acids and the total mixed fatty acids have approximately the same molecular weight, no appreciable error will be committed by taking h once for all = 95·5.

Since all the iodine absorbed by the fat is assimilated by the fatty acids, we have, letting i_1 be the iodine value of the mixed fatty acids,

$$hi_1 = 100i \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The solid fatty acids contained in the mixed fatty acids absorb no iodine ; therefore, if l be the proportion of the liquid fatty acids, we have

$$hi_1 = lJ \quad . \quad . \quad . \quad . \quad . \quad (2)$$

hence

$$lJ = 100i \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The proportion of l in L is fixed, according to the assumption made by

$$l : L = h : 100,$$

or

$$l = \frac{Lh}{100} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Substituting (4) in (3) we have

$$\frac{Lh}{100}J = 100i,$$

or

$$L = \frac{10000i}{hJ}.$$

---

[1] *Jour. Soc. Chem. Ind.* 1895, 78.

The important question whether tallow or lard stearine is the hard component of a lard substitute can, at the present state of our knowledge, only be solved by microscopical examination (cp. chap. xi. p. 584). A more definite solution of this problem may be expected from the determination of stearic acid by *Hehner* and *Mitchell's* method (cp. also "Lard," p. 584).

The quality of an edible fat, irrespective of the nature of its components, depends in a great measure on its palatableness.

The determination of the amount of free fatty acids is of great importance. Although the statements of various observers as to the digestibility of "margarine" compared with that of butter are at variance,[1] it is not disputed that very rancid fats, besides having an unpleasant taste, are digested with difficulty. On the other hand, completely neutral fats have an insipid taste;[2] therefore many manufacturers add small quantities of butyric acid to butter substitutes. According to *Stockmeier*,[3] butter containing 1·4 to 1·7 per cent of free fatty acids (calculated to oleic acid) may be considered as slightly rancid; if the free acid amounts to 2·26 per cent, the butter must be rejected as liable to cause the usual symptoms of indigestion—eructation, "heartburn," etc.

In Germany the proportion of free fatty acids is sometimes expressed in "degrees of rancidity," each degree corresponding to 1 c.c. of normal caustic potash for 100 grms. of fat (cp. table, p. 150). According to *Stockmeier*, a butter requiring more than 8 c.c. should be objected to, whereas *Halenke* and also *Schweissinger* state that butter showing a higher rancidity than 8 degrees may still be palatable and unobjectionable. However, as the rancidity does not correspond to the proportion of the free fatty acids (p. 11), no rule can at present be laid down.[4]

(*b*) *Edible Oils. Salad Oils (Sweet Oils)*

The industry of edible fats is at present in a state of transition, and as may be gathered from patent specifications new developments, necessitating new analytical methods, may be expected.

Many vegetable "cold-drawn" oils are used as salad and culinary oils, and also for preservation of food, notably olive oil, sesamé oil, arachis oil, poppy seed oil, cotton seed oil ("union salad oil"), beechnut oil, sunflower oil, nut oil, rape oil, cameline oil, and also linseed oil (in Russia!).

The examination of these oils has been treated of in chap. xi.

[1] J. König, *Die menschlichen Nahrungs- und Genussmittel*, vol. ii. 306, takes objection to A. Mayer's and A. Jolles' statement that margarine is just as easily digested as butter fat, and that both fats have the same nutritive value. Cp. also Jolles, *Jour. Soc. Chem. Ind.* 1894, 827; Moore and Rockwood, *Jour. Chem. Soc.* 1897, Abstr. ii. 150.

[2] Zuntz has shown by experiments that free fatty acids are conducive to digestion.

[3] *Vierteljahrsschr. Nahrungs- u. Genussmittel*, 1889, 428.

[4] Scala (*Staz. Sperim. Agr. Ital.*) proposes the employment of the *Reichert-Meissl* value as a measure of rancidity.

The industry of edible oils has latterly made great strides, and with the help of modern processes of refining the objectionable ingredients are successfully removed.

If an edible oil has been found free from adulterants, the estimation of free fatty acids is necessary to complete the examination.

No rule can be laid down as to what should constitute the permissible maximum of free fatty acids in a salad oil, the limit naturally depending on the demand as to taste and palatableness made in various countries or localities. An absolutely neutral oil has an insipid taste.

Nördlinger[1] gives the following proportions of free fatty acids in a few salad oils :—

Salad Oil.	Free Fatty Acids as Oleic Acid. Per cent.
Olive oil	1·66
Arachis oil	1·94
Poppy seed oil	1·92
Sesamé oil	1·97
Rape oil	1·19
Cotton seed oil[2]	0·15

3. Burning Oils

Although the enormous expansion of the mineral oil industry has greatly contributed to a reduction in the employment of fatty oils as burning oils, their use is yet considerable.

The oils chiefly used as burning oils are :—Rape oil, lard oil (American railways), seal, and whale oils (lighthouses), and the vegetable oils of the last expression (being unfit for edible purposes), such as castor oil, olive oil, etc.

The examination of these oils refers to purity and to the proportion of free fatty acids.

The absence of drying or semi-drying oils from burning oils, used in large quantities by railway companies, can be ascertained by the methods given in the foregoing chapters. The importance of such tests for large consumers may be gathered from the fact that lard oil adulterated with 25 per cent of cotton seed oil will not burn for longer than 6 to 8 hours without clogging the wick, whereas pure lard oil will burn as long as 12 to 14 hours. (Small consumers hardly note such drawbacks, and it is, therefore, easily explained that cotton seed oil, and even linseed oil (in India), and Japan wood oil (in Japan), are used as burning oils.)

The test for free fatty acids is also important (cp. "Rape Oil," chap. xi. p. 404 ; "Olive Oil," p. 452).

4. Paint Oils

Paint oils are those oils that are used as a vehicle for applying pigment colours for painting.

[1] *Jour. Soc. Chem. Ind.* 1889, 806.

[2] Refined with caustic alkali.

Practically the only oils useful for this purpose are the drying oils, and the reader will find in chap. xi., under the heads of these oils, some notes indicating the suitability of the individual oils for certain purposes. The reader is further referred to the chapter on boiled oil, p. 735.

The chief tests will be those for adulterants such as resin, resin oils, mineral oils, or a mixture of these substances with the fatty oils. All these adulterants, sometimes termed substitutes, lower the value of the paint oils, inasmuch as the lasting properties of the latter are greatly reduced.

In judging of the value of a drying oil as paint oil, the effect of the pigment with which it is to be used must not be lost sight of, inasmuch as some pigments greatly facilitate the drying, whereas others so much retard the drying that driers must necessarily be added.[1]

It should be noted that oils extracted by solvents are not fit for painting.

C. WASTE FATS

In the wider sense of this term kitchen grease, ship's fat, skin grease, slaughter-house grease, and similar fats, fall under this head. We shall, however, consider here only those fatty substances which are recovered on a large scale as by-products in various industries. Bone fat has been described already (p. 587); other waste products are: "Recovered grease," pure wool fat, "lanoline," cotton seed oil foots, fuller's grease, black oil, and sod oil or dégras.

1. Wool Fat, Wool Grease (Recovered Grease, Brown Grease)[2]

French—*Suint.* German—*Wollfett, Wollschweissfett.*

Wool fat is the natural grease contained in sheep's wool. In the course of preparing the raw wool for spinning this grease is removed by means of dilute soap (or sodium carbonate) solutions, or by extraction with volatile solvents. In this country the suds from wool-scouring are collected in large tanks, and, by acidulating with mineral acids, "brown grease," or "recovered grease," is obtained of varying composition, according as the suds from the wool are kept separate or are mixed with the soap suds from the scoured woven goods, as is the case in those woollen mills where wool is washed, spun, and woven.

The wool grease, obtained by extracting raw wool with volatile solvents, contains, of course, only the natural constituents, viz. free

[1] Cp. Lotter, *Jour. Soc. Chem. Ind.* 1895, 169.

[2] In the United States this grease is known commercially as dégras.

fatty acids, neutral compound ethers, and alcohols, in admixture with potassium salts of lower fatty acids. In the wool-scouring process by means of soap, the latter are for the most part removed by a previous steeping in lukewarm water. However, small quantities of volatile fatty acids are also found in "recovered grease."

A "recovered grease" of the latter kind is especially known under the trade term, "Yorkshire grease." This consists essentially of three groups of fatty substances :[1]—

1. *Free fatty Acids*, resulting partly from the decomposition of the waste soap and partly occurring naturally in wool fat.[2]

2. *Neutral, saponifiable Ethers.*—These consist, in the first instance, of the characteristic saponifiable constituents of wool fat, the chemical constitution of which assigns to them a place amongst waxes (p. 651). The properties of this neutral substance in its pure state have been described in the preceding chapter (p. 651). In admixture with this neutral substance there may be present glycerides, *i.e.* true neutral fats, owing their presence to fatty oils used in oiling the wool fibre. If no glycerol has been found in the "recovered grease," the neutral portion is, of course, simply a mixture of waxes.

3. *Unsaponifiable matter*, consisting of alcohols, such as ceryl alcohol, cholesterol, etc., naturally contained in wool grease. Any hydrocarbons that have found their way into the oils used for lubricating the wool will be met with in this portion of the "grease."

Yorkshire grease is a yellow or brown viscous substance of a very offensive smell; it has a specific gravity of about 0·973 at 15° C., and melts between 39° and 42° C.

The following is a complete analysis of an anhydrous "Yorkshire grease" of good quality, free from glycerides, mineral oil, and ash (*Lewkowitsch*) :—

	Per cent.
Volatile acids	1·28
Insoluble free fatty acids	20·22
Combined fatty acids	48·47
Alcohols	36·47

The methods adopted for this analysis will be fully described in the following chapter (p. 816).

Hurst[3] has given the following analyses of four samples of "Yorkshire grease." As he has neither described the method by which he has arrived at these results, nor stated which constituent has been calculated by difference, the numbers must be accepted with reserve.

[1] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1892, 134.
[2] Schulze, *Berichte*, 1872, 1076; 1873, 251; 1874, 571.
[3] *Jour. Soc. Chem. Ind.* 1889, 90.

	I.	II.	III.	IV.
Specific gravity at 15·5° C.	0·9391	0·9417	...	0·9570
,, ,, 98° C.	0·8900	0·8952	...	0·8720
	Per cent.	Per cent.	Per cent.	Per cent.
Water	0·98	1·53	1·21	0·94
Fatty acid	18·61	24·25	24·15	26·43
Neutral oil	68·62	58·25	30·02	16·86
Unsaponifiable oil	11·68	15·83	44·44	55·77
Ash	0·11	0·14	0·18	Trace
	100·0	100·0	100·0	100·0

The wool fats from various sources vary considerably within certain limits, much as other natural products do. The following table contains some characteristics of several wool fats prepared by *Herbig*[1] by extracting raw wool with ether :—

Source of Wool Fat. From	Yield of Wool Fat. Per cent.	Potash Salts in Wool Fat calculated to Potassium Oleate. Per cent.	Colour.	Odour.	Consistency.	Acid Value.	Saponific. Value.	Unsaponifiable (Total Alcohols). Per cent.
1. New Zealand wool	16·6	4·9	dark red	scarcely disagreeable, slightly aromatic.	fairly soft when fresh, becomes harder on keeping.	14·3	110·5-110·7	43·6-43·9
2. Australian wool	16·0	4·24	brownish-yellow	faint, similar to above.	fairly soft, remained so after keeping.	15·5	112·7-113·3	
3. South American wool	13·2	9·25	yellowish-olive-gre'n	faint	fairly hard.	13·2	98·7-98·9	43·1-43·6
4. Russian wool	6·6	24·4	dirty brown	..	soft at 20° C.	13·9	94·2-95·9	38·7-39·1

The efforts of several inventors (Jaffé and Darmstädter, Ekenberg and Montén) have been directed to separate the wool fat into several fractions. The last-mentioned chemists prepare three fractions :—

	Melting Point. °C.
Cholaïn	25-29
Cholepalmin	37-38
Cholecerin	49-55

Wool grease is used in the preparation of "brown cloth oils" (p. 711) by mixing it with mineral oils. The greatest part of wool grease is, however, distilled, yielding the commercial "distilled greases," which will be described further on.

[1] *Jour. Soc. Chem. Ind.* 1894, 1069.

Since the valuable property of wool fat, viz. that of yielding with water emulsions that are easily absorbed by the skin, has been rediscovered,[1] it is purified by various (patented[2]) processes, and the pure neutral wool fat is brought into commerce in the anhydrous or hydrated state.

The chemical constitution of these preparations in their anhydrous state is that given for wool wax, chap. xi. p. 651. They are sold under various names, such as Adeps lanæ, Lanoline, Agnine, etc.

The British Pharmacopœia recognises two preparations, viz. Adeps lanæ, pure wool wax, and Adeps lanæ hydrosus, hydrous wool wax, better known under the trade term "Lanoline."

(a) Pure (Anhydrous) Wool Fat. Adeps Lanæ

"Adeps lanæ" is pale yellow, translucent, and of thin unctuous consistency, with a slight but not unpleasant smell (cp. also Lanoline). It is examined in a manner identical with that described under Lanoline (see below). A sample examined by *Benedikt* gave the following numbers :—

	Per cent.
Water	0·91
Ash	0·017
Free fatty acid (as oleic acid)	0·27
Glycerol	0·0
Melting point	36°-41° C.

(b) Lanoline

Lanoline is the trade term given to a preparation consisting of about 75-80 per cent of wool wax and 25-20 per cent of water.

Lanoline has a white or slightly yellow colour and a very faint smell. Its consistency is that of a very soft ointment. Heated on the water-bath it melts, separating into two layers, viz. water and wool wax. Like a true wax, lanoline possesses the remarkable property of combining with water on being kneaded with it, without losing its salve-like consistency. For this reason, and because it does not turn rancid, it is an excellent material for the preparation of salves and ointments, the drugs incorporated with it being easily absorbed by the skin.

Dieterich has determined quantitatively its power of taking up water compared with that of other substances, by mixing 100 grms. with varying quantities of water at 15° C. until the mixtures ceased to be homogeneous. The following table contains his results :—

[1] Cp. Langbeck, *Jour. Soc. Chem. Ind.* 1890, 356.

[2] *Ibid.* Cp. also the various Letters Patent abstracted in the *Journal of the Society of Chemical Industry.*

100 Parts of	Give a complete Emulsion with Parts of Water.
Lanoline	105
Mixture of 80 parts of lanoline and 20 parts of olive oil	320
Mixtures of 20 parts of white beeswax and 80 parts of oleic acid	228
Butter fat	165
Lard	15
Paraffin wax	4

EXAMINATION OF LANOLINE

The examination of lanoline embraces the determination of water, ash, free acids, and the detection of foreign substances.

Water.—10 grms. of lanoline are weighed off accurately in a porcelain basin mixed with a small quantity of alcohol, warmed on the water-bath, and finally heated in a drying oven at 100°-110° C. until the weight remains constant. Lanoline should not contain more than 30 per cent of water.

Ash.—This is determined in the usual manner. The amount of ash should be very small; a sample of genuine lanoline gave only 0·05 per cent.

Free Acids.—10 grms. of lanoline are dissolved in ether, and titrated with decinormal alkali, using phenolphthalein as an indicator. The proportion of free fatty acids should be very small, especially if the lanoline is intended for pharmaceutical or cosmetic preparations. Genuine samples examined in the writer's laboratory required not more than 0·2 c.c. of normal potash for 15 grms. of lanoline.

Foreign Substances.—A comparison of the constants of the sample with those given in the table, p. 653, will afford the readiest means of detecting the presence of foreign substances, and will indicate the direction which further examination should take. Thus, if no glycerol has been detected in the lanoline (it should be remembered that wool wax must be saponified with alcoholic potash under pressure or with sodium alcoholate), an abnormal saponification value will point to the presence of paraffin wax or other hydrocarbons. The unsaponifiable matter must then be examined according to the directions given in chap. vii. p. 229.

(c) Distilled Grease

When the "recovered grease" is subjected to distillation with superheated steam the compound ethers are broken up, the free fatty acids undergoing partial decomposition at the same time. A light oil, consisting of hydrocarbons, is obtained first, and then follow heavier distillates, which are separated into a liquid and a solid portion by cooling and allowing to crystallise. These fractions are treated much in the same way as the distilled fatty acids in candle

works, so that the following products are finally obtained: "oleine," chiefly used as wool oil (p. 705), and "stearine," employed for sizing tallows and as inferior material in the candle and soap industries.

The changes the "recovered grease" undergoes in the distillation consist, according to *Lewkowitsch*,[1] in the first instance, in the breaking up of the compound ethers into fatty acids and hydrocarbons, the latter being formed in consequence of the fatty acids assimilating all the available oxygen in the molecule. This is illustrated by the following equation :—

$$\underset{\text{Cetyl palmitate.}}{C_{15}H_{31}CO \cdot O \cdot C_{16}H_{32}} = \underset{\text{Palmitic acid.}}{C_{15}H_{31}CO \cdot OH} + \underset{\text{Cetene.}}{C_{16}H_{32}}.$$

A portion of the neutral ethers is carried away undecomposed by the current of steam, and will be found in the "distilled grease" as such.

The free alcohols in the "recovered grease" will partly distil over as such, another portion will be broken up into hydrocarbons with loss of water; thus cholesterol, when subjected to distillation, is known to yield hydrocarbons.

The fatty acids in their turn, and especially those easily undergoing dehydration, will also contribute a portion of the hydrocarbons.

The examination of the distilled greases will therefore embrace the determination of *free fatty acids*, *neutral ethers* (*waxes*), and *unsaponifiable substances*. The latter consist chiefly of hydrocarbons, which have been erroneously returned by various chemists as mineral oil (cp. "Wool Oils"). The nature of these hydrocarbons is but very imperfectly known; being derivatives of cholesterol, they will most likely exhibit optical activity.

The methods adopted for the complete examination of distilled grease are almost the same as those employed for the complete analysis of wool fat; they will be fully described in the following chapter (p. 820).

The commercial analysis of **distilled grease oleine** used as wool oil includes the flash point and the unsaponifiable matter (cp. p. 706).

A number of analyses of distilled grease oleines will be given under the heading "Wool Oils" (p. 711).

Distilled grease stearine is a hard, whitish, solid substance, differing in its appearance from commercial stearic acid by the absence of crystalline structure. This stearine is easily identified by its strong isocholesterol reaction (p. 85) and its high iodine value, due to presence of isooleic acid. It consists chiefly of free acid, the bulk of the hydrocarbons having been removed by pressing. In commercial examination the melting and solidifying points of the stearine, the "saponifiable," and the "unsaponifiable" are required.

The "saponifiable" is ascertained by boiling an accurately weighed quantity with standard alcoholic potash, as described for the determination of the saponification value (p. 151). Each c.c. of normal

[1] *Jour. Soc. Chem. Ind.* 1892, 142.

alkali is taken as corresponding to 0·284 grm. of stearic acid. (The small quantity of neutral ethers (if any) in the stearine is thus calculated as stearic acid.) The unsaponifiable matter is determined in the manner described above (p. 218); it is most convenient to use for this test that quantity which has served for the determination of the "saponifiable."

The following table gives a few analyses of "distilled grease stearine." The free acid has been calculated as stearic acid—

Solidifying Point.	Melting Point.	Specific Gravity.		Water.	Free Acid.	Neutral Ethers.	Unsaponifiable.	Iodine Value.	Observer.
°C.	°C.	At 15·5° C.	At 98° C.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
45	48	0·9193	0·836	0·6	88·6	2·11	0·49	..	Hurst
53·5	57	0·9044	..	1·48	76·3	7·7	0·4	..	,,
..	..	..	..	2·85	72·13	..	3·12	..	,,
41·5	..	..	..	..	98·9	..	..	33·7	Lewkowitsch
..	..	..	..	..	..	..	7·2	..	,,

The residue left in the stills, **pitch** (goudron), is used as a lubricant for hot neck rollers.

2. Cotton Seed Foots

In the refining of cotton seed by means of caustic soda a precipitate is obtained, consisting of a mixture of cotton seed oil soap, colouring and resinous matters, known in this country under the trade term "mucilage."

The American cotton seed oil foots are of comparatively light colour, as the seed is pressed whilst still fresh; these "foots" can therefore be used for soap-making.

The Egyptian seed, crushed chiefly in this country, generally "heats" during the voyage and on storing; in consequence of the changes that the seed has undergone, the crude cotton seed oil has a very dark colour, and the foots obtained from it are almost black. The considerable quantity of soap and oil contained in this "mucilage" are recovered by treatment with acid, and by distilling the separated fatty mass in a current of superheated steam.

The distillate thus obtained consists chiefly of free fatty acids, and is worked up in the same manner as the distilled fatty acids of the candle-works. It yields an "oleine" and "stearine." The latter is often termed "cotton seed stearine," and must not be confounded with the true cotton seed stearine (or vegetable margarine) described p. 506.

The "oleine" and "stearine" are put to the same uses as the candle-works products, and may be similarly examined (cp. pp. 755, 766).

3. Fuller's Grease—"Seek Oil"

French—*Graisse de foule.* German—*Walkfett.*

Fuller's grease is the fatty substance recovered from the soap suds which have served for scouring silk, woollen, or cotton (dyed Turkey-red) goods by acidifying with a mineral acid.[1] The fatty mass thrown up by the acid (it is known in Yorkshire under the name "magma" or "seek," also "sake"; therefore "seek oil" means fuller's grease) is put into bags, and subjected to pressure whilst hot, when the dirt, and especially the fibres, remain behind, whereas the fatty matter is pressed out.

According to the soap used for scouring the goods, and, in the case of grease from woollen mills, according to the quality of wool oil that has been used previously in the spinning of the wool, the quality of fuller's grease will vary, and in a corresponding manner the uses it is put to. Thus, the suds from silk or best woollen goods, for which olive oil soap has been used, will yield almost pure fatty acids, which can be used for soap-making at once, whereas the suds from the lowest union goods will, as a rule, contain considerable quantities of mineral oil or other hydrocarbons and dirt, from the last of which they are freed by distillation. The distilled "oleine" is used as wool oil. An intermediate quality of fuller's grease may be used after a mechanical purification as wool oil. This must be examined for mineral acid.

The commercial examination of fuller's grease is identical with that of wool oils (p. 705).

The same remarks apply to—

4. Black (recovered) Oil,

which is expressed from the greasy waste of woollen mills, collected from underneath the carding and scribbling machines. The composition of this oil will be almost identical with that of the wool oil previously used, and may comprise all gradations from a rancid olive oil, through oleic acid, down to the lowest class wool oils, containing more than 50 per cent of unsaponifiable matter.

5. Sod Oil—Dégras[2]

French—*Dégras.* German—*Gerberfett, Lederfett, Weissbrühe, Dégras.*

Sod oil or dégras[3] is the waste fat obtained in the chamoising process, and is used for currying purposes, *i.e.* dressing bark-tanned leather.

[1] In some cases precipitation with lime is resorted to, and the lime soap is subsequently decomposed by a mineral acid.

[2] Jean, *Moniteur scientifique*, 15, 1889. Eitner, *Der Gerber*, 1890, 85; 1893, 257. Simand, *Der Gerber*, 1890, 243; 254; 266; 279. Jahoda, *Zeitsch. angew. Chem.* 1891, 325. Fahrion, *Jour. Soc. Chem. Ind.* 1891, 557; 1013; 1893, 937. Ruhsam, *Jour. Soc. Chem. Ind.* 1892, 639. Weiss, *Jour. Soc. Chem. Ind.* 1893, 937. Schmitz-Dumont, *Dingl. Polyt. Jour.* 1895, 296, Nos. 9-11; *Jour. Soc. Chem. Ind.* 1895, 815; 829. Tortelli, *Annali del Lab. Chim. Centr. delle Gabelle*, 1897, 184.

[3] It should be noted that in the United States "dégras" denotes the recovered grease from wool-scouring works.

The skins that are to be converted into chamois leather are first "limed," the hair is then removed by the aid of a blunt dressing knife, and the unhaired hides placed in a "sour bath," made of refuse malt and bran, in which they "swell" in consequence of an acid fermentation setting in. The skins are next stretched and well rubbed with whale or cod liver oil, and worked in a fulling machine, so as to become thoroughly saturated with oil. Then the skins are taken out and exposed to the air; and the same process of rubbing with oil and stamping in the stocks is repeated until enough oil has been absorbed, and the skins appear quite dry. In consequence of the exposure to the air, a portion of the oil has been somewhat changed, and has entered into "combination" with the fibre, another portion being only mechanically enclosed within the pores of the skin. The "combined oil" is that portion of altered fatty matter which cannot be extracted by carbon bisulphide.[1] In order to render the combination of the oil with the fibre more rapid, a fermentation attended with an elevation of temperature is brought about by placing the skins heaped together in a warm room, and covering them well with canvas so as to keep in the generated heat. Overheating, however, must be prevented by occasional turning over the pile so as to cool the skins. The oxidation of the oil is completed when the skins have acquired the yellow colour of chamois leather. About 50 per cent of the oil is then found to be left in the uncombined state, and is removed by one of the two following methods:—

1. *English (and German) Method.*—The skins having been treated for such a length of time that no oil can be removed by pressing or wringing are freed from the excess of oil by scraping with a blunt knife, and then washed with potash or soda lye. The emulsion thus obtained is acidified with sulphuric acid, the fatty matter skimmed off and united with the oil scraped off. This fatty substance forms the *sod oil* of commerce.

Characteristic of the sod oil, in contradistinction to dégras, is its high proportion of ash, especially of sulphates, and also the large amount of water and hide fragments (fibres).

French Method.—The skins are stocked, aired, and fermented for a shorter period than by the English or German process, so that a large proportion of the oil can be obtained from the skins by throwing them into warm water and subsequent wringing or pressing in hydraulic presses. The oil thus obtained is the *moëllon* or *dégras* of commerce. It contains less ash, less hide fibre, and also less water than the sod oil. The oil still retained by the skins is recovered by washing with alkali, as in the English and German method, and is usually added to the moëllon.

According to *Procter*,[2] many English manufacturers have adopted the French process; therefore the sod oil thus prepared should not differ from French moëllon.

Whereas genuine *moëllon* consists only of expressed oil, a second

[1] Cp. v. Schroeder and Paessler, *Jour. Soc. Chem. Ind.* 1895, 759.
[2] *Pocket-Book of the Leather Industries Laboratory.*

quality termed "secunda dégras," or shortly "dégras," is prepared by mixing genuine moëllon with blubber oils or solid fats (such as tallow, palm nut oil, etc.) This product is still included amongst better qualities of dégras. In fact, according to *Procter*, pure moëllon is never sold as such but always mixed with tallow and untreated oils; these admixtures cannot, therefore, be regarded as adulterants.

Numerous "substitutes" of dégras, or artificial dégras ("corroïne"), occur in commerce, consisting of largely adulterated dégras, or of more or less judiciously prepared mixtures of cod, whale, menhaden, sardine, Japan fish oils, blown blubber oils,[1] tallow,[2] resin, oleic acid, "recovered grease" (p. 686), etc.

In order to satisfy the demand for dégras, frequently skins are worked simply for its production, being oiled and pressed until not a rag is left. Dégras thus prepared must still be considered genuine.

Sod oil and dégras contain considerable quantities of water, which must not separate out even after long standing. The property of being easily emulsified is due, according to *Jean*, to the presence of a "resinous substance" formed during the oxidation of the oil. The greater the quantity of this substance, the more easily an emulsion is obtained. Thus a sample containing 13·9 per cent of the resinous substance yielded with 53 per cent of water an emulsion which had, even after two months' standing, the appearance of a homogeneous mixture.

This "resinous substance" has a brown colour, and melts at 65°-67° C. It is saponifiable, cannot be precipitated with common salt from its alkaline solutions (difference from fats), is insoluble in water, soluble in alcohol and ether, but *insoluble in petroleum ether* (difference from resin). According to *Jean* this substance does not occur in blubber oils, but is formed during the chamoising of the skins.

Simand describes this substance under the name "*dégras-former.*" It possesses, according to him, a light brown colour when pure, dark brown when impure. It is easily soluble in alkali and ammonia, and can be readily precipitated from these solutions by addition of acid. It is a little soluble in hot water, especially if slightly acidified, soluble in alcohol, glacial acetic acid, aniline, almost insoluble in ether, and insoluble in petroleum ether and benzene. On heating, it melts, becoming partially decomposed. It occurs chiefly in sod oil and dégras, and, according to *Simand*, also in varying quantities in all marine animal oils. Old and dark oils are said to contain larger quantities of this substance than fresh and pale oils. This, however, is, in the opinion of the writer, open to doubt; it appears to be an oxidation product (cp. p. 469).

[1] Schill and Seilacher have patented two methods for preparing artificial dégras by blowing blubber oils with air, or by treating with oxygenated water.

[2] Of course, only very low qualities of tallow or waste fats will be used for this purpose. According to Eitner (*Der Gerber*, 1890, 145), fish stearine obtained from whale oil or from Japan fish oil is very extensively employed, as the rank fishy odour which persistently adheres to this stearine renders it almost useless for soap-making, etc.

The "*dégras-former*" is not found in its free state in dégras, but is said to occur in it as part of a saponifiable substance sparingly soluble in alcohol, and readily soluble in petroleum ether, in contradistinction to the "*dégras-former*" itself.

According to *Simand* the "*dégras-former*" contains nitrogen. *Fahrion*,[1] however, has shewn that the "*dégras-former*" is free from nitrogen, if the hide fragments are removed by suitable treatment. In *Fahrion's* opinion the "*dégras-former*" is a mixture of hydroxy (oxidised) acids and of their anhydrides.

Most sod oils and dégras contain *unsaponifiable substances* originating from the marine animal oils used. Thus dégras prepared from sperm oil is characterised by considerable quantities of cetyl alcohol, and dégras from cod liver oil by an oily unsaponifiable mass, originally occurring in cod liver oil.

The proportion of *free fatty acids* in sod oils varies very much; their amount, however, does not affect the quality.

Sod oil contains, according to *Simand*, 3-4 per cent of *soap*, French dégras only 0·49-0·73 per cent, calculated in both cases to the anhydrous substance. The large amount of soap in sod oil in conjunction with the leather fibres imparts to it a viscous consistency. The proportion of *leather fibre* (*hide fragments*) should not exceed 5 per cent.

The *specific gravity* of dehydrated dégras varies from 0·945 to 0·955; it is higher than that of the oils from which it is prepared; the specific gravity of hydrous dégras approaches 1·00.

An examination of several marine animal oils, according to *Livache's* method (p. 285), proved, in satisfactory agreement with practical experience, that the oils that are best suited for the production of dégras absorb the greatest amount of oxygen. The numbers for the oxygen absorbed have been given p. 287. It will be seen from them that whale oil is most suitable, whereas sperm oil is almost useless.

The following table, due to *Eitner*,[2] is instructive, as showing the difference between oils and their corresponding sod oils:—

[1] *Jour. Soc. Chem. Ind.* 1891, 558. [2] *Der Gerber*, 1893, 257.

[TABLE

Name of Oil.	Specific Gravity.		Refractive Index.		Fatty Acids Insoluble in Petroleum Ether.		Acid Value.		Saponification Value.		Acetyl Value.[1]		Iodine Value.	
	Original Oil.	Dégras.	Original Oil.	Dégras.	Original Oil.	Dégras.	Original Oil.	Dégras.	Original Oil.	Dégras.	Original Oil.	Dégras.	Original Oil.	Dégras.
					Per cent.									
Shark liver oil . . .	0·9158	0·9212	1·4735	1·4752	0·91	1·70	7·0	8·4	157·2	143·2	45·0	45	90	82·4
Seal oil	0·9258	0·9465	1·4760	1·4790	2·70	14·41	6·1	26·1	193·8	190·5	25·6	47·8	96·5	68·4
Mixed fatty acids from seal oil	0·9354	0·9473	...	...	3·0	15·51	...	...	...	...	...	...	...	...
Cod liver oil . . .	0·9274	0·9836	1·4755	1·4780	0·87	19·40	13·6	28·3	187·9	183·4	19·4	28·3	14·8	100·5
Mixed fatty acids from cod liver oil	0·9375	0·9612	...	...	1·21	18·44	...	...	...	...	...	...	...	...
Whale oil	0·9270	0·9423	1·4755	1·4758	3·44	6·19	10·6	10·6	190·4	181·5	14·0	22·0	85	71

[1] These numbers stand greatly in need of confirmation.

EXAMINATION OF DÉGRAS

1. **Determination of Water.**—5 grms. of the sample are mixed with purified and ignited sand in sufficient quantity to give a solid and nearly dry mass. This is dried at 120° C. and weighed (*Jean*).[1]

Simand weighs 25 grms. of the sample in a small porcelain basin tared together with a short thermometer serving as a glass rod, adds 50-100 grms. of a blubber or other fatty oil, previously dried by heating to 105° C., and heats to 105° C. with constant stirring, until no more water vapour escapes. The loss in weight, ascertained after cooling, is taken as water.

French dégras contains, as a rule, 15-25 per cent of water, sod oils from 20-40 per cent (cp. tables below).

2. **Fat and Insoluble Matter.**—20 grms. of the sample are diluted with petroleum ether, and filtered through a tube closed by a cotton plug, previously dried and weighed. The petroleum ether in the filtrate is distilled off, the residue transferred to a basin, dried at 120° C., and weighed. The insoluble portion left on the cotton wool is also dried at 120° C., and weighed. It is then placed in a platinum crucible and incinerated. If a very small amount of ash is left, the insoluble portion consisted of organic matter only, otherwise the residue is weighed and further examined for clay, chalk, gypsum, magnesia,[2] etc.

3. **Ash.**—5 grms. of the sample are taken for this test. If the ash has an alkaline reaction, it should be boiled out with water, filtered, and the filtrate titrated with standard acid.

Simand weighs off 25 grms. in a platinum dish, and heats it on an asbestos plate, constantly stirring with a glass rod until the water is driven off. The glass rod is then wiped off with filtering paper, which is thrown into the dish and made to serve as a kind of wick for burning off the fat. The residue is finally incinerated and weighed.

French dégras contains but a few hundredths per cent of ash, sod oil as much as 3 per cent. The ash should be examined for iron, as iron in dégras is apt to stain the leather.[3]

4. **Mineral Acids.**—If the dégras has a strongly acid reaction (mostly due to sulphuric acid), 25 grms. of the sample are boiled with 200 c.c. of water, and, after cooling, the two layers separated by means of a separating funnel. The aqueous layer is made up to a known volume; the nature of the acid is ascertained qualitatively, and an accurately measured volume of the liquor titrated with standard alkali.

Schmitz-Dumont draws attention to the possible presence of soluble

[1] According to *Fahrion*, this method gives very erratic results.

[2] According to *Villon*, a syrupy solution of magnesium chloride is extensively used for mixing with dégras. 20 per cent of this concentrated solution may be added without being detected by the appearance of the dégras or by an abnormal proportion of water.

[3] *Simand* states that as little as 0·05 per cent of ferric oxide has an injurious action. Addition of 500 c.c. of one per cent oxalic acid solution to 100 kg. of dégras is said to remedy this defect.

fatty acids. Instead of exhausting with ether, as he advises, it would be more expeditious to titrate the mineral acids, methylorange being the indicator, until neutral, then to add phenolphthalein, and to again titrate until the solution becomes pink.

5. **Hide Fragments.**—The sample is exhausted repeatedly with petroleum ether, and the residue, consisting of water, sand, soap, and hide fragments, washed, first with water and then with alcohol, dried, weighed, incinerated, and weighed again. The difference between the two weights gives roughly the amount of hide fragments.

6. **Unsaponifiable Matter.**—This is prepared and examined according to the methods described, chap. vii. pp. 217-233.

7. **"Resinous Substance." "Dégras-former." Oxidised Acids.**—For the determination of the resinous substance *Jean* proceeds as follows:—The soap solution which has been extracted with ether for the determination of unsaponifiable matter, as under 6, is heated to drive off the ether, and precipitated whilst hot with an excess of common salt. After cooling, the deeply coloured solution is filtered from the separated soap into a flask and hydrochloric acid added. The resinous substance is precipitated in the form of flocks, which unite on boiling the solution, and, on cooling, adhere to the sides of the flask, so that the aqueous liquid may be decanted. The resinous substance is then dissolved in ether, the ethereal solution transferred to a tared porcelain basin, the ether evaporated off, and the residue weighed.

Simand determines the amount of the dégras-former in the following manner:—

20 to 25 grms. of the sample, according to the proportion of water in the dégras, are saponified in an Erlenmeyer flask, provided with a small funnel, with 5-6 grms. of solid caustic soda, previously dissolved in 10 c.c. of water and 50-60 c.c. of alcohol, by boiling for half an hour. The alcohol is then evaporated off, the soap dissolved in water, and the fatty acids liberated by acidulation with hydrochloric acid. The solution is heated until the fatty acids form a clear supernatant layer and the dégras-former has coagulated to lumps. After cooling, the acid liquid is poured off from the fatty acids, and, in order to recover a small quantity of dégras-former held in solution, neutralised with ammonia, and boiled down. The mixed fatty acids and dégras-former are boiled out repeatedly with water, and the washings after neutralisation with ammonia added to the first aqueous liquid. The residue obtained on boiling down is dissolved in a little water, the solution acidulated with hydrochloric acid, and the small quantity of precipitated dégras-former filtered off, washed, dried, and brought into the Erlenmeyer flask, the contents of which have been dried in the meanwhile at 105° C. The fatty mass is then repeatedly shaken out with 100 to 120 c.c. of petroleum ether, which dissolves the fatty acids whilst the dégras-former and small quantities of albuminoid substances remain undissolved. Next the residue is dissolved in alcohol, and the albuminoid substances separated by filtration. The filtrate is boiled down to drive off the alcohol, and the residue, consisting of the purified dégras-former, weighed. The petroleum ether washings may be boiled

down and the fatty acids thus determined. They may be further examined for the melting point, etc.

A sample may be considered as pure if it yields at least 12 per cent of dégras-former, calculated to a dégras of 20 per cent of water. Good samples contain higher proportions of dégras-former.

The results of *Simand's* method are stated to be accurate to 0·5 per cent.

8. **Free Fatty Acids.**—They are determined in the usual manner (p. 182) by titrating with standard alkali, using phenolphthalein as an indicator. The free fatty acids are calculated to oleic acid. The fatty matter obtained from dégras contains, as a rule, 15-19 per cent of free fatty acids.

Jean gives the following analyses of samples of dégras :—

		1	2	3	4	5	6	7
Water .	per cent	18·90	14·84	12·93	28·90	19·20	5·39	8·90
Ash . . .	,,	0·25	0·13	0·55	0·70	0·07	0·25	1·21
Hide fragments .	,,	0·30	0·30	0·09	0·58	0·27	...	1·59
Oils . . .	,,	69·71	74·65	80·00	66·93	75·66	84·87	72·15
Unsaponifiable .	,,	6·84	6·05	...	...	...	...	...
Resinous substance	,,	4·00	4·05	5·81	3·52	4·80	9·46	16·15

The following tables give *Simand's* analyses of samples of dégras and of sod oil :—

	Dégras-former.	Melting Point of Fatty Acids.	Soap.	Original Dégras.	
				Hide Fragments.	Water.
	Per cent.	°C.	Per cent.	Per cent.	Per cent.
French dégras, anhydrous No. 1	19·14	18·0-28·5	0·73	0·07	16·5
,, ,, ,, 2	18·43	28·5-29·0	0·49	0·12	20·5
,, ,, ,, 3	18·10	31·0-31·5	0·68	0·18	12·0
Sod oil ,, ,, 1	20·57	33·5-34·0	3·95	5·7	35·0
,, ,, ,, 2	18·63	27·5-27·0	3·45	5·9	28·0
,, ,, ,, 3	17·84	28·0-28·5	3·00	4·5	30·5

The quantitative reactions, such as saponification and iodine number, have been used by several chemists in the examination of dégras ; yet they have but little discriminative value. A large quantity of mineral oils is more readily detected by the determination of unsaponifiable matter than by the saponification value.

An exhaustive examination of a number of dégras, using the quantitative reactions, has been made by *Ruhsam.*[1] His results are given in the following table :—

[1] *Jour. Soc. Chem. Ind.* 1892, 639.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
No. of Sample.	Water.	Iodine Value.				Acid Value.		Saponification Value.		Ether Value.		Constant Acid Value.	Constant Saponification Value.	Constant Ether Value (Difference between 13 and 14).
		Original Dégras.	Anhydrous Dégras.	Insoluble Fatty Acids.	Acetylated Fatty Acids.	Original Dégras.	Anhydrous Dégras.	Original Dégras.	Anhydrous Dégras.	Original Dégras (Difference between 7 and 9)	Anhydrous Dégras (Difference between 8 and 10).			
	Per cent.													
1	19·1	60·4	74·7	70·5	73·1	30·5	37·7	...	...	...	...	185·5	224·3	38·8
2	12·9	55·9	64·2	58·6	52·7	63·3	72·7	96·2	110·4	32·9	37·7	102·8	131·5	28·7
3	12·4	67·8	77·4	75·4	90·4	35·2	40·2	97·0	110·7	62·2	70·5	129·6	172·9	43·4
4	15·9	65·9	78·4	70·2	66·6	42·1	50·1	113·4	134·8	71·3	84·7	162·9	193·7	30·8
5	16·4	65·0	77·8	78·5	76·2	44·1	52·7	114·9	137·4	70·8	84·7	163·5	185·9	22·4
6	11·5	67·8	76·6	76·5	75·7	57·4	64·9	96·3	108·8	38·9	43·9	175·8	229·6	53·8
7	13·9	83·3	96·7	95·9	88·9	...	...	...	...	...	...	182·5	215·6	33·1
8	17·3	69·2	83·7	93·4	102·7	23·9	28·9	83·4	100·8	59·5	71·9	96·7	197·1	100·4
9	16·6	67·5	80·9	...	...	43·4	52·0	117·8	141·2	74·4	89·2	...	...	...
10	5·3	70·5	74·4	79·3	73·0	51·2	54·1	118·6	125·2	67·4	71·1	179·5	210·2	30·7
11	...	127·7	127·7	142·3	127·4	..	...	...	163·8	...	...	180·8	212·2	31·4
12	...	...	126·7	106·0	101·9	...	...	...	186·0	...	...	159·3	213·2	53·9
Mean of 1-10	...	...	78·5	77·6	77·7	...	50·4	...	121·2	...	70·8	153·2	195·6	42·4

The samples 1-9 are French artificial dégras. No. 10 is a so-called "emulsion fat," No. 11 a moëllon prepared by *Ruhsam* from whale oil No. 12. The acetyl values given in the original paper have been omitted here for reasons given p. 164.

Schmitz-Dumont's figures for a number of dégras and commercial products giving high proportions of unsaponifiable matter are contained in the following table :—

No.			Water.	Ash.	Insoluble in Petroleum Ether.	Fatty Matter.	Unsaponifiable Matter.	Oxidised Acids (Dégras-former).	Anhydrous Fat.		
									Acid Value.	Saponific. Value.	Iodine Value.
			Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.			
1		Dégras	13·31	0·32	0·31	86·1	3·1	11·03	108·0	185·8	69
2		,,	10·05	0·18	0·24	89·5	3·4	14·13	119·0	188·0	52·8
3		,,	10·24	0·28	0·28	89·2	1·0	1·49	104·0	181·8	70·7
4		,,	8·49	0·06	0·31	91·1	0·91	9·25	34·5	208·5	106·0
5		,,	17·33	0·27	0·14	82·3	2·51	0·95	29·2	206·0	122·0
6		,,	10·59	0·20	0·10	89·1	3·1	10·93	112·0	181·2	63·9
7		,,	1·53	0·70	0·04	97·7	1·85	16·17	112·0	170	62·5
8		Moëllon, pure	18·45	0·07	0·09	81·4	2·04	11·65	25·7	215·5	89·1
9		,,	19·88	0·03	0·46	79·63	0·45	1·46	47·4	214·0	115·0
10		Moëllon-dégras	11·65	0·63	0·98	86·74	3·27	2·01	17·4	196·7	126·0
11		Oxidised blubber oil	10·43	0·50	0·21	88·86	1·44	1·61	17·0	192·3	129·0
12		Oxidised emulsion fat	7·45	0·41	0·08	92·1	2·72	9·74	17·0	196·3	107·8
13	Of French origin.	Dégras	13·88	0·14	0·22	86·8	40·6	4·06	35·0	99·8	52·9
14		,,	14·16	0·58	0·97	84·3	18·9	3·73	32·4	137·4	80·6
15		,,	25·46	0·07	1·25	73·22	14·29	5·99	33·0	206·4	101·8
16		,,	18·79	0·46	0·31	80·44	23·61	5·33	31·0	135·4	72·3
17		Dégras-moëllon	15·79	0·05	0·22	83·94	28·1	1·84	40·5	113·2	72·1
18		Dégras	7·59	0·26	0·38	91·8	33·12	3·39	39·7	93·0	49·9
19		"Mutton dégras"	16·49	0·31	0·74	82·5	8·5	5·51	39·4	194·0	104·5
20		Dégras-moëllon	14·29	0·29	0·38	85·04	14·1	4·96	38·4	180·0	102·0
21		Dégras	20·37	0·08	0·45	79·1	40·3	2·95	24·0	86·0	49·5
22		,,	30·29	0·25	0·22	69·24	2·23	6·55	54·6	201·0	90·0
23		Fat from sod oil	..	..	..	100·0	0·71	16·84	71·3	234·0	61·0

Similar analyses, published by *Tortelli*, are reproduced here :—

[TABLE

No.		Specific Gravity at 18° C.	Water. Per cent.	Ash. Per cent.	Insoluble in Petroleum Ether. Per cent.	SO_3. Per cent.	Unsaponifiable Matter. Per cent.	Oxidised Acids (Dégras former)		Acid Value of		Saponification Value of		Iodine Value of	
								in Original Substance.	in Anhydrous Substance.	Original Substance.	Anhydrous Substance (calculated).	Original Substance.	Anhydrous Substance (calculated).	Original Substance.[1]	Anhydrous Substance (calculated).
1	Natural dégras from chamoising .	1·0025	31·13	1·83	5·07	0·47	2·36	18·03	26·38	35·75	51·75	155·0	221·0	35·7	52·3
2	,, ,, ,,	0·9993	39·60	1·79	5·18	0·20	1·26	14·09	23·44	25·08	41·72	144·0	239·0	34·0	56·4
3	Fish oil, used in dégras manufacture	0·9172	0·20	0·03	...	0·0	1·30	3·79	3·80	9·39	...	192·3	192·3	139·7	139·7
4	Commercial "dégras," German .	0·9435	17·74	0·11	0·15	0·0	1·16	9·66	11·77	16·64	20·02	172·0	209·0	69·0	83·8
5	,, ,, French .	0·9495	18·13	0·32	trace	0·0	19·61	2·03	2·48	22·49	27·46	131·2	160·0	64·4	78·9
6	,, ,, French .	0·9445	17·35	0·49	trace	0·03	2·25	6·65	8·04	11·72	14·18	164·0	198·0	95·6	115·6
7	,, ,, French .	0·9466	20·78	0·38	trace	0·04	1·88	9·44	11·92	11·55	19·62	160·0	193·0	53·8	65·3
8	,, ,, German .	0·9493	22·89	0·60	0·23	0·02	8·75	9·11	11·81	11·83	15·35	126·0	163·4	44·7	58·0
9	,, ,, German .	0·9493	21·33	0·55	0·30	0·06	15·77	4·30	5·47	11·49	14·61	105·0	129·0	39·6	50·4
10	,, ,, French .	0·9498	21·40	0·10	0·12	0·02	30·56	5·40	6·87	19·29	24·54	95·0	120·9	45·4	57·7
11	,, ,, Belgian .	0·9506	22·70	0·08	0·32	0·04	22·26	6·18	7·99	18·77	24·28	92·5	119·2	46·1	59·6
12	,, ,, Belgian .	0·9516	10·89	0·31	0·86	0·02	17·59	4·90	5·50	12·63	14·27	136·0	152·6	50·2	50·7

[1] The iodine value was determined in the substance containing water.

ARTIFICIAL DÉGRAS.—Presence of foreign fatty substances in a sample of dégras may be suspected, according to *Jean*, if the specific gravity of the separated fatty matter is lower than 0·920, genuine samples of dégras having a specific gravity of 0·945-0·955, and according to *Tortelli* (see table) about 1·0. **Tallow** may be detected by the high melting point of the mixed fatty acids of dégras, as will readily be seen from the following table :—

Mixed Fatty Acids from	Melting Point. °C.
Tallow	above 40
Whale oil	24·9
Cod liver oil	18·5
Japan fish oil	30·8

Hydrocarbons and **resin** in a dégras are detected by examining the fatty matter according to the directions given in chaps. vii. and viii. pp. 217, 234.

The estimation of **wool grease** or **distilled grease** is, in the present state of our knowledge, not yet possible. Detection of cholesterol is not sufficient proof of their presence, since fish and liver oils contain notable proportions of this alcohol; but the appearance of a green fluorescence would point to the presence of isocholesterol and inferentially to that of wool grease or of distilled grease. Raw wool fat would most likely escape complete saponification, and part of the waxes would pass into the unsaponifiable portion. By again saponifying the latter, preferably under pressure, a definite saponification value would point to the presence of wool wax. A very rough approximation of the quantity of the adulterant may be obtained by isolating the cholesterol in the form of its acetate (see p. 231).

"Corroïne," an artificial dégras, is stated to consist of a mixture of vaseline and wool fat emulsified with water.[1] Another artificial dégras is made by heating blubber oils to 120° C. and blowing air through.

D. WOOL OILS—CLOTH OILS[2]

Under the trade term wool oils or cloth oils are comprised all those oils that are used by woollen manufacturers for lubricating the wool before spinning, or for oiling the rags before grinding and pulling.

The wool oils may be conveniently subdivided into three classes (*a*) fatty oils, including fatty acids; (*b*) emulsified oils; (*c*) solutions of soap.

The following is a list of the fatty oils used in the woollen industry, arranged in the order of their suitability and quality, commencing with olive oil, which is used for best qualities of wool, and ending with oils consisting in great part of unsaponifiable matter :—

[1] *Jour. Soc. Chem. Ind.* 1895, 815.

[2] Cp. Lewkowitsch, *Jour. Soc. Dyers and Colourists*, 1896, 60; *Jour. Soc. Chem. Ind.* 1896, 459.

Olive (Gallipoli) oil, lard oil, neat's foot oil, oleine (= oleic acid) [saponification or saponified oleine, distillation or distilled oleine], distilled grease oleine, black recovered oil, "seek oil," and brown [grease] oil.

Emulsified oils are largely used on the Continent; they are prepared from neutral oils, oleic acid, and aqueous ammonia or a solution of sodium carbonate, or, in other words, they consist of oil and oleic acid emulsified by a soap solution.

Solutions of soap are represented by concentrated solutions of castor oil soap or a neutral alkali salt of sulpho-ricinoleic acid.

The tendency for cheap wool oils has led to the production of a large number of "manufactured oils," which represent mixtures ("blends") of the above-named wool oils with mineral oils.

Before discussing the several wool oils we may broadly lay down the principles upon which the analysis and valuation of wool oils has to be based.

Wool oils *should be easily removable in the scouring*, they should therefore be free from *drying-oils* (or their fatty acids) *and resinifying substances* (resin acids), as these offer great resistance to their removal in the scouring process, become sticky, leave an unpleasant odour on the fabric, and cause stains in the finished cloth. Even small quantities of hydrocarbons in the oils for finer goods are objectionable.

Although the mineral oils readily form emulsions with soap solutions, practical experience shows that they are not so easily removable as one might anticipate. Therefore, for best goods wholly saponifiable wool oils should be used. The low class oils contain large proportions of hydrocarbons, but they can be removed with comparative ease, as in the manufacture of the goods for which these oils are employed strongly alkaline soaps are used.[1]

Wool oils should develop as little heat as possible both in the stored raw material and during the working of the oiled material. *Drying and even semi-drying oils* may easily give rise to a development of heat sufficient to cause spontaneous combustion. Heat may be also produced in the scribbling and carding process, and the action of free fatty acids on the metal of the scribblers must be taken into account. Therefore the *flash point* and in general the *liability of an oil to cause a fire*, or to favour the spreading of it, is of the greatest commercial importance. This point will have to be considered especially by the analyst, as the fire insurance offices put great strictures on the users of wool oils, assessing as they do the insurance premium according to the quality of the oil.

It may therefore be found useful in this connection to quote the order in which the schedules of the fire insurance companies in this country arrange the oils:—

Free from any extra charge are—Olive (Gallipoli) oil, lard oil, oleine ("saponified" or "distilled") not containing more than 10 per cent of unsaponifiable matter, fish oil, or a manufactured oil ("purified

[1] Cp. Lewkowitsch, *Jour. Soc. Dyers and Colourists*, 1894, March; *Jour. Soc. Chem. Ind.* 1894, 258; *Jour. Soc. Dyers and Colourists*, 1896, 60; *Jour. Soc. Chem. Ind.* 1896, 459; and Spennrath and Walther, *Jour. Soc. Chem. Ind.* 1895, 362.

by distillation or saponification," whatever this may mean) containing not more than 30 per cent of unsaponifiable matter,[1] and having a flash point of not under 340° F. (167·8° C.)

A higher rate is charged for—Manufactured oils containing more than 30 per cent, but not more than 50 per cent, of unsaponifiable matter.

A still higher rate is charged for—Black (recovered) oil (p. 693), containing not more than 50 per cent of unsaponifiable matter.

The highest rate is charged for—Manufactured oils containing more than 50 per cent of unsaponifiable matter, or mineral oil, oil of pine, linseed oil, rape oil, cotton seed oil, or any other seed oil.

Neat's foot oil and tallow oil are not mentioned in these schedules, although they are very useful wool oils and quite harmless, whereas, curiously enough, fish oil is permitted free of extra charge; yet cotton seed oil, which is equally dangerous, is placed amongst the oils charged at the highest rate. Nor has regard been taken of the fact that the permission to use fish oil offers an opportunity for adding cotton seed oil with impunity.

Although mineral oils in themselves are not liable to spontaneous combustion, still experience has shown that once a fire has broken out, they cause a rapid spreading of it; it is for this reason that strictures are laid on extensive use of mineral oils.

Therefore *the determination of the unsaponifiable matter and of the flash point* are of the greatest importance in the analysis of wool oils.

The methods for the determination of the *unsaponifiable matter* have been detailed above (p. 218).

Some analysts ascertain the "saponifiable"[2] by boiling with alcoholic potash (p. 151), and calculating the amount of KOH used to oleic acid, then obtaining the "unsaponifiable matter" by difference.[3] This method should be rejected as leading to erroneous results in many cases, and the unsaponifiable matter should be determined direct by extraction.

Another error committed by some analysts is to return the "unsaponifiable matter" as mineral oil, a misnomer which may lead to great inconvenience to the user of the oil. If neutral oil be required besides free fatty acid, it is determined as described p. 752.

The *flash point* is determined by heating 50 c.c. of the oil under examination in a porcelain basin ("open test"), constantly stirring with a thermometer, and from time to time bringing a small flame towards the surface of the oil. That temperature is noted as flash point when there is a slight explosion or "flash." Of course, any other apparatus may also be used (cp. "Lubricating Oils," p. 716). The flash point should not be below 170° C. (340° F.)

A rapid method for the determination of the liability of wool oils to spontaneous combustion is afforded by using *Mackey's* "Cloth Oil Tester."[4]

[1] The Austrian fire insurance companies allow only 15 per cent of unsaponifiable matter.

[2] *I.e.* the sum of the neutral fat and free fatty acids.

[3] Cp. Lewkowitsch, *Jour. Soc. Chem. Ind.* 1892, 142.

[4] Supplied by Reynolds and Branson, Leeds.

This apparatus is illustrated by Fig. 45, and consists essentially of a cylindrical metal water-bath, provided with a lid having a nozzle for inserting a thermometer, and fitted with two tubes A and B for air currents in the directions of the arrows. Inside the apparatus is placed a cylinder C of wire gauze, containing a ball of cotton wool oiled with the sample under examination. In testing proceed as follows :—

Weigh out 14 grms. of the sample into a shallow dish containing 7 grms. of pure cotton wool. Tease out carefully the cotton wool by hand, so that the oil is thoroughly distributed throughout the mass. This teasing and incorporation of the oil with the cotton cannot be

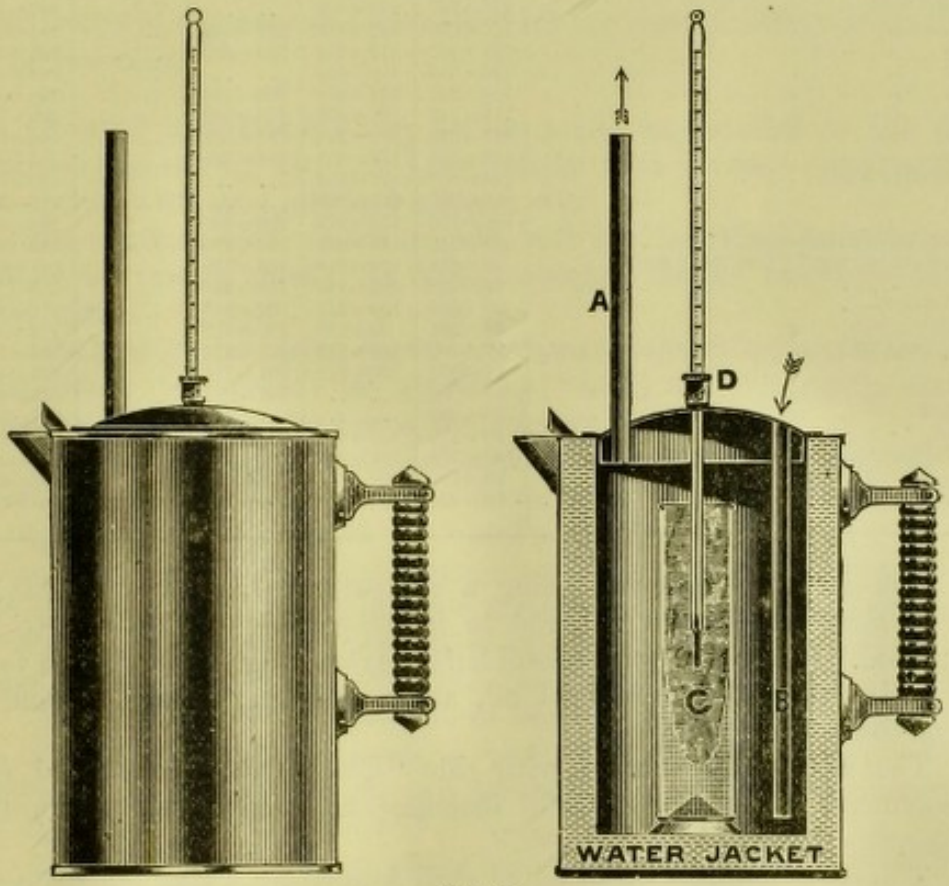


Fig. 45.

done too carefully, as much of the success of the experiment depends on the even distribution of the oil. Transfer the oiled cotton wool to the cylindrical cage C, holding the thermometer in its place, while the cotton wool is packed around it. Bring the water in the jacket to vigorous boiling, place the cage in the bath, slip the lid down over the stem of the thermometer, and fix it in its place [1] by means of the clamp D. Keep the water in the bath boiling, and note the temperature after the lapse of one hour. Care must be taken that no moisture enters the bath.

[1] The thermometer provided with the apparatus bears a red mark on the stem ; it should be so fixed that the red mark is just visible.

If the thermometer registers over 100° C. at the end of the first hour, the oil under examination must be considered as dangerous. In the case of very dangerous oils the temperature will run up to 200° C. within one hour and a half. If the temperature rises very rapidly above 150° C. it is best to withdraw the thermometer, as the oiled cotton wool may fire.

The following table gives a number of tests :[1]—

No.	Oil Used.	Temperature in 1 hr.	Temperature in 1 hr. 15 m.	Temperature in 1 hr. 30 m.	Temperature in 2 hrs.	Maximum.
		°C. = °F	°C. = °F.	°C. = °F.	°C. = °F.	°C. = °F. H. M.
1	Cotton seed	125=257	242=468	.. ..	.. ..	242=468 1 15
2	,, ,,	121=250	242=468	282=540	.. ..	284=543 1 35
3	,, ,,	128=262	212=414	225=437	.. ..	225=437 1 30
4	,, ,,	124=255	210=410	.. ..	.. ..	248=478 1 35
5	,, ,,	116=241	192=378	200=392	.. ..	200=392 1 30
6	,, ,,	118=244	191=376	202=396	.. ..	202=396 1 30
7	,, ,,	117=243	190=374	194=381	.. ..	194=381 1 30
8	,, ,,	112=234	177=351	204=399	.. ..	211=412 1 45
9	Olive fatty acids	114=237	177=351	.. ..	.. ..	196=385 1 25
10	,, ,,	105=221	165=329	.. ..	.. ..	293=559 1 55
11	,, ,,	102=216	135=275	208=406	.. ..	226=439 1 45
12	White Australian olein	103=217	115=239	191=376	.. ..	230=446 1 45
13	Olive (containing 1% free fatty acids)	98=208	102=216	104=219	.. ..	241=466 3 25
14	Oleine	98=208	101=214	102=216	.. ..	110=230 2 8
15	97% oleine	98=208	100=212	102=216	.. ..	172=342 3 15
16	Belgian oleine	98=208	99=210	100=212	.. ..	173=343 3 16
17	Olive (neutral)	98=208	100=212	101=214	.. ..	235=455 5 15
18	,, ,,	97=207	100=212	101=214	.. ..	228=442 4 30
19	,, ,,	97=207	.. ..	101=214	.. ..	235=455 4 55
20	Cotton	139=282	.. ..	.. ..	.. ..	200=392 1 4
21	Olive	99=210	101=214	102=216	103=217	113=235 4 30
22	Mixture of 50% of No. 20 and 50% of No. 21	102=216	117=243	.. ..	.. ..	200=392 1 29
23	,, 25 ,, ,, 75 ,,	99=210	105=221	112=234	.. ..	200=392 1 52
24	,, 10 ,, ,, 90 ,,	99=210	102=216	105=221	127=261	200=392 2 9

The method described being a comparative one, the directions given must be strictly adhered to if comparable results are to be expected. It will be found useful before examining the sample to test, say, olive oil and cotton seed oil, as representing a safe oil and a dangerous oil respectively.

The writer has worked with this "Cloth Oil Tester," and can recommend it as a very useful instrument, much simpler than the apparatus described by *Richards*.[2]

The latter consists of an outer shell formed by a six-inch wrought iron tube, which can be closed at each end by discs of wood. Into this tube is inserted an inner four-inch tube of sheet-iron, with overlapping metal covers at each end. Thus there is left an air space of one inch around the inner tube and of three inches at each end. The whole apparatus is conveniently placed on a tripod, and heated by a Bunsen burner. Three thermometers, which are inserted into the inner shell through the outer one, allow the temperature to be read.

To test an oil, 50 grms. are evenly distributed over, say, 50 grms. of cotton waste, and the waste carefully pushed into one end of the

[1] Mackey, *Jour. Soc. Chem. Ind.* 1896, 90. Similar but very rough experiments were made before him by Gellatly (1874) to test the liability to spontaneous combustion of lubricating oils. Cp. also Kissling, *Jour. Soc. Chem. Ind.* 1895, 479.

[2] *Jour. Soc. Chem. Ind.* 1892, 547.

inner tube, and a thermometer inserted into the middle of the ball. A second ball of unoiled waste is placed similarly at the other end of the tube. On heating, the thermometer inserted into this blank waste should not rise above 100°-101° C.; this can be easily controlled by the readings of the middle thermometer. The latter should be kept at about 125° C.

The results obtained by means of this apparatus are stated to have been of the greatest use for determining the cause of fires and for gauging the degree of safety of oils. For instance, the percentage of fatty oil which may be safely mixed with mineral oil was easily determined. The experiments showed that neat's foot oil and best lard oil may be mixed with mineral oil to the extent of 50-60 per cent, while in the case of cotton seed oil the limit of safety is reached at 25 per cent.

Olive oil and lard oil may be examined as detailed in the preceding chapter (pp. 451, 584), especially with a view to detecting admixture with seed oils and mineral oils.

The examination of oleic acid will be described p. 765. It should be tested chiefly for unsaponifiable matter and linseed oil fatty acids.

Distilled grease oleine (p. 691), as also all the other manufactured oils—black (recovered) oil (p. 693), "seek oil" (p. 693), brown (grease) oil (p. 686), are tested for unsaponifiable matter.

The unsaponifiable matter should not be returned as mineral oil, without the detailed examination warranting such a statement. Even if the unsaponifiable matter be liquid and fluorescent, it may consist of hydrocarbons formed by destructive distillation of wool fat.[1] In the latter case, the unsaponifiable matter will show the isocholesterol reaction (p. 86), and the molecular weight of the fatty acids will be found considerably higher than 282, the molecular weight of oleic acid.

As the fire insurance companies charge according to the amount of unsaponifiable matter, *resin* is now added fraudulently. This is detected and determined in the saponifiable part (*i.e.* soap solution) as described chap. viii. p. 235.

Emulsion wool oils are tested for soda or ammonia (cp. "Turkey-red Oil," p. 726); the oily substance is separated by a mineral acid, and examined for "saponifiable" and "unsaponifiable."

In order to produce a more complete emulsion, occasionally gum or gelatin-like substances have been added. They are detected by adding alcohol, which precipitates these adulterants. The following table (p. 710) contains the analysis of several emulsified oils.

A number of analyses of lower class wool oils are given in the following table (p. 711); it has not been considered necessary to add any analyses of olive and lard oils. The oleines given below (p. 767) are, of course, also suitable for oiling wool.

[1] Cp. Lewkowitsch, *Jour. Soc. Chem. Ind.* 1892, 142. The importance of this question with regard to insurance risk has been clearly stated in a paper by *Mackey*, read before the Insurance Institute of Yorkshire. Cp. *The Textile Manufacturer*, 1894, 18.

Emulsion Wool Oils.

Name of Oil.	Na_2O. Per cent.	NH_3. Per cent.	Water. Per cent.	Fatty Matter. Per cent.	Fatty Acids. Per cent.	Neutral Fat. Per cent.	Unsaponifiable. Per cent.	Soda Soap Anhydrous. Per cent.	Gummy Substances. Per cent.	Observer.
...	0·91	0·32	84·45	16·16	...	...	...	...	...	Horwitz[1]
...	...	...	76·67	20·86	...	...	...	0·91	0·72[2]	Morawski
"Patent oil"	0·41	1·36	...	...	70·0[3]	8·7	6·9	...	...	Lewkowitsch
...	...	12·50	34	...	45·0	7·0	...	1·5	...	Fuchs and Schiff

[1] *Jour. Soc. Chem. Ind.* 1890, 937. This paper contains many errors. [2] This substance is most likely a decoction of Carrageen moss.
[3] Calculated as oleic acid.

The "Soluble Neoline" prepared according to Patent Specification 21,976, November 17, 1893, belongs to this class of oils. From the proportions given in the specification the writer has calculated the following percentage composition :—

Water	56·18
Soap	8·40
Heavy paraffin oil	16·82
Potassium carbonate	4·55
Glycerin	14·05

Analyses of Wool Oils

Source or Name.	Flash Point.	Specific Gravity at 15·5° C.	Free Fatty Acids.	Unsaponifiable.	Neutral Fat.		Observer.
					Direct.	By Difference.	
	°F.		Per cent.	Per cent.	Per cent.	Per cent.	
Distilled oleine from recovered grease	..	0·8894	77·2[1]	26·8	..	4·0	Allen
,, ,, ,,	..	0·9083	55·3[1]	35·9	11·6	8·8	,,
,, ,, ,,	..	..	54·9[2]	34·5	11·28[3]	..	Lewkowitsch
,, ,, ,,	338	0·9031	55·02	34·66	..	9·2	Hurst
,, ,, ,,	342	0·8980	56·26	29·46	..	11·95	,,
,, ,, ,,	322	0·9050	53·65	16·32	..	28·65	,,
,, ,, ,,	..	0·9000	59·83	38·92	..	..	,,
,, ,, ,,	..	0·9091	64·42	9·95	..	25·63	,,
,, ,, ,,	415	0·941	..	41·7	..	..	Hess

	Flash Point.	Moisture.	Saponifiable.[4]	Unsaponifiable.			Observer.
	°F.	Per cent.	Per cent.	Per cent.			
Brown oleine, compound oil of English distilled and foreign oil	396	0·77	86·28	12·95	..	..	Mackey
Brown foreign oleine, Belgian	354	0·75	80·56	18·69	..	..	,,
Brown "oleine cloth oil," "manufactured"	349	0·64	73·78	25·58	..	..	,,
"Black oil," recovered after using foreign and English distilled oleine, (flannel district, Lancashire)	367	1·27	69·08	29·65	..	..	,,
"Brown grease" recovered after using Gallipoli oil	419	1·07	69·16	29·77	..	..	,,
Distilled oleine from brown grease and once recovered olive oil	342	0·77	62·04	37·19	..	..	,,
"Black oil" recovered after using oleine and better class "cloth oils" (half "seek," half waste)	369	1·11	60·39	38·50	..	..	,,
Brown oleine, distilled from brown grease	338	0·69	46·96	52·35	..	..	,,
"Black oil," recovered after using recovered and low cloth oils (from waste)	331	0·67	32·03	67·30	..	..	,,
"Brown pulling oil" (for rags), brown grease and hydrocarbons	374	0·74	21·01	78·25	..	..	,,

[1] Calculated as oleic acid. [2] Mean molecular weight 286. [3] Consisting of 7·02 per cent of fatty acids and 4·26 per cent of combined alcohols. [4] By difference.

E. LUBRICATING OILS

A good lubricating oil should fulfil the following conditions :—

1. It should diminish friction.
2. It should not lose its lubricating power on exposure to the atmosphere.
3. It should have no deleterious chemical action on the metal surfaces.
4. It should possess a sufficient degree of viscosity, so that it is neither squeezed out between the moving surfaces, nor wasted by rapid motion of the running machinery. In other words, the lubricant should have just sufficient viscosity to keep the moving surfaces apart under the maximum pressure.[1]
5. It should not give off combustible gases or vapours at the temperature it is heated to in practical use.
6. It should be free from grit and suspended matter.

The following are used as lubricants :—Fats and oils (as tallow, lard oil, tallow oil, sperm oil, olive oil, rape oil), mineral oils, and mixtures of fatty and mineral oils. Resin oils are unsuitable on account of their liability to "gum," and their presence in lubricating oils must, therefore, be considered as an adulteration.

Solid lubricants are mixtures of fats, fatty oils, and mineral oils, solidified by sodium carbonate, lime resinate, soaps, etc.

For very heavy work pitches (pp. 692, 755) are employed as the most suitable lubricant.

"Dead" tar oils were used formerly for adulterating lubricating oils; but owing to the cheapness of mineral oils they are now but rarely met with in lubricating oils.

For purposes of **valuation** it is necessary to determine the following **physical constants** of a lubricating oil: (1) the specific gravity (p. 123), (2) the viscosity[2] (p. 103), (3) the freezing point (p. 135),

[1] Cp. B. Redwood, *Jour. Soc. Chem. Ind.* 1886, 121 ; Lew, *ibid.* 1891, 777 ; Künkler, *ibid.* 1891, 1014.

[2] Petroff (*Grossmann Die Schmiermittel*, pp. 42-49) determines the internal friction of oils, *i.e.* the absolute viscosity. The following table shows the co-efficients of internal friction at different temperatures for some lubricating oils :—

Temperature.	Sperm Oil.	Olive Oil.	Palm Oil.	Mineral Oil (Rososine).	Mineral Oil.	Mineral Oil.	Mixed Cylinder Oil.	Water.
°C.	0·884 at 19° C.	0·955 at 18° C.	0·963 at 17° C.	0·885 at 18° C.	·900 at 18° C.	9·918 at 18° C.	0·922 at 18° C.	
20	0·00360	0·00845	0·09900	0·00237	0·03034	0·08360	0·28500	0·000103
30	0·00246	0·00541	0·04636	0·00152	0·01530	0·03800	0·08930	0·000082
40	0·00177	0·00361	0·02331	0·00102	0·00844	0·02070	0·04240	0·000066
50	0·00132	0·00257	0·01306	0·00069	0·00504	0·01180	0·02250	0·000051
60	0·00107	0·00190	0·00777					

The conclusion Petroff draws from his observations are the following :—

At a given temperature the order of the oils regarding their internal frictions is the same as their lubricating power and their viscosity, as ascertained in the usual manner. The absolute viscosity of oils diminishes rapidly with increase of temperature.

"cold-test," *i.e.* liability to thicken in the cold, if the lubricant should be used at low temperatures. With regard to test (1) it may be pointed out again, that the specific gravity has little or no value in relation to the lubricating value of an oil, and serves, therefore, chiefly to direct attention to adulteration.

The *freezing point* or "*cold-test*" may be determined by the methods given above (chap. v. p. 135.)

The "cold-test" is not of such great importance in this country as in the United States and on the Continent, where the danger exists of damage to machinery being done by oil becoming solid in the lubricators. In these countries the specifications of the railway companies fix, therefore, the temperature at which the lubricating oil must remain fluid.

According to the directions of the New York Produce Exchange the sample to be tested is poured into a beaker 4 in. deep by 3 in. in diameter until nearly filled. The beaker is immersed in a freezing mixture, the temperature of which is controlled by a fixed thermometer; and a second thermometer is immersed in the oil, reaching half way down the beaker. When both thermometers register the same temperature (viz. the specified cold-test), the oil must still flow on inclining the beaker.

It should be noted that the oil is not stirred, and that thus the conditions obtaining in practice are simulated although the factor of the length of time is neglected. More complicated than the American test is the cold-test prescribed by the Prussian State Railway Direction. According to their rules winter oil must remain fluid at -15° C. This is considered to be the case if the oil, cooled to -15° C., and subjected to the constant pressure of a water column of 50 mm., will rise in a glass tube of 6 mm. internal diameter at a minimum rate of 10 mm. per minute. The apparatus adopted for this test (made by G. A. Schultze, Berlin), is far too complicated for so simple a determination.

Railway companies and other large consumers of lubricants test the lubricating value by means of specially designed apparatus, simulating as nearly as possible the conditions obtaining in practice. As to the value of these tests, and a description of the apparatus, the reader must be referred to the sources given in the footnote.[1]

Chemical tests have for their object the determination of the liability to "gum" or resinify and to spontaneous combustion, the flash point, ignition point, loss by evaporation, origin, and purity.

Liability to "gum."—A good lubricant should neither dry on exposure nor "gum" (causing, in the first instance, more fuel to be consumed in consequence of the drag upon machinery), nor have a tendency to become acid. A practical test for ascertaining the liability of a lubricating oil to gum may be made in the manner

[1] Redwood, *Jour. Soc. Chem. Ind.* 1886, 121; Cameron-Leask, *Soaps and Candles*, pp. 258-313; Thorpe's *Dictionary of Applied Chemistry*, vol. ii. p. 474; Thurston, *Treatise on Friction and Lubrication*, pp. 248-263; B. Redwood, *Petroleum*, p. 634; Goodman, *Recent Researches in Friction; Proc. Inst. Civil Engineers*, vol. 85.

proposed by *Nasmith* and *Albrecht*, by placing at the same time equal quantities of oils to be compared on an inclined plane.[1] The oil flowing for the longest time will be the best; bad oils cease to flow after a few days, becoming thick or "gummy." A table containing a few results obtained in that fashion, given in Appleton's *Dictionary of Mechanics*, is reproduced here :—

Lubricant.	Run of Oil in Inches after Days.								
	1	2	3	4	5	6	7	8	9
Sperm oil, best	32	50	53·5	54	54	54	54	54	...
Sperm oil, com.	19	45	55	59	62	64	67	67·5	68
Olive oil, Gallipoli	10	14	18	18·5	19·5	20·5	21	21·25	21·5
Lard oil	10·25	10·5	10·75	10·75	11·75	still	...	...	...
Rape oil	14	18	19	19	19·25	19·25	19·75	still	...
Linseed oil	17·5	18	18	18·25	18·5	still	...	...	...

O. Bach,[2] adopting a method originally proposed by *Fox*, estimates the capacity for absorbing oxygen as a measure of the liability to gumming or becoming acid. A known quantity of oil is heated for ten hours with oxygen in a sealed tube, of about 100-125 c.c. capacity, in an air-bath at a temperature of 110° C. The point of the tube is then broken under a measured volume of water, and the absorbed oxygen found from the difference in volume. The presence of excess of oxygen after the experiment must be ascertained in the usual manner with a glowing splinter of wood.

The following are *Bach's* results :—

1 Grm. of	Absorbed Oxygen. c.c.
"Valve" oil	0·10
"Valvoline" oil	0·45
"Refined cylinder" oil	0·34
Mineral oil, Russian	0·74
"Lubricating oil," sp. gr. 0·877	0·70
,, ,, ,, 0·865	4·80
90 parts "lubricating oil," with 10 parts of "cod oil"[3]	9·40
90 ,, "oleonaphtha" ,, ,, ,, ,,	8·60
"Cod oil,"[3] sp. gr. 0·963	76·30
Resin oil	181·00
Olive oil	144·00
Rape oil	166·00
Cotton seed oil	111·00

More convenient comparative tests for the drying power are unquestionably afforded by the determination of the iodine value

[1] Cp. Daw. *Chem. News*, 1894 [70], 42. [2] *Jour. Soc. Chem. Ind.* 1889, 990.
[3] This is a trade term for redistilled resin oil.

(p. 170), the rise of temperature in *Maumené's* test (p. 291), and the oxygen absorption determined by placing a weighed quantity in a watch glass and ascertaining the increase in weight after exposing to, say, 100° C. for twelve to twenty-four hours. Of course, it is necessary to work with perfectly dry oils. The oxygen absorption may also be determined by *Livache's* method.

As the oils exhibiting a pronounced tendency to gum are those liable to **spontaneous combustion,** the value of a lubricating oil under this head may be determined by means of the "Cloth Oil Tester" (see p. 707).

The **flash point** is determined by the "open test," as already described for wool oils (p. 706). This method is sufficiently accurate for practical purposes, it being only necessary to ascertain whether the oil is dangerous or not.

Oils containing even small quantities of water give, according to *Holde*,[1] very irregular values for their flash points. The presence of moisture may be recognised by heating the sample in an oil-bath to 140° C., when at about 120° C. frothing or even bumping will be noticed. In such a case *Holde* dehydrates the oil by shaking with calcium chloride and allows to stand for twenty-four hours.

The lowest value for the flash point by the "open test" should be about 175° C. (350° F.) for lubricating oils, and about 260° C. (500° F.) for cylinder oils. The following table gives *Künkler's*[2] observations on a few lubricating oils, comprising mineral and fatty oils :—

Oils.	Spec. Grav. at 17·5° C.	Flash Point °C.	Viscosity (Engler)	
			At 50° C.	At 100° C.
Russian cylinder oils .	0·911-0·923	183-238	10·2-16·2	2·0-2·8
,, machine oils .	0·893-0·920	138-197	5·8-6·3	1·5-1·8
,, spindle oils .	0·893-0·895	163-167	3·1-3·4	1·4-1·5
American cylinder oils .	0·886-0·899	280-283	...	4·1-4·8
,, machine ,, .	0·884-0·920	187-260	4·2	1·6
,, spindle ,, .	0·908-0·911	187-200	3·1-3·3	1·4-1·6
Rape oil, crude . .	0·920	265	4·0	1·7
,, ,, refined . .	0·911	305	4·9	2·0
Olive oil . . .	0·914	305	3·7	1·8
Castor oil . . .	0·963	275	16·4	3·0
Linseed oil . . .	0·930	285	3·2	1·7
Tallow	0·951	265	5·2	2·5

It will be seen from this table that mineral oils suffer a greater loss in viscosity with increase of temperature than fatty oils.

When greater accuracy is required than is furnished by the "open test," the adoption of "close test" apparatus is necessary. In this country *Gray's* flash-point apparatus is used for this purpose.

Gray's apparatus[3] is illustrated by Fig. 46. It consists of a

[1] *Jour. Soc. Chem. Ind.* 1889, 735. [2] *Ibid.* 1890, 197.

[3] Supplied by Baird and Tatlock, 14 Cross Street, London, E.C.

brass oil cup, A, of 2 in. diameter by $2\frac{2}{10}$ in. in depth, and has, therefore, the same dimensions as the Abel Petroleum Tester. The height to which the cup is to be filled is indicated by a line cut round the inside; it runs $1\frac{1}{2}$ in. from the bottom. The cup is closed by a tightly fitting lid, through the centre of which a steel shaft passes to the bottom, carrying two sets of stirrers, one above and the other below the surface of the oil. On the top of the steel shaft there is fixed a small bevelled wheel, H, with milled edge, and geared with a vertical bevelled wheel, G, actuated by a small handle, B. Thus the stirrers are set in motion. The lid is provided with four openings, one of which serves for the insertion of a thermometer, whereas the other three provide means for producing the flash. These three orifices are, as a rule, closed by a loose flat cover, S, provided with openings which, when the cover is turned one quarter round, coincide with the ports in the fixed lid. One of the latter is immediately in front of the test-lamp, D, which can be tilted whenever required, whereas the other two ports, one on each side, admit air to produce the explosive mixture.

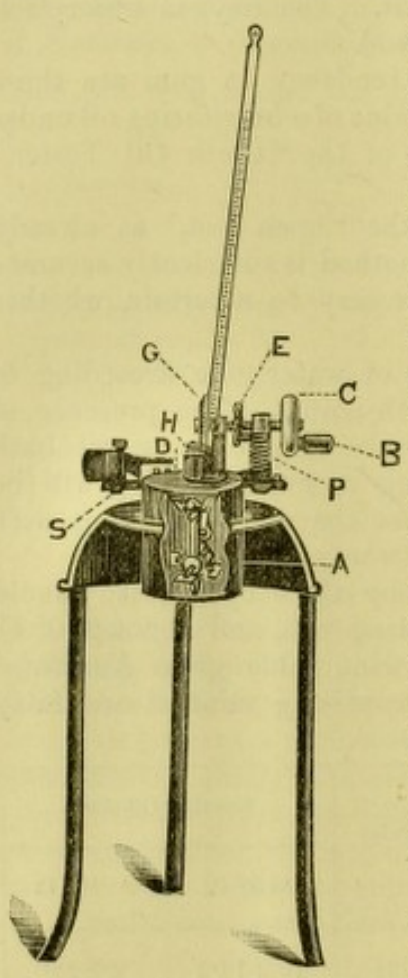


Fig. 46.

To perform the test, fill the cup to the mark with the sample, light the test-lamp and adjust the flame to about $\frac{1}{8}$ in. in size. Then heat the oil cup by means of a Bunsen burner or a sand-bath, whilst rotating the stirrers, so that the temperature of the oil rises about 5° C. per minute at first, but less when the point is reached at which the oil is expected to flash. Whilst the bevelled wheels are in gear the sliding cover is held in its normal position by the spring P. Then draw the horizontal shaft, which has a little lateral play in its bearings, slightly to the right, whereby the stirrers are thrown out of gear. Turn the handle a quarter of a round, when the loose cover is rotated, the ports opened, and at the same time the test-lamp tilted into the opening. Reverse the handle immediately, whereby the ports are closed automatically. If a slight explosion was produced, note the temperature; this is the flash point of the oil. If no flash was produced, continue the heating; throw the stirrers into gear, and proceed as before.

The following table gives a number of flash points,[1] together with some other constants :—

[1] Cameron-Leask, pp. 263-291.

	Specific Gravity at 60° F.	Viscosity at			Flash Point. Close Test.	Cold Test.	Remarks.	
		70° F.	120° F.	180° F.	°F.	°F.		
Refined Mineral Oils—		Standard for Viscosity. Sperm Oil at 70° C. = 100						
Scotch	0·890-0·895	100-130	40-50	..	320-350	32		
	0·885-0·890	75-100	35-40	..	300-325	32		
	0·875-0·880	50-60	25-30	..	300-325	32		
American	0·915-0·920	400-425	90-100	35-40	375-425	32		
	0·905-0·910	200-225	55-65	..	350-400	32		
	0·885-0·890	75-100	35-40	..	325-350	32		
	0·875-0·880	65-75	30-35	..	325-350	32		
Russian	0·910-0·915	1200-1500	200-250	50-70	400-425	25		
	0·905-0·912	700-800	125-150	45-50	350-375	25		
	0·895-0·900	220-250	60-65	..	325-350	15		
	0·895-0·900	125-175	..	..	300-325	10		
Natural (dark) Mineral Oils—		Standard for Viscosity. Tallow at 180° C. = 100.						
American summer, dark	0·890-0·895	..	250-300	70-75	400-425	40-50		
,, medium	0·880-0·885	550-700	110-125	40-50	350-400	25-30		
,, winter	0·880-0·885	350-400	90-100	35-40	325-375	25-30		
Russian residuum	0·910-0·915	750-1000	150-200	45-60	250-300	25-30		
Natural and Filtered Mineral Oils—								
American heavy dark	0·900-0·905	..	1750-2000	350-400	500-550	40-45		
,, extra dark	0·900-0·905	..	2000-2500	400-450	525-575	35-40		
,, medium dark	0·895-0·900	..	1200-1400	300-350	500-525	40-45		
,, heavy filtered	0·890-0·895	..	1400-1500	300-350	500-550	60-70		
,, medium filtered	0·890-0·895	..	1000-1200	250-300	500-525	65-70		
,, light filtered	0·885-0·890	..	885-1000	200-250	450-500	75-80		
,, fluid filtered	0·885-0·890	..	1200-1400	300-350	500-550	40-45		
,, ,,	0·885-0·890	..	900-1000	225-275	450-500	45-50		
							No. of Samples	Flash Points
Southern sperm oil	0·8807	100·1	45·4	..	457·5 *	41·7	34	420-485
Arctic sperm oil	0·8804	105·3	47·2	..	446·2 *	39·2	59	390-485
White whale oil	0·9207	187·7	71·3	..	476·0 *	27·2	35	430-530
Neat's foot oil	0·9170	247	82·4	..	470·3 *	34·4	17	410-540
Lard oil	0·9172	223·2	79·4	..	493·9 *	39·6	18	425-545
Olive oil	0·9167	213·2	75·0	..	437·5 *	27	24	410-465
Rape oil, East India, refined	0·916	250·4	88·1	..	478·6 *	26·4	89	410-510
,, Black Sea, refined	0·9209	226·9	78·8	..	465·4 *	27	25	430-490
Cotton seed oil, refined	0·9235	190·4	69·8	..	523 *	30	22	500-540
Castor oil	0·963	2500	390	..	487 *	0		

* Mean values.

In Germany the *Abel-Pensky-Martens* apparatus is used,[1] as also the *Treumann* open cup.[2]

The **ignition point** is determined, according to *Martens*, by filling a crucible of about 40 mm. diameter, and 40 mm. high, within 5 mm. of its brim, and embedding it to half its height in a sand-bath. The crucible is heated at first rapidly until the flash point has been reached, then the gas-burner is turned low and the temperature allowed to gradually rise 10°-15° C. above the flash point; after every rise of 2° C. a small flame is approached to the surface until the oil burns

[1] *Jour. Soc. Chem. Ind.* 1889, 736. [2] *Ibid.* 1895, 284.

calmly. The crucible must be protected from draught by a convenient arrangement.

As we subdivide here for the sake of convenience the lubricating oils into (1) Fatty oils and liquid waxes, (2) Mineral oils, (3) Mixtures of (1) and (2), (4) Solid lubricants, other tests will be mentioned under the separate heads.

1. Fatty Oils and Liquid Waxes

The most important fatty oils used for lubricating are tallow oil, lard oil, neat's foot oil, olive oil, rape oil, castor oil; less important are whale and seal oils, latterly also porpoise and blackfish oils are being employed. The liquid waxes are excellent lubricants, and are almost exclusively used as such.

Apart from the conditions laid down above, the suitability of these oils is determined by their action on metals when in contact with them under approximately the same conditions as obtain in practice.

Experiments made by *I. J. Redwood*[1] have established the following facts:—Iron is acted on by tallow oil the most, and by seal oil the least. Bronze was not attacked at all by rape oil, and but very slightly by olive oil; it was, on the other hand, vigorously corroded by cotton seed oil. Copper was not attacked by any of the mineral oils; sperm oil had the least and tallow oil the most action on it. In the case of lead, the most deleterious lubricant was whale oil; the best, olive oil. Whale, lard, and sperm oils were about equally corrosive. For zinc the best oil was lard oil, and the worst sperm oil.

The experiments were carried out in the following manner:—The metals were first thoroughly cleaned by means of ether and then dried. Next they were weighed accurately and placed in closed vessels filled with oil, and kept for a year at a uniform temperature, in summer at 80° F., and in winter at about 50° F.

It would, however, not be permissible to draw from these experiments the conclusion that the oils would behave in the same manner if used for lubricating bearings, etc., the conditions being essentially different. Therefore similar experiments instituted by *Donath*,[2] *Aisinmann*, *a. o.*, need not be detailed here, as being of little practical use.

The larger the proportion of **free acids** in an oil, the greater is the liability to corrode metal. The determination of free fatty acids in lubricating oils is, therefore, very important. It is carried out by titrating with caustic alkali, using phenolphthalein as an indicator (p. 182).

It should be borne in mind that fatty oils undergo hydrolysis in high-pressure steam cylinders, and that the fatty acids thus set free will corrode the iron cylinder.

The acidity is expressed in various ways, as shown in the table, p. 150. In this country it is customary to calculate the alkali used

[1] *Jour. Soc. Chem. Ind.* 1886, 362. [2] *Ibid.* 1895, 283.

to oleic acid, and return it as per cents of free fatty acids. It should, however, be remembered that acidity of an oil may be due to mineral acid used in refining, as in the case of rape oil. Therefore the test for mineral acids should not be omitted.

The examination of the various oils for adulterants has been dealt with exhaustively in the preceding chapter. It should be remembered that if liquid waxes are present the proportion of unsaponifiable matter will be high.

2. Mineral Oils

The mineral oils used for lubricating are derived from crude petroleum or from shale. The oils from the latter are mostly distilled products, the oils derived from the former are either distilled oils or the still residues refined by treatment with animal char.

Besides applying the tests mentioned above, the following points deserve attention :—

Loss by Evaporation.—In the case of fatty oils the point at which evaporation commences almost coincides with the temperature at which decomposition takes place, whereas in the case of mineral oils, consisting as they do of oils of different boiling points, evaporation—and consequently loss to the user of the oil—may begin below the temperature at which the bulk of the mineral oil volatilises.

The method ordinarily adopted to determine the loss by evaporation was to heat for several hours an accurately weighed quantity on a watch glass and to weigh the residue. Oils intended for the lubrication of machinery at normal temperatures would be heated for, say, five hours at 100° C., and in the case of cylinder oils the tests should be made in the drying oven at a temperature of say 180° C.[1]

Archbutt[2] recommends as a safer method to heat the oil in a current of air or superheated steam. 0·5 grm. of the sample are placed in a platinum tray, which for convenience of manipulation is brought into a glass tube, and so introduced into a copper tube $\frac{7}{8}$ in. internal diameter, and 2 ft. long. Round the copper tube is coiled a tube $\frac{3}{8}$ in. diameter, and about 10 ft. long, one end of which enters the wider copper tube and serves to heat the current of air or steam which is passed over the oil. The coiled tube is fixed in an air-bath and heated by a row of small gas jets to the desired temperature, controlled by a thermometer. A measured quantity of air is passed over the oil at the rate of 2 litres per minute for exactly one hour; the oil is then withdrawn and reweighed. Good locomotive cylinder oils should not lose more than 0·5 per cent at a temperature of 370° F. (188° C.) under the conditions described above.

Presence of **water** is recognised by frothing or bumping, on heating in a test-tube. Oils containing notable proportions of water have a turbid appearance. Turbidity due to separated paraffin wax or impurities, etc., may disappear on heating, but will reappear in the cooled oil after standing.

[1] *Cameron-Leask*, p. 295. [2] *Jour. Soc. Chem. Ind.* 1896, 326.

Acidity.—In their pure state mineral oils should be practically free from acids, and therefore have but slight action on metals when compared with fatty lubricating oils. Small quantities of *mineral acids* left in the oil in consequence of faulty washing after refining are detected by shaking the sample with water, to which a drop of methylorange solution has been previously added. The so-called petroleum acids are not removed by washing with water. Their proportion is determined, according to *Zaloziecki*,[1] by shaking 100 grms. of oil with 50 c.c. decinormal alkali, consisting of equal volumes of aqueous and alcoholic solutions, and titrating back the free alkali.

Allen[2] heats in special cases 50 grms. of the oil for six to eight hours with an equal volume of water in a closed vessel immersed in boiling water, shaking the contents of the bottle from time to time. When the two layers have separated the aqueous liquid is titrated with decinormal alkali, using phenolphthalein as indicator. The acidity will be due in most cases to sulphuric acid, produced by the decomposition of sulphonates in the oil; if a notable amount has been found, the oil must be rejected. In the case of cylinder oils the vessel should be immersed in a boiling calcium chloride solution.

Ash.—The ash is determined by igniting an accurately weighed quantity in a platinum dish and weighing the residue. This should be *nil*. In case a soda or potash soap was added, the residue treated with water will give a strongly alkaline reaction when tested with litmus paper. An alkaline reaction may be also due to lime. If the ash is considerable it should be examined. In case an "oil thickener" has been added, say aluminium oleate, notable proportions of alumina will be found.

Schweitzer and *Lungwitz*[3] recommend as a reagent for the detection of soaps in lubricating oils a saturated solution of metaphosphoric acid in absolute alcohol.

The determination of **paraffin—paraffin wax**—will but rarely be required. Lubricating oils containing too much paraffin would not prove satisfactory in the cold-test, and would therefore be rejected at the outset.

Holde has examined the processes proposed by *Pawlewski* and *Filemonewicz*, *Zaloziecki*, and *Höland* for the estimation of small quantities of paraffin;[4] he rejects them as not admitting of general application, and recommends the following method, being a modification of the one originally proposed by *Engler* and *Boehm*, as yielding satisfactory results:—

10 to 20 c.c. of oils poor in paraffin (such as Russian distilled oils, solidifying below -5° C.), or 5 grms. of oils rich in paraffin (such as American, Scotch, Galician, solidifying at or above 0° C.) are dissolved in an equal number of c.c. of a mixture of equal parts of absolute alcohol (98·5 per cent) and ether in an Erlenmeyer flask of 150-200 c.c. capacity at the ordinary temperature. The flask is then immersed in a freezing mixture registering from -18° to -20°

[1] *Chem. Revue*, 1897, 37.
[2] *Comm. Org. Anal.* ii. 205.
[3] *Jour. Soc. Chem. Ind.* 1894, 1178.
[4] Cp. Eisenlohr, *ibid.* 1897, 701.

C., and whilst the solution is vigorously agitated, so much of the alcohol-ether mixture is added until oily drops just disappear and the liquid exhibits only crystals or flocks of paraffin wax. The crystals are filtered off at the same low temperature and washed with the alcohol-ether mixture previously cooled down to -18° to -20° C. until 5 to 10 c.c. of the filtrate no longer give an oily residue. Prolonged washing beyond this point will lead to loss. The paraffin wax retained on the filter is washed with benzene into a capsule, the solvent is evaporated off, and the residue dried at 105° C., prolonged heating in the air-bath being avoided.

Impurities due to incomplete purification of the oils may be tested for by one of the following methods. In some cases these impurities are left purposely in the oils, as a complete removal of the asphalt-like and mucilaginous substances, naturally occurring in the crude oils, tends to reduce the viscosity and consequently the apparent lubricating value. On the other hand badly refined oils have a tendency to resinify easily. *Schaedler*, and also *Martens*, shake equal measures of the sample and of sulphuric acid, specific gravity 1·53; in the case of a pure oil the acid should separate as a colourless or, at most, slightly yellow layer; there should be no separation of black flocks in the oil, nor should it be coloured brown. If the acid remains colourless, or is but slightly coloured, the experiment should be repeated, the cylinder containing the mixture being heated this time to 100° C.; pure oils should not turn brown even under these conditions. It has been attempted to convert this test into a quantitative one by operating as follows:—

20 c.c. of the sample are well shaken in a graduated stoppered cylinder with 10 c.c. of concentrated sulphuric acid and 20 c.c. of petroleum ether; the increase in volume of the acid is then read off after settling out. Oils of good quality should yield to the acid no more than 1·2 to 2·4 c.c., *i.e.* 6 to 12 per cent. But it should be understood that these results are a rough approximation only, as the "naphthenes" are soluble in concentrated sulphuric acid.[1] *Holde*[2] showed that by treating lubricating oils with a mixture of alcohol and ether (3 : 4) resinous or asphaltic bodies containing oxygen are precipitated, but no reliable quantitative method has been worked out hitherto.[3]

Fatty oils in mineral oils are present, if the sample has yielded a definite saponification value; very small quantities of glycerides are detected according to *Lux's* method (p. 223).

Resin oil, as also *tar oils*, are detected by the methods given above (p. 225). Resin oil is determined quantitatively, according to *Storch*,[4] as follows:—

10 to 15 grms. of the mineral oil, which must be free from fatty oils, are gently warmed in a flask with five times their weight of 96 per cent alcohol, the mixture being occasionally shaken and allowed to

[1] In the presence of fatty oils the sulphuric acid treatment leads to altogether unreliable results.

[2] *Jour. Soc. Chem. Ind.* 1895, 894.

[3] Cp. also Aisinmann, *ibid.* 1895, 282; Singer, *Chem. Revue*, 1897, 93.

[4] *Jour. Soc. Chem. Ind.* 1891, 276.

cool. The alcoholic solution, containing all the resin oil present, is then transferred to a tared Erlenmeyer flask, about 7 cm. high; the mineral oil is again washed, without agitating, with a few c.c. of 96 per cent alcohol, which are added to the main washing. The Erlenmeyer flask is now gently heated, surrounded by a beaker so as to prevent too rapid condensation, on the water-bath until the residue in the flask is free from bubbles. It is then cooled and weighed. The weight of this residue (A) will be that of the resin oil *plus* a portion of mineral oil dissolved by the alcohol. To remove the greatest part of the mineral oil, the residue (A) is treated next with ten times its weight of alcohol, and the solution boiled down as before, when a second residue (B) is obtained, which still contains a small quantity of mineral oil. The correction necessary for this is found in the following manner:—Suppose 11·2 grms. of the sample have been treated with 50 grms., and subsequently residue A with 15·5 grms. of alcohol. Let the weight of A be 1·51 grms., and that of B 1·15 grms., then $50 - 15{\cdot}5 = 34{\cdot}5$ grms. of alcohol had dissolved $1{\cdot}51 - 1{\cdot}15 = 0{\cdot}36$ grms., hence 15·5 grms. had dissolved 0·162 grms. of mineral oil. There are therefore present in the sample $1{\cdot}15 - 0{\cdot}162 = 0{\cdot}988$ grms., or 8·8 per cent of resin oil. The true quantity lies between the two weights of the second residue, viz. between B and its corrected value.

Nitrobenzene is readily detected in debloomed oils by its smell, especially on warming.

For the detection of **nitronaphthalene** in mineral oils, *Leonard*[1] gives the following method based on the reduction of nitronaphthalene to naphthylamine:—A small quantity of the oil is gently warmed with zinc-dust and dilute hydrochloric acid, and the mixture agitated from time to time. During this process the fæcal odour characteristic of *a*-naphthylamine will be perceived. After the reduction is complete the acid aqueous liquid is drawn off by the aid of a separator. A portion of this liquid, when neutralised with ammonia, gives with ferric chloride a blue precipitate which rapidly becomes purple. The remainder of the solution may be rendered alkaline with soda and extracted with ether. The latter is then evaporated, and the residue dissolved in a little alcohol. On the addition of a drop of a sodium nitrite solution, acidified with acetic acid, a yellow colour is produced, which is changed to crimson by hydrochloric acid.

3. Mixtures of Fatty and Mineral Oils

Mineral oils are miscible with all fatty oils, castor oil excepted (p. 421).[2] Extensive use is made of this miscibility in practice, and by far the greatest number of commercial lubricating oils consist of such mixtures. Latterly also "blown oils" (p. 733) are largely mixed with mineral oils, or with mixtures thereof and of fatty oils,

[1] *Jour. Soc. Chem. Ind.* 1894, 69; cp. also Holde, *ibid.* 1894, 906.

[2] Castor oil can, however, be made miscible with mineral oils by mixing it first with a fatty oil, say tallow oil.

their high viscosity and specific gravity rendering them especially suitable for this purpose. Also soap and "oil thickeners" are added fraudulently to give the oil more "body," and the fluorescence of mineral oils is concealed by "deblooming" the oil by means of nitronaphthalene, nitronaphthol, or nitrobenzene.

Such mixtures are examined and their constituents determined quantitatively by means of the "quantitative reactions" described in chaps. vii., viii. (cp. also "Soaps," p. 785).

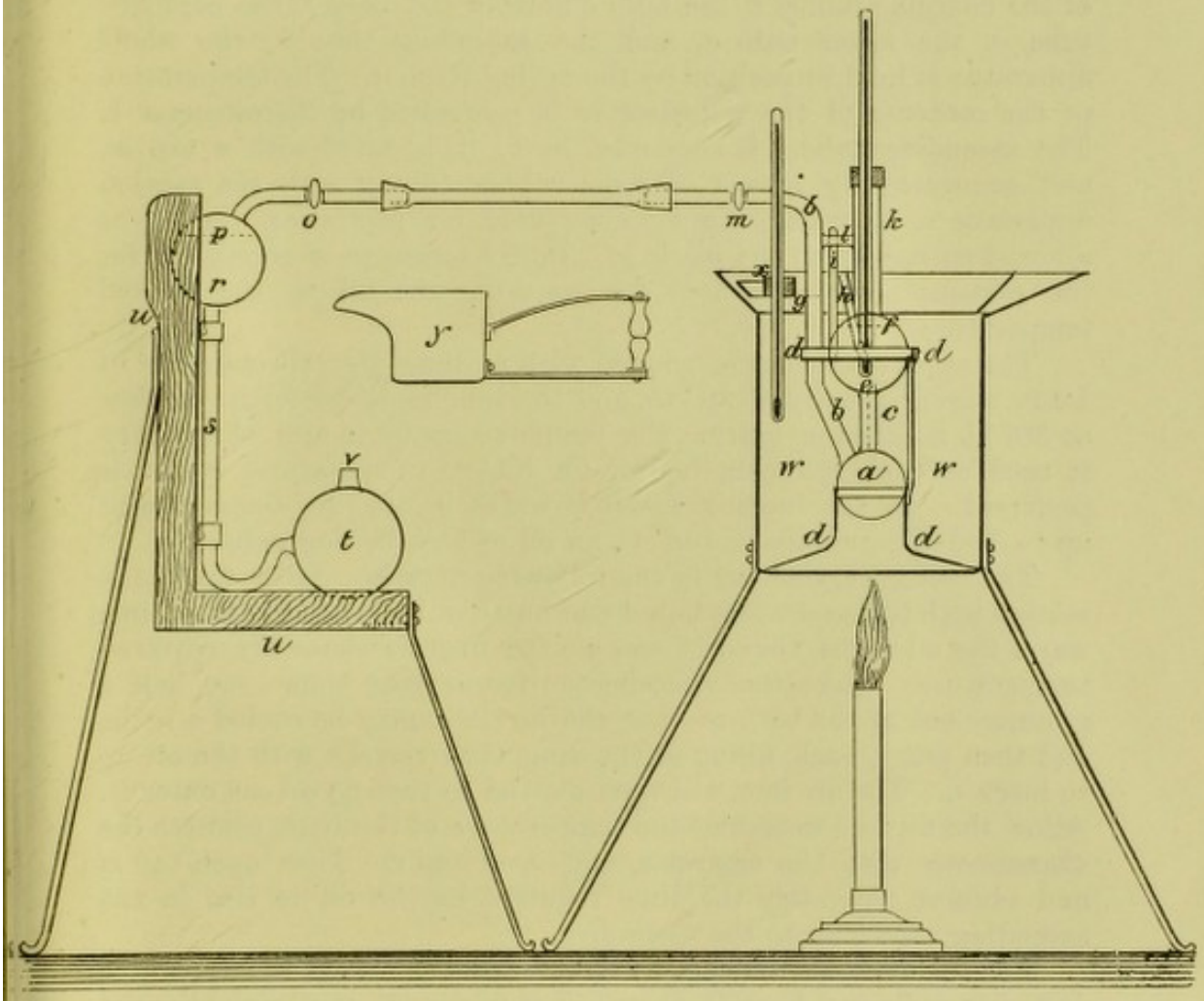


Fig. 47.

The nature of the fatty oils may be ascertained by separating the unsaponifiable matter from the soap solution, which contains also any resin acids present, liberating the free fatty acids, and examining them systematically. A definite acetyl value will point to the presence of "blown oils," if castor oil be absent.

The unsaponifiable matter is tested for resin oil as already described.

According to *Künkler*,[1] the viscosity of the mineral oil (unsaponifiable portion) should also be determined. The quantity required for

[1] *Jour. Soc. Chem. Ind.* 1894, 543.

this test being somewhat large when the existing viscosimeters are used, *Künkler* has designed a new apparatus requiring only 30 c.c.

This apparatus (Fig. 47) consists of a sheet brass (oil- or) water-bath, *w*, provided with a copper bottom, the contents of which may be heated by a gas burner; the temperature of the heating liquid is read off a thermometer held by *x*; *w* contains the removable stand *d* placed firmly on four legs, and supported by two brackets *h*. In this stand fits the viscosimeter, made of strong glass and consisting of the charging-funnel *k*, the bulb *e* bearing the mark *f*, the capillary tube *c*, the lower bulb *a*, and the ascending tube *b*; the whole apparatus is held in position by the spring-clamp *i*. The temperature of the contents of the viscosimeter is controlled by thermometer *k*. The ascending tube *b* is supported by *l*; it is fitted with a tap *m*, and connected by means of india-rubber tubing with the suction apparatus *r*, in which the mercury used for aspirating the oil is allowed to rise up to the mark *p*. Bulb *t* serves as a receptacle for the mercury; can *y* is used for warming the oil to the desired temperature.

The apparatus must be gauged with a dilute glycerin solution of 1·110 specific gravity at 20° C., and the time required for its outflow at 20° C. is taken as unity. For temperatures up to 100° C. mercury is used as the aspirating liquid, for higher temperatures water is preferred. In the heating vessel *w* water is used for temperatures up to 100° C., and above 100° C. an oil of high boiling point.

The test is carried out in the following manner: Fill *r* up to the mark *p* with the aspirating liquid and heat the bath. In the meantime warm the oil to be tested in can *y* a few degrees above the required temperature. Take the viscosimeter for a short time—say half a minute—out of the bath so that the air in *a* may be cooled a little, and then put it back, filling at the same time vessel *e* with the oil up to mark *f*. The air in *a* will then expand so that no oil can enter it. Allow the oil in *e* to assume the temperature of the bath, connect the viscosimeter with the aspirator, and open tap *o*. Then open tap *m* and observe accurately the time required by the oil to rise in the ascending tube *b* up to the mark *g*.

For the accurate dimensions of the various parts of the apparatus (which may be had from *C. Desaga* of Heidelberg), the original paper must be consulted.

The following table contains a few viscosimetric constants as determined with the new apparatus, contrasted with the numbers obtained by means of *Engler's* viscosimeter:—

[TABLE

Kind of Oil.	Künkler's Viscosimeter.						Engler's Viscosimeter.					
	Seconds at °C.			Glycerin Solution, Spec. Grav. 1·110 at 20° C. (66 seconds) = 1. °C.			Seconds at °C.			Water at 20° C. (54 seconds) = 1. °C.		
	20	50	100	20	50	150	20	50	150	20	50	150
Rape oil, refined	1220	380	...	18·48	5·76	...	660	224	...	12·22	4·15	...
Cod liver oil	760	262	...	11·51	3·97	...	430	165	...	7·96	3·06	...
American lubricating oil, pale, 0·905	905	215	...	13·71	3·26	...	475	140	...	8·80	2·59	...
Russian lubricating oil, pale, 0·908	4320	595	...	65·5	9·01	...	2340	355	...	43·33	6·57	...
American cylinder oil, pale	...	...	750	...	...	11·36	...	...	75	...	...	1·39
,, ,, ,, dark	...	...	1005	...	...	15·23	...	...	95	...	...	1·76
"Valvoline" cylinder oil	...	...	885	...	...	13·41	...	...	85	...	...	1·57

4. Solid Lubricants—Greases

Under this head fall the **solidified oils** and the **solid lubricants** (greases). The former are mostly mineral oils gelatinised by soda or lime soap, the latter consist of mixtures of solid fats, fatty oils, mineral oils, resin oils, and lime and aluminium soaps (of fatty acids or resin acids). These lubricants contain a certain proportion of **water.** "**Weighting substances**" are added fraudulently or, as in the case of talcum or plumbago, with a view to increase the lubricating power of the "grease." **Galena oils** (plumbago oils) consist of lead soaps dissolved in mineral oils.

The analysis of these solid lubricants offers no difficulty. The lubricant is first dried and then extracted with a suitable volatile solvent when the mineral matters and soaps remain undissolved, the mixed fatty and mineral (and resin) oils passing into solution. Small quantities of dissolved soaps may be removed from the latter by washing the mixed oils after evaporating off the solvent with water or with dilute mineral acid. The mixed oils are examined as described already (p. 722); the insoluble part is examined in a similar way to soaps (p. 785). But it should be borne in mind that in these cases, as also in the case of locomotive or waggon greases, the chemical analysis gives no clue as to the lubricating value.

Hot neck grease (p. 692).

F. TURKEY-RED OILS[1]

Turkey-red oil is a fatty substance used in the preparation of the cotton fibre for dyeing and printing Turkey-red. The part which the Turkey-red oil plays is not fully understood yet; it is explained as a physical or as a chemical action. In the light of the former explanation it is assumed that the oil protects the lake formed on the fibre, much as linseed oil may be looked upon in painting. In the latter case the oil is said to combine with alumina and finally with the colouring matter, forming a compound lake. In these cases, however, where chemical combination with formation of a lake is excluded on account of the chemical constitution of the colouring matter, the physical theory appears to commend itself. Thus the oil is not a mordant proper, but acts as a fixing agent in so far as it

[1] Frémy, *Ann. de Phys. et de Chim.* 65. 121; *Annalen*, 19. 296; 20. 50. Müller-Jacobs, *Jour. Soc. Chem. Ind.* 1884, 257; 412. 1885, 18; 21; 115. Liechti and Suida, *Jour. Soc. Chem. Ind.* 1886, 662. H. Schmid, *Dingl. Polyt. Jour.* 254. 346. Sabanejeff, *Berichte*, 19, Ref. 239. M. and A. Saytzeff, *Berichte*, 19, Ref. 541. Benedikt and Ulzer, *Jour. Soc. Chem. Ind.* 1887, 543; 1888, 328. Scheurer-Kestner, *Jour. Soc. Chem. Ind.* 1891, 471, 555. Juillard, *Jour. Soc. Chem. Ind.* 1892, 355; 1893, 528. Wilson, *Jour. Soc. Chem. Ind.* 1891, 26; 1892, 495. Löchtin, *Jour. Soc. Chem. Ind.* 1890, 498. Juillard, *Jour. Soc. Chem. Ind.* 1894, 820. Wolff, *Chem. Revue*, 1897, 103.

imparts to the dyed fabric a better and superior lustre, which does not belong to the unoiled fibre.

Turkey-red oil is usually prepared by the action of concentrated sulphuric acid on *castor oil*, the acid being allowed to run into the oil slowly with constant stirring, so that the temperature of 35° C. is not exceeded. If necessary, the mass must be cooled, as at a higher temperature secondary reactions take place with liberation of sulphurous acid. The product is next mixed with water and allowed to settle out. The lower layer is then drawn off and washed with brine, or, better still, with a solution of Glauber salt, until the washings are only slightly acid. Finally ammonia is added, until a sample gives a complete emulsion with water. Instead of ammonia some manufacturers use soda, or a mixture of ammonia and soda.

The resulting product is not completely neutralised by the alkali, and consequently still possesses a strong acid reaction. The crude product as obtained before the partial neutralisation can be easily resolved into two portions, one being readily soluble, the other insoluble in water. The separation is effected as follows :—

The product obtained after mixing castor oil with sulphuric acid is dissolved in ether, washed with brine until free from sulphuric acid, and then repeatedly shaken out with water. The aqueous solutions are united and treated with sodium chloride, when the *water-soluble portion* separates as an oily layer. On evaporating off the ether from the ethereal solution the *water-insoluble portion* is obtained.

Benedikt and *Ulzer* have shown that the *water-soluble portion* of castor Turkey-red oil consists of ricinoleo-sulphuric acid, an acid sulphonic acid ether of ricinoleic acid, formed according to the following equation :—

$$\underset{\text{Ricinoleic acid.}}{C_{18}H_{33}O_2 . OH} + SO_4H_2 = \underset{\text{Ricinoleo-sulphuric acid.}}{C_{18}H_{33}O_2 . O . SO_3H} + H_2O.$$

This ricinoleo-sulphuric acid is miscible with water in all proportions ; the aqueous solutions give a lather like soap solutions. Brine, moderately dilute sulphuric acid, and hydrochloric acid precipitate it from its aqueous solution, the ricinoleo-sulphuric acid forming a heavy oily layer on the bottom of the containing vessel. On shaking with ether three layers are formed ; the middle layer consists of the acid mixed with large quantities of ether, whereas the uppermost ethereal layer contains smaller quantities of the acid.

Lead, copper, calcium, and barium salts added to the solution of the acid produce viscous precipitates.

Ricinoleo-sulphuric acid is not decomposed on boiling its aqueous or alkaline solutions ; but boiling with dilute hydrochloric or sulphuric acid decomposes it readily into ricinoleic and sulphuric acids.

The *water-insoluble* portion of castor Turkey-red oil consists chiefly of free ricinoleic acid mixed with small quantities of neutral (unacted on) fat, and perhaps also of anhydrides of ricinoleic acid.

Scheurer-Kestner is of the opinion that castor Turkey-red oil consists of ricinoleo-sulphuric acid (as stated by *Benedikt* and *Ulzer*) and of monoricinoleic and diricinoleic acids, polymerisation of the free ricinoleic acid having taken place.

According to *Juillard*, polymerisation proceeds further, giving rise to the formation of di-, tri-, tetra-, and penta-ricinoleic acids, an opinion at variance with *Scheurer-Kestner's* views, who maintains that polymerisation extending beyond the formation of the di-acid is due to a secondary action of hydrochloric acid liberated on washing the product with brine instead of Glauber salt. In *Juillard's* opinion castor Turkey-red oil is a mixture of varying proportions of poly-ricinoleic acids of alkali salts of mono- and poly-ricinoleo-sulphuric acids, of anhydrides of the latter acids, and of their products of decomposition.[1]

Besides castor oil also other fatty oils, such as olive oil, arachis oil, and cotton seed oil, are used in practice for the production of Turkey-red oils.

According to *Benedikt*, castor Turkey-red oil cannot be replaced by these oils for the reason that by treatment with sulphuric acid saturated hydroxy acids and their sulphuric acid ethers are formed, thus (taking oleic acid as an example)—

$$\underset{\text{Oleic acid.}}{C_{18}H_{34}O_2} + SO_4H_2 = \underset{\text{Hydroxystearo-sulphuric acid.}}{C_{18}H_{35}(O \cdot SO_3H)O_2}.$$

The latter acid is then decomposed for the most part according to the following equation—

$$\underset{\text{Hydroxystearo-sulphuric acid.}}{C_{18}H_{35}(O \cdot SO_3H)O_2} + H_2O = \underset{\text{Hydroxystearic acid.}}{C_{18}H_{35}(OH)O_2} + SO_4H_2.$$

Whereas, therefore, Turkey-red oil from olive, arachis, and cotton seed oils, and consequently also from oleic acid, contains *saturated* acids, castor Turkey-red oil consists solely of *unsaturated* fatty acids; hence the superior effect of the latter may be due to the oxidisability of the castor Turkey-red oil fatty acids.

This last statement of *Benedikt* may require some qualification, since *Schmitz* and *Tönges*[2] have prepared a Turkey-red oil by mixing oleic acid with sulphuric acid and heating the product to 105°-120° C., whereby hydroxy acids are supposed to be formed with loss of sulphurous acid, and since *Werner*[3] has stated that this Turkey-red oil is, in certain cases, superior to castor Turkey-red oil.

The chemistry of Turkey-red oils requires, therefore, further elucidation; it may be added that *Geitel* (p. 69) has proved the presence of stearolactone and of the anhydride of the ordinary hydroxystearic acid in Turkey-red oil prepared from oleic acid.

The commercial Turkey-red oils are more or less thickish fluids, appearing yellow in thin and brown in thick layers.

[1] *Jour. Soc. Chem. Ind.* 1894, 820. [2] *Ibid.* 1892, 827.
[3] *Ibid.* 1893, 40.

Since their composition depends on the mode of manufacture and on the raw material used, the Turkey-red oils have no constant composition.

The commercial examination of Turkey-red oil divides itself into two parts, viz. (1) the preliminary examination, the most important part of which consists in dyeing samples prepared with the oil, and (2) the chemical tests.

Preliminary Examination

The sample should give a complete emulsion with water; separation of oily drops may take place after long standing only. This test is performed by mixing, in a graduated cylinder, one measure of oil, at first with a little warm water, gradually increasing the quantity until ten measures have been added, and comparing the appearance of the sample with an emulsion prepared side by side in exactly the same way with a standard sample of known purity. Both emulsions should act in a like manner on litmus paper, showing a slightly acid reaction. In case the reaction should be neutral or alkaline, acetic acid must be added, drop by drop, until the intensity of the reaction and of the turbidity in both samples is alike.

Good oils should give a clear solution with ammonia, and exhibit no turbidity even if large quantities of ammonia are added.

The *alcoholic* solution of a Turkey-red oil is the more turbid the larger the amount of unchanged oil (neutral fat) in the sample.

The sample dyeing is carried out in the following manner:—Two pieces of cotton of equal size are prepared with the sample and with a standard oil respectively by allowing them to soak in an emulsion made from 1 part of oil and 15-20 parts of water (some experimenters add ammonia until the emulsion just becomes clear). After drying, the fabric is mordanted with alum and dyed in alizarin (blue shade), or, as the case may be, steam red is printed on. The samples are then brightened by soaping and finished in the usual manner. It is evident that this mode of comparison will be only resorted to in a works laboratory, or by an analyst who has special experience in that branch of work.

Chemical Examination

The value of a Turkey-red oil depends, in the first instance, on the proportion of *total fatty matter* in the sample, comprising under the latter term the sum of the *water-insoluble portion* obtained after acidifying the oil (viz. fatty acids, hydroxy acids, and neutral fat) and of the hydroxy acids obtained on decomposing the soluble sulphuric ethers of the fatty acids.

Next, the proportion of *neutral fat*, *sulphuric ethers of fatty acids*, *ammonia or soda*, and *sulphuric acid*, may be estimated.

Indications as to the nature of the raw material used are obtained from the iodine and the acetyl values of the total fatty matter

1. Total Fatty Matter.—The older processes, proposed by *Brühl* and *Stein*, do not yield accurate results, and are therefore omitted here. The best method is that recommended by *Benedikt*.[1]

About 4 grms. of the sample are weighed off accurately in a half-circular porcelain basin of about 125 c.c. capacity, previously tared together with a glass rod. The oil is mixed with 20 c.c. of water, added gradually; should the liquid be turbid, a drop of phenolphthalein is added and then ammonia run in, until slightly alkaline, when a clear solution will be obtained, or, at any rate, only a few flocks will remain undissolved. If the addition of ammonia is omitted the results will be too high. 15 c.c. of sulphuric acid, consisting of equal measures of concentrated acid and water, are then run in with stirring, and an accurately weighed quantity of stearic acid, say 6 to 8 grms., added. The mixture is then heated until a clear fatty layer has separated on the top. This is allowed to solidify by cooling; the cake is then lifted up by means of the glass rod, rinsed off with a little water, and placed meanwhile on filter paper. The contents of the dish are warmed on the water-bath, so that the particles of fatty matter adhering to the sides and floating in the water collect into one drop, which is conveniently made to adhere to the sides of the vessel on cooling. The liquid is then poured off, the basin rinsed out, and the cake of fatty matter placed in it. Now the basin is heated over a very small flame, which must not touch its bottom, and the melted fat continually stirred with the glass rod, until the crackling noise has ceased and white vapours are just beginning to escape. The fat is then allowed to cool and weighed.

Of course, the separated fatty matter may be collected and dried by any other convenient method, such as that described by *Hehner* for the determination of the percentage of fatty acids in a fat (p. 160), or as is the practice in the analysis of soaps, or according to the method proposed by *Guthrie*.[2]

For the purposes of a rapid determination the following process, due to *Finsler*, has been recommended by *Breindl*.[3] This process is largely employed in practice, and yields approximately the same results as *Benedikt's* method. A flask of about 200 c.c. capacity provided with a long neck, which is graduated to $\frac{1}{5}$ or $\frac{1}{10}$ c.c., is used for this test; the lowest graduation represents a capacity of 150 c.c., the uppermost 200 c.c. 30 grms. of the sample are weighed off accurately, washed into the flask with hot water, the volume made up to about 100 c.c., then 25 c.c. of sulphuric acid of spec. grav. 1·563 (52° Bé.) are added, and the mixture heated to boiling with frequent

[1] *Zeitsch. f. angew. Chem.* 1887, 325.

[2] The process recommended by Guthrie (*Chem. News*, 1890, 52) is stated by R. Williams (*Chem. News*, 1890, 76) to yield erroneous results. If, however, the above-given definition of total fatty matter be accepted, his criticism falls to the ground.

[3] *Jour. Soc. Chem. Ind.* 1889, 573.

shaking until the fatty matter forms a clear and transparent layer. A hot concentrated solution of common salt or Glauber salt is next added in small portions, until the separated layer of fat rises into the neck of the flask. After half an hour's standing the volume of fat is read off; the number of c.c. multiplied by 3·33 corresponds to per cents of total fatty matter.

2. Neutral Fat.—About 30 grms. of the sample are dissolved in 50 c.c. of water, 20 c.c. of ammonia and 30 c.c. of glycerin are added, and the mixture exhausted with ether twice, using 100 c.c. each time. The ethereal solution is freed from small quantities of dissolved soap by washing with water, and the ether evaporated off. The residue is transferred to a tared beaker of about 150 c.c. capacity, dried at first on the water-bath, then in an air-bath at 100° C., and weighed.

3. Soluble Fatty Acids (Sulphonated Fatty Acids).—5 to 10 grms. of the oil under examination are dissolved in a strong-walled flask in 25 c.c. of water, 25 c.c. of fuming hydrochloric acid are added, and the contents of the closed flask heated in an oil-bath to 130°-150° C. for one hour. Water is added next, the mixture transferred to a beaker and the fatty layer filtered off, most conveniently after some stearic acid has been melted with it. The sulphuric acid in the filtrate is then determined by precipitation with barium chloride. From the amount thus found the quantity of sulphuric acid, as determined under **5** (see below), is subtracted and the difference calculated to ricinoleic acid, 80 parts of SO_3 corresponding to 378 parts of ricinoleo-sulphuric acid, $C_{18}H_{33}O_2 . O . SO_3H$. Even in the case of the Turkey-red oil under examination not having been prepared from castor oil, this calculation will be correct, as the molecular weight of hydroxystearo-sulphuric acid—380—almost coincides with that of ricinoleo-sulphuric acid.

4. Ammonia and Caustic Soda.—7 to 10 grms. of the sample are dissolved in a little ether, and shaken four times with dilute sulphuric acid (1 : 6), using 5 c.c. each time.

For the determination of ammonia, the acid liquors are distilled with caustic potash in the well-known manner, and the ammonia received in an accurately measured quantity of standard acid; after titrating back the excess of acid the amount of ammonia is calculated.

For the estimation of caustic soda the acid liquors are concentrated in a platinum dish on the water-bath, and the excess of sulphuric acid driven off by heating on the sand-bath; the residue is ignited after mixing with ammonium sulphate and the formed sodium sulphate weighed.

5. Sulphuric Acid.—The quantity of sulphuric acid present in the form of ammonium or sodium sulphate is found by dissolving a weighed quantity of the sample in ether, and shaking it several times with a few c.c. of concentrated brine free from sulphates. The several washings are united, diluted, filtered, and the filtrate precipitated with barium chloride.

Another method would be to determine the total sulphur in the

sample by *Liebig's* method (p. 95), when the amount of sulphuric acid (or of sulphonated fatty acids) may be found by difference.

The method for the detection of **iron** in Turkey-red oils has been described p. 99.

The examination of a sample of Turkey-red oil, with a view to determining the nature of the raw material used—whether pure castor oil, or another fatty substance—is best based on the iodine and acetyl values of the total fatty matter. This is prepared as described above under **1**, with the only difference that no stearic acid is added.

If the iodine value is not much below 80, pure castor oil has been used; otherwise an adulterated castor oil may have been employed, or olive oil, arachis oil, cotton seed oil, oleic acid, etc. It should be remembered that these substances yield saturated acids; consequently, a very low iodine value will point to the absence of castor oil.

An acetyl value of 140 or above will point to pure castor oil; in the case of other oils lower values will be obtained.

The following is the percentage composition of a very good sample of Turkey-red oil :—

		Per cent.
Water-soluble fatty matter		9·5
Water-insoluble fatty matter	Neutral fat	1·3
	Fatty acids	47·2
Total fatty matter		58·0
Ammonia		1·8
Total sulphuric acid		4·6

A sample of genuine castor oil examined in the writer's laboratory gave the following result :—

Total fatty matter	40·1 per cent.
Unsaponifiable	0·15 ,,

The following constants were ascertained for the fatty acids obtained by saponification :—

Specific gravity at 15° C.	0·9449
Iodine value	82·1
Acid value	174·3
Saponification value	189·3
Acetyl value	126·9

It may be mentioned here that latterly *Scheurer*[1] has proposed metallic sulpholeates—sulpholeate of aluminium—as mordants for steam colours.

[1] *Jour. Soc. Chem. Ind.* 1893, 1025.

G. OXIDISED OILS

1. Blown Oils

Under the terms "blown oils," "base oils," "thickened oils," "soluble castor oil," a number of oils are brought into commerce, prepared by treating fixed oils with air at a somewhat elevated temperature. The oils are heated in a jacketed pan by steam to 70° C., in some cases to 110°-115° C., and air is blown through. The temperature rises beyond that of the steam used for heating, and in some cases it is necessary to cool the blown oil by a cooling worm.

The oils increase under this treatment in density and also in viscosity. They approach in these respects castor oil, but differ from it in that they are miscible with mineral oils, and are but sparingly soluble in alcohol. They are, however, more soluble in alcohol than the original oils, as shown in the following table, due to *Benedikt* and *Ulzer*:[1]—

1 Part of	Dissolved in parts of Absolute Alcohol at 18° C.
Cotton seed oil	35·7
Blown cotton seed oil, laboratory sample . .	22·9
,, ,, commercial sample . .	14·9

The nature of the chemical change taking place is not fully known. *Benedikt* and *Ulzer* have obtained high acetyl values on examining the two blown oils mentioned in the table, and are therefore of opinion that the fatty acids are partially converted into hydroxy acids; at the same time the iodine absorptions decreased considerably. No glycerol appears to be destroyed by the blowing (cp. "Boiled Oil").

Thomson and *Ballantyne*[2] have examined a number of "blown oils," confirming a few earlier experiments made by *Fox* and *Baynes*.[3] The changes which a sample of rape oil and of sperm oil underwent on blowing are shown in the following table, to which are added a few analyses of commercial blown oils:—

[1] *Zeitsch. angew. Chemie*, 1887, 245. [2] *Jour. Soc. Chem. Ind.* 1892, 506.
[3] *Analyst*, 1887, 33.

No.	Oil.	Specific Gravity at 15·5° C. (Water 15·5° = 1).	Free Acid calculated as Oleic.	Unsaponifiable Matter.	Saponification Value.	Iodine Value.	Specific Temperature Reaction.[1]	Insoluble Acids.	Soluble Volatile Acids.	Soluble Non-Volatile Acids.	Iodine Value of Insoluble Acids.	Molecular Weight of			Observer.
												Insoluble Acids.	Soluble Non-Volatile Acids.	Soluble Volatile Acids.	
1	Rape	0·9141	Per cent. 5·10	Per cent. 0·65	173·9	100·5	135	Per cent. 94·76	Per cent. 0·52		..	..	..	..	Thomson and Ballantyne
2	No. 1, blown 5 hours .	0·9275	5·01	..	183·0	88·4	..	..	..	..	..	..	..	..	
3	No. 1, blown 20 hours .	0·9615	7·09	0·76	194·9	63·2	..	85·94	9·20	0·82	66·5	327	241	72	,,
4	Sperm . . .	0·8797	1·97	36·32	130·4	82·1	..	..	..	..	..	..	..	..	,,
5	No. 4, blown 25 hours .	0·8989	3·27	34·65	142·3	67·1	..	..	..	..	..	..	..	..	,,
6	Commercial Blown Rape	0·9672	4·93	2·80	197·7	63·6	253	82·40	11·16	9·00	70·2	317	..	76	,,
7	Commercial Blown Cotton seed	0·9740	3·38	1·00	213·2	56·4	227	84·97	1·90	1·94	62·7	296	..	104	,,
		At 20° C. Water 20° = 1													
8	Commercial Blown Seal	0·9815	16·5	..	221·0	78·2	..	73·4	..	..	..	..	..	..	Chapman and Rolfe[2]

[1] Page 296. [2] *Chem. News*, 1894 [70], 2.

"Blown oils" are said to be very suitable for lubricating purposes on account of their high specific and viscosity; but opinions conflict as to their suitability, the principal objection appearing to be that they are liable to gum. Nevertheless, they are extensively used, mixed with mineral oil, and even with resin oil.

The examination of blown oils chiefly consists in the determination of the unsaponifiable matter and detection of resin oil.

2. Boiled Oil

French—*Huile cuite.* German—*Gekochtes Leinoel, Leinoelfirniss.*

Boiled oil is prepared by "boiling," *i.e.* heating linseed oil to a temperature from 210° to 260° C., whereby it acquires the property of more rapidly drying into a varnish, when exposed to the air, than raw linseed oil.

This property of absorbing oxygen is further increased if "driers" (such as manganese dioxide, manganese borate, manganese oxalate, litharge, etc.) are added to the oil whilst being heated. These "driers" seem to act as oxygen carriers;[1] at any rate it is proved that the lead salts of unsaturated fatty acids dry better than the fatty acids themselves.[2]

The suitability of a raw linseed oil for making "boiled oil" is chiefly determined by its age. Fresh oils give a scum on boiling, and effervesce very strongly; therefore only old "tanked" oil, from which solid glycerides, as also water, have separated out as "mucilage," can be used. Chemical tests, apart from tests for purity, are of little use for the valuation of raw oil. The higher the specific gravity the better it will be. According to *Allen*, it should not be less than 0·935 at 15·5° C. The *Livache* and the *Maumené* tests may also furnish useful indications.[3]

What action takes place during the process of boiling is not known yet. A slight decomposition of the linseed oil undoubtedly does take place, as proved by the evolution of acrolein vapours. This decomposition, however, is a limited one, as boiled oil still yields 8·9 per cent of glycerol. Oxidation seems also to take place to some extent, but cannot go very far, as the boiling oil comes in contact with but a limited quantity of air. The lower iodine value of the boiled oil may either point to oxidation or, as *Fahrion*[4] assumes, to polymerisation. The "driers" appear to form linolates, which dissolve in the remainder of the oil and increase its oxygen absorption power.[2]

Boiled oil has a darker colour than raw oil, being more of a red-brown shade. The higher the oil has been heated, the darker as a

[1] The comparative action of various driers has been studied by Thorpe (*Jour. Soc. Chem. Ind.* 1890, 628). Recent researches have shown that only lead and manganese driers are useful.

[2] Cp. Eng. Pat. 1891, 7251, and Eng. Pat. 1893, 9315.

[3] According to Lippert, linseed oil for boiling should not give flocks on heating to about 300° C.

[4] *Jour. Soc. Chem. Ind.* 1892, 696.

rule will be the colour of the product. Boiled oil is more viscous than raw linseed oil; it has a higher specific gravity, ranging from 0·9389 to 0·9433, according as it was boiled with a manganese- or a lead-drier. The iodine value of boiled oil is lower than that of raw oil (see below). A sample of boiled oil examined in the writer's laboratory had the iodine value 127 (cp. also below).[1] It is very likely that boiled oil will show a higher acetyl value than raw oil.

Boiled oil is adulterated in the same manner as linseed oil; the adulterants most frequently used are resin, and mineral and resin oils.[2] They are detected as described under the heading "Linseed Oil" (p. 343). The so-called "patent boiled oils" are, as a rule, adulterated oils. A rapid method,[3] suitable as a preliminary test, to detect *unsaponifiable matter* is to add water after saponification with alcoholic potash, when a strong turbidity will indicate presence of adulterants.[2]

Resin could, of course, not be thus detected; if its presence be suspected, the writer recommends to determine the acid value of the sample, using phenolphthalein as indicator, and to calculate the number of c.c. used to resin, molecular weight 346. The small proportion of free fatty acids, if any, is neglected. For the *Liebermann-Storch* reaction an alcoholic extract of the oil, but not the oil itself, should be used.

The employment of the butyro-refractometer[4] has been proposed, but it would be easy to prepare mixtures having correct deviations.

The distinction between linseed oil and boiled oil may be based on the iodine and specific gravity tests.

A practical test is to allow the sample to dry on a watch-glass side by side with a sample of raw linseed oil. Boiled oil dries within twenty-four hours, whereas raw linseed oil at most becomes more viscous. This practical test would also indicate adulteration with fatty oils, such as rape oil and cotton seed oil.

Boiled oil is, as a rule, mixed with raw linseed oil, as, used alone, it would give a somewhat "hard" coat, liable to crack, whereas the addition of raw linseed oil renders the coat more elastic and durable. The detection of small quantities of raw linseed oil in boiled oil has therefore little practical importance.

For the rapid distinction of linseed oil from boiled oil *Finkener* recommends for custom-house purposes the following test, by which 25 per cent of boiled oil can be detected in raw oil. The following reagents are required:—A 20 per cent ammonia solution, and a solu-

[1] R. Williams (*Analyst*, 1895, 277) gives the following iodine values for boiled oils at different stages of boiling:—

	Thin.	Thin.	Stout.	Very Stout.
Iodine value .	111·3	112·4	65.6	59·9

It should be noted that these numbers are very likely too high, as the Hübl solution was allowed to act on the oil for 18 to 20 hours.

[2] Cp. paint oils, p. 686.

[3] Amsel (*Jour. Soc. Chem. Ind.* 1895, 605; 1896, 222) unnecessarily proposes for this well-known phenomenon the term "water-reaction." It should be noted that oils prepared with liquid driers (see p. 737) may legitimately contain small proportions of oil of turpentine.

[4] Hefelman and Mann, *ibid.* 1896, 475.

tion containing 100 grms. of lead acetate and 32 grms. of glycerin in 120 c.c. of water. One operates as follows:—1 c.c. of the ammonia solution is mixed with 5 c.c. of the lead solution, 12 c.c. of the suspected sample are added, and the whole is vigorously shaken together and then heated for three minutes to 100° C. On standing, if the sample be pure linseed oil, it will form two layers, the lower one being as clear as water, while if the sample contain boiled oil it will set to a soft viscous mass.

Boiled oil may be readily differentiated from raw linseed oil by the presence of metals ("driers"), which are absent from the latter.

The nature of the metal in the "drier" is ascertained by boiling, say, 30 grms. of the sample with dilute hydrochloric acid, and allowing to separate into two layers. The acid layer is syphoned off, and tested for metals (lead, manganese), or acids (boric, oxalic, etc.), in the usual manner.

The solid "driers" (siccatives) are of late being replaced by "soluble" driers, which offer the advantage that they can be incorporated with linseed oil not only at a comparatively low temperature —120° C.—but even in the cold, if they have been dissolved previously in oil of turpentine. The "boiled oils"[1] prepared by either method possess equally high drying properties, provided the same amount of metal has been added. According to *Weger*,[2] commercial soluble driers are either "fused" or "precipitated" driers, consisting of linoleates (salts of the mixed fatty acids from linseed oil) or resinates; it should be noted that the metals are exclusively lead and manganese, other metals, such as copper, zinc, etc., yielding useless products. Lead salts alone are not used, as not imparting such drying properties as are yielded by manganese salts. In practice either manganese salts are used, or mixtures of manganese and lead salts.

The following are the commercial products used as soluble driers: —Manganese resinate, mangano-lead resinate, manganese linoleate, and mangano-lead linoleate.

"Fused" manganese resinate but rarely contains more than 3·2 per cent of soluble manganese, whereas the "precipitated" salt may contain as much as 6 to 7 per cent Mn.; "fused" manganese linoleate contains 9-9·5, sometimes even 11 per cent Mn. "Precipitated" manganese linoleate is not a commercial product.

In the manufacture of boiled oil 2 to 3 per cent of "fused" manganese resinate, or mangano-lead resinate are used, or in their place 1 per cent of "fused" manganese linoleate, or 1 to 1·5 per cent of "precipitated" manganese resinate. The best proportion of lead salts to manganese salts appears to be 5 : 1, and the best commercial products contain 8 to 9 per cent of soluble lead and 1·5 to 2 per cent of soluble manganese.

The valuation of a "soluble" drier cannot be based on the proportion of the metal as determined by incineration, inasmuch as oxide

[1] The oils thus prepared are still termed by the trade "boiled oils."
[2] *Journ. Soc. Chem. Ind.* 1896, 728.

held in suspension, and therefore not chemically combined with the linseed oil fatty acids or resin fatty acid, is useless as a drier. A good soluble drier must therefore be soluble in ether and (in the case of lead resinate) chloroform.

In the analytical examination burn off the organic matter and determine the lead and manganese in the ash; as the driers often contain sand, etc., the weighing of the ash would be useless. If calcium be present in any quantity, after separating the lead, estimate the manganese and calcium together as carbonates, and titrate the manganese; the calcium is then found by difference. Then extract a fresh portion of the sample with ether or chloroform (in the case of a lead resinate), filter, wash, incinerate, and determine the manganese in the ash. The difference between the two amounts of manganese corresponds to the manganese present as soluble drier; the result may be checked by determination of the soluble manganese in an aliquot part of the ethereal extract. The soluble lead must be determined by difference, since the chloroform is only driven off completely from the resinate solution at a red heat, when the greater part of the lead also volatilises as chloride.

The chemical change that takes place when boiled oil (or any drying oil) "dries" is very imperfectly understood. According to *Bauer* and *Hazura*[1] the glyceride of linolenic acid (and perhaps in a higher degree the glycerides of linolenic acids) is at first converted into the glyceride of hydroxylinolic (resp. hydroxylinolenic acid); then anhydrides are formed. *Mulder's* older statement that, in the first instance, all the glycerol is oxidised, is incorrect, as boiled oil contains considerable proportions of glycerol. (It has been pointed out already (p. 211) that the glycerol cannot be estimated by *Benedikt* and *Zsigmondy's*, or by *Hehner's* method, as boiled oil contains, besides glycerol, other soluble substances that yield oxalic acid and are easily oxidised by chromic acid.) The last product of oxidation was hitherto assumed to be *Mulder's* linoxyn, a neutral substance, insoluble in ether and possessed of somewhat elastic properties. *Reid*,[2] however, has shown that in course of time the "linoxyn" in its turn is converted into a viscous liquid heavier than water, and soluble in the latter to a considerable extent. This liquid is termed by *Reid* "superoxidised linseed oil."

Fahrion is of the opinion[3] that, on drying, hydroxy acids are formed, basing his view on the fact that fatty acids insoluble in petroleum ether are obtained from boiled oil and linseed oil varnish (cp. Dégras-former, p. 699). Whether these acids are really hydroxy acids, or have a more complex constitution, is open to doubt (cp. p. 204).

Fahrion gives the following analyses of three samples of boiled oil; the oxidised acids[4] (hydroxy acids?) have been determined by the method described page 204 :—

[1] *Jour. Soc. Chem. Ind.* 1888, 680. [2] *Ibid.* 1894, 1020. [3] *Ibid.* 1894, 404.
[4] I prefer this term to hydroxy acids, as the constitution of these acids is not known yet.

Boiled Oil.	Consistency.	Iodine Value.	Acid Value.	Oxidised Acids.	Oxidised Acids in Dried Oil.
				Per cent.	Per cent.
No. 1	Somewhat thin and fluid	101·3	13·4	0·5	30·6
No. 2	Very viscid	77·3	24·9	4·1	20·8
No. 3	Tacky; yielding "strings"	73·7	32·6	7·6	16·4

The "dried oil" was obtained by spreading the boiled oil on a glass plate in a very thin film, and exposing it to the air for ten days at a temperature slightly higher than the ordinary. *Fahrion* draws from these figures the conclusion that a boiled oil dries the better, and consequently is the more valuable, the less oxidised acids it contains. This opinion is confirmed by some statements of *Leeds*[1] on various qualities of linseed oil varnishes (lithographic varnishes), showing that the drying power of linseed oil varnishes diminishes as the boiling of the raw oil progresses. Thus, whereas "thin" lithographic varnishes dry about as well as raw linseed oil, the "extra strong" varnish can hardly be said to dry at all (cp. below).

Boiled oil is extensively used in the manufacture of fatty (fixed) oil **varnishes**, made from linseed oil, various gum-resins, and oil of turpentine. The latter would be determined approximately, according to *M^{c}Ilhiney*,[2] by distilling 25 grms. of the varnish with 100 c.c. of water in a distilling flask, when the whole of the ethereal oil is stated to come over with the first 90 to 95 c.c. of distillate.

The residue would, in the writer's opinion, be best treated with alcohol in order to separate the gum-resin from the boiled oil. No test experiments having been made yet, this must be accepted with due reserve.

3. Lithographic Varnish

Lithographic varnish is a perfectly clear, transparent substance; if of the best quality it is but slightly darker than raw linseed oil. It often has a faintly reddish tint, and when prepared by boiling over fire (see below) it exhibits a more or less strongly marked green fluorescence.

Lithographic varnish is obtained by boiling linseed oil at a higher temperature (say 260° to 300° C.) than that at which "boiled oil" is prepared. It further differs from the latter in that it is free from metals, no "drier" being added to the oil whilst boiling.

According to the degree of consistency of the product several varieties are discerned in commerce. They are given in the following table (p. 740).

"*Burnt oil*" is a fairly quick drying varnish, which will form a strong skin in twenty-four to forty-eight hours at the ordinary

[1] *Jour. Soc. Chem. Ind.* 1894, 203. [2] *Ibid.* 1895, 78.

temperature. It is obtained by heating raw linseed oil up to its flash point, and allowing it then to burn quietly, with constant stirring, until the required consistency is reached.

I subjoin the result of an examination of several lithographic varnishes, to which, for the sake of comparison, is added that of raw linseed oil. The oxidised acids, termed "*Fahrion's* acids" by *Leeds*, have been determined as described page 204.

Lithographic Varnishes prepared by Boiling over Fire.

	Specific Gravity at 15° C.	Free Acids calculated as Oleic Acid.	Saponification Value. Mgrms. KOH.	Unsaponifiable Matter.	Oxidised Acids.	Iodine Value.
		Per cent.		Per cent.	Per cent.	
Raw linseed oil . .	0·9321	0·85	194·8	...	0·30	169·0
"Tint" varnish .	0·9584	1·46	197·5	...	1·50	113·2
"Thin" varnish .	0·9661	1·76	196·9	0·62	2·50	100·0
"Middle" varnish .	0·9721	1·71	197·5	0·85	4·20	91·6
"Strong" varnish .	0·9741	2·16	190·9	0·79	6·50	86·7
"Extra strong" varnish	0·9780	2·51	188·9	0·91	7·50	83·5
"Burnt" thin varnish	0·9675	6·93	195·5	1·35	0·85	92·7

The mixed fatty acids, derived from the raw linseed oil and the varnishes, and freed from the unsaponifiable matter, gave the following results :—

Mixed Fatty Acids from Lithographic Varnishes.

	Specific Gravity at 15·5° C.	Melting Point. °C.	Solidifying Point. °C.	Mean Combining Weight.	Saponification Value. Mgrms. KOH.	Iodine Value.
Raw linseed oil . .	0·923	24-26·5	...	286·5	195·8	145·5
"Tint" varnish . .	0·941	20·5	15	...	...	118·3
"Thin" varnish .	0·949	22	18	...	...	108·8
"Middle" varnish .	0·950	24	22	272·6	205·8	97·7
"Strong" varnish .	0·953	25·5	24	270·1	207·7	87·3
"Extra strong" varnish	0·955	27	23	269·8	207·9	90·8
"Burnt" thin varnish	...	23	19	...	...	99·3

Another method of preparing linseed oil varnish consists in treating linseed oil with oxygen in jacketed pans heated by steam. The oil gains thereby in weight, and the product obtained is a pale oil, not darker than the raw oil, and free from the fluorescence characteristic of the oils obtained by boiling over fire.

The following table gives the physical and chemical characteristics of these oxidised oils and of their mixed fatty acids, in juxtaposition with those of a sample of a dried oil, obtained from a raw linseed oil by exposure in a flat dish to a moderate current of air at 45° C. for about five weeks, the skin formed being daily broken up and mixed

with the bulk. This dried linseed oil had a jelly-like consistency, lumps of comparatively hard material and skin alternating with a small quantity of oil of the consistency of "middle" varnish :—

Varnishes prepared by Treatment with Oxygen

Oils.	Specific Gravity at 15° C.	Free Acid calculated as Oleic Acid.	Saponification Value. Mgrms. KOH.	Unsaponifiable Matter.	Oxidised Acids.	Iodine Value.
		Per cent.		Per cent.	Per cent.	
Oxidised oil, weak	1·03	18 - 28·4[1]	221	0·89	42·82	58·8
„ „ strong	1·05	18·49-28·9[1]	223·5	0·97	44·19	53·5
Dried linseed oil .	...	12·67	171·6	0·81	31·58	93·9

Mixed Fatty Acids.	Melting Point.	Solidifying Point.	Mean Combining Weight.	Saponification Value.	Iodine Value.
	°C.	°C.			
Oxidised oil, weak .	28	26	241·4	232·4	63·2
„ „ strong .	27	25	242·5	231·3	60·6
Dried linseed oil .	26	22	268·8	208·7	100·3

The oxidised oils are much more readily soluble in alcohol, and, especially the sample "oxidised oil, weak," possessed more strongly marked drying powers than the ordinary varnishes. They are saturated with gas which causes them to effervesce on heating.

Linoleum [2]

Linseed oil intended for the manufacture of **linoleum** is exposed to air or treated with oxygen until the maximum amount of oxygen has been absorbed. The product thus obtained forms a yellow gelatinous mass, which can be drawn into "strings." It is heavier than water, and insoluble in alcohol, ether, chloroform, and carbon bisulphide.

This mass, mixed with resin, rasped cork, and "fillers," serves as the raw material for linoleum.

Linoleum is, as a rule, valued by so-called "practical" tests.[3] Still, chemical analysis will reveal an excessive amount of ash, and extraction of linoleum with ether will show whether the oil used had been dried completely. The larger the amount of extract the less valuable is the linoleum.

[1] The first of these figures was found when the pink colour of the phenolphthalein remained after a vigorous shaking ; but it disappeared after a short time, and more alkali was run in until the pink colour remained constant for two or three minutes ; thus the second figure was obtained (cp., however, *Jour. Soc. Chem. Ind.* 1890, 847).

[2] Cp. W. F. Reid, *Jour. Soc. Chem. Ind.* 1896, 75.

[3] Cp. also Buchartz, *ibid.* 1895, 587.

The following three analyses of linoleum are due to *Pinette*;[1] it may be added that this observer erroneously considers the sample No. 3, yielding the largest amount of ether-soluble oil, the best :—

Samples of Linoleum

		No. 1.	No. 2.	No. 3.
Water		3·39	3·01	3·41
Linseed oil (ether-soluble)		10·43	10·60	19·58
Cork (by difference)		77·24	73·63	54·16
Ash	Silica	2·94	3·99	4·31
	Alumina	1·91	4·94	0·61
	Ferric oxide	1·78	1·79	8·86
	Lime	...	...	6·17
	Alkalis, etc.	1·31	2·04	2·90
		100·0	100·0	100·0

H. VULCANISED OILS

Rubber Substitutes

French—*Gomme factice.* German—*Faktis.*

Vulcanised oils are prepared from fatty oils either by heating with sulphur, or by treatment with sulphur chloride in the cold.[2] According to the process used they are distinguished in the trade as "brown" (black) and "white substitutes" respectively. The "white substitutes" contain, therefore, a considerable proportion of chlorine, which is, of course, absent in the "brown (black) substitutes"; thus it is possible to easily distinguish the two classes of substitutes by chemical means.

The substitutes are india-rubber like substances, and serve, as their name indicates, to replace india-rubber. The white substitutes form a yellowish, elastic, crumbly substance of oily smell and neutral reaction; the brown (black) substitutes occur in commerce either as sticky lumps or in a ground state.

Being derivatives of fatty oils, the quantitative reactions naturally lend themselves as suitable methods for their examination, supplemented, of course, by such tests as the nature of the substance requires.[3]

Thus the sulphur is determined by treating the substitute with fuming nitric acid in the presence of silver nitrate and subsequent fusing with caustic potash and potassium nitrate, the insoluble silver compounds retaining the chlorine.

The following table contains a number of analyses of india-rubber substitutes by *Henriques*[3] :—

[1] *Jour. Soc. Chem. Ind.* 1892, 550. [2] Cp. p. 282.
[3] *Jour. Soc. Chem. Ind.* 1894, 47, 70.

Oils vulcanised with S_2Cl_2.	Sulphur.	Chlorine.	Water.	Residue on Ignition.	Fatty Acids.	Iodine Value.	Acetyl Value.	Fatty Acids.		
								Sulphur.	Chlorine.	Iodine Value.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.		Per cent.	Per cent.	
Linseed oil rubber substitute from raw oil . .	9·34	8·84	3·02	...	79·6	56·3	21·0	9·88	Trace	160·3
Linseed oil ,, ,, ,, blown oil .	4·78	4·85	0·85	...	81·67	52·6	19·6	4·06	0·60	141·2 / 121·0
Rape oil ,, ,, ,, commercial oil .	8·28	7·62	...	...	86·89	32·5	31·0	8·34	Trace	101·5
Rape oil ,, ,, ,, blown oil . .	6·59	5·95	...	...	87·95	26·9	...	6·54	Trace	102·8
Poppy seed oil ,, ,, ,, blown oil . .	7·68	7·44	...	...	74·90	33·6	...	8·32	...	133·3
Cotton seed oil ,, ,, ,, blown oil . .	6·23	5·36	...	...	...	30·3	51·3	6·44	Trace	91·5
Castor oil ,, with minimum of S_2Cl_2 .	4·82	6·70	...	...	85·35	35·2	...	5·32	Trace	136·2 / 147·4 / 152·1
Castor oil ,, ,, maximum ,, ,, . .	10·60	8·95	...	...	...	21·9	105·6	...	0·26	105·6
Commercial Products.										
White substitute, No. 1	6·4	5·0	0·85	0·8	90·45	30·9	...	6·12	0·83	91·3
,, ,, No. 2	6·17	5·86	1·0	5·51	73·58	31·0	...	6·45	0·43	91·2
,, ,, No. 3	8·25	8·88	...	...	...	32·6	...	8·15	...	102·3
Brown substitute, No. 1	15·48	0·7	...	...	...	42·0	...	14·14	...	129·0
,, ,, No. 2	17·71	0·36	...	...	...	42·0	...	15·20	...	125·6

The nature of the chemical change taking place on treating oils with sulphur chloride is not understood yet, and little can be added to the notes given above (chap. ix. p. 284), under the head of sulphur chloride. *Henriques* has shown that blown oils require much less sulphur chloride than the original oils to form vulcanised oils; this would favour the opinion that the white substitutes are addition products. On saponification, the chlorine only is eliminated as hydrochloric acid, the sulphur remaining in chemical union with the oils and unsaturated substances are again obtained, as is proved by the high iodine numbers of the sulphurised fatty compounds. The sulphur cannot be present as an SH group, since such substances should assimilate "acetyl" like hydroxy acids, but experiments have proved that this is not the case.

Nor is the reaction of sulphur on oils fully understood. Whereas melted sulphur does not interact with a saturated fatty acid, such as stearic acid, at about 130° C., oleic acid[1] readily absorbs ten per cent of sulphur at 130°-150° C. The sulphur does not crystallise out on cooling, and no sulphuretted hydrogen is evolved. The reaction taking place appears therefore to consist in true addition. It differs most essentially from the action of sulphur on oils at higher temperatures, for even stearic acid is attacked by sulphur at 200° C. with evolution of sulphuretted hydrogen, much as oleic acid heated with sulphur to 200°-300° C. is converted into sulpho-oleic acid with concomitant formation of sulphuretted hydrogen (cp. chap. iii. p. 55).

Altschul states that all oils behave in the same manner, viz. form addition compounds with sulphur, which on saponification yield salts of sulphurised fatty acids, the latter being separated in their free state on decomposing with a mineral acid.

Henriques[2] has, however, shown that the reaction is not so simple, addition and substitution taking place concurrently, the former preponderating at lower temperatures, the latter at high ones. Also Michael[3] has shown that the action of sulphur on unsaturated organic compounds is of a complicated nature.

It should be noted that the saponification of the sulphurised oil must be carried out in the cold in order to avoid loss of sulphur. For this operation *Henriques'* method of cold saponification described above (chap. ii. p. 21) will be found suitable.

[1] Altschul, *Jour. Soc. Chem. Ind.* 1896, 282.
[2] *Jour. Soc. Chem. Ind.* 1896, 282. [3] *Berichte*, 1895, 1633.

I. CANDLES

1. Tallow Candles

The once flourishing tallow candle industry has almost completely succumbed to the competition of the stearine and paraffin candle. The tallow dip candle has therefore but an insignificant local importance. As a rule, it is not adulterated. Its commercial examination is identical with that of tallow (p. 596).

2. Stearine Candles

For the manufacture of stearine candles the solid fats are resolved into three portions: 1. The solid fatty acids, or the candle material (candle grease), also termed "stearine," or commercial stearic acid; 2. The liquid fatty acids, "oleine," or "elaine" as the term runs, used chiefly for soap-making and as wool oil (p. 704); and 3. Glycerin.

The fats chiefly used are tallow and palm oil. In France these two fats are usually mixed in equal proportions. Also bone fat is largely employed on the Continent. A very valuable raw material is "tallow stearine" (p. 591). Of minor importance are Malabar tallow and other less-known vegetable fats, these not having been imported hitherto in sufficient quantities to Europe.

The processes used on the manufacturing scale are the following:—

1. Lime Saponification.—The fats mixed with water are saponified by means of burnt lime, either in open vats (old process) or in autoclaves at pressures varying from 10 to 12 atmospheres. In the former case 12-14 per cent of lime are required, whereas in the latter the proportion of lime may be as low as 3 per cent. The resulting product is lime soap ("rock"), in the latter process mixed with free fatty acid, and glycerol. The glycerol dissolved in the water is drawn off and recovered by concentration. The lime soap, or the mixture of lime soap and free fatty acids, is decomposed by sulphuric acid, when the lime is precipitated as calcium sulphate and the free fatty acids float on the top. The fatty acids are washed with hot water, allowed to solidify in shallow trays, and pressed in hydraulic presses, at first in the cold, and finally at a higher temperature. The press-cakes are remelted, washed first with dilute sulphuric acid, to decompose any lime soap present, and finally with water. The product thus obtained—"stearine," "commercial stearic acid"—is a mixture of stearic and palmitic acids with small quantities of oleic acid.

The oil expressed in the hot holds considerable proportions of "stearine" in solution; this is recovered by cooling the oil and filter-pressing the deposited crystals.

The expressed liquid acids, or the "red oil," is termed "oleine";

with special reference to this saponification process it is called "saponification oleine," or "saponified oleine."

The yield of candle material by this process is about 50 per cent of the fat employed.

In place of lime other bases such as magnesia, zinc oxide, are employed.

2. **"Acid Saponification," or "Sulphuric Acid Saponification."**—In some candle-works this process is used exclusively; in others, however, only impure or inferior raw material, such as bone fat, is subjected to this process, as otherwise it would not yield a colourless product. In the "acid saponification" process the raw material is mixed with several per cents (varying from 4 to 12) of concentrated sulphuric acid at the temperature of 120° C., for a short time, then run into water and boiled up. The fatty acids floating on the top of the acid liquid are collected and purified by distillation in a current of steam. The distillate thus obtained is resolved into two portions, viz. "distilled stearine," and "distilled oleine."

The yield of candle material is notably higher than in the lime process (by 13 to 20 per cent), a considerable quantity of oleic acid being converted into isooleic acid[1] (p. 57). The *rationale* of the reaction taken place will be explained below.

The glycerin, termed "distillation glycerin" (not to be confounded with distilled glycerin), obtained in this process is of inferior quality; its yield is also greatly diminished, the sulphuric acid having destroyed a portion of it.

In order to obtain the full quantity of glycerin of good quality it has become the practice to saponify the fats by the lime saponification method (or by the following process 3), and subsequently to treat the free fatty acids as in the sulphuric acid process, so as to increase the yield of candle material.

3. **Saponification by Means of Water.**—Fats are also saponified by means of water under a pressure of 15 to 18 atmospheres (220 to 270 lb.), or by distillation in a current of superheated steam *in vacuo*, when fatty acids and glycerol distil over.[2]

Oleic acid being a by-product of no value for candlemaking, various processes have been proposed for the **conversion of oleic acid into candle material.**[3]

The first attempts were directed to the conversion of oleic acid into one of the solid acids—*elaïdic acid*, *palmitic acid*, or *stearic acid*.

By means of nitrous acid a solid acid is only obtained in the case of *fresh* oleic acid; but, even at best, *elaïdic* acid is a very poor candle material.

The conversion of oleic acid into *palmitic acid*, according to *Varrentrapp's* reaction (p. 46), has been tried repeatedly on a large scale; latterly by *Radisson*,[4] but no economical advantages have resulted, the product not being suitable for candle-making.[5]

[1] Benedikt, *Jour. Soc. Chem. Ind.* 1888, 754. [2] Lewkowitsch, Eng. Pat. 5985, 1888.
[3] Cp. Lewkowitsch, *Jour. Soc. Chem. Ind.* 1897, 389. [4] *Jour. Soc. Chem. Ind.* 1884, 200.
[5] Cp. Lewkowitsch, Technical Report on the Paris Exhibition, *Chem. Zeit.* 1889, 1190.

P. de Wilde and *A. Reychler* proposed to convert oleic acid into stearic acid by treatment with small quantities of iodine, bromine, or chlorine (cp. p. 56). The action of chlorine on oleic acid with a view to converting it into candle material has been patented by *Zürrer*.[1]

M. v. Schmidt heats ten parts of oleic acid with one part of zinc chloride to 180° C., boils the product repeatedly with dilute hydrochloric acid, and finally with water. The fatty substance is then distilled in a current of superheated steam, and the distillate is separated by pressure into candle material and oleic acid.

A product thus prepared for candle-making gave on analysis (*Benedikt*[2]) the following numbers (cp. chap. xiii. p. 812):—

Stearolactone	75·8 per cent
Isooleic acid	15·7 ,,
Solid fatty acids	8·5 ,,
	100·0

Zinc chloride seems to act on oleic acid in a manner analogous to concentrated sulphuric acid. Very likely two isomeric zinc chloride-addition compounds are formed, which are subsequently decomposed on boiling with dilute hydrochloric acid into zinc chloride and two isomeric hydroxystearic acids, one of which is changed into stearolactone with loss of one molecule of water.

The same hydroxystearic acids have been obtained by *Geitel* on treating oleic acid with concentrated sulphuric acid in the cold, with this difference, however, that stearolactone is formed in small quantities, the chief product being ordinary hydroxystearic acid. On distilling in a current of steam, the stearolactone passes over unchanged, whereas the hydroxystearic acids yield isooleic acid.

The most promising process for the conversion of oleic acid into candle material seems to lie at present in the action of concentrated sulphuric acid, assisted perhaps by a small proportion of fuming acid,[3] in the cold.

In fact, the higher yield of candle material obtained by the acid saponification process (see above) is caused by the action of the vitriol on oleic acid, producing partial conversion of it into solid products.

The *rationale* of the chemical action[4] taking place in the cold may be explained as follows:—

In the first instance sulphuric acid is assimilated by oleic acid, much as bromine is absorbed by it with formation of saturated products. But in the present case there is this important difference, that as the two atom groups SO_3H and OH are different, two products may be expected, according as the SO_3H group is assimilated by the β or the γ carbon atom, thus—

[1] German Patent, No. 62,407, 1892.
[2] *Monatshefte f. Chem.* 1890, 90; cp. chap. xiii. p. 812.
[3] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1897, 392. David, Eng. Pat. 3700, 1897.
[4] Geitel, however, has shown that stearosulphuric acid is formed.

$$C_{14}H_{29}-CH=CH-CH_2-COOH$$
Oleic acid.

yields

$$(1)\ C_{14}H_{29}-\overset{\gamma}{C}H(SO_3H)-\overset{\beta}{C}H(OH)-CH_2-COOH$$
γ-Sulphostearic acid.

and

$$(2)\ C_{14}H_{29}-\overset{\gamma}{C}H(OH)-\overset{\beta}{C}H(SO_3H)-CH_2-COOH$$
β-Sulphostearic acid.

As there is no reason why one acid should be formed in preference to the other, it may be assumed that both acids are formed in equal proportions. These acids are not very stable, and by merely allowing the crude product to stand, enough moisture is absorbed to produce a partial splitting up into SO_4H_2 and hydroxy acids, thus—

$$(1)\ C_{14}H_{29}-\overset{\gamma}{C}H(SO_3H)-\overset{\beta}{C}H(OH)-CH_2-COOH+H_2O=C_{14}H_{29}-CH_2-\overset{\beta}{C}H(OH)-CH_2-COOH+SO_4H_2$$
β-Hydroxystearic acid.

$$(2)\ C_{14}H_{29}-\overset{\gamma}{C}H(OH)-\overset{\beta}{C}H(SO_3H)-CH_2-COOH+H_2O=C_{14}H_{29}-\overset{\gamma}{C}H(OH)-CH_2-CH_2-COOH+SO_4H_2$$
γ-Hydroxystearic acid.

The latter acid — γ-hydroxystearic acid — immediately undergoes dehydration with formation of γ-stearolactone (p. 69).

Another portion of the sulphostearic acid remains unchanged, but on boiling the crude mass with water the undecomposed portion is also converted into β-hydroxystearic acid and stearolactone, as shown.

In the subsequent distillation of the washed product the stearolactone already formed passes over unchanged, as also part of the β-hydroxystearic acid, whereas another part is converted by dehydration into oleic *and* isooleic acids, thus—

$$(1)\ C_{14}H_{29}-CH_2-CH(OH)-CH_2-COOH-H_2O=C_{14}H_{29}-CH=CH-CH_2-COOH$$
Oleic acid.

$$(2)\ C_{14}H_{29}-CH_2-CH(OH)-CH_2-COOH-H_2O=C_{14}H_{29}-CH_2-CH=CH-COOH$$
Isooleic acid.

It is evident that unless distillation can be avoided, a complete conversion of oleic acid into solid products cannot be thus obtained.

In the "acid saponification" process the interaction takes place at a high temperature, and it is therefore readily intelligible that, the chemical changes involved being of a reversible nature, a limit is reached beyond which the proportion of oleic acid cannot be reduced.

David's[1] statement that 18-20 per cent of stearolactone are formed in the cold by washing the product of interaction of oleic and sulphuric acids with an equal volume of water, removing the acid layer, dissolving the oily layer in an equal volume of water, and allowing to stand for twelve hours, has been controverted by *Lewkowitsch*,[2] who has shown that the separated crystals are practically nothing but β-hydroxystearic acid.

Examination of the Raw Material of the Candle Industry

The raw material of the candle industry is valued on the solidifying point of the fatty acids; the higher this is, the greater will be the yield of solid fatty acids. The proportion of water and of non-fatty substances is also taken into account.

In the following lines the methods employed for the valuation are shortly summarised.

The sample is drawn carefully in the manner described page 87. Water may be determined, according to *H. Norman Tate*,[3] by heating 50 grms. in a porcelain crucible, or better in a silver crucible, to 130° C., and keeping it thereat until bubbles cease to be given off, and the melted fat is in a condition of calm fusion without giving off vapour. The fat is then allowed to cool, and is weighed. The loss indicates the moisture (cp. also p. 88).

Impurities—not-fats—are determined as described p. 88. It should, however, be mentioned that in the case of bone fat containing glue and lime soaps, different results are obtained according as the fat is extracted after previous drying, or is extracted undried. The method employed should, therefore, be stated distinctly when returning the results of the analysis. According to the "French method" the undried fat is extracted.

Solidifying Point of the Fatty Acids. Tallow Titer

The "titer test" has been fully described p. 134. It is necessary to pay the greatest attention to this determination, the practical yield of candle material depending in a great measure on its accuracy. *Dalican* weighs off 50 grms. of fat, and employs the mixed fatty acids obtained from it for the "titer test." The following is an empirical table compiled by *Dalican*, giving the percentages of stearic and oleic acids for the solidifying points of tallow stated. The total yield of fatty acids is taken as 95 per cent, and that of the (9·68 per cent glycerol-yielding) radicle C_3H_2 as 4 per cent, 1 per cent being allowed for water and impurities.

[1] *Jour. Soc. Chem. Ind.* 1897, 339. [2] *Ibid.* 1897, 390.
[3] *The Examination of Tallow*, Liverpool, 1888.

Solidifying Point.	Stearic Acid.	Oleic Acid.
C.	Per cent.	Per cent.
35	25·20	69·80
35·5	26·40	68·60
36	27·30	67·70
36·5	28·75	66·25
37	29·80	65·20
37·5	30·60	64·40
38	31·25	63·75
38·5	32·15	62·85
39	33·44	61·55
39·5	34·30	60·80
40	35·15	59·85
40·5	36·10	58·90
41	38·00	57·00
41·5	38·95	56·05
42	39·90	55·10
42·5	42·75	52·27
43	43·70	51·30
43·5	44·65	50·35
44	47·50	47·50
44·5	49·40	45·60
45	51·30	43·70
45·5	52·25	42·75
46	53·20	41·80
46·5	55·10	39·90
47	57·95	37·05
47·5	58·90	36·10
48	61·75	33·25
48·5	66·50	28·50
49	71·25	23·75
49·5	72·20	22·80
50	75·05	19·95
50·5	77·10	17·90
51	79·50	15·50
51·5	81·90	13·10
52	84·00	11·00
52·5	88·30	6·70
53	92·10	2·90

De Schepper and *Geitel*[1] recommend each candle-works chemist to construct an empirical table for his own use, from which the yield of candle material may be found at once. It goes, of course, without saying that a table of this kind holds good only for the particular works for which it is constructed, as the solidifying points of the mixed fatty acids and the yields of candle material naturally vary considerably according as lime saponification or sulphuric acid saponification is employed.

Such an empirical table is made by mixing "stearine" and oleic acid, prepared in the works, in known proportions, and determining the solidifying points of these mixtures. Of course, for each kind of fat a separate table must be constructed. As an example we give the following table of *Y. de Schepper* and *Geitel*, used in the candle-works of Gouda (Holland) for tallow and palm oil. The process employed is sulphuric acid saponification. The yields of "stearines" of

[1] *Dingl. Polyt. Jour.* 245. 295.

different solidifying points are recorded as obtained from the saponified mass by expressing it at different temperatures. The "stearines" solidifying at 48° C., 50° C., and 52° C. differ from those having a higher solidifying point most likely by a higher proportion of isooleic acid.

Solidifying Point.	Percentage of "Stearine" of Solidifying Point stated.							
	Palm Oil.				Tallow.			
°C.	48°	50°	52°	55·4°	48°	50°	52°	54·8°
5	...	...	...	...	...	...	...	...
10	4·2	3·6	3·3	2·6	3·2	2·7	2·3	2·1
15	10·2	9·8	7·8	6·6	7·5	6·6	5·7	4·8
20	17·4	15·0	14·4	11·0	13·0	11·4	9·7	8·2
25	26·2	22·4	19·3	16·2	19·2	17·0	14·8	12·6
30	34·0	30·5	26·6	22·3	27·9	23·2	21·4	18·3
35	45·6	40·8	35·8	29·8	39·5	34·5	30·2	25·8
36	48·5	43·2	38·0	31·8	42·5	36·9	32·5	27·6
37	51·8	45·5	40·3	33·6	46·0	40·0	34·9	29·6
38	55·5	48·8	42·6	35·8	49·5	42·6	37·5	32·0
39	59·2	51·8	45·6	38·2	53·2	45·8	40·3	34·3
40	63·0	55·2	48·6	40·6	57·8	49·6	43·5	37·0
41	66·6	58·7	52·0	43·0	62·2	53·5	47·0	40·0
42	70·5	62·2	55·2	45·5	66·6	57·6	50·5	42·9
43	74·8	66·0	58·8	48·5	71·8	62·0	54·0	46·0
44	79·2	70·2	62·0	51·4	77·0	66·2	58·4	49·8
45	84·0	74·5	66·0	54·3	81·8	71·0	62·6	53·0
46	89·4	78·8	69·8	57·8	87·5	75·8	67·0	56·8
47	94·3	83·0	74·0	61·0	93·3	80·9	71·5	60·8
48	100·0	88·0	78·6	65·0	100·0	87·2	76·6	65·0
49	...	94·2	83·5	69·1	...	93·0	84·7	69·5
50	...	100·0	89·0	73·4	...	100·0	87·0	74·5
51	...	...	94·5	78·0	...	...	93·5	79·8
52	...	...	100·0	82·8	...	...	100·0	84·8
53	...	...	...	87·6	...	...	...	90·1
54	...	...	...	92·2	...	...	...	95·3
55	...	...	...	97·5	...	...	(54·8)	100·0
55·4	...	...	...	100·0	...	...	...	...

The actual proportion of true **stearic** acid in the mixed fatty acids is ascertained by *Hehner* and *Mitchell's* method (chap. viii. p. 198).

As a measure of the proportion of **oleic acid** or **"oleine,"** the iodine value may be determined; the lower this is, the more valuable the material will be for candle-making. It should, however, be borne in mind that also **isooleic** acid, absorbing as much iodine as ordinary oleic acid, is suitable for the candlemaker's purposes on account of its high melting point, 45° C.

The amount of **glycerol** obtainable in the saponification process is calculated from the ether value (p. 208), if neutral fats be used.

Adulterants in the raw material of candle-works are detected according to the methods detailed above under tallow (p. 596).

Control of the Saponification Process in Candle-Works and Examination of the Intermediate Products

In order to ascertain how far saponification of the fats has proceeded in the autoclaves, a sample is drawn from time to time, and the ratio of neutral fat to free fatty acids determined. The sample is boiled with water in the case of products from the acid process, and in the case of lime saponification with dilute sulphuric acid, so as to isolate the fatty substance. Then the acid value, A, and the saponification value, K, of the sample are determined. Adopting 95 per cent of fatty acids as the yield from neutral fats, the ratio in which the free fatty acids, F, stand to the undecomposed neutral fat, N, at the time the sample was taken is given by the following proportion :—

$$F : N = A : 1{\cdot}053(K - A).$$

A shorter method, naturally commending itself in those cases where palm oil (containing large proportions of free fatty acids) is mixed with neutral fats, is to determine K once for all at the outset, or, to save calculation, the number of c.c. of a potash solution, which need not be standardised, and then to ascertain the number of c.c. required for neutralising the free acids of the sample with the same potash solution. The quotient then gives the percentage of free fatty acids in the sample.

The following table illustrates the sampling of tallow saponified in an autoclave, 3 per cent of lime being used :—

The Sample taken after	Free Fatty Acids. Per cent.
The 1st hour contained	38·55
,, 2nd ,, ,,	77·40
,, 3rd ,, ,,	83·9
,, 4th ,, ,,	87·5
,, 5th ,, ,,	88·6
,, 6th ,, ,,	89·3
,, 7th ,, ,,	93·0
,, 8th ,, ,,	97·5
,, 9th ,, ,,	98·1
,, 10th ,, ,,	98·6

The proportion of **oleic acid** in the press-cakes and in the "red oil" is determined in the case of products from the lime saponification process by *Hübl's* iodine absorption method. In the case of products from the sulphuric acid saponification separation of the lead salts by means of ether must be resorted to (p. 192). *Y. de Scheppel* and *Geitel* use also for press-cakes the table given p. 751. They find the "stearine" in "red oils" from the following table after saponifying the sample in order to hydrolyse any undecomposed neutral fat, and determining the solidifying point of the liberated fatty acids. The table has been compiled empirically by mixing together "oleine" of

solidifying point 5·4° C. and "stearine" of solidifying point 48° C. in the proportions stated, and subsequently determining the solidifying points of the mixtures.

Solidifying Point of the Mixture.	Stearine of Solidifying Point 48° C.	Solidifying Point of the Mixture.	Stearine of Solidifying Point 48° C.	Solidifying Point of the Mixture.	Stearine of Solidifying Point 48° C.
°C.	Per cent.	°C.	Per cent.	°C.	Per cent.
5·4	...	20	12·1	35	39·5
6	0·3	21	13·2	36	43·0
7	0·8	22	14·5	37	46·9
8	1·2	23	15·7	38	50·5
9	1·7	24	17·0	39	54·5
10	2·5	25	18·5	40	58·9
11	3·2	26	20·0	41	63·6
12	3·8	27	21·7	42	68·5
13	4·7	28	23·3	43	73·5
14	5·6	29	25·2	44	78·9
15	6·6	30	27·2	45	83·5
16	7·7	31	29·2	46	89·0
17	8·8	32	31·5	47	94·1
18	9·8	33	33·8	48	100·0
19	11·1	34	36·6		

The following table, calculated by *Mangold*,[1] gives the proportions of "stearine" and oleic acid for the iodine values found. It refers to the products obtained from tallow and palm oil by means of lime saponification :—

[1] Marazza-Mangold, *Die Stearinindustrie*, p. 168.

[TABLE

Iodine Value.	Product contains		Iodine Value.	Product contains		Iodine Value.	Product contains	
	Oleic acid. Per cent.	"Stearine." Per cent.		Oleic acid. Per cent.	"Stearine." Per cent.		Oleic acid. Per cent.	"Stearine." Per cent.
0	0	100	31	34·41	65·59	62	68·83	31·17
1	1·11	98·89	32	35·52	64·48	63	69·94	30·06
2	2·22	97·78	33	36·63	63·37	64	71·05	28·95
3	3·33	96·67	34	37·74	62·26	65	72·16	27·84
4	4·44	95·56	35	38·85	61·15	66	73·27	26·73
5	5·55	94·45	36	39·96	60·04	67	74·38	25·62
6	6·66	93·34	37	41·07	58·93	68	75·49	24·51
7	7·77	92·23	38	42·18	57·82	69	76·60	23·40
8	8·88	91·12	39	43·29	56·71	70	77·71	22·29
9	9·99	90·01	40	44·40	55·60	71	78·82	21·18
10	11·10	88·90	41	45·51	54·49	72	79·93	20·07
11	12·21	87·79	42	46·62	53·38	73	81·04	18·96
12	13·32	86·68	43	47·73	52·27	74	82·15	17·85
13	14·43	85·57	44	48·84	51·16	75	83·26	16·74
14	15·54	84·46	45	49·95	50·05	76	84·37	15·63
15	16·65	83·35	46	51·06	48·94	77	85·48	14·52
16	17·76	82·24	47	52·17	47·83	78	86·59	13·41
17	18·87	81·13	48	53·28	46·72	79	87·70	12·30
18	19·98	80·02	49	54·39	45·61	80	88·82	11·18
19	21·09	78·91	50	55·50	44·49	81	89·93	10·07
20	22·20	77·80	51	56·62	43·38	82	91·04	8·96
21	23·31	76·69	52	57·73	42·27	83	92·15	7·85
22	24·42	75·58	53	58·84	41·16	84	93·26	6·74
23	25·53	74·47	54	59·95	40·05	85	94·37	5·63
24	26·64	73·36	55	61·06	38·94	86	95·48	4·52
25	27·75	72·25	56	62·17	37·83	87	96·59	3·41
26	28·86	71·14	57	63·28	36·72	88	97·70	2·30
27	29·97	70·03	58	64·39	35·61	89	98·81	1·19
28	31·08	68·92	59	65·50	34·50	90·07	100	0
29	32·19	67·81	60	66·61	33·39			
30	33·30	66·70	61	67·72	32·28			

Candle Material—Candles

The commercial examination of the candle material, or of the finished stearine candles, embraces the determination of the melting and solidifying points of the fatty substance, the determination of any unsaponified fat, and the detection of carnaüba wax, paraffin wax, cerasin, and cholesterol.

Neutral fat and hydrocarbons are detected qualitatively as described p. 100.

Neutral fat may be due either to incomplete saponification or to intentional admixture, as in the case of "composite candles" (night lights), consisting of a mixture of "stearine" and cocoa nut stearine. If the quantity of neutral fat is but small, the determination of the ether value does not lead to accurate results. In such cases it is safer to saponify 20 to 50 grms. of the sample and to determine the glycerol (p. 207). The amount of glycerol multiplied by ten gives the proportion of neutral fat.

Hydrocarbons in candle material may be either due to destruction of the fatty acids having taken place in the distillation process to some extent or to admixture with paraffin wax or cerasin.

Cholesterol may be due to presence of "distilled grease stearine." These substances are detected as described p. 224.

Carnaüba wax may have been added to increase the solidifying point of the candle material (chap. xi. p. 651). It is easily detected by employing the methods given in chaps. vii. and viii.

Colouring matter will but rarely engage the attention of the analyst. At present aniline colours are used chiefly for fancy candles, and poisonous colours containing arsenic and copper have almost disappeared from candle-works.

It is also possible to decide by which process a given candle material has been prepared if the following points are borne in mind.

Saponification stearine ("saponified stearine") consists of stearic and palmitic acids, with but insignificant amounts of oleic acid.

Distillation stearine ("distilled stearine") contains considerable amounts of isooleic acid (the candle material obtained by the zinc chloride process consists chiefly of stearolactone and oleic acid).

Distilled grease stearine contains notable quantities of cholesterol (cp. also p. 691).

The determination of each of these substances has been described in chap. vii., and it may therefore suffice to state that "*distillation stearine*" has a considerable iodine number, say up to 15, due to presence of isooleic acid, and that stearolactone is detected by its constant ether value (p. 206).

The proportion of **stearic acid** is estimated by *Hehner* and *Mitchell's* method described p. 198, the amount of **oleic acid** is determined as described p. 197, and the proportion of palmitic acid is taken by difference.

By-products of the technical saponification processes are *glycerin* (cp. p. 786), *oleic acid* (cp. Wool Oils, p. 704, Textile Soaps, p. 784), and *stearine pitch*, the residue left in the stills after the fatty acids have been distilled off.

Stearine pitch[1]**—candle tar** (*Goudron*)—contains small quantities of free fatty acids and neutral fat—together about 10 per cent—and chiefly hydrocarbons due to destructive distillation. It is used for making oil gas, as a lubricant for hot neck rollers, and as insulating material for electric cables[2] by mixing with sulphur and heating from 120° to 175° C.

3. Wax Candles

The examination of wax candles is identical with that of beeswax: the reader is therefore referred to the section on "Beeswax"

[1] *Jour. Soc. Chem. Ind.* 1894, 380. [2] Eng. Pat. No. 3045, 1894.

(p. 655). As wax candles are not moulded, but "drawn," it may be advisable in some cases to peel off the several concentric layers and examine each layer separately, or at least the innermost and outermost layers.

Under the name "wax candles" a material is sometimes sold not containing any beeswax whatever; the following analysis gives the composition of a candle of this kind:—

Carnaüba wax	60 per cent.
"Stearine"	25 ,, ,,
Cerasin	15 ,, ,,

4. Sperm Candles

Sperm candles, *i.e.* candles made from "spermaceti," are at present almost exclusively used as the standard for photometrical measurements by gas examiners in this country.

Pure spermaceti cannot be employed very well for candles, the material being too brittle; beeswax, tallow, stearine, paraffin wax, and cerasin are therefore admixed with it. These admixtures are detected according to the directions given pp. 664-669.

The rules for the preparation of standard sperm candles for photometrical purposes, published by the Metropolitan Gas Referees,[1] prescribe that for the purpose of rendering spermaceti less brittle, best air-bleached beeswax, melting at or about 144° F. (62° C.), shall be used (and no other material), and that the proportion of beeswax to spermaceti shall be not less than 3 per cent, nor more than 4·5 per cent. The spermaceti itself shall be so refined as to have a melting point lying between 112° F. and 115° F. (45°-46° C.) The melting point is to be determined as follows:—

"A small portion of the spermaceti is melted by being placed in a short test-tube, the lower end of which is then plunged in hot water. A glass tube drawn out at one end into a capillary tube about 1 mm. in diameter is dipped, narrow end downwards, into the liquid spermaceti, so that when the tube is withdrawn 2 or 3 mm. of its length are filled with spermaceti, which immediately solidifies. The corresponding part of the exterior of the tube is also coated with spermaceti, which must be removed. The narrow part of the tube is then immersed in a large vessel of water of a temperature not exceeding 100° F. (37·8° C.) The lower end of the tube, which contains the spermaceti, should be three or four inches below the surface, and close to the bulb of a thermometer. The upper end of the tube must be above the surface, and the interior of the tube must contain no water. The water is then slowly heated, being at the same time briskly stirred, so that the temperature of the whole mass is as uniform as possible. When the plug of spermaceti in the tube melts, it will be forced up the tube by the pressure of the water. The temperature at the moment when this movement is observed is the melting point."

[1] *Jour. Soc. Chem. Ind.* 1894, 65.

5. Paraffin Wax Candles

Paraffin wax consists principally of a mixture of hydrocarbons, being the higher members of the ethane series, C_nH_{2n+2}.

Paraffin wax is white, translucent, crystalline, and free from taste and odour; it can be distilled unchanged.

The melting and solidifying points, as also the specific gravities of various qualities of paraffin, vary very much, according as hydrocarbons of lower or higher melting points preponderate. In commerce two brands are recognised: *hard paraffin wax* and *soft paraffin wax*. The subjoined table, due to *Tervet*,[1] gives the melting points of each of twenty successive fractions into which three paraffin waxes of the melting points given below had been resolved. The temperatures are degrees Fahrenheit.

Melting Points of Fractions obtained from Paraffin Waxes

No. of Fraction.	Of Melting Point 126° F.	Of Melting Point 111° F.	Of Melting Point 102° F.
1	119·0	103·0	94·0
2	120·0	104·0	94·0
3	120·5	104·5	95·0
4	121·0	105·0	96·0
5	121·0	106·0	96·0
6	121·0	107·0	97·5
7	121·5	107·5	98·0
8	122·0	108·0	98·5
9	122·5	108·5	99·0
10	123·0	109·0	99·0
11	124·0	110·5	100·0
12	125·0	112·0	102·0
13	126·0	113·0	103·5
14	127·0	113·5	105·0
15	128·0	114·5	106·5
16	129·0	116·0	108·0
17	130·0	117·0	109·0
18	132·0	119·0	110·0
19	134·0	123·0	112·5
20	138·0	125·0	113·0

The melting and solidifying points of paraffin waxes almost coincide.

The relation between the solidifying point of paraffin wax and its density in the solid and liquid state is shown in the following table:—

[1] *Jour. Soc. Chem. Ind.* 1887, 356.

Specific Gravity of Paraffin Waxes (Allen)[1]

No.	Origin of Sample.	Specific Gravity.		Solidifying Point.
		Solid, at 15° C.	Liquid, at 99° C.	°C.
1	Shale oil . . .	0·8666	0·7481	44·0
2	,, ,, . . .	0·8961	0·7494	47·0
3	,, ,, . . .	0·9000	0·7517	52·0
4	,, ,, . . .	0·9111	0·7572	58·5
5	American petroleum .	0·9083	0·7535	53·8
6	Ozokerit . . .	...	0·7531	61·5
7	Rangoon tar . .	0·8831	0·7571	49·0

The following table gives the specific gravities of refined American paraffin waxes, determined in the melted state at the temperatures stated :—

Specific Gravities of Melted Paraffin Waxes (I. I. Redwood)[2]

°F. at which determined.	Melting Point 108° F.	Melting Point 114° F.	Melting Point 120·5° F.	Melting Point 122·25° F.	Melting Point 122·75° F.	Melting Point 128·25° F.	Melting Point 133·25° F.
160	0·77069	0·77193	0·77391	0·77079	0·77023	0·77573	0·77723
155	0·77119	0·77330	0·77531	0·77149	0·77163	0·77653	0·77853
150	0·77309	0·77473	0·77657	0·77319	0·77283	0·77803	0·78003
145	0·77509	0·77620	0·77777	0·77519	0·77463	0·77973	0·78153
140	0·77679	0·77763	0·77847	0·77689	0·77633	0·78133	0·78333
135	0·77899	0·77953	0·78147	0·77869	0·77843	0·78303	...
130	0·78049	0·78113	0·78267	0·78029	0·77973	...	...
125	0·78199	0·78343	0·78441	...	...	...	...
120	0·78359	0·78473	...	...	...	...	...
115	0·78529	...	...	...	...	...	...

Specific Gravities of Solid Paraffin Waxes at 60° *F. (I. I. Redwood)*

Melting Point 106° F.	Melting Point 111·5° F.	Melting Point 120·5° F.	Melting Point 122·25° F.	Melting Point 125·75° F.	Melting Point 131° F.
0·87525	0·88230	0·89895	0·90105	0·90350	0·90865

The behaviour of paraffin wax with solvents has been studied by *Pawlewski* and *Filemonewicz*.[3] The following table gives the solubility at 20° C. of ozokerit paraffin, of spec. grav. 0·9170 at 20° C., melting at 64°-65° C., and solidifying at 61°-63° C. :—

[1] *Comm. Org. Anal.* vol. ii. 411. [2] *Jour. Soc. Chem. Ind.* 1889, 163.
[3] *Jour. Chem. Soc.* 1889, Abstr. 82.

Solvent.	Grms. of Ozokerit Paraffin Wax dissolved by		Weight of Solvent required to dissolve completely 1 Part of Paraffin Wax.
	100 grms.	100 c.c.	
Carbon bisulphide	12·99	...	7·6
Petroleum ether, boiling up to 75° C.; spec. grav. = 0·7233	11·73	8·48	8·5
Oil of turpentine; spec. grav. = 0·857, boiling point 158°-166° C.	6·06	5·21	16·1
Cumene comm. up to 160° C.; spec. grav. = 0·867	4·28	3·72	23·4
Cumene fraction., 150°-160° C.; spec. grav. = 0·847	3·99	3·39	25·0
Xylene comm. B.P., 135°-143° C.; spec. grav. = 0·866	3·95	3·43	25·1
Xylene fract., 136°-138° C.; spec. grav. = 0·864	4·39	3·77	22·7
Toluene comm., 108°-110° C.; spec. grav. = 0·866	3·83	3·34	26·1
Toluene fract., 108·5-109·5° C.; spec. grav. = 0·866	3·92	3·41	25·5
Chloroform	2·42	3·61	41·3
Benzene	1·99	1·75	50·3
Ethyl ether	1·95	...	50·8
Isobutyl alcohol, spec. grav. = 0·804	0·285	0·228	352·9
Acetone, 55·5°-56·5° C.; spec. grav. = 0·797	0·262	0·209	378·7
Ethyl acetate	0·238	...	419·0
Ethyl alcohol, 99·5° Tr.	0·219	...	453·6
Amyl alcohol, 127°-129° C.; spec. grav. = 0·813	0·202	0·164	495·3
Propionic acid	0·165	...	595·3
Propyl alcohol	0·141	...	709·4
Methyl alcohol, 65·5°-66·5° C.; spec. grav. = 0·798	0·071	0·056	1447·5
Methyl formate	0·060	...	1648·7
Glacial acetic acid	0·060	0·063	1668·6
Ethyl alcohol, 64·3° Tr.	0·046	...	2149·5
Acetic anhydride	0·025	...	3856·2
Formic acid (cryst.)	0·013	0·015	7689·2
Ethyl alcohol, 75° Tr.	0·0003	...	330000·0

Holde[1] records the following data :—

100 c.c. of 95·5 per cent alcohol dissolve 0·031 grm.
100 „ of 98·5 „ „ 0·029 grm.

of paraffin wax, melting point 55°-56° (origin not stated).

EXAMINATION OF THE RAW MATERIAL

In crude paraffin wax, or "scale," as the term runs, there are present varying quantities of impurities or "dirt," water, and hydrocarbons of lower melting point, consisting mostly of "soft" paraffin. The latter, being valueless to the candlemaker, is termed "oil." There

[1] *Chem. Revue*, 1897, 6.

is no sharp line of demarcation between the solid hydrocarbons and the "oil," these passing gradually through "soft" or low melting point paraffins into each other. The amount of "oil" pressed out in practical working depends naturally on various circumstances, such as temperature, pressure, length of time during which pressure is applied, and it will thus be readily understood that a laboratory test for "oil" must be an arbitrary one.

In commerce, methods of testing must, therefore, be arranged by buyer and seller.

A method of this kind agreed upon by the *Scottish Mineral Oil Association* and certain *Representative Purchasers* for the sampling and testing of scale is the following:[1]—

Sampling of Scale.—The sample is taken by means of a metal tube, slightly conical, so that a cylindrical core of paraffin is obtained. Immediately after the sample has been drawn it is thoroughly mixed, placed in suitable wide-mouthed bottles, which may be closed either with glass stoppers or good corks; if the latter are used, they should be covered with paraffin paper or soaked in melted paraffin wax before being inserted. The scale should be tightly packed into and completely fill the bottles, as otherwise partial evaporation may occur, and moisture may condense in the upper portion. The bottles are then finally sealed in the usual manner.

Determination of Dirt in Scale.—The amount of dirt (fibres of press cloths, sand, etc.) in scale is determined by melting a weighed quantity—not less than 7000 grains (453·58 grms.)—and, after subsidence, pouring off the clear paraffin. The residue is then mixed with naphtha or petroleum ether, thrown on a weighed dry filter paper, washed with naphtha or petroleum ether, dried, and weighed.

Determination of Water in Scale.—The amount of water present in scale may be determined by either of the following processes, the determination by "subsidence"[2] having been abandoned as leading to erroneous results:—

(*a*) *Distillation from a Copper Flask.*—From 1 to 2 lbs. of the scale are heated in a copper flask connected to an ordinary Liebig condenser. The flask should be about 11″ high, 8″ in diameter at the bottom, and 1¼″ at the mouth. By means of a powerful Bunsen burner the water is volatilised and then condensed, a small quantity of light oil passing over at the same time. The distillate is received in a narrow graduated measure, so that the volume of water can be readily ascertained. As a little water usually adheres to the sides of the condenser tube, this must be washed off with petroleum ether or naphtha, previously saturated with water, and added to the principal quantity.

(*b*) *Price's Company's Method.*—500 grains (32·4 grms.) of the scale to be tested are weighed in a porcelain basin, and heated with constant stirring to 230° F. (110° C.), until bubbles cease to be given off; the loss is then determined.

500 grains (32·4 grms.) of the same scale, which has been freed of

[1] *Jour. Soc. Chem. Ind.* 1891, 346. [2] Sutherland, *ibid.* 1887, 123.

its water and dirt by melting at a gentle heat and by subsidence, are heated in the same way to the same temperature for the same length of time, and the loss is determined. The loss in the second instance is now deducted from the loss in the first experiment, and the difference is taken as the quantity of water present.

Determination of Oil in Scale.—A quantity of the scale, after having been freed from water and dirt by melting and subsidence, is allowed to cool over night to a temperature of 60° F. (15·5 C.) The solid mass is then ground to a fine powder, a portion of which is used in the determination of the oil.

250 grains (16·2 grms.) of the scale, or 150 grains (9·6 grms.) in the case of the scale containing much oil, say over 7 per cent, are then wrapped in fine linen pressing cloths and a number of layers of filter paper, sufficient to absorb all the oil. The oil is then removed by pressure in a press,[1] which must have some arrangement for indicating the pressure applied.

The cup in which the scale is placed during the application of pressure must have an area of 20 square inches; the maximum pressure is to be 10 cwts. per square inch, and the working pressure 9 cwts. per square inch. The scale is to remain under pressure for fifteen minutes; the temperature of the scale and of the press is to be 60° F.

As the oil is determined on scale which has been freed from water and dirt, the result must be calculated to the original scale containing water and dirt.

Determination of the Melting (Setting) Point of Solid Paraffin.—This is determined by what is known as the "English test":—A test-tube, about 1 inch in diameter, is filled to the depth of about 2 inches with the melted paraffin, a small thermometer is inserted, and the whole steadily stirred, while the test-tube and its contents are allowed to cool slowly. The temperature at which the thermometer remains stationary for a short time is the melting (setting) point. It should be noted that paraffin wax does not exhibit the peculiarity of mixed fatty acids, viz. to remain stationary at the melting point and then to rise for a short time. With paraffin wax the mercury remains stationary at the melting point for about half a minute; but no rise takes place and the mercury then steadily falls.

The *American method* is as follows:—Compress 500 grains (32·4 grms.) of the untreated scale under a pressure of 9 tons over the whole surface of the circular press-cake,[2] five and five-eighth inches in diameter. This pressure is maintained for five minutes at the temperature of 60° F. The melting point is determined as follows:—A sufficient quantity of the scale is melted to fill three parts of a half-round dish, three and three-fourth inches in diameter. A thermometer with a round bulb is suspended in the melted mass so that

[1] No one special form of press is recommended for general adoption. A description of several forms of press is given *Jour. Soc. Chem. Ind.* 1891, 346. Cp. also Cameron-Leask, *Soap, Candles, etc.*, p. 324.

[2] This is the same pressure as that employed in the "Scotch test."

the bulb is only three-fourths immersed. The melted paraffin is then allowed to cool slowly, and the temperature at which the first indication of "filming," extending from the sides of the vessel to the thermometer, occurs, is taken as the melting point.[1]

The *German method* for testing paraffin wax (obtained from lignite), known as the "*Hallenser Vorschrift*," is the following:—

A small beaker, 7 cm. high, and 4 cm. in diameter, is filled with water and warmed to about 70° C. A small piece of the sample of paraffin wax is then thrown on the water so as to form, after melting, a bubble of about 6 mm. diameter. A centigrade thermometer,[2] made according to the directions of the "Halle Association," is then immersed in the water so that the bulb is entirely covered by water, and the mass allowed to cool slowly. The temperature at which a film is noticed on the paraffin is read off as the solidifying point.[3]

It is evident that the method of determining the solidifying point according to the American and German methods must lead to very uncertain results. The best plan would be to adopt one of the methods described above (chap. iv. p. 130). *L. Weinstein*[3] has ascertained that the results obtained by the capillary tube method are very concordant indeed.

CANDLE MATERIAL

In the Scottish Paraffin Industry scale setting below 48° C. (118° F.) is classed as soft scale. As a rule, the setting point is stipulated for. In the Saxo-Thuringian industry the candle material has, as a rule, the melting point 53°-56° C.; material of lower melting point (50°-52° C.) or higher melting point (60° C.) being but rarely employed.[4]

Paraffin wax must be mixed with a small proportion of stearic acid, from 2 to 15 per cent, to prevent the softening and bending of the candle.

The stearic acid is determined by titrating an accurately weighed quantity with normal potash, using phenolphthalein as an indicator. Each c.c. of normal potash corresponds to 0·284 grm. of stearic acid.

The melting point of a mixture of paraffin and stearic acid lies, of course, below the calculated means of the melting points of the components, just like in the case of other mixtures. The following table, due to *Scheithauer*,[4] gives the melting points of a number of mixtures of paraffin wax and stearic acid of known melting points:—

[1] Garrigues (*Jour. Soc. Chem. Ind.* 1895, 281) proposes to take this point by melting 30 to 50 grms. of the sample in a beaker, inserting the thermometer so that the bulb is completely immersed, and twirling the beaker continuously in one direction until the mercury ceases to fall or rise. At first it falls rapidly and regularly, but then more steadily at the rate of 0·1° to 0·2° C. per minute after it has reached the highest point, at which it remains stationary for about half a minute. This highest point is taken as the melting point.

[2] This thermometer is supplied by Ferd. Dehne, or J. H. Schmidt, Halle a/S.

[3] *Jour. Soc. Chem. Ind.* 1887, 567.

[4] Scheithauer, *Die Fabrikation der Mineralöle*, Braunschweig, 1895.

Paraffin Wax. Per cent.	Of Melting Point. °C.	Stearic Acid of Melting Point 54° C. Per cent.	Melting Point of Mixture. ° C.
90·0	36·5	10·0	36·5
66·6	,,	33·3	39·0
33·3	,,	66·6	45·75
10·0	,,	90·0	51·75
90·0	37·5	10·0	36·5
66·6	,,	33·3	35·5
33·3	,,	66·6	47·0
10·0	,,	90·0	52·0
90·0	40·75	10·0	39·75
66·6	,,	33·3	40·50
33·3	,,	66·6	47·50
10·0	,,	90·0	52·0
90·0	45·0	10·0	44·0
66·6	,,	33·3	40·75
33·3	,,	66·6	48·0
10·0	,,	90·0	52·5
90·0	48·5	10·0	47·5
66·6	,,	33·3	45·0
33·3	,,	66·6	47·75
10·0	,,	90·0	52·50
90·0	50·0	10·0	49·0
66·6	,,	33·3	47·0
33·3	,,	66·6	47·5
10·0	,,	90·0	52·5
90·0	54·0	10·0	53·0
66·6	,,	33·3	49·0
33·3	,,	66·6	47·0
10·0	,,	90·0	52·5
90·0	56·5	10·0	55·5
66·6	,,	33·3	52·0
33·3	,,	66·6	47·5
10·0	,,	90·0	52·5

6. Cerasin Candles

Raw Material.—The raw material used for the manufacture of cerasin is *ozokerit*, a natural bituminous product occurring in many parts of the globe in the vicinity of petroleum springs. The ozokerit

known best is found in Galicia. Formerly the ozokerit was distilled with a view to obtaining paraffin wax; at present, at any rate on the Continent, it is exclusively worked up for the preparation of cerasin.

The colour of ozokerit varies from a pure yellow to dark brown, depending on the admixed oxygenated resinous products. A rough test for specimens of great purity is that they can be kneaded between the fingers. The specific gravity varies from 0·91 to 0·97. The melting point is conditioned by the proportion of liquid hydrocarbons; therefore it is difficult to fix the lower limit of the melting point. The upper limit of about 100° C. is reached by the so-called "marble-wax." The ordinary commercial cerasins melt at 60°-75° C.; some very hard specimens ("Sprungwachs") at 75°-80° C.[1]

Pure ozokerit, *i.e.* the substance freed from water and mineral matter, varies much in its composition; it consists chiefly of hydrocarbons, but contains also oxygenated and wax-like bodies; in case the liquating process has been faulty, asphalt-like substances are also present.

Impurities naturally occurring in ozokerit are chiefly water, liquid hydrocarbons, and clay. The longer ozokerit has been kept at a temperature above 70° C., and the more carefully the liquation process has been conducted, the purer the cerasin will be. Fraudulently added impurities are: asphaltum (mineral pitch), and residues from paraffin oil distilleries.

The examination of ozokerit consists in the determination of the loss on heating to 150° C. (which should not exceed 5 per cent), of its melting and solidifying points, and of the proportion of mineral matters. For the estimation of the latter small pieces are cut from the bottom of the blocks of ozokerit and treated with petroleum ether.

Ozokerit can, therefore, only be properly valued by closely following the process of refining adopted on the large scale.

Lach[2] proceeds as follows:—100 grms. of ozokerit are treated in a tared porcelain basin with 20 grms. of fuming sulphuric acid at a temperature of 170°-180° C. with constant stirring, until no more sulphur dioxide escapes. On re-weighing, the difference gives the volatile substances, viz. water and hydrocarbons. Into the melted substance 10 grms. of animal char, previously dried at 140° C., are stirred, and the mass is allowed to cool. A tenth part of the mixture is then weighed off and put in a weighed small cylindrical filter, closed at the bottom, and extracted in a Soxhlet apparatus with petroleum ether, boiling from 60° to 80° C. The filter is dried at 130° C. and re-weighed; from the loss the percentage of wax is calculated. By evaporating the petroleum ether solution and drying the residue at 180° C. this result may be verified; the melting point of the isolated cerasin may then be ascertained.

The proportion of fuming sulphuric acid may be varied, according as the colour of the refined product is desired to be yellow or white.

The refined product is termed CERASIN.

[1] Berlinerblau, *Das Erdwachs*. Braunschweig, 1897.
[2] *Jour. Soc. Chem. Ind.* 1885, 488.

Cerasin (French, *Cérésine;* German, *Ceresin, Erdwachs*) resembles in its physical characters beeswax; it is yellow or white, and odourless. It melts between 61° and 78° C., sometimes also at a higher temperature; its specific gravity is 0·918-0·922.

Commercial cerasin is frequently coloured with turmeric and other colouring matters. On shaking the melted sample with alcohol the colouring matters pass into the alcoholic solution.

Cerasin is adulterated with "soft" paraffin and bleached colophony. An acid value of the sample may point to the presence of resin. In order to raise its melting point it is also mixed with carnaüba wax (p. 651).

Paraffin Wax is detected in cerasin by heating the sample with absolute alcohol, allowing to cool, and placing a few drops of the alcoholic solution on an object glass, when the residue will appear crystalline under the microscope.

The following table, due to *Berlinerblau*,[1] may prove of use for practical purposes:—

Cerasin. Per cent.	Paraffin. Per cent.	Melting Point. ° C.	Solidifying Point. ° C.	Specific Gravity at		
				15° C.	83°-85° C.	95° C.
100	0	70-73	69·5	0·921	0·7835	0·774
95	5	69-73	68·5	0·919		
90	10	68-72	66·5	0·9175	0·7800	
80	20	66-71·5	65·0	0·914	0·7775	
70	30	64·5-70	63·0	0·910	0·7750	
60	40	62-69	62·0	0·907		
50	50	58·5-67	60·0	0·904	0·7705	
40	60	56·5-65	59·0	0·900		
30	70	54·5-62	57·0	0·897		
20	80	52·5-58·5	54·0	0·894		
10	90	49·5-54·5	49·0	0·892		
0	100	47-52	47·0	0·889	0·7655	0·756

Other adulterants are detected by proceeding according to the processes given for the examination of beeswax (p. 664).

For a thorough examination of the unsaponifiable matter the methods described in chap. vii. (p. 229) must be used.

K. COMMERCIAL OLEIC ACID. OLEINE, ELAÏNE

Commercial oleic acid (p. 745) is in its purest state transparent, and of a yellow or light brown colour; if turbid it has a dark brown colour. The former quality is termed "pale oleine" (French,

[1] *Loc. cit.*

Oléine blonde; German, *Blondes Elaïn*); the latter "red oil." Commercial oleic acid contains notable quantities of solid fatty acids, viz. palmitic and stearic; if the oleic acid has been obtained by acid saponification (p. 746) there may be present, besides these acids, isooleic acid, and also hydrocarbons to the extent of 3 to 7 per cent. These hydrocarbons are produced by partial decomposition of the crude fatty acids during distillation; it is, therefore, possible to infer from their presence and their amount the mode of manufacture and the care exercised in distilling. But the converse, that a commercial oleic acid, if free from hydrocarbons, is a "saponified oleine," does not hold good, there being in commerce carefully prepared "distilled oleines" that are practically free from unsaponifiable matter.

Commercial oleic acid contains varying proportions of unsaponified (neutral) fat, solid fatty acids, and hydrocarbons.

The neutral fat is determined as described for commercial stearic acid; the hydrocarbons are estimated by the methods given in chap. vii., and the solid fatty acids as described p. 192.

The following table contains a few analyses of typical "oleines," as obtained in the saponification of neutral fats:—

[TABLE

Commercial Oleine from	Condition.	Colour.	Spec. Grav. at 15·5° C.	Free Fatty Acids.	Unsaponifiable.	Neutral Fat.		Iodine Value.	Observer.
						Direct.	By Difference.		
				Per cent.	Per cent.	Per cent.	Per cent.		
Tallow by autoclave process	Clear	Pale brown	0·8996	96·3	1·3	...	2·5	...	Allen
,, ,, ,,	Fluid, with slight deposit	Brown	0·9055	80·3	2·2	...	17·5	...	,,
,, ,, ,,	,, ,, ,,	Dark brown	...	88·2	...	11·5	...	...	Lewkowitsch
Tallow and palm oil (Belgian)	Clear	Dark brown	...	86·6	...	14·0	...	...	,,
,, (?) ,,	Clear	Pale brown	...	93·8	3·9	...	2·3	...	Allen
,, (?) ,,	Semi-solid	Brown	0·9085	83·7	2·9	13·4	17·0	...	,,
Autoclave oleine ,,	,,	Pale brown	0·9014	96·2	4·8	...	...	...	,,
,, ,, French .	Contained much solid	Pale brown	0·8987	84·5	10·3	3·3	2·0	...	,,
Tallow by lime saponification	...	...	...	89·4	2·0	...	8·6	...	,,
Tallow and palm oil by acid saponification . . .	Clear	Pale brown	...	92·2	3·2	...	5·6	...	Lewkowitsch
Tallow and palm oil by acid saponification . . .	Solid at 15° C.	White	...	97·8	1·0	...	1·2	...	,,
Tallow and palm oil by lime saponification . . .	Clear	Pale brown	...	94·6	2·6	3·4	...	...	,,
Tallow by autoclave process	,,	,,	...	...	...	...	...	80	,,

Other oleines obtained from waste products of the fat industries, and containing large proportions of unsaponifiable matter, have been described under the headings: "Wool Fat" (p. 691), "Cotton Seed Foots" (p. 692), and "Wool Oils" (p. 704).

If the oleine be intended for the manufacture of soap the unsaponifiable matter only need be determined, a certain proportion of solid fatty acids or of neutral fat being rather desirable than otherwise. For rapid valuation of oleine intended for soap-making it is therefore sufficient to saponify with alcoholic potash, and divide the saponification value found into 200 × 100,[1] when the percentage of saponifiable fat is obtained in sufficient approximation.

If it be required to ascertain whether a sample of oleine has been obtained from tallow only, or from a mixture of tallow with a vegetable fat, the methods described chap. ix. p. 317, may be employed.

High-class oleines for the wool industry have been stated to occasionally contain linseed oil acids, due according to *Granval* and *Valser*,[2] to admixture of linseed oil with tallow stearine in order to induce the press-cakes to part more readily with the liquid fatty acids. A somewhat considerable proportion of linseed oil fatty acids is detected by a high iodine value of the sample.

Hazura[3] proceeds as follows:—50 grms. of the sample are saponified on the water-bath with dilute alcoholic potash. The alcohol is driven off by boiling down, and the residuary soap is dissolved in 1000 c.c. of water. Into this strong alkaline solution 1000 c.c. of a 5 per cent solution of potassium permanganate are gradually run in with constant shaking. After ½ to 1 hour the hydrated manganese peroxide is filtered off, the filtrate acidified with sulphuric acid, and again filtered. The filtrate thus obtained is neutralised with caustic potash, concentrated to about 300 c.c., and again acidified with sulphuric acid, whereby a precipitate is obtained. The acid liquid and the precipitate are then shaken out with ether.

If the precipitate dissolves in ether, it consisted of pure azelaic acid, $C_9H_{16}O_4$, and the sample of oleine is free from linseed oil acids; but if the precipitate does not dissolve in ether, this may be owing to the presence of these acids. The precipitate is filtered, recrystallised several times from water or alcohol, and decolourised by animal charcoal; after drying in a desiccator its melting point is determined. If the latter be above 160° C., linseed oil acids are undoubtedly present.

If a somewhat large quantity of this oxidation product be available, its acid value may be also determined; this should not exceed 150, the acid value of hexahydroxystearic acid being 147·3.

Amagat and *Jean*[4] detect the presence of linseed oil fatty acids in oleine with the aid of the oleo-refractometer. The following are their results:—

[1] Taking 200 as the saponification value of oleic acid.
[2] *Jour. Pharm. Chem.* 1889, 232; *Jour. Soc. Chem. Ind.* 1889, 425.
[3] *Jour. Soc. Chem. Ind.* 1889, 641. [4] *Monit. Scient.* 1890, 346.

	Degrees.
Oleine from tallow or from mixed tallow and palm oil .	−36 to −34
Oleine with 10 per cent of mixed linseed oil fatty acids .	−29
,, ,, 20 ,, ,, ,, ,, .	−24
,, ,, 35 ,, ,, ,, ,, .	−23
,, ,, 40 ,, ,, ,, ,, .	−11
Mixed fatty acids from linseed oil	+29

The detection of "distilled grease oleine" in commercial oleic acid may be also effected by means of the oleo-refractometer :—

	Degrees.
Oleic acid from tallow or from mixed tallow and palm oil . .	−34
,, ,, with 10 per cent of distilled grease oleine . .	−28
,, ,, ,, 20 ,, ,, ,, ,, . . .	−23
,, ,, ,, 30 ,, ,, ,, ,, . . .	−17
,, ,, ,, 40 ,, ,, ,, ,, . . .	−11
,, ,, ,, 50 ,, ,, ,, ,, . . .	− 5
Distilled grease oleine	+25

Presence of "distilled grease oleine" is, however, detected with greater certainty by means of the cholesterol or isocholesterol reaction (p. 84).

The metallic salts of oleic acid will be mentioned under the heading "Insoluble Soaps."

L. SOAPS

It has been pointed out already (p. 33) that the metallic salts of higher fatty acids are termed *soaps*; hence we speak of potash soap, lime soap, lead soap, etc.

In particular, the term "soap" is applied to the salts of the alkali metals, and as the resinates of these metals have also the property of lathering and acting as good detergents, they are included under this generic term.

I.—Soaps of the Alkali Metals. Soaps

The commercial soaps are either *hard* or *soft* soaps, according as the base combined with the fatty acids is *soda* or *potash*.

Soaps are manufactured by boiling glycerides with caustic alkalis. In the event of the raw material being fatty acids (oleic acid, p. 768) or resin, soap-making consists, chemically speaking, in neutralising an acid by a base.

If potash be used as base, the resulting **potash soap** retains all the glycerol contained originally in the glycerides, and, on account of the chemical properties of the potash salts of the fatty acids, also

a large amount of water. Potash soaps made with the greatest care will be devoid of free alkali; as a rule, however, the commercial potash soaps contain an excess of alkali. Besides, the commercial soaps will naturally retain any impurities occurring in the fats and in the alkali used—notably sulphates, carbonates, chlorides, etc.

100 parts of neutral glycerides yield, when saponified on the large scale, 240 parts of commercial potash soap.

Soda soaps are made by saponifying glycerides with caustic soda. The older process of preparing the potash soap first, and subsequently converting it by means of common salt into soda soap, is at present only practised where cheap supplies of wood ashes admit of the economical working of this method. In practice we discern chiefly two processes for making hard soap—(1) by the "cold process," and (2) by boiling.

In the former process cocoa and palm nut oils are chiefly used, having the property of being easily saponified by strong caustic lyes in the cold (p. 538). The resulting hard soap, like potash soap, contains the entire mass of fat and alkali brought together; consequently all the glycerol formed during saponification is found in the soap.

In the second process the fats are boiled with the caustic soda lye, the resulting soap paste is "cut" by addition of salt, and by suitable treatment is brought into the form of the familiar cake or bar. The glycerol is in this case separated; and as an excess of free alkali can be easily avoided, the final product should be the pure sodium salt of fatty acids (with only small quantities of mineral salts) combined with so much water as is necessary to form commercial soap. This soap is termed "*curd soap*," "*genuine soap.*"

100 parts of neutral glycerides yield about 150 parts of finished soda soap.

The data given for the yields of soaps enable us to calculate the theoretical composition of pure commercial soaps.

Suppose a fat has been saponified, the saponification value of which is 195, or, in other words, which requires 19·5 per cent of KOH = 16·42 per cent of K_2O for saponification.

The 240 parts of potash soap obtained from 100 parts of this fat contain, of course, 16·42 parts of K_2O; therefore we have in the soap 6·843 per cent of K_2O [240 : 16·42 : : 100 : x].

Let the mean molecular weight of the fatty acids be 275; hence the corresponding amount of the fatty anhydride 275 − 9 = 266. As 47·1 parts of K_2O combine with 266 parts of fatty anhydride, we have in the soap 38·7 per cent of fatty anhydride [47·1 : 266 : : 6·843 : x]. The remainder consists of glycerol and water.

The composition of a pure potash soap should therefore be—

	Per cent.
Fatty anhydride	38·700
K_2O	6·843
Glycerol and water	54·457
	100·000

As in the course of analysis (see below) the fatty acids are isolated in their hydrated state, we should find on analysing a pure commercial potash soap 40 per cent of fatty acids [266 : 275 : : 38·7 : x].

Similarly, the composition of a pure commercial soda soap may be calculated.

100 parts of the same fat require 10·81 parts of Na_2O [47·1 : 31 : : 16·42 : x] ; consequently the finished soap contains 7·21 per cent of Na_2O [150 : 10·81 : : 100 : x], with which are combined 61·8 per cent of fatty anhydrides [31 : 266 : : 7·21 : x], corresponding to 63·9 per cent of fatty acids [266 : 275 : : 61·8 : x].

(K_2O Na_2O)

The percentage composition of a pure "curd soap" is therefore—

	Per cent.
Fatty anhydride	61·80
Na_2O	7·21
Water	30·99
	100·00

If the mean molecular weight of the fatty acids be different from 275, as in the case of, say, rape or castor oil, the result will be somewhat different. In the case of cocoa nut oil soap, made by the cold process, the soap would have the following composition, for the saponification value of a cocoa nut oil 240, and the mean molecular weight of the fatty acids 200 :—

	Per cent.
Fatty anhydride	54·50
Na_2O	8·86
Glycerol and water	36·64
	100·00

Pure commercial soda soaps made by the processes mentioned contain the proportion of water given above—which might be called their water of constitution, inasmuch as a soap cannot be made with less water—when freshly prepared. On exposure to the air, however, they lose water, and naturally the proportion of fatty acids will be found higher.

In the manufacture of good toilet soaps—**milled soaps**—the drying is carried out intentionally, and the soaps thus produced may contain as little or even less than 10 per cent of water, with a corresponding increase in the proportions of fatty anhydride and soda, which of course remain in the same ratio.

More frequently, as in low class household soaps, the proportion of water is increased with the aid of caustic alkalis or carbonates, etc. Cocoa nut oil soaps (marine soaps) in particular are able to combine with such enormous quantities of water that those soaps may contain as little as 16 to 20 per cent of true soap.

Although the nature of the fatty material plays a very important part indeed in the manufacture of soap, different fats of varying

degrees of purity being employed for soaps intended for special purposes (toilet soaps, household soaps, textile soaps, etc.), it does not frequently come within the scope of a commercial analysis to give an exhaustive report as to the nature of the fatty raw material.

In commercial analysis it is usually sufficient to estimate the **total fatty matter**, or, in short, **fatty matter**, perhaps with a further discrimination into **fatty acids, neutral fat,** and **unsaponifiable matter.** As a rule, the fatty matter is returned as **fatty acids**, if no further examination be instituted, and in the case of pure soaps, such as good household soaps, this will meet all that is required for a *rapid* valuation of the soap. Any **resin acids** present in the fatty matter are in that event looked upon as so much fatty acids, and consequently included in the fatty acids, unless a separate determination of the resin acids be desired.

The more fatty acids a sample contains the more actual soap is present. A comparison of the result of the analysis with the theoretical composition of soaps given above will render the valuation an easy matter. Any hard soap containing more than 64 per cent of fatty acids has either dried spontaneously on keeping, or has been dried artificially, as in the case of milled toilet soaps. Hard soaps containing less than that amount have been reduced intentionally, and may contain an excess of water or alkali, or any of that well-nigh endless number of adulterants that are incorporated with soap.

Almost equally important is the estimation of the quantity of the base, especially with a view to determining whether any alkali is present other than is requisite to combine with the fatty acids. Any excess of alkali beyond that quantity is objectionable in toilet and household soaps. In special cases, however, an excess of alkali is demanded, as in scouring soaps (see Textile Soaps, p. 784).

In the case of PURE ("GENUINE") SOAPS the estimation of fatty matter and alkali in its various forms will suffice for all practical purposes, and the **water** in the soap may be found by difference.

In the present condition of the soap trade, and in view of the demands made by the public taste, it is difficult to say what constitutes adulteration.

Resin is a legitimate substitute of fatty matter, the resinates of sodium possessing valuable detergent properties. **Sodium silicate** and **borate** also possess detergent properties, but these substances must be considered as standing on the border-line between legitimate constituents and adulterants.

Colouring matters in soaps cannot be considered as illegitimate, as coloured soaps are demanded in commerce. If the colouring matter be harmless no objection can therefore be raised, and the analyst will, at most, only be desired to state whether certain colouring matters contain poisonous metals or not.

Ethereal oils in soaps have almost become a necessity, even as regards better class household soaps. Their quantity will naturally

be very small, and need not, as a rule, occupy the attention of the analyst.

MEDICATED SOAPS contain ingredients which, if sold under their proper names, cannot be objected to, soap being made in those cases the most convenient vehicle for the application of medicaments to the skin. *Carbolic soap* falls under this head, as also those "superfatted" soaps which contain iodine, iodoform, etc. Where the line has to be drawn between a true and a spurious medicated soap must be left to special examination that falls outside the scope of this work. It may, however, be added, that a great many soaps stated to contain valuable medicaments are entirely devoid of them.

In TRANSPARENT SOAPS a small quantity of alcohol may be present, left in consequence of incomplete evaporation of the alcohol used in the process. If the transparency is due to presence of *sugar*, this substance must be considered an adulterant.

The number of substances that are acknowledgedly incorporated with soaps in order to impart to them some valuable properties, real or supposed, is almost legion. It must be left to the analyst to decide in each individual case whether petroleum, paraffin wax, tar oils, sulphur, etc., are to be classed amongst adulterants or not.

There can, however, be no doubt as to adulteration in the case of "fillers" or "weighting substances" having been found in soaps, these substances being added solely for the purposes of substituting a worthless material for soap. Starch, clay, talcum, chalk, barytes, fall under this category. If sand in a soap be stated or sold as such, it can, of course, not be considered a fraudulently added material.

In the following lines I describe the best methods (leaving out a number of more or less valueless processes and methods) used for the detection and estimation of the several constituents of soaps and various foreign substances, in the order of their importance as regards the purposes of commercial analysis.

No attempt is made to indicate a scheme of procedure that would include the examination for all substances that may possibly be present, as such a course would be of little practical use.

Sampling of the Soap

Great care must be exercised in sampling if gross errors are to be avoided. As pointed out already, soap exposed to the air dries on the surface, the outer portions of a cake protecting the inner portions to some extent. The sample of hard soap should therefore be taken from the centre of the cake by cutting away all the outer portions; to what extent this must be done will be seen in most cases by

inspecting the sample, a transverse section showing to what depth drying to any serious extent has taken place. Such devices as taking a sample by means of a cork borer, or by cutting a transverse slice out of the cake in order to obtain an "average" sample, lead to erroneous results. If the soap under examination be freshly made (with 30 per cent of water) the sample should be fairly large and weighed off rapidly, as it is apt to give up perceptible quantities of moisture to the dry atmosphere of the balance case, if the weighing is done slowly. For the same reason the sample should not be sliced before weighing, except perhaps in cases of a milled toilet soap or of a very dry soap.

The well-known contrivances for preventing loss of moisture during weighing are therefore best resorted to.

Similar precautions must be taken in the case of soft soap. If a barrel of potash soap has to be sampled, the soap must be taken from the centre.

Quantitative Analysis of Soap

(*a*) *Determination of Fatty Matter*

A rapid, and for the purposes of commercial analysis sufficiently accurate process is the following:—

Weigh off accurately 5 to 10 grms. of the sample (or a larger quantity, say 30 to 50 grms., on a balance sensitive to centigrammes), and dissolve in hot water in a beaker or porcelain basin by heating gently; stir continually with a glass rod so as to prevent the soap from caking on to the bottom of the vessel. When the solution is gently boiling add a few drops of methylorange, and run in gradually hydrochloric, or dilute sulphuric (or nitric acid if chlorides and sulphates are to be determined), until there is an excess of mineral acid. Heat with constant stirring until the separated fatty acids have melted into oily drops, add about 5 grms. of dry beeswax (or stearic acid) weighed accurately on a tared watch-glass (to be used again afterwards), and heat again until the mixture of fatty acid and wax has collected on the top of the liquid as a clear, transparent oily layer free from any white specks. Rinse off the glass rod, boil until the fatty matter has again collected into one mass, remove the vessel from the source of heat, and allow to solidify by cooling. A white precipitate on the bottom of the beaker will indicate the presence of silicate or "fillings" insoluble in mineral acids.

The solidified cake is then detached from the vessel by means of a platinum spatula, lifted out of the liquid, rinsed off with cold water, and placed on filter paper. Any small quantity of fatty substance adhering to the sides of the vessel is carefully scraped off and added to the cake. Dry the cake carefully with filter paper, place it on the watch-glass used before with its bottom side upwards, allow to dry in a desiccator, and weigh (or—with less accuracy—weigh

immediately after drying with filter paper, taking care that no moisture remains in any cavities of the cake). If the cake should contain any cavities (which occurs only when the fatty matter has not been boiled sufficiently), enclosing water and perhaps also acid, the cake may be remelted in a basin over water, lifted off and dried again, and heated in a tared porcelain dish over a very small flame until the crackling noise has ceased, which indicates that all moisture has been driven off.

From the weight thus found the weight of the beeswax is deducted, and the difference returned as **fatty matter.** As a rule, it is returned as **fatty acids** if no closer examination is made. This would, however, be only correct if the absence of *neutral fat*, *wax*, and *unsaponifiable matter* has been proved, *resin acids* being looked upon as so much fatty acids, unless determined separately.

The addition of beeswax may, of course, be omitted if the fatty matter will set to a solid cake on cooling. Unless this be ascertained by a preliminary experiment it will be best to add beeswax at the outset.

The determination of the **total alkali** in the soap can be conveniently combined with this process if an accurately measured volume of standard acid is used for the decomposition of the soap. The acid liquid is then filtered to separate traces of fatty acids adhering to the vessel, and the excess of acid titrated back by standard alkali (see below).

If the process given here should not be considered accurate enough, the fatty matter may be collected on a filter, as in *Hehner's* process, and further treated as has been described page 160. If the aqueous liquid contains any suspended matter, or if a precipitate has been formed, it is best to use a separating funnel, drawing off the liquid from the fatty layer, and then throwing the latter on a filter. If any foreign matter, say fibres, be noticed in the fatty matter, it is best to dissolve it in alcohol, or petroleum ether, etc., and to filter.

Any *soluble* fatty acids present will have passed partly into the acid liquid; as a rule, they may be altogether neglected, except perhaps in the case of soaps from cocoa nut and palm nut oils. In that event it is best to work with concentrated solutions, or, if convenient, to add brine or common salt, which will throw out the bulk of the soluble acids, so that the remainder may be disregarded. If the greatest accuracy be required the acid liquor is titrated with standard alkali until it is neutral to methylorange. Phenolphthalein is then added, and decinormal or half-normal alkali run in until pink. The quantity of alkali used in the second titration is calculated to, say, caprylic acid, $C_8H_{16}O_2$, molec. weight 144, and its amount added to the chief quantity found before.

A large number of processes have been recommended by various observers purporting to introduce greater accuracy, but in my opinion these unnecessarily complicate the analysis without anything being gained. Thus it has been proposed to decompose the soap in a

separating funnel, shake out with ether, and evaporate the ethereal solution containing the fatty matter, etc.

If by subsequent examination the soap has been found free from neutral fat, wax, and unsaponifiable matter (cp. 780), as is mostly the case, the fatty matter is returned as **fatty acids**. If a complete analysis of the soap is desired they must be calculated to fatty anhydrides. Since 100 parts of stearic acid, $C_{18}H_{36}O_2$, correspond to 96·83 parts of stearic anhydride, $(C_{18}H_{35}O)_2O$, and similarly 100 parts of palmitic acid, $C_{16}H_{32}O_2$, to 96·48 parts of palmitic anhydride, $(C_{16}H_{31}O)_2O$, and 100 parts of oleic acid, $C_{18}H_{34}O_2$, to 96·81 parts of oleic anhydride, $(C_{18}H_{33}O)_2O$, no appreciable error is committed if 3·25 per cent are deducted, or, what amounts to the same, the percentage of fatty acids be multiplied by 0·9675, and the result returned as fatty anhydride.

(*b*) *Total Alkali*

Total alkali is the sum of the several amounts of alkali present in the soap as (1) alkali combined with fatty (and resin) acids, (2) free caustic alkali, (3) alkali in the form of carbonate, silicate, or borate.

The total alkali is found by titration with standard acid, and is conveniently combined with the determination of the fatty matter, the indicator used being methylorange (see above (*a*)).

The alkali is calculated in the case of soft soaps as caustic potash, K_2O, and in the case of hard soaps as caustic soda, Na_2O. There may be present in hard soaps small quantities of potash, but this is, as a rule, disregarded. More frequently soft soaps contain notable proportions of soda. If a separate determination of soda and potash be required, a weighed quantity of soap is decomposed with hydrochloric acid, the acid liquor separated from the fatty acids by filtration, and the potash estimated as potassium platinic chloride in the usual way. From the amount of potash, and from the quantity of acid required to saturate the total alkali, the caustic soda is easily calculated. Of course, any other method used in mineral analysis may be employed.

(*c*) *Free Caustic Alkali and Alkaline Salts*

A preliminary test is made by dropping an alcoholic solution of phenolphthalein on a freshly cut surface of the soap. Pink colouration indicates presence of free caustic soda, and, if the soap is not too dry, also of carbonate, silicate, and borate. If the soap is very dry the last-mentioned salts cannot be thus detected. If a colouration has been obtained, any free caustic alkali is separated from the alkaline salts by dissolving a portion of the sample in absolute alcohol, and filtering. The alkaline salts remain on the filter, and the alcoholic filtrate may now be tested with phenolphthalein.

Free caustic alkali should be absent from well-made soaps, especially from toilet soaps. The "fitting" of a soap without an excess

of free alkali requiring a great deal of circumspection, most of the ordinary commercial soaps contain an excess of alkali. If this be small the free caustic soda will be converted on exposure to the atmosphere into carbonate, so that no free alkali will be found in many cases, especially if the outer portions of a cake be tested. If, however, the excess of free caustic soda in the soap be large, as notably in scouring soaps and cheap toilet soaps made by the cold process, the detection of free alkali will offer no difficulty.

It should be borne in mind that under the term free alkali frequently all that alkali is understood which is not combined with fatty acids to form true soap, so that carbonate, silicate, and borate is included in "free alkali." We understand here under free alkali free caustic alkali, thus distinguishing it from the alkaline salts.

Free caustic alkali is determined quantitatively, according to *Hope*,[1] by dissolving 30 grms. of the sample in hot alcohol, as free as possible from water. For very moist soaps absolute alcohol should be used. Highly watered soaps are best dehydrated first to some extent. The hot solution is filtered rapidly, lest any soap-jelly should separate on the filter; if the operation is carried out judiciously, a hot water funnel may be dispensed with.[2] The filter is well washed, and the filtrate received in a narrow-mouthed flask so as to prevent as much as possible contact with air. Phenolphthalein is then added to the solution, and decinormal hydrochloric acid dropped in until the colour is discharged. If no preliminary test has been made it may happen that the alcoholic solution exhibits an acid reaction to phenolphthalein at this stage. This acidity is due to the soap containing, in consequence of faulty "fitting," an acid stearate (palmitate or oleate, cp. p. 34), or to free fatty acid having been added to "kill" an excess of alkali. In either case the analytical report will state that the soap contains *free fatty acids.*

The precipitate left on the filter contains carbonate, silicate, and borate, possibly mixed with sodium chloride and sulphate,[3] and other insoluble substances, added as "fillers," such as starch, sand, clay, etc., or colouring matters, etc. For the *complete* examination of this precipitate see below. For the determination of the alkaline salts only the precipitate on the filter is washed with cold (see (*f*) 1) water, and the alkalinity of the filtrate determined by titration with standardised acid, using methylorange as indicator. The acid required is calculated to Na_2O.

We have thus determined—

(1) *Total alkali.*
(2) *Free caustic alkali.*
(3) *Alkali present as carbonate, silicate, borate.*

[1] *Chem. News*, 43 (1881), 219.

[2] *Spaeth* recommends to use Soxhlet's extractor (cp. *Jour. Soc. Chem. Ind.* 1896, 139), but in the writer's opinion his process only complicates matters.

[3] Horn, *Jour. Soc. Chem. Ind.* 1887, 681, recommends in the case of highly watered soaps to remove the greatest part of the water by preliminary drying of the sample, as otherwise carbonate (and also chloride and sulphate) passes into the filtrate.

The alkali combined with fatty (and resin) acids may now be found by difference, *i.e.* by subtracting the sum of the amounts of alkali obtained for (2) and (3) from the total alkali (1). It can, however, be found direct by titrating the alcoholic solution of the soap, after neutrality has been established to phenolphthalein, with normal acid, using methylorange as indicator. This may be done to check the results of the analysis, or in order to dispense with the determination of the alkali present as carbonate, silicate, and borate, which obviously can then be found by difference.

(*d*) *Determination of Water*

Highly watered soaps must not be dried at once at 100° C., as they melt at this temperature, and become coated with a dry skin which prevents the escape of water from the inner portions. For this reason and those mentioned under "Sampling," the method of reducing the soap to shavings, and drying on a watch-glass at first from 60°-70° C., and then to 100° C., should be abandoned in favour of one of the following processes :—

(1) Tare accurately a beaker of 100 c.c. capacity, the bottom of which is covered with recently ignited sand about half an inch high, together with a small glass rod, then weigh off in a beaker about 5 grms. of the sample, add 25 c.c. of alcohol, dissolve the soap on the water-bath with occasional stirring, evaporate the alcohol, and finally dry in an oven at 110° C. until the weight remains constant (*Gladding*).[1]

(2) A rapid, and for technical purposes sufficiently accurate process is that proposed by *Watson Smith*.[2] Heat 5-10 grms. of the sample in a large porcelain crucible on the sand-bath, stirring constantly with a glass rod (weighed with the crucible), having a roughed and jagged end, whereby the lumps formed towards the end of the operation are conveniently broken up. The drying is usually complete after twenty to thirty minutes ; all the water is expelled, when a cold watch-glass held over the crucible, after removal of the flame, is no longer bedewed with moisture. The crucible should be heated by a small flame, and care must be taken not to burn the soap ; this would be recognised by the characteristic smell.

The loss found is calculated as water, but it should be remembered that ethereal oils present in toilet soaps (and also in household soaps) volatilise with the water ; so also would alcohol (present in small quantities in some kinds of transparent soaps), and appreciable amounts of glycerol if present in notable quantities, as in some toilet soaps. Besides, if the soap contains considerable proportions of free caustic soda, part of the loss will be compensated by the absorption of carbonic dioxide.

As the sample of soap when it reaches the analyst's laboratory, as

[1] *Chem. Zeit.* 7. 568. [2] *Jour. Soc. Dyers and Colourists*, i. 31.

a rule, has lost more or less water by drying, I am of the opinion that, excepting milled toilet soaps and potash soaps and special cases, the direct determination of water in soaps is of little use, and that it is preferable to find the water by difference.

For ordinary purposes of valuation of a sample of soap the determinations described under (*a*) to (*d*) will suffice. Further tests will embrace the examination of the fatty matter, and detection and determination of other constituents of the soap, legitimate and fraudulent.

(*e*) *Examination of the Fatty Matter* ("*Soap Stock*")

If no wax has been employed in the separation of the fatty matter, the latter may be used direct for the following tests. Otherwise a fresh quantity of fatty matter must be prepared, for which purpose most conveniently the cuttings are used up.

The fatty matter may contain, besides fatty acids, (1) resin acids, (2) neutral fat, (3) unsaponifiable matter.

(1) **Resin Acids.**—Resin acids are detected qualitatively by the *Liebermann-Storch* reaction (p. 226). For their quantitative estimation *Twitchell's* method should be used (p. 244).

(2) **Neutral Fat.**—A well-made soap will but rarely contain any unsaponified fat. Sometimes, however, neutral fatty substances are added purposely to the finished soap, as in the case of the "superfatted" soaps for medicinal purposes (admixture with olive oil), or in the case of certain toilet soaps (wool wax). The neutral fat is obtained together with any unsaponifiable matter present, and must be separated from it subsequently.

The neutral fat *plus* unsaponifiable may be isolated direct from the sample of soap by dissolving a weighed quantity in water or alcohol, adding caustic potash to neutralise any free fatty acids present, using phenolphthalein as indicator, and exhausting the soap solution as directed chapter vii. p. 218; or the *dried* soap may be exhausted with solvents. About 10 grms. of the sample are weighed off, dissolved in a beaker in alcohol, and mixed with five to seven times its weight of sand, previously washed with acid and ignited. The alcohol is then evaporated off, and the dried mass transferred to a *Soxhlet* extractor and exhausted. The extract contains, besides neutral fat and unsaponifiable matter, also free fatty acids, if present. Their quantity may be determined at this stage (see above) by titration with alkali, using phenolphthalein as indicator. If the soap contains at the same time neutral fat and free caustic soda, which may occur to a notable extent in a badly made cocoa nut oil soap by the "cold process," obviously saponification will take place in the alcoholic solution, and the method becomes valueless. Considering that the weighing off of a fresh sample may, in view of the difficulty of obtaining several samples of exactly the same amount of moisture, cause considerable errors, I prefer, although

it entails a little more calculation and one more operation, to determine the neutral fat in the isolated fatty matter. To this effect the fatty matter is dissolved in alcohol, neutralised exactly, using phenolphthalein as indicator, and the solution then shaken out with ether. The residue from the ethereal solution consists of neutral fat *plus* unsaponifiable. Their separation is effected by saponification and extraction of the saponified substance (p. 218).

If unsaponifiable matter be absent the total ether residue consists of neutral fat, otherwise the neutral fat is found by difference after saponification and estimation of the unsaponifiable matter.

A complication arises if the soap contains wool wax also. If wool wax be suspected, and confirmation has been obtained by a qualitative test for cholesterol or isocholesterol, it will be best to boil the ether residue with dilute alcoholic potash on the water-bath so as to obtain part of the wool wax as unsaponifiable matter.

(3) **Unsaponifiable Matter.** — This is isolated and estimated together with neutral fat. If no neutral fat has been found the total ether residue consists of unsaponifiable matter. In the case of certain toilet soaps this may be wool wax; it will be identified by its physical characters, and chiefly by its qualitative reactions (cholesterol or isocholesterol reactions).

Other unsaponifiable substances present may be paraffin wax, vaseline, paraffin oil, oil of turpentine, tar oils, naphthalene, hydrocarbons from "distilled grease" (p. 690) and from other sources, all of which substances have been and are being mixed with soaps. Methods for their identification have been described in chapter viii.

Waxes will hardly be added to soaps, on account of the difference of price. Carnaüba wax, stated in some text-books as being usually admixed with soaps in order to render incorporation of large proportions of paraffin oil possible, is not used, as the same object may be attained by cheaper methods.

The examination of the FATTY ACIDS themselves, after separation from resin acids, neutral fat, and unsaponifiable matter, with a view to determining the nature of the "stock" the soap has been made from, is a complicated problem, which will hardly come within the scope of a commercial analysis. Still, if such a research be required, the methods detailed in chapters ix. and x. must be applied systematically, and they will, as a rule, lead, if not to strictly accurate, at any rate to approximately accurate results.

(*f*) *Substances insoluble in Alcohol*

The estimation of the total amount of substances insoluble in alcohol is conveniently combined with the determination of the free caustic alkali described under (*c*), the insoluble being collected on a tared filter previously dried at 100° C. The filter, together with the precipitate, is then dried again at 100° C., and weighed.

Good soaps will yield but insignificant traces of residue. Only those soaps which have been rendered transparent by the "alcohol process" will be absolutely free from insoluble matter.

The residue obtained on the filter may consist of—

1. Water-soluble salts, such as chloride, sulphate, carbonate, silicate, and borate of the alkalis.

2. Mineral substances insoluble in water, viz. colouring matters and "filling" and "weighting" substances, such as clay, chalk, sand, etc.

3. Organic substances, especially starch, dextrin, gelatin (carrageen mucilage).

1. **Water-soluble Substances.**—The estimation of alkali present in the form of *carbonate*, *silicate*, and *borate*, has been already described under (*c*). Cold water is used so as not to dissolve any gelatin, if present. If silicate is present this will have been noticed when decomposing the soap by acid (see above under (*a*)). The silicate may be estimated simultaneously with the fatty matter, if no other water-insoluble substance is present, or it can be determined at this stage by acidifying the neutralised (titrated) filtrate with hydrochloric acid and evaporating to dryness in the usual way. The filtrate from the separated silica may be tested for boric acid.

If boric acid is absent, it is easy to calculate from the alkali and the silica found the amounts of carbonate and silicate. If boric acid be present and the proportion of borate be also required, the water-soluble portion is best divided into three parts. In one portion the carbon dioxide is determined, in a second the silica, and the third is titrated for alkali and tested qualitatively for boric acid.[1]

Chlorides and *sulphates* are best determined in aliquot portions of the acid liquor, obtained as in (*a*) after separation of the fatty matter in the usual manner. It should be remembered that in that case, of course, nitric acid must be used to decompose the soap.

2. **The water-insoluble portion** is ignited, so as to get rid of any organic substances, and the residue weighed. The ash may be examined qualitatively and quantitatively in the usual manner.

3. **Organic Substances.**—The microscopical examination of the total residue insoluble in alcohol may furnish useful hints. *Starch* will be detected in this manner; a corroborative test may then be made with iodine. It is determined quantitatively by conversion into glucose. The residue, insoluble in alcohol, is washed with cold water to remove the water-soluble substances and *dextrin*, and boiled with dilute sulphuric acid, replacing the water as it boils away. The liquid is then neutralised with barium carbonate, filtered, and the glucose estimated by titration with *Fehling's* solution in the usual way.

Dextrin will have been washed out simultaneously with the soluble salts by cold water. The proportion of dextrin is estimated by precipitating it from the aqueous solution by means of alcohol. This is done best in a beaker, tared with a glass rod, so that the

[1] Waltke and Co.'s method, see *Jour. Soc. Chem. Ind.* 1896.

liquid may be agitated vigorously, when all the dextrin will adhere to the sides of the vessel. The aqueous liquid is then poured off, the dextrin washed with alcohol, and determined by re-weighing the beaker after drying at 100° C.

Gelatin will be dissolved by washing the alcohol-insoluble residue with hot water. The filtrate is tested for it with tannic acid.

(*g*) *Other Substances occurring in Soaps*

1. **Glycerol.**—The minute quantity of glycerol left in hard soaps, made by the boiling process, can only be determined with accuracy if a large quantity of soap be employed. It is contained in the aqueous liquid from the separated fatty matter, and may be determined as described under estimation of glycerol in spent soap-lyes (p. 809), but as a rule its determination is not required. In special cases, however, it may indicate by its amount that a hard soap has been made by the cold process, when about 5 per cent of glycerol and more will be found; its *absence* in soft soaps will prove that oleic acid has been used as "stock."

Considerable quantities of glycerol occur in certain toilet soaps, being intermixed with them in special machines; on account of its cosmetic properties, the glycerol must be considered a valuable ingredient of such soaps.

In the last-mentioned cases the glycerol is determined by dissolving the soap in water, separating the fatty matter by an acid, and filtering off. The filtrate is neutralised with barium carbonate, and boiled down to the consistency of a syrup. The residue is then extracted with a mixture of three parts of 95 per cent alcohol and of one part of ether, the alcoholic solution filtered and evaporated on the water-bath to a small bulk, and finally dried under a desiccator. The glycerol in the crude glycerin thus obtained is determined by the acetin process[1] (p. 213).

The estimation of the glycerol in the solution by the permanganate process (p. 208) may also be resorted to, but there is always the possibility that some other organic substances may be present yielding oxalic acid on oxidation.

If sugar be present at the same time, as in cheap transparent soaps, these methods are obviously useless unless the sugar be first removed (cp. 3. below).

2. **Alcohol.**—Alcohol, if present at all, is found, as a rule, in such minute quantities that it is unnecessary to determine it. If larger amounts be suspected, 50 to 60 grms. of the soap are mixed with pumice, according to *Valenta*,[2] and the alcohol distilled off by immersing the flask in a paraffin bath, heated at first to 110° C., and afterwards to 120° C. The distillate is tested for alcohol by the iodoform test, carried out, according to *Hager*, in the following manner:—Add to the liquid 5-6 c.c. of a 10 per cent caustic potash

[1] Lewkowitsch, *Chem. Zeit.* 1889, 659. [2] Jacobsen's *Repertorium*, 1884, i. 244.

solution, warm to 40°-50° C., and add a 16-20 per cent solution of potassium iodide, saturated with iodine till the liquid appears yellowish-brown. If the colour should not disappear on shaking, introduce caustic potash by means of a glass rod till discolouration just ensues. If alcohol be present yellow crystals of iodoform separate either at once or after some time; examined under the microscope they appear as hexagonal plates.

3. **Sugar** is present to a considerable extent (25 per cent) in some transparent soaps, hence its determination may be required. This is best effected by boiling the filtrate (or a measured portion of it) obtained in (*a*) with dilute sulphuric acid to invert the sugar, making alkaline, and boiling after previous dilution so as to prevent oxidation of glycerol by *Fehling's* solution. The separated Cu_2O is estimated in the usual way and calculated to sugar.

If glycerol and sugar be present conjointly, and both substances are to be estimated, separation is effected, according to *Donath* and *Mayrhofer*,[1] by adding to the solution a quantity of slaked lime sufficient to combine with the sugar present, and an equal quantity of washed and ignited sand, then boiling down to the consistency of a syrup, pulverising the residue after cooling, and exhausting it in a corked flask with 80-100 c.c. of a mixture of equal volumes of alcohol and ether. The solution will then contain all the glycerol, free from sugar, and it may be estimated as described under (*g*) 1.

4. **Carbolic Acid.**—As the use of *carbolic soap* in this country is somewhat extensive, the estimation of phenols (carbolic acid, cresylic acid) may be sometimes required. *Allen*[2] proposes the following method:—

5 grms. of the sample are dissolved in warm water, and a sufficient quantity of a 10 per cent caustic soda solution added to neutralise the phenols. The soap solution is then shaken out with ether to remove any coal-tar hydrocarbons, introduced into the soap with impure cresylic acid (their amount may be determined by evaporating the ether and weighing the residue). The alkaline liquid separated from the ether is next treated in a separating funnel with excess of strong brine, which throws out the dissolved soap as a granular mass, the sodium phenates remaining in solution. If the soap refuses to coagulate (as in presence of much resin), addition of a small quantity of dissolved tallow or palm curd will remedy the defect. The solution is separated from the soap by filtering, the soap washed on the filter with brine, and the filtrate made up to 1000 c.c. A portion of this liquid, say 100 c.c., is tested first for complete removal of soap by shaking in a separating funnel with dilute sulphuric acid, when no turbidity should appear. Standard bromine water is then run in gradually with occasional shaking, until the yellowish colouration of the liquid indicates a slight excess of bromine. The bromine solution is standardised by means of pure crystallised phenol or by cresylic acid, according as phenol or cresol is contained in the soap. In the former case the precipitated tribromophenol forms snow-white crystal-

[1] *Zeitsch. analyt. Chem.* 20. 383. [2] *The Analyst*, 1886, 103.

line flocks, whereas, in the latter case, the precipitate is milky and does not separate well from the liquid. The remaining portion of the 1000 c.c. may be boiled down to a small bulk, acidulated with sulphuric acid, and treated with a slight excess of bromine. The liquid is then shaken out repeatedly with small quantities of carbon bisulphide—5 c.c. each time—until the solvent no longer acquires a red or yellow colour, and the carbon bisulphide evaporated off, when the bromo-derivatives of the phenols remain behind. If pure crystallised phenol has been mixed with the soap, fine, long, almost colourless needles are obtained. By multiplying their weight by 0·281 the proportion of phenol is found approximately. If cresylic acid has been used the residue will be deep yellow, orange, or red, with little or no tendency to crystallise; in that case its weight need not be determined, as it would not furnish even a rough approximation to the actual quantity of cresylic acid present.[1]

In practice the writer considers the following method sufficiently accurate:—Weigh off a somewhat large amount of the sample, say 100 grms., treat as described to separate the soap, boil down the solution of the phenate to a small bulk, transfer to a stoppered measuring cylinder of 50 or 100 c.c. capacity, add sufficient salt so that some remains undissolved, and acidify with sulphuric acid. The volume of the separated phenols is then read off and the number of c.c. taken as so many grams.

Textile soaps[2] are often submitted to the analyst to obtain an opinion as to their suitability.

Soap intended for *scouring raw wool* should be devoid of free caustic alkali, as the free alkali has an injurious action on the wool, destroying its surface by pitting the scales and taking away its lustre.

Potash soap is preferable to soda soap, *cæteris paribus*. A small amount of alkaline carbonate may be permissible if the raw wool is of inferior quality. Unsaponified fat, unsaponifiable matter, resin, silicate, and "fillers" should be absent. A good many "secret powders" consist of sodium carbonate and inert substances with a minimum of palm oil soap.

Soaps for *scouring the woven woollen fabric* should fulfil the same conditions, if they are intended for best class goods. A potash soap would also be preferable to a soda soap, *cæteris paribus*.

For the scouring of low class goods, such as union goods for which mungo and shoddy are used, strongly alkaline soaps are demanded by manufacturers, and a certain amount of free caustic alkali and carbonates may be permissible under these circumstances, although it would be preferable to use a pure soap and add such

[1] Fresenius and Makin (*Jour. Soc. Chem. Ind.* 1896) modify Allen's method by distilling the "carbolic" acid off in a current of steam and estimating the phenol by Koppeschaar's method. Obviously this elaborate method will not give greater accuracy.

[2] Lewkowitsch, *Jour. Soc. Dyers and Colourists*, 1894, 42; *Jour. Soc. Chem. Ind.* 1894, 258.

quantities of alkali as are considered necessary in the special case. Silicate and resin should, however, not occur in soaps of that kind, nor should the soap contain any unsaponified fat or unsaponifiable substances.

Calico printers require a neutral soap, as any free alkali will act injuriously on the colour of the printed calico.

Soap powders, dry soaps, washing powders are mixtures of sodium carbonate with anhydrous soap reduced to a powder. They are largely adulterated with sand, sodium sulphate, and other inert substances.

II.—Insoluble Soaps (Metallic Soaps)

The metallic soaps are used for various purposes in the arts. Thus **aluminium soaps,** especially **aluminium oleate,** are employed as "oil thickeners." They are dissolved, with the aid of heat, in mineral oils, in order to impart to them a greater consistency with a view to producing oils of higher viscosity, or, as the term runs, having more "body."

Lead and **manganese** soaps are used as "driers" in the manufacture of varnish from linseed oil (cp. p. 737); **zinc, iron, nickel, cobalt,** and **chromium** soaps are employed in the manufacture of coloured varnishes, or for water-proofing leather and canvas.[1] *Lead* soaps, in their pure state, are principally used in the preparation of lead plaster.

In this class of soaps must be also included the **metallic resinates.** Manganese resinate and lead resinate are soluble in warm linseed oil; these two salts are therefore used as liquid driers (cp. p. 737). Copper resinate is used as a rust preventive and for painting ships. Lime resinate is largely employed in the manufacture of solid lubricants (p. 726).

All these soaps are prepared by double decomposition of the alkali soaps with aqueous solutions of the metallic salts.

For analytical purposes the metallic soaps are decomposed by means of a suitable mineral acid (hydrochloric, nitric, sulphuric), when the fatty acids are obtained as an oily layer, and the metal passes into the acid solution. Both the fatty acids and the acid liquor are then examined in the usual way. (Cp. also "Boiled Oil," p. 735.)

In the examination of *lead plaster* ether is the reagent employed to ascertain the origin of the fatty material. Lead plaster prepared from oleic acid is completely soluble, whereas plasters made from olive oil or lard leave, according to *Kremel*,[2] an ether residue of 17-20 and 40-50 per cent respectively.

[1] Cp. Villon, *Jour. Soc. Chem. Ind.* 1895, 802. [2] *Pharm. Post*, 20. 190.

M. GLYCERIN

Under the term "glycerin" we understand all those commercial products consisting of more or less pure "glycerol," $C_3H_8O_3$.

Glycerin is the waste product of the candle and soap industries. It is obtained originally in dilute aqueous solutions, which contain various impurities depending on the process of saponification (cp. p. 745) employed. The purest raw material results from saponification by means of lime (magnesia), or water, the most impure in the soap manufactory, notably so if the fats and oils have been saponified by means of black ash lyes. Modern processes have, however, overcome the difficulties caused by the various impurities in such a manner that, *e.g.*, chemically pure glycerins from soap-lyes and lime saponification cannot be distinguished. The glycerins obtained by the sulphuric acid saponification process retain some organic impurities which seem to have hitherto defied all attempts to remove them, as the writer has ascertained in the case of a number of "chemically pure" glycerins originating from that process.

The weak solutions of glycerol are concentrated after suitable purification, and refined by distillation in a current of superheated steam.

Ranged according to purity, the following kinds of glycerin are distinguished in commerce:—

1. Chemically pure glycerin.
2. Dynamite glycerin. Distilled glycerin.
3. Crude glycerin.

A fourth kind, *refined glycerin*, occupying an intermediate position between 2 and 3, was formerly manufactured from crude candle glycerins by treating with charcoal. It has, however, all but disappeared from the market during the last few years.

1. Chemically Pure Glycerin

Chemically pure glycerin, in its most concentrated form, should approach as nearly as possible the chemical substance "glycerol," the properties of which have been described p. 77.

Crystallised glycerin has been manufactured for some time, but its production has been abandoned latterly, owing to the high cost, the best brands of chemically pure glycerin fully equalling it, if not even surpassing it, since crystals are apt to enclose impurities.

Chemically pure glycerin is prepared by repeated distillation of a carefully refined crude material. It is manufactured in varying concentrations, discerned according to their specific gravities as *chemically pure glycerin* 1·260, *chemically pure glycerin* 1·250, etc. These glycerins should be colourless, odourless, and of a pure sweet taste, and as free

from impurities as it is possible to make a chemically pure substance on a large scale. They should, therefore, consist of glycerol and water, with only infinitesimal quantities of impurities. The preparation demanded by the Pharmacopœia is the purest commercial article.

Qualitative Tests

The following impurities should be tested for :—

(*a*) *Lime.*—A few c.c. of the sample are mixed with twice the volume of distilled water, and a few drops of a solution of ammonium oxalate added. No turbidity must appear even after violent agitation and standing for some time. A precipitate would point to the admixture with badly distilled or even with "refined glycerin."

(*b*) *Lead.*—Dilute the sample and add a solution of freshly prepared sulphuretted hydrogen, and afterwards some acetic acid. Ammonium sulphide, if used instead of sulphuretted hydrogen, would also indicate iron, insignificant traces of which cannot be objected to.

(*c*) *Arsenic.*—This metal should be wholly absent. It should be borne in mind that, once arsenic has found its way into glycerin, it cannot be removed by the usual processes of refining,[1] as glycyl arsenite, $AsO_3(C_3H_5)$, the substance formed when arsenious acid is dissolved in glycerin, distils over with the latter. Hence many commercial brands are contaminated with arsenic, some to such an extent that they are decidedly harmful when used for medicinal preparations, or are otherwise taken inwardly.

Marsh's well-known test for arsenic is not sensitive enough, and it is better to substitute for it *Gutzeit's* test, which combines with greater accuracy the advantage of rapidity.

Place 1 c.c. of the sample in a high test-tube, add some zinc, free from arsenic, and a few c.c. of pure dilute sulphuric acid. The test-tube is then covered with a tightly fitting cap of filtering paper, two or three layers thick, the innermost layer having been previously moistened, by the aid of a glass rod, with a 50 per cent solution of silver nitrate. In presence of arsenic arseniuretted hydrogen is given off. After ten minutes' standing the paper cap is taken off and examined. No deep yellow stain must be noticeable on the inner fold, a slight yellowish colouration only being permissible. This test is so extremely sensitive, that it is absolutely necessary to make side by side with it a blank test, using the same reagents. The silver nitrate test is almost too delicate (although there are commercial glycerins which will not show any colouration after ten minutes), and has therefore been replaced by less rigorous tests. A glycerin may be considered as free from arsenic if no yellow colouration appears after ten minutes, if in *Gutzeit's* test a concentrated solution of mercury bichloride is substituted for silver nitrate. In case

[1] Lewkowitsch, *Year-Book of Pharmacy*, 1890, 380.

the latter reagent be used, hydrochloric acid may be employed instead of sulphuric acid. With silver nitrate hydrochloric acid is objectionable, as hydrochloric acid gas may possibly be given off if the liquid becomes too hot.

Nagelwoort has stated recently [1] that coal gas, or even the quality of filter paper, may affect the test, and recommends therefore to conduct the current of hydrogen and arseniuretted hydrogen over powdered silver nitrate placed in a U tube between two plugs of slag wool. This is an unnecessary complication of a simple test.

It should, however, be noted that sulphuretted hydrogen, evolved if sulphides be present, also produces a yellow stain. In order to exclude errors sulphides must be oxidised to sulphates. I test for presence of sulphides by proceeding, as in *Gutzeit's* test, but substituting a paper cap moistened with lead acetate instead of silver nitrate; a black stain points to sulphides.

(*d*) *Chlorine.*—Mix a few c.c. of the sample with twice the volume of pure water, acidify with nitric acid, and add a solution of silver nitrate; no turbidity must then appear.

(*e*) *Iron.*—Tested with a solution of tannic acid no bluish colouration must appear.

(*f*) *Ash.*—The last traces of metals (iron, copper) cannot be removed from a product manufactured on a large scale. The determination of the ash in a sample will prove whether the permissible minimum has been exceeded.

The table given p. 790 shows the amounts of ash found in chemically pure glycerins of commerce.

(*g*) *Organic impurities.*[2]—These impurities are due to faulty manufacture, and may either consist of *acrolein* and volatile fatty acids, as *butyric acid*, or of substances having a higher boiling point than glycerol itself. The latter substances may be comprised under the name *polyglycerols.*

A rapid "practical" test for volatile fatty acids is to spread a few drops of the sample on the back of the hand, and rub it gently into the skin. No smell of acrolein or butyric acid should be then noticeable. A better method is to mix the sample with alcohol and concentrated sulphuric acid, when in presence of butyric acid the characteristic smell of pine apples, due to ethyl butyrate, will be noticed at once.

Acrolein, as also other reducing substances, is best detected by adding a few drops of a silver nitrate solution to the aqueous solution of glycerin. No blackening or browning should appear after standing for twenty-four hours at the ordinary temperature.

The German Pharmacopœia, edit. iii., prescribes the silver test in the following form:—Heat 1 c.c. of glycerin with 1 c.c. of ammonia to boiling and add three drops of silver nitrate solution. No discolouration should be noticeable within five minutes.

This test was originally intended to detect presence of arsenic, but

[1] *Pharm. Rund.* 1894, 109.

[2] Lewkowitsch, *Year-Book of Pharmacy*, 1890, 382.

is absolutely unreliable for this purpose. It is also worthless for the detection of other impurities, as it depends so much on the mode of operating, that on the one hand an impure glycerin, one even that has not been distilled, may conform to the test, whereas on the other hand a pure glycerin may have to be rejected. At the temperature of boiling water a mixture of glycerol and silver nitrate *does* become reduced at once on addition of ammonia (p. 82). If the enormous excess of ammonia is mixed with glycerol, according to the directions of the Pharmacopœia, ebullition of the liquid may take place before the temperature of 100° C. is reached, and in that case silver nitrate subsequently added will not be reduced.

This method should therefore be abandoned,[1] or, at any rate, used with great caution.

From these remarks it will be understood that the silver nitrate test described, viz. addition of silver nitrate in the cold, can be made far more sensitive if, instead of neutral silver nitrate, an ammoniacal silver nitrate solution be used in the cold. Even the minutest traces of organic impurities, such as acrolein, may be thus detected.

Acrolein may be also detected by means of *Schiff's* reagent. This is prepared by dissolving 1 grm. of magenta crystals in a 1000 c.c. flask in about 700 c.c. of water, adding 10 grms. of sodium bisulphite previously dissolved in 100 c.c. of water and 15 c.c. of strong hydrochloric acid, and finally making up to 1000 c.c. The test is made by placing a few c.c. of the sample in a test-tube, and carefully pouring on to it, so that no mixing takes place, a few c.c. of the reagent. No violet-coloured zone should appear between the two layers.

(*h*) *Sugar.*—Adulteration of glycerin with sugar (cane sugar or glucose) does occur when glycerin is high in price. The presence of sugars is detected by the polarimeter.

Quantitative Tests

The *polyglycerols* are tested for[2] by allowing an accurately weighed quantity of the sample to evaporate gently at 160° C. Care should be taken not to heat too rapidly, otherwise even the purest glycerin may become polymerised with the production of that very substance that is to be detected. From the weight of the residue the weight of ash, subsequently found on incineration, must be deducted. The difference (the "organic residue") gives a fair indication as to the care with which the glycerin has been manufactured,

The following table gives the "organic residue" and ash of a number of "chemically pure glycerins" examined in the writer's laboratory,[2] and arranged according to the amount of organic residue :—

[1] It may be added here that the Pharmacopœia test has met with a strenuous objection on the part of a number of German glycerin manufacturers, who declared in a circular that they could not supply an article satisfying the Pharmacopœia test.

[2] Cp. Lewkowitsch, *Year-Book of Pharmacy*, 1890, 382.

No.	Residue at 160° C.	Ash.	Organic Residue.
	Per cent.	Per cent.	Per cent.
1	0·03033	0·00603	0·0243
2	0·0276	0·00300	0·0246
3	0·0377	0·005	0·0327
4	0·0498	0·0138	0·0360
5	0·0452	0·0081	0·0371
6	0·0509	0·0066	0·0443
7	0·0656	0·0139	0·0517
8	0·0748	0·0140	0·0738
9	0·0905	0·0154	0·0751
10	0·1047	0·0190	0·0857
11	0·1236	0·0305	0·0931
12	0·1621	0·0183	0·1438
13	0·8060	0·2090	0·5970

Rules for the valuation of commercial chemically pure glycerins may be derived from this table. The first seven samples certainly deserve the name of chemically pure glycerin, the following four samples represent lower qualities unfit for pharmaceutical purposes, whereas the last two samples are simply glycerins refined by distillation; the last sample would be rejected as unsuitable even by dynamite makers.

Sample No. 2 represents chemically pure glycerin manufactured by the writer on a large scale from soap-lye glycerin.

The **percentage of glycerol** in a sample may be determined either by physical or chemical methods.

A. Physical Methods

(*a*) **Specific Gravity.**—Tables for the specific gravities of aqueous solutions of glycerin have been given by *Fabian*, *Metz*, *Schweikert*, *a.o.* The most accurate numbers are those published by *Lenz*,[1] *Strohmer*,[2] *Gerlach*,[3] *Skalweit*,[4] and *Nicol*.[5]

The following tables contain the numbers of *Lenz*, *Strohmer*, *Gerlach*, and *Nicol*; those given by *Skalweit* will be found on p. 796.

[1] *Zeitsch. analyt. Chem.* 19. 302. [2] *Monatshefte für Chemie*, 5. 61.
[3] *Chemische Industrie*, 7. 281. [4] *Repert. analyt. Chem.* 5. 18.
[5] *Pharm. Jour. and Transact.* 1887. 297.

[TABLE

Specific Gravities of Aqueous Solutions of Glycerin

Glycerol. Per cent.	Lenz.	Strohmer.	Gerlach.		Nicol.
	Spec. Grav. at 12°-14° C. Water at 12° C. = 1.	Spec. Grav. at 17·5° C. Water at 17·5° C. = 1.	Spec. Grav. at 15° C. Water at 15° C. = 1.	Spec. Grav. at 20° C. Water at 20° C. = 1.	Spec. Grav. at 20° C. Water at 20° C. = 1.
100	1·2691	1·262	1·2653	1·2620	1·26348
99	1·2664	1·259	1·2628	1·2594	1·26091
98	1·2637	1·257	1·2602	1·2568	1·25832
97	1·2610	1·254	1·2577	1·2542	1·25572
96	1·2584	1·252	1·2552	1·2516	1·25312
95	1·2557	1·249	1·2526	1·2490	1·25052
94	1·2531	1·246	1·2501	1·2464	1·24790
93	1·2504	1·244	1·2476	1·2438	1·24526
92	1·2478	1·241	1·2451	1·2412	1·24259
91	1·2451	1·239	1·2425	1·2386	1·23990
90	1·2425	1·236	1·2400	1·2360	1·23720
89	1·2398	1·233	1·2373	1·2333	1·23449
88	1·2372	1·231	1·2346	1·2306	1·23178
87	1·2345	1·228	1·2319	1·2279	1·22907
86	1·2318	1·226	1·2292	1·2252	1·22636
85	1·2292	1·223	1·2265	1·2225	1·22365
84	1·2265	1·220	1·2238	1·2198	1·22094
83	1·2238	1·218	1·2211	1·2171	1·21823
82	1·2212	1·215	1·2184	1·2144	1·21552
81	1·2185	1·213	1·2157	1·2117	1·21281
80	1·2159	1·210	1·2130	1·2090	1·21010
79	1·2122	1·207	1·2102	1·2063	1·20739
78	1·2106	1·204	1·2074	1·2036	1·20468
77	1·2079	1·202	1·2046	1·2009	1·20197
76	1·2042	1·199	1·2018	1·1982	1·19925
75	1·2016	1·196	1·1990	1·1955	1·19653
74	1·1999	1·193	1·1962	1·1928	1·19381
73	1·1973	1·190	1·1934	1·1901	1·19109
72	1·1945	1·188	1·1906	1·1874	1·18837
71	1·1918	1·185	1·1878	1·1847	1·18565
70	1·1889	1·182	1·1850	1·1820	1·18293
69	1·1858	1·179	...	...	1·18020
68	1·1826	1·176	...	...	1·17747
67	1·1795	1·173	...	...	1·17474
66	1·1764	1·170	...	...	1·17201
65	1·1733	1·167	1·1711	1·1685	1·16928
64	1·1702	1·163	...	...	1·16654
63	1·1671	1·160	...	...	1·16380
62	1·1640	1·157	...	...	1·16107
61	1·1610	1·154	...	...	1·15834
60	1·1582	1·151	1·1570	1·1550	1·15561
59	1·1556	1·149	...	...	1·15288
58	1·1530	1·146	...	...	1·15015
57	1·1505	1·144	...	...	1·14742
56	1·1480	1·142	...	...	1·14469
55	1·1455	1·140	1·1430	1·1415	1·14196
54	1·1430	1·137	...	...	1·13923
53	1·1403	1·135	...	...	1·13650
52	1·1375	1·133	...	...	1·13377
51	1·1348	1·130	...	...	1·13104
50	1·1320	1·128	1·1290	1·1280	1·12831
45	1·1183	...	1·1155	1·1145	1·11469
40	1·1045	...	1·1020	1·1010	1·10118
35	1·0907	...	1·0885	1·0875	1·08786
30	1·0771	...	1·0750	1·0740	1·07469
25	1·0635	...	1·0620	1·0610	1·06166
20	1·0498	...	1·0490	1·0480	1·04884
15	1·0374	...	...	...	1·03622
10	1·0245	...	1·0245	1·0235	1·02391
5	1·0123	...	...	...	1·01184
0	1·0000	...	1·0000	1·0000	1·00000

Lenz has made his determinations with a sample of chemically pure glycerin, the glycerol in which had been estimated by ultimate analysis. *Strohmer* employed crystallised glycerin freed from water by pressing repeatedly between folds of filter paper. *Gerlach*, again, prepared his most concentrated glycerin by boiling down chemically pure glycerin 1·220, until its boiling point remained constant at 290° C.

The specific gravities of aqueous solutions for each degree below 50 per cent are given in the tables pp. 795, 796.

Specific gravities found at temperatures other than those mentioned in the table may be corrected by reference to the following table, due to *Gerlach* :—

Expansion of Aqueous Solutions of Glycerin. Volume at 0° C. = 10,000

Glycerol	Volume at 0° C.	Volume at 10° C.	Volume at 20° C.	Volume at 30° C.
Per cent.				
0	10,000	10,001·3	10,016·0	10,041·5
10	10,000	10,010	10,030	10,059
20	10,000	10,020	10,045	10,078
30	10,000	10,025	10,058	10,097
40	10,000	10,030	10,067	10,11[illegible]
50	10,000	10,034	10,076	10,124
60	10,000	10,038	10,084	10,133
70	10,000	10,042	10,091	10,143
80	10,000	10,043	10,092	10,144
90	10,000	10,045	10,095	10,148
100	10,000	10,045	10,090	10,150

The numbers for intermediate temperatures are found by interpolation. For temperatures lying between 15° and 20° C. the specific gravity can be calculated from the numbers given in *Gerlach's* table (p. 791) by means of the following formula :—

$$s_t = s_1 + \frac{t-15}{5}(s_2 - s_1),$$

where

s_1 is the specific gravity of the glycerin at 15° C. Water at 15° C. = 1.
s_2 ,, ,, ,, 20° C. ,, 20° C. = 1.
s_t ,, ,, ,, t° C. ,, t° C. = 1.

A few of the numbers contained in the table p. 791 have been controlled by *Morawski*[1] by means of ultimate analysis. His results show that *Lenz's* figures are, as a rule, a little too low, those of *Strohmer* a little too high, whereas *Gerlach's* and *Skalweit's* values agree both amongst themselves and with the results of elementary analysis.

[1] *Jour. Soc. Chem. Ind.* 1889, 424.

The specific gravity of the sample is taken in the usual manner, using one of the methods described page 124. In the case of the most concentrated glycerin a slight complication arises, inasmuch as air bubbles easily become entangled, which rise only very slowly in the viscous liquid at the ordinary temperature. Thus if the hydrostatic balance be used, as is stipulated in many contracts (especially for dynamite glycerin, p. 802), the determination may take hours, if the glycerin has not been poured into the cylinder carefully, allowing the substance to flow along the side of the vessel.

Hehner[1] recommends to fill a *Sprengel* tube with the glycerin at a higher temperature than the ordinary with the aid of the filter-pump, and then to immerse the tube in water of the normal temperature; for any other temperature a correction of 0·00058 for each degree centigrade must be made. By means of this factor *Richmond* has calculated *Lenz's* table to 15·5° C.—

Glycerol.	Specific Gravity at 15·5° C.	Glycerol.	Specific Gravity at 15·5° C.
Per cent.		Per cent.	
100	1·2674	87	1·2327
99	1·2647	86	1·2301
98	1·2620	85	1·2274
97	1·2594	84	1·2248
96	1·2567	83	1·2222
95	1·2540	82	1·2196
94	1·2513	81	1·2169
93	1·2486	80	1·2143
92	1·2460	79	1·2117
91	1·2433	78	1·2090
90	1·2406	77	1·2064
89	1·2380	76	1·2037
88	1·2353	75	1·2011

The writer prefers the following method:—The sample is warmed in a closed bottle by immersing in warm water until all air bubbles have risen to the top. The glycerin is then allowed to cool in the closed bottle, preferably to the normal temperature, and then carefully filled into the ordinary specific bottle provided with a perforated stopper. If this has been pushed home, after the last filling up, the very small drop of glycerin squeezed out is wiped off with a linen cloth, and the bottle taken out of the water-bath. A number of comparative experiments, those made with the *Sprengel* tube being used as the standard, has proved that the specific gravities are correct to the fourth decimal if the weights are reduced to vacuum. Any complicated calculation is avoided by determining once for all the necessary corrections for the picnometer when filled with water. Suppose the weight p has been found in air, then the corrected weight, P, will be

$$P = p + pR.$$

[1] *Jour. Soc. Chem. Ind.* 1889, 8.

If brass weights are used, the correction, R, for the specific gravities likely to occur is found in the following table :[1]—

Correction for Weights in Vacuo

Specific Gravity.	R.
1·00	0·00106
1·02	0·00103
1·04	0·00101
1·06	0·00099
1·08	0·00097
1·10	0·00095
1·15	0·00090
1·20	0·00086
1·25	0·00082
1·30	0·00078

(*b*) **Refractive Index.**—If a refractometer be available, the glycerol in the sample can be determined very rapidly and with very great accuracy. The refractometric constant is found in a shorter time than that at which a specific gravity determination can be made. It has the further advantage that only one drop is required.

The values given in the following tables, due to *Lenz*, *Strohmer*, and *Skalweit*, have been determined with *Abbe's* refractometer. Of course, the butyro-refractometer (p. 116) may also be used. According to *Lenz*, the several observations agree amongst each other to a few units of the fourth decimal, whilst the difference in the refractive indices corresponding to 1 per cent of glycerin amounts to 13·5 units of the fourth decimal. By reference to the tables, the percentage of glycerol in a sample can therefore be determined accurately to about 0·5 per cent.

[1] Landolt, *Optisches Drehungsvermögen*, p. 131.

Specific Gravities and Refractive Indices of Aqueous Solutions of Glycerin (Lenz)

Glycerol.	Sp. Gr. at 12°-14° C.	Ref. Ind. at 12·5°-12·8° C.	Glycerol.	Sp. Gr. at 12°-14° C.	Ref. Ind. at 12·5°-12·8° C.	Glycerol.	Sp. Gr. at 12°-14° C.	Ref. Ind. at 12·5°-12·8° C.
Per cent.			Per cent.			Per cent.		
100	1·2691	1·4758	66	1·1764	1·4249	32	1·0825	1·3745
99	1·2664	1·4744	65	1·1733	1·4231	31	1·0798	1·3732
98	1·2637	1·4729	64	1·1702	1·4213	30	1·0771	1·3719
97	1·2610	1·4715	63	1·1671	1·4195	29	1·0744	1·3706
96	1·2584	1·4700	62	1·1640	1·4176	28	1·0716	1·3692
95	1·2557	1·4686	61	1·1610	1·4158	27	1·0689	1·3679
94	1·2531	1·4671	60	1·1582	1·4140	26	1·0663	1·3666
93	1·2504	1·4657	59	1·1556	1·4126	25	1·0635	1·3652
92	1·2478	1·4642	58	1·1530	1·4114	24	1·0608	1·3639
91	1·2451	1·4628	57	1·1505	1·4102	23	1·0580	1·3626
90	1·2425	1·4613	56	1·1480	1·4091	22	1·0553	1·3612
89	1·2398	1·4598	55	1·1455	1·4079	21	1·0525	1·3599
88	1·2372	1·4584	54	1·1430	1·4065	20	1·0498	1·3585
87	1·2345	1·4569	53	1·1403	1·4051	19	1·0471	1·3572
86	1·2318	1·4555	52	1·1375	1·4036	18	1·0446	1·3559
85	1·2292	1·4540	51	1·1348	1·4022	17	1·0422	1·3546
84	1·2265	1·4525	50	1·1320	1·4007	16	1·0398	1·3533
83	1·2238	1·4511	49	1·1293	1·3993	15	1·0374	1·3520
82	1·2212	1·4496	48	1·1265	1·3979	14	1·0349	1·3507
81	1·2185	1·4482	47	1·1238	1·3964	13	1·0332	1·3494
80	1·2159	1·4467	46	1·1210	1·3950	12	1·0297	1·3480
79	1·2122	1·4453	45	1·1183	1·3935	11	1·0271	1·3467
78	1·2106	1·4438	44	1·1155	1·3921	10	1·0245	1·3454
77	1·2079	1·4424	43	1·1127	1·3906	9	1·0221	1·3442
76	1·2042	1·4409	42	1·1100	1·3890	8	1·0196	1·3430
75	1·2016	1·4395	41	1·1072	1·3875	7	1·0172	1·3417
74	1·1999	1·4380	40	1·1045	1·3860	6	1·0147	1·3405
73	1·1973	1·4366	39	1·1017	1·3844	5	1·0123	1·3392
72	1·1945	1·4352	38	1·0989	1·3829	4	1·0098	1·3380
71	1·1918	1·4337	37	1·0962	1·3813	3	1·0074	1·3367
70	1·1889	1·4321	36	1·0934	1·3798	2	1·0049	1·3355
69	1·1858	1·4304	35	1·0907	1·3785	1	1·0025	1·3342
68	1·1826	1·4286	34	1·0880	1·3772			
67	1·1795	1·4267	33	1·0852	1·3758			

[TABLE

Specific Gravities and Refractive Indices of Aqueous Solutions of Glycerin (Strohmer)

Glycerol. Per cent.	Sp. Gr. at 17·5° C.	Ref. Ind. at 17·5° C.	Glycerol. Per cent.	Sp. Gr. at 17·5° C.	Ref. Ind. at 17·5° C.	Glycerol. Per cent.	Sp. Gr. at 17·5° C.	Ref. Ind. at 17·5° C.
100	1·262	1·4727	83	1·218	1·4478	66	1·170	1·4206
99	1·259	1·4710	82	1·215	1·4461	65	1·167	1·4189
98	1·257	1·4698	81	1·213	1·4449	64	1·163	1·4167
97	1·254	1·4681	80	1·210	1·4432	63	1·160	1·4150
96	1·252	1·4670	79	1·207	1·4415	62	1·157	1·4133
95	1·249	1·4653	78	1·204	1·4398	61	1·154	1·4116
94	1·246	1·4636	77	1·202	1·4387	60	1·151	1·4099
93	1·244	1·4625	76	1·199	1·4370	59	1·149	1·4087
92	1·241	1·4608	75	1·196	1·4353	58	1·146	1·4070
91	1·239	1·4596	74	1·193	1·4336	57	1·144	1·4059
90	1·236	1·4579	73	1·190	1·4319	56	1·142	1·4048
89	1·233	1·4563	72	1·188	1·4308	55	1·140	1·4036
88	1·231	1·4551	71	1·185	1·4291	54	1·137	1·4019
87	1·228	1·4534	70	1·182	1·4274	53	1·135	1·4008
86	1·226	1·4523	69	1·179	1·4257	52	1·133	1·3997
85	1·223	1·4506	68	1·176	1·4240	51	1·130	1·3980
84	1·220	1·4489	67	1·173	1·4223	50	1·128	1·3969

Specific Gravities and Refractive Indices of Aqueous Solutions of Glycerin (Skalweit)

Glycerol. Per cent.	Sp. Gr. at 15° C.	$n_{[D]}$[1] at 15° C.	Glycerol. Per cent.	Sp. Gr. at 15° C.	$n_{[D]}$ at 15° C.	Glycerol. Per cent.	Sp. Gr. at 15° C.	$n_{[D]}$ at 15° C.
0	1·0000	1·3330	34	1·0858	1·3771	68	1·1799	1·4265
1	1·0024	1·3342	35	1·0885	1·3785	69	1·1827	1·4280
2	1·0048	1·3354	36	1·0912	1·3799	70	1·1855	1·4295
3	1·0072	1·3366	37	1·0939	1·3813	71	1·1882	1·4309
4	1·0096	1·3378	38	1·0966	1·3827	72	1·1909	1·4324
5	1·0120	1·3390	39	1·0993	1·3840	73	1·1936	1·4339
6	1·0144	1·3402	40	1·1020	1·3854	74	1·1963	1·4354
7	1·0168	1·3414	41	1·1047	1·3868	75	1·1990	1·4369
8	1·0192	1·3426	42	1·1074	1·3882	76	1·2017	1·4384
9	1·0216	1·3439	43	1·1101	1·3896	77	1·2044	1·4399
10	1·0240	1·3452	44	1·1128	1·3910	78	1·2071	1·4414
11	1·0265	1·3464	45	1·1155	1·3924	79	1·2098	1·4429
12	1·0290	1·3477	46	1·1182	1·3938	80	1·2125	1·4444
13	1·0315	1·3490	47	1·1209	1·3952	81	1·2152	1·4460
14	1·0340	1·3503	48	1·1236	1·3966	82	1·2179	1·4475
15	1·0365	1·3516	49	1·1263	1·3981	83	1·2206	1·4490
16	1·0390	1·3529	50	1·1290	1·3996	84	1·2233	1·4505
17	1·0415	1·3542	51	1·1318	1·4010	85	1·2260	1·4520
18	1·0440	1·3555	52	1·1346	1·4024	86	1·2287	1·4535
19	1·0465	1·3568	53	1·1374	1·4039	87	1·2314	1·4550
20	1·0490	1·3581	54	1·1402	1·4054	88	1·2341	1·4565
21	1·0516	1·3594	55	1·1430	1·4069	89	1·2368	1·4580
22	1·0542	1·3607	56	1·1458	1·4084	90	1·2395	1·4595
23	1·0568	1·3620	57	1·1486	1·4099	91	1·2421	1·4610
24	1·0594	1·3633	58	1·1514	1·4104	92	1·2447	1·4625
25	1·0620	1·3647	59	1·1542	1·4129	93	1·2473	1·4640
26	1·0646	1·3660	60	1·1570	1·4144	94	1·2499	1·4655
27	1·0672	1·3674	61	1·1599	1·4160	95	1·2525	1·4670
28	1·0698	1·3687	62	1·1628	1·4175	96	1·2550	1·4684
29	1·0724	1·3701	63	1·1657	1·4190	97	1·2575	1·4698
30	1·0750	1·3715	64	1·1686	1·4205	98	1·2600	1·4712
31	1·0777	1·3729	65	1·1715	1·4220	99	1·2625	1·4728
32	1·0804	1·3743	66	1·1743	1·4235	100	1·2650	1·4742
33	1·0831	1·3757	67	1·1771	1·4250			

[1] $n_{[D]}$ is the refractive index for the sodium line D.

It must be distinctly understood that the refractive indices are accurate only for the temperatures stated, the indices varying with the temperature, as may be gathered from the following table :—

Specific Gravity.	Variation of Refractive Index for 1° C.	Observer.
1·25350	0·00032	Listing
1·24049	0·00025	Van der Willigen
1·19286	0·00023	,,
1·16270	0·00022	,,
1·11463	0·00021	,,

The variation in the case of pure water is 0·00008 for 1° C.

With a view to eliminating slight errors due to the adjustment of the instrument, and to reduce the influence of temperature, *Lenz* recommends to take, immediately after the sample has been examined, the refractive index of water, having, of course, the same temperature. Thus the numbers of the following table have been obtained :—

Difference between Refractive Indices of Aqueous Solutions of Glycerin and Pure Water (Lenz)

Glycerol	$n_{[D]}$ Glycerol − $n_{[D]}$ Water.	Glycerol	$n_{[D]}$ Glycerol − $n_{[D]}$ Water.	Glycerol	$n_{[D]}$ Glycerol − $n_{[D]}$ Water.	Glycerol	$n_{[D]}$ Glycerol − $n_{[D]}$ Water.
Per cent.		Per cent.		Per cent.		Per cent.	
100	0·1424	74	0·1046	48	0·0645	22	0·0288
99	0·1410	73	0·1032	47	0·0630	21	0·0275
98	0·1395	72	0·1018	46	0·0616	20	0·0261
97	0·1381	71	0·1003	45	0·0601	19	0·0238
96	0·1366	70	0·0987	44	0·0587	18	0·0225
95	0·1352	69	0·0970	43	0·0572	17	0·0212
94	0·1337	68	0·0952	42	0·0556	16	0·0199
93	0·1323	67	0·0933	41	0·0541	15	0·0186
92	0·1308	66	0·0915	40	0·0526	14	0·0173
91	0·1294	65	0·0897	39	0·0510	13	0·0160
90	0·1279	64	0·0889	38	0·0495	12	0·0146
89	0·1264	63	0·0861	37	0·0479	11	0·0133
88	0·1250	62	0·0842	36	0·0464	10	0·0120
87	0·1235	61	0·0824	35	0·0451	9	0·0108
86	0·1221	60	0·0806	34	0·0438	8	0·0096
85	0·1206	59	0·0792	33	0·0424	7	0·0083
84	0·1191	58	0·0780	32	0·0411	6	0·0071
83	0·1177	57	0·0768	31	0·0398	5	0·0058
82	0·1162	56	0·0757	30	0·0385	4	0·0046
81	0·1148	55	0·0745	29	0·0372	3	0·0033
80	0·1133	54	0·0731	28	0·0358	2	0·0021
79	0·1119	53	0·0717	27	0·0345	1	0·0008
78	0·1104	52	0·0702	26	0·0332	0	0·0000
77	0·1090	51	0·0688	25	0·0318		
76	0·1075	50	0·0663	24	0·0315		
75	0·1061	49	0·0659	23	0·0302		

(*c*) **Vapour Tension.**—The percentage of glycerol in aqueous solutions may be also estimated by the tension of the vapour given off.

Gerlach has designed for this purpose the vaporimeter[1] shown in Fig. 48. It consists of the hollow cylinder A, made of copper or

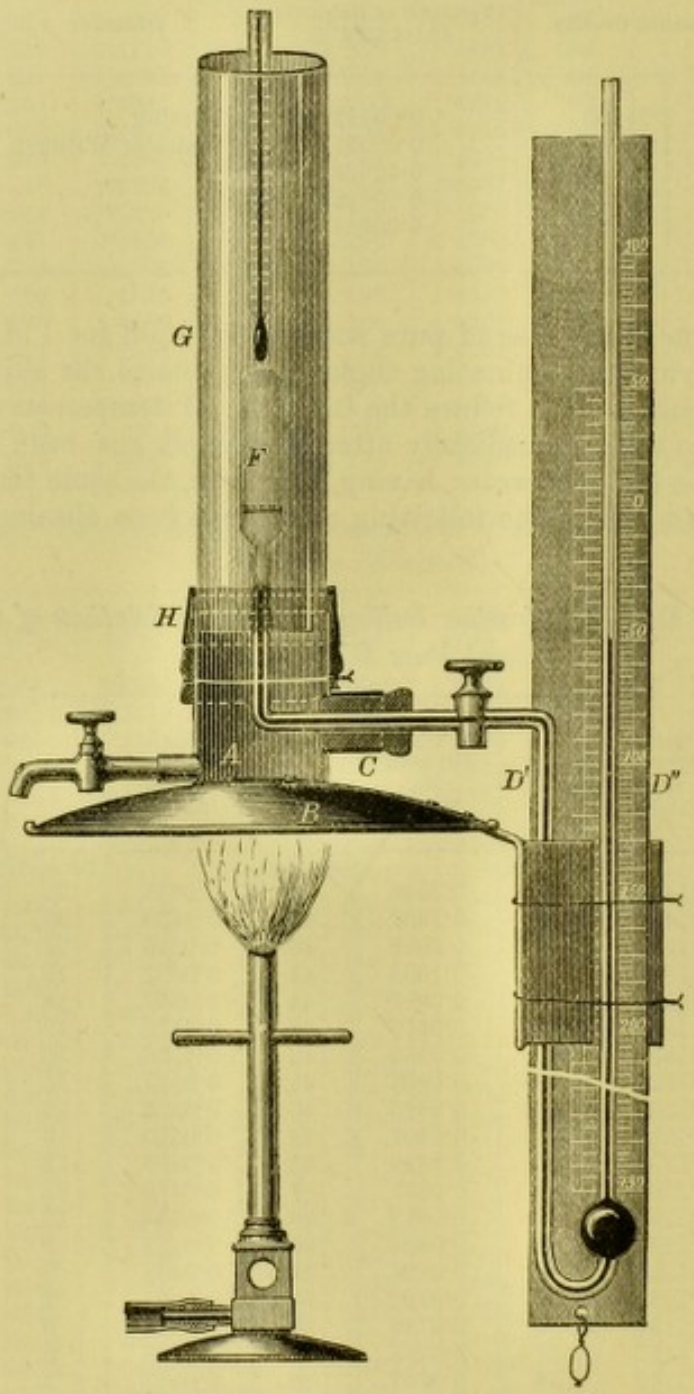


Fig. 48.

German silver, braized on to the metal dish B. The glass cylinder G is fastened to A by means of stout india-rubber tubing, tied on with wire, and then secured by the conical clamp H. Nozzle C is fitted

[1] Made by F. Müller, Dr. Geissler's Nachfolger, Bonn a/Rh.

with an india-rubber stopper, through which passes one end of the gauge (manometer) D′ D″.

To use the instrument, the glass cylinder G and bottle F are detached, the plug taken out of the tap, and the instrument hung up by the hook fastened to its bottom. F is then rinsed out with the sample of glycerin, and filled with mercury up to a mark on the neck, and then completely with glycerin. After allowing to stand until all air-bubbles have escaped the bottle is attached to the end of D′, which is well ground so as to fit into the neck of F. When the glycerin has ceased to drain out, the plug is put in its place, G is attached to A, and filled with water. This is then heated to boiling, when the sample will emit vapour which drives mercury into the gauge D′ D″. A short thread of glycerin precedes the mercury; by suitable adjustment, effected by taking out the plug for a moment, the thread is made equally long in all experiments.

If the bottle F has been charged in a blank experiment with water, the mercury will rise so high in D″ that its level is the same as the mercury in the bottle, since the vapour tension of water, at its boiling point, equals the atmospheric pressure. This point is marked on the scale as the zero point, its position being, of course, the same for all pressures of the atmosphere, since a change in the latter influences both the boiling point of the water in G and the vapour tension in F in the same manner. From the zero point downwards (and also upwards) the scale is divided into millimetres.

On examining glycerin in the vaporimeter, the zero point will, of course, not be reached. The number read off the scale requires, however, a correction, the level of the mercury in the bottle F being now higher than in the blank test. This increase in height must be added to the reading. Each instrument is provided by the maker with a table, stating this correction for the interval from 0 to 500 mm., from which the correction for each experiment can be calculated.

Example.—Let the correction for an interval from 0-500 mm. be given as 21 mm., and in an actual experiment with glycerin 492 mm. be read off the scale of the vaporimeter as the level of the mercury. The correction is then calculated by means of the proportion $500 : 21 = 492 : x$, hence $x = 20{\cdot}6$. Consequently, the actual decrease of the vapour tension of the sample of glycerin equals $492 + 20{\cdot}6 = 512{\cdot}6$. From the table given p. 800 we find that the sample contains 70 per cent of glycerol.

Specific Gravities, Boiling Points, and Vapour Tensions of Aqueous Solutions of Glycerin (Gerlach)

Glycerol.	Parts of Glycerol compared with 100 parts of Water.	Specific Gravity.		Boiling Point. At 760 mm. Pressure.	Vapour Tension at 100° C.
		At 15° C. Water 15° C. = 1.	At 20° C. Water 20° C. = 1.		
Per cent.				°C.	mm.
100	Glycerin	1·2653	1·2620	290	64
99	9900	1·2628	1·2594	239	87
98	4900	1·2602	1·2568	208	107
97	3233·333	1·2577	1·2542	188	126
96	2400	1·2552	1·2516	175	144
95	1900	1·2526	1·2490	164	162
94	1566·666	1·2501	1·2464	156	180
93	1328·571	1·2476	1·2438	150	198
92	1150	1·2451	1·2412	145	215
91	1011·111	1·2425	1·2386	141	231
90	900	1·2400	1·2360	138	247
89	809·090	1·2373	1·2333	135	263
88	733·333	1·2346	1·2306	132·5	279
87	669·231	1·2319	1·2279	130·5	295
86	614·286	1·2292	1·2252	129	311
85	566·666	1·2265	1·2225	127·5	326
84	525	1·2238	1·2198	126	340
83	488·235	1·2211	1·2171	124·5	355
82	455·555	1·2184	1·2144	123	370
81	426·316	1·2157	1·2117	122	384
80	400	1·2130	1·2090	121	396
79	376·190	1·2102	1·2063	120	408
78	354·500	1·2074	1·2036	119	419
77	334·782	1·2046	1·2009	118·2	430
76	316·666	1·2018	1·1982	117·4	440
75	300	1·1990	1·1955	116·7	450
74	284·615	1·1962	1·1928	116	460
73	270·370	1·1934	1·1901	115·4	470
72	257·143	1·1906	1·1874	114·8	480
71	244·828	1·1878	1·1847	114·2	489
70	233·333	1·1850	1·1820	113·6	496
65	185·714	1·1710	1·1685	111·3	553
60	150	1·1570	1·1550	109	565
55	122·222	1·1430	1·1415	107·5	593
50	100	1·1290	1·1280	106	618
45	81·818	1·1155	1·1145	105	639
40	66·666	1·1020	1·1010	104	657
35	53·846	1·0885	1·0875	103·4	675
30	42·857	1·0750	1·0740	102·8	690
25	33·333	1·0620	1·0610	102·3	704
20	25	1·0490	1·0480	101·8	717
10	11·111	1·0245	1·0235	100·9	740
0	0	1·0000	1·0000	100	760

In the case of samples containing more than 70 per cent of glycerol an india-rubber tubing should be attached to limb D″, and suction applied, so as to expedite vaporising. But in the case of anhydrous glycerin even this device fails.

It is evident that for practical purposes this method of ascertaining the percentage of glycerol in a sample will but rarely be resorted to, the other processes yielding more accurate results in a shorter time.

B. Chemical Methods

If very dilute solutions of chemically pure glycerin have to be examined the physical methods lose in accuracy, and it is preferable to resort to chemical methods.

Oxidation of Glycerol.—The methods falling under this heading have been fully described p. 207.

As only the minutest traces of organic impurities are present in a chemically pure glycerin, all those processes will yield accurate results.

Of concentrated glycerins, 0·2 to 0·4 grms. are weighed off; of dilute solutions, of course, more is taken.

Benedikt and *Zsigmondy* state that, when employing their process (p. 208), the proportion of glycerol in a solution containing but 0·03 per cent can be estimated with accuracy to 0·0003 per cent.

Morawski[1] bases a method of determining glycerol on its property of combining with lead oxide to form monoplumbo-glyceroxide (p. 79). 50-60 grms. of litharge are weighed into a large crucible together with a short glass rod, then about 2 grms. of the sample are added, and enough alcohol to facilitate the thorough mixing of the glycerin with the litharge. The crucible is heated at first in a vacuum water-oven, and then to 120°-130° C. in an air-bath, being covered with a watch-glass having an aperture for the glass rod, until the weight becomes constant. The increase in weight multiplied by 1·2432 ($C_3H_8O_3 : C_3H_6O = 92 : 74$; $\frac{92}{74} = 1{\cdot}2432$) gives the amount of glycerol in the sample.

This process cannot be considered satisfactory when compared with the oxidation method. *Lewkowitsch*[2] has shown that errors up to 10 per cent may occur. If the litharge contains "red lead," or has had an opportunity of absorbing carbonic dioxide from the atmosphere, the results become inaccurate, Even *Morawski's* own results show a mean difference of 0·6 per cent, *in maximo* 1·5 per cent. The necessity of preventing contact with the atmosphere during the drying, which takes three to four hours, renders this method inconvenient.

Also *Muter's*[3] process, based on the solubility of copper oxide in glycerol; *Diez's*[4] method, based on the conversion of the glycerol in the sample into its benzoate; and *Boulez's* process, based on the conversion of glycerol into calcium glycero-phosphate,—are not accurate enough to deserve further notice here.

[1] *Jour. Soc. Chem. Ind.* 1889, 424.
[2] *Chem. Zeit.* 1889, 94.
[3] *Analyst*, 1881, 41.
[4] *Jour Soc. Chem. Ind.* 1887, 609.

2. Dynamite Glycerin—Distilled Glycerin.

Dynamite glycerin is a distilled glycerin, chiefly used in the manufacture of high explosives having nitroglycerin as a basis or containing it as an ingredient.

Being a product obtained by distillation, it contains a very small amount of ash only, and is hereby easily distinguished from crude glycerin. It is further differentiated from it by not giving a precipitate with lead acetate.

The best brands of dynamite glycerin approach in purity chemically pure glycerin; they differ from it in colour, being yellowish to straw coloured, and also in the somewhat larger amount of ash and organic impurities which is permissible.

The conditions dynamite glycerin should fulfil are, in consequence of the risks to which the manufacturer of dynamite is exposed if the glycerin be impure, usually laid down in contracts between buyer and seller. Thus the following points are stipulated :—

Specific Gravity.—This should be not less than 1·261 at 15·5° C. For its determination see p. 793. This is a very important test, as high percentage of glycerol found by the bichromate method may be caused by presence of trimethylene-glycol, detected in a sample of commercial glycerin by *Noyes* and *Watkin*.[1] Presence of trimethylene-glycol may be suspected if low specific gravity is combined with apparently high percentage of glycerin.[2]

Lime, *Magnesia*, and *Alumina* should be absent.

Chlorine.—Only traces are permissible; the glycerin must not become milky by silver nitrate.

Arsenic.—Only minute traces are tolerated. The test is made by making the glycerin *just* alkaline with a minute quantity of ammonia, and adding silver nitrate. No yellow precipitate must appear. This precipitate being soluble in ammonia, an excess of this reagent must be avoided. Of course, *Gutzeit's* reaction (see p. 787), using mercuric chloride, may also be employed.

Organic Impurities.—Tested with silver nitrate, the glycerin must not become brown or black within ten minutes.

Total Residue.—This is determined as described p. 789. It must not exceed 0·25 per cent.

Free Acids.—The glycerin should not be acid to litmus, nor should it contain fatty acid; cp. Test for Volatile Fatty Acids, p. 788. On passing nitrous acid fumes through it, it should not curdle; it is supposed that oleic acid would thus be detected.

[1] *Jour. Soc. Chem. Ind.* 1896, 207.

[2] Barton, *ibid.* 1895, 516, proposes to heat the glycerin to 225°-230° C. for 2 hours, and then again to take the specific gravity, which he terms "permanent specific gravity." *Barton* assumes that hydrocarbons are volatilised, but their occurrence is more than doubtful except in glycerins from bone fat. The "permanent specific gravity" will always be higher than the specific gravity of the sample, as the last traces of water volatilise; also trimethylene-glycol (boiling point 214°-217°) will most likely be driven off.

Nitration and Separation Test.—A sample of glycerin may prove good in all preceding tests, and yet be totally unfit for the manufacture of nitroglycerin. The suitability of a sample of dynamite glycerin must therefore be determined by the following process, simulating the operations on a manufacturing scale :—

375 grms. of a mixture, consisting of one part (by weight) of nitric acid, specific gravity 1·5, and two parts (by weight) of sulphuric acid, specific gravity 1·845, previously cooled down to the ordinary temperature in a closed vessel, are weighed off in a beaker of about 500 c.c. capacity. A thermometer, used during the nitration as a stirrer, is then introduced into the acid, and the beaker immersed in a capacious vessel filled with cold water, or, if necessary, with ice. A stream of cold water is kept running through the vessel by means of a stout india-rubber tubing, say $\frac{3}{4}''$ diameter, coiled at the bottom of the vessel. It is very important that the india-rubber tubing should be securely fastened to the water-tap, if the latter be near the operator, as it may easily happen that the tube is thrown off the tap by the pressure of the water in the pipe, when any water accidentally coming into contact with the acid may raise the temperature to such a point that explosion will ensue. The writer uses, therefore, thin-walled beakers, so that they may be rapidly broken in case the temperature rises to a point of danger ; the rapid discharge of the mixed acids and nitroglycerin into the large mass of water will then effectively prevent an explosion.

When the temperature of the acids has fallen to about 12° to 15° C. 50 grms. of the sample of glycerin, weighed off in a beaker having a spout, are allowed to fall into the acids, drop by drop, constantly stirring with the thermometer, and observing the temperature after the addition of every single drop of glycerin. Considering the danger attending this operation, the inexperienced analyst had perhaps best be shown the test by an experienced operator. If this be not feasible, the safest plan will be to proceed in the manner described, *i.e.* add cautiously drop by drop, stirring all the while, so that no overheating may take place *locally*, and never allowing the temperature to exceed 30° C. No addition of another drop of glycerin must be made until the temperature has fallen below 25° C. (An experienced operator will, of course, proceed a little more rapidly.)

If all the glycerin has been dropped in in this manner, the mixture is stirred for a short period, until the temperature has fallen to about 15° C., and transferred to a separating funnel, which must be absolutely dry. The safest plan is to have the funnel rinsed out beforehand with concentrated sulphuric acid.

If the dynamite glycerin is good, the nitroglycerin will rapidly rise to the top and separate in a few minutes as an oily, somewhat turbid layer on the top of the spent acids. The quicker the separation into two well-defined layers takes place the better is the glycerin. If flocculent matter is noticeable in the nitroglycerin layer, if the separation is slow, and an intermediate layer of this flocculent substance renders the line of separation indistinct, the sample is unsuitable for

dynamite making. In some cases the time of separation cannot be stated, owing to the nitroglycerin being honeycombed with this flocculent substance, requiring hours for separation. Such a sample must of course be rejected.

The *quantitative* determination of the yield of nitroglycerin is conveniently combined with this nitration test. In that case the accurate quantity of glycerin used is either determined by re-weighing the beaker containing the glycerin, or the beaker is rinsed out with the mixture of acids and nitroglycerin. The former method is the better. After separation of the nitroglycerin the acid layer is carefully drawn off, and the nitroglycerin slightly agitated without shaking, so that any drops of acid adhering to the vessel are brought into one mass. This is carefully drawn off, and the nitroglycerin washed with water of 35°-40° C. once, then once or twice with a 20 per cent solution of sodium carbonate, and then again with water. The nitroglycerin is then transferred to a suitable burette, in which the adhering water rises to the top. The volume is read off, and the quantity determined by multiplying the number of c.c. by 1·6, the specific gravity of nitroglycerin (the specific gravity of the product may be determined, if desired), or by weighing the product after separation from water by filtering over salt.

It is evident that this process yields only approximate results, especially so as nitroglycerol is slightly soluble in water. The method is, however, satisfactory for the commercial valuation of dynamite glycerin. The yield of nitroglycerin should be at least from 207-210 per cent of the glycerin weighed off, the more the better. The quantity of nitroglycerin contained in the washings (recovered on the large scale by the so-called after-separation) is disregarded. The theoretical yield of nitroglycerol from glycerol is 246·7 per cent.

It is, of course, necessary to destroy the nitroglycerin. This is done best by spreading out a sufficient quantity of dry sawdust in not too thick a layer in an open space (say in the yard and not too near the wall of buildings), and running the nitroglycerin out of a separating funnel on to it whilst the operator carries it along the sawdust, so as to distribute the nitroglycerin in a slender continuous trail, taking care that no pool is formed. By applying a lighted match to one end of the trail the nitroglycerin will burn away quietly. The waste acids should be destroyed in a similar manner; when they are brought into contact with sawdust a violent reaction sets in, but there is no danger if the nitroglycerin has been separated off carefully.

The glycerol in the sample of dynamite glycerin may also be determined by oxidation, see p. 208. The results are, of course, not so accurate as in the case of chemically pure glycerin.

Distilled glycerin is used for various purposes in the arts. The proportion of glycerin in a sample is usually determined with sufficient accuracy by taking its specific gravity and referring to the tables pp. 791, 795, 796.

3. Crude Glycerin

The composition of commercial crude glycerins varies considerably with the process of saponification from which it originates. In commerce the following three qualities are discerned :—

1. *Crude Saponification Glycerin.*—This is prepared by concentrating the "sweet water" obtained in the saponification by lime (p. 745) or water (p. 746). This crude glycerin usually contains about 0·5 per cent of ash and small quantities of organic impurities. Its colour varies from yellow to dark brown ; its taste is sweet.

Tested with basic lead acetate it gives but a slight precipitate ; on addition of hydrochloric acid to good samples no turbidity appears. It is usually concentrated in the candle-works to 1·240-1·242 specific gravity, and sold as "saponification glycerin," 28° Bé. ; it contains about 90 per cent of glycerol. By refining with charcoal the "refined" glycerin is obtained. If the lime has been precipitated by oxalic acid, the excess of the latter will be found in the glycerin.

2. *Distillation Glycerin.*—This glycerin is recovered from the acid waters of the sulphuric acid saponification process (p. 746). The amount of ash is higher than that of saponification glycerin, sometimes as much as 3·5 per cent, and the organic impurities also reach several per cents. Its colour is usually pale yellow ; its taste is sharp and astringent, and it emits an unpleasant smell when rubbed between the hands. Tested with basic lead acetate a voluminous precipitate is obtained ; on addition of hydrochloric acid a turbidity, due to fatty acids, appears.

The specific gravity is the same as that of the saponification glycerin ; it contains, as a rule, from 84 to 86 per cent of glycerol. It is sold as distillation glycerin, 28° Bé.

3. *Soap-lye Glycerin.*—This glycerin is obtained on purifying the soap-maker's spent lyes, and concentrating to the specific gravity of 1·3. It contains about 10 per cent of ash, chiefly common salt, if pure ; if impure, sodium carbonate, caustic soda, sodium sulphide, sodium thiocyanate, and sodium thiosulphate are also present. The proportion of organic impurities in soap-lye glycerin varies considerably, depending on the process of purification used, etc. Some commercial glycerins contain less than 2 per cent of organic impurities, thus representing a crude glycerin of better quality than distillation glycerin ; others, again, contain large quantities of impurities, consisting of fatty acids, resin acids, and albuminoid substances, gelatin, and hydrocarbons (from bone fat). Its colour is pale yellow to brown or almost black, according to the purity. The taste of good samples is sweet, qualified, of course, by the proportion of salt in the sample ; impure samples have a most unpleasant, garlic-like taste, although sulphides may be absent.

Good soap-lye glycerin should have a specific gravity 1·3, and contain 80-82 per cent of glycerol and 10 per cent of ash. It should not become turbid on addition of hydrochloric acid.

Soap-lye glycerin can, therefore, be rapidly distinguished from saponification *and* distillation glycerin by the large proportion of common salt (heavy precipitate with silver nitrate), and by its high specific gravity; saponification and distillation glycerins are differentiated by the lead acetate, the hydrochloric acid, and the organic residue tests.

COMMERCIAL ANALYSIS OF CRUDE GLYCERIN

(*a*) **Estimation of Glycerol.** — The crude glycerin is valued on the proportion of glycerol in the sample, allowance having been made for the difference in quality due to the different origin of the sample.

The best methods for the quantitative estimation are *Benedikt* and *Cantor's*[1] "Acetin method" and *Hehner's*[2] "Bichromate method." *Benedikt* and *Zsigmondy's* permanganate process (p. 208) does not yield reliable results in this case owing, no doubt, to the presence of organic impurities yielding oxalic acid on oxidation, even if the bulk of the organic impurities be first removed by diluting the sample and precipitating with lead acetate. *Morawski's* method (p. 801) is in this case useless, as also are the other methods mentioned, p. 801.

Acetin Method.—This process is based on the quantitative conversion of glycerol into triacetin (p. 3), when concentrated glycerin is heated with acetic anhydride. If the product of this reaction is then dissolved in water, and the free acetic acid has been carefully neutralised with alkali, the dissolved triacetin can be easily estimated by saponifying with a known volume of standard alkali and titrating back the excess. The solutions required are—

1. Half-normal or normal hydrochloric acid (*accurately* standardised).

2. Dilute caustic soda, containing about 20 grms. of NaOH in 1000 c.c. Its strength need not be known accurately.

3. A 10 per cent solution of caustic soda. Solutions 2 and 3 are best kept in large bottles connected by means of syphon tubes with burettes, so that the filling of the latter may take place automatically. To prevent absorption of carbon dioxide from the air the bottles are provided with soda-lime tubes through which the air has to pass.

The estimation of the glycerol is carried out as follows:—

About 1·5 grms. of the crude glycerin weighed off accurately are heated with 7-8 c.c. of acetic anhydride and 3 grms. of anhydrous sodium acetate (dried previously in an oven) for 1½ hours in a round-bottomed flask, of about 100 c.c. capacity, connected with an inverted condenser. The mixture is then allowed to cool a little, 50 c.c. of

[1] *Jour. Soc. Chem. Ind.* 1888, 696; cp. also Lewkowitsch, *ibid.* 1889, 574; *Chem. Zeit.* 1889, 13, 93, 191, 659.

[2] *Jour. Soc. Chem. Ind.* 1889, 6; cp. also Bordas and Raczkowski, *ibid.* 1897, 167.

warm water are poured down through the tube of the condenser, and the acetin made to dissolve by shaking the flask; if necessary, the contents of the flask may be slightly warmed, but must not be boiled.[1] These operations must be done with the condenser, as triacetin is volatile with water vapours. The solution is next filtered from a flocculent precipitate, containing most of the impurities of the sample, into a wide-mouthed flask of about 500-600 c.c. capacity, and the filtrate allowed *to cool down* to the ordinary temperature. Phenolphthalein is then added, and the free acetic acid neutralised with the dilute caustic soda solution. Whilst running in the soda the solution must be agitated continually, so that the alkali may not be in excess locally longer than is unavoidable. The point of neutrality is reached when the slightly yellowish colour of the solution just changes into reddish-yellow. If the solution is allowed to become pink, the point of neutrality has been exceeded, and the test must be started afresh; the excess of soda cannot be titrated back, as partial saponification of the acetin takes place in presence of the slightest excess of alkali. The change of colour is very characteristic, and is easily noticed after some little practice.

25 c.c. of the strong soda solution are now run in and the solution boiled for a quarter of an hour. The excess of soda is then titrated back with the standard acid. Side by side with it, operating in the same manner, 25 c.c. of the caustic soda are boiled and titrated with acid. The difference between the two titrations corresponds to the amount of alkali required for the saponification of the triacetin. From this the quantity of glycerol in the sample can be calculated, as shown in the following example :—Suppose 1·324 grms. of the sample have been treated as described above. Let 25 c.c. of the strong alkali require 60·5 c.c. of normal hydrochloric acid, and let the number of c.c. required for titrating back the excess of soda in the sample be 21·5 c.c., then $60{\cdot}5 - 21{\cdot}5 = 39{\cdot}0$ c.c. have been used. 1 c.c. of normal acid corresponds to $\frac{0{\cdot}092}{3} = 0{\cdot}03067$ grms. of glycerol. Hence the sample contained $0{\cdot}03067 \times 39 = 1{\cdot}1960$ grms. or 90·3 per cent of glycerol.

Bichromate Method.—About 1·5 grms. of crude glycerin are weighed off in a 100 c.c. flask, and silver oxide added to precipitate any chlorine (present in the sample as sodium chloride), and to oxidise aldehydes. A little water is then run in and the mixture allowed to stand for ten minutes. Basic lead acetate is added next in slight excess, and the volume made up to 100 c.c. A portion of the solution is filtered through a dry filter, and 25 c.c. of it placed in a beaker previously cleaned with concentrated sulphuric acid and bichromate solution, so as to remove traces of adhering fat. Then proceed as described page 212.

As the bichromate solution is necessarily a strong one, the measuring must be done with the greatest care. Attention must also be paid to the temperature of the solution at the time of measuring.

[1] Hehner, *Jour. Soc. Chem. Ind.* 1889, 6.

Hehner states that the strong bichromate solution expands 0·05 per cent for each degree C. The writer obviates corrections by bringing the standard solutions to the normal temperature in a large water-bath, and keeping thereat until the titration is finished.

Hehner has shown by a number of comparative experiments, using both the acetin and the bichromate processes, that the results agree very well. This has been borne out by a large number of experiments made by the writer. *Hehner* advises to use both methods in the examination of a sample, and to take the mean of the two results. This, however, entails too much unnecessary work in commercial analysis, and it will therefore be preferable to make two tests by the acetin method.

(*b*) **Specific Gravity.**—This is taken as described page 793. Saponification and distillation glycerin should have a density of 1·240-1·242; soap-lye glycerin of 1·3.

(*c*) **Ash.**—3-5 grms. of the sample are weighed off accurately in a platinum dish, and the glycerol burnt away. This determination may be combined with that of the organic impurities, except, perhaps, in the case of soap-lye glycerin, when it will be found preferable to make two separate determinations.

The platinum dish is placed over a small burner, which must not touch its bottom, and the glycerol allowed to evaporate off slowly. More heat should only be applied after the bulk of the glycerol has been driven off. In the case of soap-lye glycerin a bulky carbonaceous residue is obtained, which is heated high enough to just destroy the organic matter. After cooling, the charred mass is exhausted with water and transferred to a filter, the filtrate boiled down in the platinum dish on the water-bath, the residue, which must be white, heated (not above 400° C. to avoid loss by volatilisation of sodium chloride), and weighed. The carbon on the filter may as a rule be disregarded. *Vizern*[1] recommends to ignite also the carbon; this may be necessary if the sample contains large proportions of lime.

H. D. Richmond[2] estimates the ash by carbonising, as described above, adding a little concentrated sulphuric acid, and heating over a good Bunsen flame until the ash is burnt white. The "sulphated" ash is then multiplied by 0·8. This method is less accurate, and cannot be recommended.

(*d*) **Organic Impurities.**—They are determined as described page 789. In the case of soap-lye glycerin, the drying at 160° C., until constant weight is obtained, requires a somewhat long time. The process is shortened by adding to the residue occasionally a few drops of water.

(*e*) **Fatty acids** are detected by acidifying the sample, after diluting with three measures of water, with hydrochloric acid.

(*f*) **Arsenic** is tested for as described pages 787, 802.

If a *soap-lye glycerin* contains considerable quantities of **sulphides, thiosulphates,** or **sulphites,** it is almost valueless to the refiner. The

[1] *Jour. Chem. Soc.* 1890, Abstr. 835. [2] *Jour. Soc. Chem. Ind.* 1889, 7.

detection of these impurities is, therefore, of great importance for purposes of valuation. According to *Ferrier*,[1] 50 grms. of the sample are conveniently made up to 500 c.c., and the solution tested for *sulphides* with paper saturated with alkaline lead nitrate solution. To detect traces of sulphides down to $\frac{1}{100000}$th part, a few c.c. of the solution are placed in a small flask, four or five drops of hydrochloric acid added, as well as a pinch of sodium bicarbonate, the liquid heated carefully to boiling, and a paper moistened with alkaline lead nitrate held over the flask.

Hyposulphites and *sulphites* are detected by treating a sample of the solution with a few c.c. of a solution of barium chloride, and filtering off the precipitate containing carbonate, sulphate, and sulphite. As soon as the filtrate has been obtained clear, if necessary by repeated filtrations, two or three drops of hydrochloric acid and a few drops of a potassium permanganate solution are added. If the glycerin contains even less than $\frac{1}{10000}$th part of thiosulphate, a distinct turbidity is produced.

The detection of the *sulphites* is effected by washing the precipitate on the filter with boiling water, stirring it up with a little water, and adding to this mixture a little starch solution and a few drops of iodine solution. In the presence of sulphites the blue colouration disappears with more or less rapidity, whilst in their absence the blue colour is permanent.

The process given by *Ferrier* for the quantitative determination is not accurate, and need therefore not be referred to here.[2]

The **residues from the distillation of glycerin** are used in the manufacture of shoe-blacking. They contain large proportions of ash and polyglycerols. The proportion of glycerol is best determined by the acetin method.[3]

The valuation of **soap-maker's spent lyes** is made on the basis of the proportion of glycerol they contain, provided sulphur compounds are absent.

For the estimation of glycerol 1000 c.c. are heated to boiling and acidified with hydrochloric acid, when any fatty acids, etc., separate as an oily liquid on the top. This is filtered off, the filtrate made neutral, and lead acetate added. The precipitate is filtered off and the clear solution boiled down. The salt separating out is fished out and sucked dry by means of a filter-pump. When a few c.c. of solution are left finally, this is added to the salt, and the latter exhausted with a mixture of three measures of methylated spirit and one measure of ether. The alcoholic filtrate is evaporated down on

[1] *Jour. Soc. Chem. Ind.* 1893, 471.
[2] Cp. Richardson and Aykroyd, *Jour. Soc. Chem. Ind.* 1896, 171.
[3] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1890, 479.

the water-bath, and the crude glycerin thus obtained examined by the acetin method.

If but small quantities of soap-lye are available, so many grams are weighed off in a 100 c.c. flask as will approximately correspond to 1·2 grms. of pure glycerol, and the glycerol is then determined by *Hehner's* bichromate method (p. 807).

CHAPTER XIII

EXAMPLES [1]

THE manner in which the methods described in the preceding chapters can be employed in the examination of technical products may be illustrated by the following examples :—

1. TOURNANT OIL (TURKEY-RED OIL)

An oil sold as Tournant Turkey-red oil gave on examination the following results :—

Specific gravity at 17·5° C. . . .	0·933
Acid value	54·9
Saponification value	186·4
Iodine value	90·5
Acetyl value	54·9

The high acetyl value, the high specific gravity, the high iodine value, and the low saponification value, point unmistakably to the presence of *castor oil.*

Taking the acetyl value of castor oil as 153, the oil contains approximately an amount of

$$\text{Castor oil} = \frac{54{\cdot}9 \times 100}{153} = 36 \text{ per cent.}$$

The nitric acid test revealed the presence of *cotton seed oil.* Assuming that the sample contained, besides castor oil, some true Turkey-red oil, or a mixture of olive oil and oleic acid, all of which absorb about 83 per cent of iodine, then the proportion of cotton seed oil may be calculated according to the formula given p. 311, the iodine value of cotton seed oil being taken as 108.

$$\text{Cotton seed oil} = \frac{100\,(J - n)}{m - n} = \frac{100\,(90{\cdot}5 - 83)}{108 - 83} = 30 \text{ per cent.}$$

---

[1] Cp. also the examples given pp. 149, 152, 165.

As the acid value of oleic acid is 199 (p. 150), the acid value of the sample, 54·9, will correspond to about 27·6 per cent of free oleic acid. Consequently the oil cannot contain more than about 6·4 per cent [100 – (36 + 30 + 27·6)] of neutral fat due to true Tournant oil. Tournant oil contains, however, about 26 per cent of free fatty acids (p. 464); therefore about 1·6 per cent of free fatty acids must be added to the amount of neutral oil, and, of course, deducted from the amount of free oleic acid. Accordingly, an oil exactly similar to the sample could be prepared by mixing the following fatty substances in the proportions stated :—

	Per cent.
Castor oil	36
Cotton seed oil	30
Tournant oil	8
Commercial oleic acid	26
	100

2. Commercial Acetine

See p. 677.

3. Composition of Butter Fat

See p. 607.

4. Product obtained by the action of Zinc Chloride on Oleic Acid

Oleic acid may be converted by *v. Schmidt's* process (p. 747) into a solid substance. A sample[1] was prepared in the laboratory by heating 500 grms. of oleic acid with 50 grms. of zinc chloride to exactly 185° C. in an oil-bath, until a drop of the mixture, after boiling with hydrochloric acid, solidified on cooling. The contents of the flask were then decomposed with hydrochloric acid, and the fatty substance purified by repeatedly boiling out with water.

(*a*) *Crude Product*

The fatty substance thus prepared had the consistency of lard; on examination it gave the following constants :—

Acid value	124·9
Saponification value	179·7
Ether value	54·8
Constant acid value	125·7

[1] Benedikt, *Monatshefte f. Chemie*, 1890, 71; *Jour. Soc. Chem. Ind.* 1890, 658.

Constant saponification value	180·8
Constant ether value	55·1
Acetyl acid value	114·9
Acetyl saponification value	201·0
Acetyl value	86·1
Iodine value	36·0

From these numbers the following conclusions may be drawn :—

The *acid value* of the sample is considerably lower than that of the original oleic acid (198·6); therefore a portion of the oleic acid has either been polymerised or has been converted into anhydrides.

The definite *ether value*, found by the difference of the saponification and acid values, points to the presence of *saponifiable anhydrides*.

Still, the *saponification value*, 179·7, is too low for a mixture of monobasic fatty acids, containing no more than 18 atoms of carbon in the molecule, and of anhydrides of the same order. We must, therefore, conclude that either polymerisation has taken place or that *unsaponifiable anhydrides* have been formed.

For the determination of *unsaponifiable anhydrides* 100 grms. of the sample were dissolved in alcohol and boiled with 40 grms. of caustic soda previously dissolved in a little water. The soap solution was then shaken out with petroleum ether, the ethereal solution washed with water, the solvent distilled off, and the residue dried, at first on the water-bath, being repeatedly moistened with alcohol, and finally at 105° C. in a drying oven. Thus 8 grms. of substance, equal to 8 per cent, were obtained. This anhydride could only be saponified by alcoholic potash at 150° C., and may, therefore, for practical purposes be considered as unsaponifiable. It is a yellow viscous liquid insoluble in alcohol. It absorbs no iodine, and has neither an acid nor a saponification value.

The *constant ether value* (p. 206) points distinctly to the presence of that class of anhydrides which are converted by alkalis into the potassium salts of the corresponding acids, but are re-formed whenever the salts are decomposed by an acid.

This easily *saponifiable anhydride* was isolated from the soap solution after extracting the unsaponifiable liquid anhydride with petroleum ether in the following manner :—The solution was diluted with hot water, acidulated with hydrochloric acid, and boiled down on the water-bath until the alcohol was evaporated off. The oily layer floating on the top (corresponding to 100 grms. of the sample) was separated from the aqueous layer and neutralised most carefully with caustic soda in the manner described (p. 207), as the slightest excess of alkali was liable to saponify a portion of the anhydride, and thus vitiate its quantitative determination. By extraction with petroleum ether 28 grms. of a white crystalline substance were obtained, forming curved needles (from dilute alcohol), melting point 51·2° C. The substance absorbed no iodine, its acid value was *nil*, and its saponification value was 199. The crystals were therefore identical with the *stearolactone* described by *Geitel* (p. 69), a conclusion

which was further confirmed by the numbers furnished by ultimate analysis.

The quantitative composition of the product of the interaction of zinc chloride and oleic acid can now be calculated in the following manner :—

The *constant ether value* being identical with the ordinary *ether value*, anhydrides of the type of acetic anhydride (*i.e.* anhydrides saponifiable by alkalis and not re-formed on acidifying) are absent.

Since the ether value of pure stearolactone (according to theory) is 198·9, the amount of stearolactone in the sample can be calculated from the *constant ether value* of the sample, viz. 55·1, using the proportion $198{\cdot}9 : 100 :: 55{\cdot}1 : x$; hence $x = 27{\cdot}7$ per cent, or *rot.* 28 per cent. This number agrees perfectly with that found by direct determination (comp. above).

From the *iodine value* of the sample the proportion of oleic acid—oleic *plus* isooleic acid—is found. Pure oleic acids absorb, according to theory, 90·07 per cent of iodine; consequently the iodine value, 36, of the sample corresponds to 40 per cent of oleic acids.

The *true* acetyl value of the sample is found by subtracting the constant ether value, 55·1, from the above given acetyl value, 86·1; it equals $86{\cdot}1 - 55{\cdot}1 = 31{\cdot}0$. From this acetyl value the proportion of β-hydroxystearic acid, molecular weight = 300, can be found by substituting in the equation (p. 205)—

$$x = \frac{100 \,.\, c \,.\, \mathrm{M} \,.\, (\mathrm{M}+42)}{56100(\mathrm{M}-42)}$$

for c and M, 31 and 300 respectively. Hence $x = 21{\cdot}97$, or about 22.

The product of the interaction of zinc chloride and oleic acid has, therefore, the following composition :—

	Per cent.
Liquid anhydride	8
Stearolactone	28
Oleic acids	40
β-Hydroxystearic acid	22
Saturated fatty acids (by difference)	2
	100

That there is a small amount of saturated fatty acids (other than hydroxy acids) present may be proved by means of the saponification values in the following manner :—

40 per cent of oleic acid correspond to the acid value	79·6
22 ,, ,, β-hydroxystearic acid ,, ,,	41·1
	120·7

The acid value of the sample having been found = 124·9, the difference, $124{\cdot}9 - 120{\cdot}7 = 4{\cdot}2$, must be accounted for by the presence of saturated acids. This conclusion is further supported by the behaviour of oleic acid when heated with zinc chloride to 200° C.

(*b*) *Crude distilled Product*

The crude product (*a*) was distilled under diminished pressure, and the distillate, after washing with water, examined, when the following numbers were obtained :—

Acid value	126·3
Saponification value	188·1
Ether value	61·8
Acetyl acid value	127·0
Acetyl saponification value	189·0
Acetyl value	62·0
Iodine value	47·1
Unsaponifiable	13·6 per cent.

The proportion of "unsaponifiable" was determined, on the one hand, in a direct way, by extracting the alcoholic solution of the soap with petroleum ether and weighing the residue, and, on the other hand, by difference, the extracted soap having been decomposed with acid and the separated fatty mass weighed.

The *unsaponifiable* portion forms a mobile, light yellow oil, consisting chiefly of hydrocarbons, with which small quantities of oxygenated substances are admixed, as proved by ultimate analysis :—C = 84·10 per cent ; H = 13·70 per cent ; O = 2·20 per cent. The iodine value of the unsaponifiable matter was 74·1.

The composition of the crude distillate may now be inferred as follows :—

The *ether value*, 61·8, corresponds to 31 per cent of *stearolactone*.

The ether value being identical with the *acetyl value*, *hydroxy acids* must be absent.

Iodine is absorbed both by the "unsaponifiable" and the oleic acids. The 13·6 per cent of unsaponifiable—iodine value 74·1—require 10·08 per cent of iodine. Consequently there are left for the oleic acids 47·1 – 10·08 = 37·02 per cent of iodine. This corresponds to 41·13 per cent of oleic acids.

Hence we find the crude distilled product to have the following percentage composition :—

	Per cent.
Unsaponifiable	13·6
Stearolactone	31·0
Oleic and isooleic acids	41·1
Saturated acids (by difference)	14·3
	100·0

Also in this case presence of saturated acids is indicated by the saponification value of the distillate, the number 126·3 being considerably higher than that required for 41·1 per cent of oleic acids, viz. about 82.

The changes the crude product (*a*) has undergone on being distilled consist, therefore, in the decomposition of the liquid anhydride, and in the conversion of β-hydroxystearic acid into isooleic and oleic acids.

(*c*) *Solid Portion of the Distillate* (*Candle Material*)

The candle material obtained from the crude distillate (on the large scale by cold and hot pressing, in the laboratory by the use of unglazed porcelain) is a hard, crystalline mass, melting point 41°-42° C. It caused no grease-spot on paper, and contained only traces of liquid oleic acid. On examination the following numbers were obtained :—

Acid value	53·3
Saponification value	204·3
Ether value	151·0
Acetyl saponification value	205·0
Iodine value	14·0

From these data the following composition is calculated :—

	Per cent.
Stearolactone	75·8
Isooleic acid	15·7
Saturated fatty acids	8·5
	100·0

5. "Recovered Grease"[1]

(*Crude Wool Fat*)

In technical analysis the determination of the following constituents of recovered grease would be required (cp. p. 687) :—

(*a*) Free fatty acids.
(*b*) Neutral fat.
(*c*) Unsaponifiable matter.

(*a*) *Free Fatty Acids*

The amount of alkali required to saturate the free fatty acids in 1 grm. of the "recovered grease" was 0·71 c.c. normal KOH (acid value = 39·8). A larged weighed quantity of "recovered grease" was then nearly neutralised with the greater part of the alkali required, as calculated from the acid value, and then carefully titrated with half-normal alkali, until the solution became pink to phenolphthalein. A large proportion of neutral fat and unsaponifiable matter rose to the top as an oily layer, and was separated from the soap solution,

[1] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1892, 134 ; cp. also *ibid.* 1896, 14.

after having been dissolved in ether. The remainder of the neutral fat and unsaponifiable matter was removed from the soap solution by shaking out with ether. The ethereal solutions were united, freed from adhering soap by washing with water, and the solvent was then distilled off. Thus the neutral fat (*b*) and the unsaponifiable matter (*c*) were obtained together.

Between the aqueous and the ethereal layers there appeared a flocculent stratum, which was found to consist of an insoluble soap. It was isolated by filtering off from the soap solution. The fatty acids of both the soap solution and the insoluble soap were separated in the usual manner by decomposing with a mineral acid. Thus the free fatty acids of the "recovered grease" were obtained in two fractions, viz. (1) acids, forming soluble soaps; (2) acids, forming insoluble soaps.

Both kinds of acids were found to contain inner anhydrides or lactones (increase of weight on boiling with acetic anhydride, cp. p. 206); for the determination of the molecular weight the acids had therefore to be boiled with standardised alcoholic potash. The molecular weights were found to be respectively 326 and 520. The proportion of the acids (1) to the acids (2) being 9 : 1, the mean molecular weight of *all* free fatty acids may be taken as—

$$\frac{9 \times 326 + 520}{10} = 345.$$

The *Reichert-Meissl* value of the recovered grease was 6·2, or, in other words, 1 grm. required 0·124 c.c. normal KOH for saturation of the volatile fatty acids. Assuming as their mean molecular weight 102 ($C_5H_{10}O_2$), the "recovered grease" contains $10{\cdot}2 \times 0{\cdot}124 = 1{\cdot}26$ per cent of *volatile acids.*

The insoluble free fatty acids in 1 grm. were saturated by 0·71 – 0·124 c.c. = 0·586 c.c. normal KOH. Their mean molecular weight being 345, we find $34{\cdot}5 \times 0{\cdot}586 = 20{\cdot}22$ per cent of *insoluble free fatty acids.*

(*b* and *c*) *Neutral Fat and Unsaponifiable Matter*

A somewhat large quantity of the substance (*b*) and (*c*), prepared as already described, was saponified, and the soap solution tested for *glycerol.* The negative result proved *absence of glycerides.* The neutral fat had, therefore, to be considered a *wax.*

The ether residue obtained by extracting the saponified mass with ether, and evaporating off the latter, was completely dissolved by acetic anhydride, no oily layer separating on cooling (p. 230). Therefore, *hydrocarbons* were absent, and the *unsaponifiable matter* (*c*) could only consist of alcohols.

The wax (*b*) was separated from the unsaponifiable matter (*c*) by judicious boiling out with alcohol,[1] in which the wax is almost in

[1] Preferably acetic anhydride, cp. p. 230.

soluble. The latter was thus obtained as a viscous wax-like substance, melting into a thick liquid at about 40° C.

On saponification with double normal alcoholic potash under pressure (p. 23), 1 grm. of the wax was found to require 1·825 c.c. of normal KOH, or, in other words, its saponification value was 102·4.

The alcohols (unsaponifiable) were determined in the usual manner by extracting the saponified mass with ether; the fatty acids were then estimated in the soap solution by *Hehner's* method. Thus the composition of the wax was found in two analyses as follows:—

	I. Per cent.	II. Per cent.
Fatty acids	56·3	54·1
Alcohols	43·2	44·0
	99·5	98·1

The sum of the constituents of the wax should have been higher than 100, several per cents of water being assimilated on saponification. The deficiency must be looked for in the number obtained for the fatty acids, this having been found too low, owing to the property of these acids of easily losing water on drying, with formation of inner anhydrides or lactones. The molecular weight of these fatty acids was found to be 327·5 when using *alcoholic* potash for the determination, wherefrom the percentage composition of the wax may be calculated as follows:—

	Per cent.
Fatty acids, $1{\cdot}825 \times 32{\cdot}75 =$ . . .	59·77
Alcohols (mean of values in Analyses I. and II.) .	43·60
	103·37

The *mean molecular weight of the alcohols* calculated from the equation

$$M = \frac{43{\cdot}6 \times 327{\cdot}5}{59{\cdot}77}$$

was found to be 239.

The fatty acids absorbed only 17 per cent of *iodine;* they consist, therefore, for the most part of saturated acids.

(*c*) *Unsaponifiable Matter*

The proportion of unsaponifiable matter was found *approximately* by analysing the mixture of (*b*) and (*c*) in the same manner as (*b*), and comparing the numbers obtained as follows:—

1 grm. of the mixture of (*b*) and (*c*) required 1·73 c.c. of normal KOH on saponification. Its percentage composition was found as follows:—

	I. Per cent.	II. Per cent.
Fatty acids	50·7	49·8
Alcohols	47·5	47·6
	98·2	97·4

From these numbers we calculate—

	Per cent.
Fatty acids, 1·73 × 32·75	56·66
Alcohols	47·55
	104·21

The 56·66 parts of fatty acids require 41·34 per cent of alcohols, mean molecular weight 239, to form wax. Consequently there are present in the "recovered grease" 47·55 − 41·34 = 6·21 per cent of *unsaponifiable matter.*

The composition of the "recovered grease" is therefore—

	Per cent.
Volatile fatty acids	1·26
Insoluble free fatty acids	20·22
Unsaponifiable matter (uncombined alcohols) .	6·21
Wax (wool fat) by difference	72·31
	100·00

To check the result the sum of the alcohols and of the wax could have been determined direct.

The number 72·31 for wax can be resolved, with the help of its above-given percentage composition (fatty acids, 59·77 per cent; alcohols, 43·60 per cent), into two numbers expressing its component parts, viz. 72·31 × 0·5977 = 41·81 per cent of fatty acids, and 72·31 × 0·436 = 30·5 per cent of alcohols. The total unsaponifiable matter obtainable from the "recovered grease" on complete saponification is, therefore, 30·5 + 6·21 = 36·71 per cent. Hence we express the analytical result as follows:—

		Per cent.	
Volatile fatty acids		1·26	
Insoluble free fatty acids . . .		20·22	
Unsaponifiable matter (uncombined alcohols)		6·21	Total unsaponifiable matter. 36·71
Wax	Combined alcohols	30·50	
	Combined fatty acids . . .	41·81	

The percentage of the *total unsaponifiable matter*—36·71—can, of course, be verified by direct determination, which can be suitably combined with that of the saponification value. Direct experiment gave the number 36·47 (see below).

A more rapid, and for technical purposes sufficiently accurate, method would be to determine the *acid value*, the *saponification value*

(the *ether value* by difference), the proportion of *total unsaponifiable matter*, the *mean molecular weight of the total insoluble acids*,[1] and, if required, the *Reichert-Meissl value*. The following numbers were thus obtained :—

1 grm. required for the saturation of the volatile acids	. 0·124 c.c. of normal KOH	
1 ,, ,, ,, ,, ,, free insoluble acids	0·586 c.c.	,, ,,
1 ,, ,, ,, ,, ,, total insoluble acids .	. 2·19 c.c.	,, ,,
1 ,, ,, ,, ,, ,, combined insoluble acids (by difference)	1·48 c.c.	,, ,,
Mean molecular weight of the total insoluble acids .	. 332[2]	
Unsaponifiable matter	. 36·47 per cent.	

From these analytical data we obtain :—The percentage of the free insoluble acids, $0{\cdot}586 \times 33{\cdot}2 = 19{\cdot}45$; the percentage of the combined fatty acids, as hydrated acids, $1{\cdot}48 \times 33{\cdot}2 = 49{\cdot}13$; and the percentage of volatile acids, $0{\cdot}124 \times 10{\cdot}2 = 1{\cdot}26$ as before.

In the following table these numbers are collated :—

	Per cent.
Volatile fatty acids	1·26
Insoluble free fatty acids	19·45
Combined fatty acids (as hydrated acids) . .	49·13
Total unsaponifiable matter	36·47
	106·31

Part of the surplus over 100 is due to the proportion of water assimilated on saponification ; the remainder is due to an error in the number found for the molecular weight of the total insoluble fatty acids, caused by the difficulty of titrating accurately the dark alcoholic solutions.

It would not have been permissible to determine the proportion of the total fatty acids by *Hehner's* method, the result obviously coming out too low owing to the formation of inner anhydrides.

6. Distilled Grease[3]

(*Liquid Portion*)

The liquid portion of the distillate obtained on a large scale by subjecting the "recovered grease" to distillation gave on examination the following results :—

[1] This must be determined with *alcoholic* potash (cp. above).

[2] This number is somewhat too high, owing to the dark colour of the alcoholic solution of the fatty acids.

[3] Lewkowitsch, *Jour. Soc. Chem. Ind.* 1892, 141.

(*a*) 1 grm. required for the saturation of the free fatty acids . 1·92c.c. of normal KOH
(*b*) 1 ,, ,, ,, ,, ,, total fatty acids on saponification . . . . . 2·10 c.c. ,, ,,
(*c*) 1 grm. required therefore for the saturation of the combined fatty acids . . . . . 0·18 c.c. ,, ,,
(*d*) Mean molecular weight of the total fatty acids[1] . 300·5
(*e*) Total unsaponifiable matter . . . . 38·8 per cent.

From the numbers recorded under (*c*) and (*d*) and (*e*) the composition of the distilled grease may be expressed thus :—

	Per cent.
Fatty acids (as hydrated acids), 2·1 × 30·05 . .	63·1
Total unsaponifiable matter	38·8
	101·9

The low number obtained for the combined fatty acids shows that the greater portion of the wax had been decomposed during distillation.

The free fatty acids were isolated as described p. 816; their mean molecular weight was 286; they may, therefore, be considered as consisting of a mixture of oleic, stearic, and palmitic acids, with a small proportion of higher fatty acids. The proportion of free fatty acids in the "distilled grease" was, therefore, 1·02 × 28·6 = 54·91 per cent.

The wax *plus* the unsaponifiable matter was isolated in the same manner as described p. 817. The separation of these two constituents was, however, impossible, the unsaponifiable matter being also insoluble in alcohol. The mixture of the two substances was therefore saponified, so as to isolate the fatty acids contained in the wax. They possessed the molecular weight 394, as determined by means of *alcoholic* potash. The proportion of combined fatty acids in the "distilled grease" was therefore (2·10 – 1·92) × 39·4 = 7·09 per cent.

The alcohol combined with the latter acids was contained in the total unsaponifiable matter. Its presence was proved, on the one hand, by boiling an accurately weighed portion with acetic anhydride, and ascertaining that an increase in weight had taken place; and, on the other hand, by isolating the alcohol from the total unsaponifiable matter by means of alcohol.

Adopting the molecular weight for the alcohols that had been found (p. 818) for the combined alcohols in the "recovered grease," we can calculate the proportion of *alcohols* from the equation

$$\frac{7{\cdot}09 \times 239}{394} = x\,;$$

hence $x = 4{\cdot}3$.

The amount of *undecomposed wax* in the "distilled grease" is, therefore, neglecting the small amount of water assimilated on saponification, 7·09 + 4·3 = 11·39 per cent.

[1] Determined with *alcoholic* potash.

The remainder of the unsaponifiable matter, 38·8 – 4·3 = 34·5 per cent, consists of hydrocarbons formed in consequence of the free fatty acids and of the wax of the "recovered grease" having been decomposed during distillation.

The composition of the "distilled grease" is expressed by the following numbers:—

	Per cent.	
Free fatty acids	54·91	
Combined fatty acids	7·09	Undecomposed Wax. 11·39
Combined alcohols	4·30	
Unsaponifiable matter (hydrocarbons)	34·50	
	100·80	

INDEX

Abietic acid, 235, 236
Absolute iodine value, 195, 312
Absorption spectra, 113
Acetic acid, 42
Acetin, 3, 26
Acetine, 677
Acetyl value, 162
  acid value, 163
  saponification value, 163
Acid, acetic, 42
  acrylic, 52
  aldepalmitic, 24, 604
  angelic, 53
  arachidic, 49
  asellic, 54, 279, 479
  azelaic, 73
  behenic, 49
  behenolic, 60
  brassidic, 59
  butyric, 42
  capric, 44
  caproic, 43
  caprylic, 44
  carnaübic, 50
  cerotic, 50
  cocceric, 64
  crotonic, 176
  crotonoleic, 26, 414
  daturic, 47
  dihydroxyasellic, 170
  dihydroxybehenic, 71
  p-dihydroxybehenic, 71
  dihydroxyheptadecylic, 70
  dihydroxyjecoleic, 70
  dihydroxypalmitic, 70
  dihydroxystearic, 66, 67, 70
  p-dihydroxystearic, 70
  dihydroxystearidic, 70
  dihydroxystearo-sulphuric, 65
  dihydroxytiglic, 69
  diricinoleic, 65
  doeglic, 59
  elæomargaric, 60
  elæostearic, 60
  elaïdic, 57
  erucic, 59
  formic, 527
  gaïdic, 53
  hexahydroxystearic, 72
  hyænic, 50
Acid, hydroxyoleic, 55
  hydroxystearic, 68
  hypogæic, 53
  isanic, 63
  isobutylacetic, 43
  isocetic, 45
  isodihydroxybehenic, 71
  isoerucic, 60
  isolinolenic, 62
  isolinusic, 72
  isooleic, 57
  isoricinoleic, 65
  isotrihydroxystearic, 71
  isovaleric, 43
  jecoleic, 59, 279
  jecoric, 62, 279
  lanoceric, 66
  lanopalmic, 63
  lauric, 44
  lignoceric, 49
  linolenic, 62
  linolic, 60, 144, 202
  linusic, 72
  lycopodic, 54
  margaric, 47
  medullic, 587
  melissic, 50
  millet oil, 61
  moringic, 26
  morrhuic, 481
  myristic, 45
  oleic, 54, 197, 201, 202, 765
  p-oleic, 57
  oxyoleic, 61
  palmitic, 46, 199, 201
  palmitolic, 60
  pentadecylic, 76
  pentaricinoleic, 728
  physetoleic, 53
  pimaric, 235
  rapic, 58
  ricinelaïdic, 65
  ricinic, 66
  ricinisoleic, 64
  ricinoleic, 64
  ricinoleo-sulphuric, 725
  salicylic, 616
  sativic, 72, 142
  stearic, 47, 198, 201
  stearolic, 60

Acid, suberic, 73
sylvic, 235
tariric, 61
tetrahydroxystearic, 72
theobromic, 26, 527
therapic, 63, 279
tiglic, 53
tigliceric, 67
trihydroxystearic, 71
triricinoleic, 728
umbellulic, 27, 44, 508
Acid saponification, 746
Acid value, 148
Acids, acetic series, 42
acrylic series, 52
dibasic, 72
dihydroxylated, 66, 69
hexahydroxystearic, 72
hydroxylated, 63, 64, 68
linolenic series, 62
linolic series, 60
monohydroxylated, 68
oleic series, 52
ricinoleic series, 64
tetrahydroxylated, 72
trihydroxystearic, 71
Acorn oil, 434
Acroleïn, 80
detection in glycerin, 788
Acrylic series, 52
Adeps lanæ, 689
Agnine, 689
Alcohol, carnaübyl, 74
ceryl, 75
cetyl, 74
cocceryl, 76
isoceryl, 75
lanolin, 76
melissyl, 75
myricyl, 75
octodecyl, 74
psyllostearyl, 76
Alcohol, detection in soap, 782
methylated, 20
purification of, 19
Alcohols, 73-86
aliphatic, 213
allylic series, 75
aromatic series, 83
detection of, in unsaponifiable matter, 230
ethane series, 73
free, in waxes, 16
Alde-acids, 53
Aldepalmitic acid, 24, 604
Aliphatic alcohols, 73-82
alcohols, detection of, in unsaponifiable matter, 230
alcohols, determination of, 213
Allylic series of alcohols, 75
Almond oil, 435
Amyl stearate, 4
Angelic acid, 53
Anhydrides, inner, 206
Animal fats, 550
Animal oils, 468
distinction between, and vegetable oils, 317
waxes, 651
Annatto, 614
Apricot kernel oil, 428
Arachidic acid, 49
Arachin, 5
Arachis oil, 441
Arctic sperm oil, 278, 647
Aromatic series of alcohols, 83
Asellic acid, 54, 279, 479
Aselline, 481
Azelaic acid, 73

Badger fat, 551
Baryta value, 159
Base oils, 13, 733
Basswood oil, 393
Baudouin's test for sesamé oil, 390
Becchi's test for cotton seed oil, 382
Beechnut oil, 393
Beef marrow fat, 586
Beef tallow, 592
stearine in lard, 584
Beeswax, 655
Beeswax oil, 657
Behenic acid, 49
Behenolic acid, 60
Ben oil, 467
Bieber's reagent, 439
Blackcock fat, 551
Black fish oil, 495
Black mustard oil, 407
Black oil, 693
Blown oils, 13, 733
Blubber oils, 278, 469, 490
Boiled (linseed) oil, 735
Boiling points of fatty acids, 30
Bone fat, 587
lime soaps in, 749
Borneo tallow, 533
Bottlenose oil, 647
Brassidic acid, 59
Brassidin, 5
Brazil nut oil, 395
Bromine, action on fats, 14
addition number, 169
substitution number, 169
thermal test, 300
value, 167
value of oils and liquid waxes, 307
value of solid fats, 329
Brown grease, 686
Brown substitutes, 742
Burning oils, 685
Butter, 604
adulteration of, 609
cacao (cocoa), 527
fat, 601
galam, 513
goa, 531
kokum, 531
mace, 523
mahwah, 511

Butter, nutmeg, 523
oil, 609
phulwara, 511
shea, 513
substitutes, 679
vegetable, 541, 682
Butterine, 621, 678
Butyric acid, 42
Butyrin, 3
Butyro-refractometer, 116
in analysis of butter, 626

Cacao butter, 527
Californian nutmeg oil, 441
Cameline oil, 367
Candle material, 754
Candle nut oil, 362
Candles, 745
cerasin, 763
paraffin wax, 757
sperm, 756
stearine, 745
tallow, 745
wax, 755
Candle tar, 755
Capric acid, 44
Caprin, 44
Caproic acid, 43
Caproin, 607
Caprylic acid, 44
Caprylin, 607
Carapa oil, 509
Carbolic acid as solvent in the examination of oils, 274
Carbolic acid in soap, 783
Carnaüba wax, 649
Carnaübic acid, 50
Carnaübyl alcohol, 74
Castor oil, 420
oil group, 413
oil rubber substitute, 743
oil, soluble, 733
Celosia oil, 365
Cerasin, 765
candles, 763
detection in unsaponifiable matter, 230
Cerotic acid, 50
Cerotin, 5
Ceryl acetate, 75
alcohol, 75
cerotate, 15
palmitate, 15
Cetin, 15, 669
Cetyl acetate, 74
alcohol, 74
alcohol, quantitative determination, 230
benzoate, 74
palmitate, 15
stearate, 15
Ceylon oil, 538
Chamois fat, 551
Chaulmoogra oil, 508
Chemical constitution of fats, 2
constitution of waxes, 14
Chemical methods of examining fats and waxes, 137-216
methods of examining fatty oils and liquid waxes, 253, 277-318
methods of examining solid fats and waxes, 328
Cherry kernel oil, 426
laurel oil, 428
Chicken fat, 551
Chinese wax, 672
Chloride of sulphur, *see* Sulphur chloride
Chlorine, action of, on fats, 13
colour reactions, 316
estimation of, in fats, 97
Cholesterol, 83
determination of, in unsaponifiable matter, 231
in animal oils, 317
in cod liver oil, 487
Cholesterones, 233
Cholesteryl acetate, 84, 232
benzoate, 84, 231
oleate, 16
palmitate, 16
stearate, 16
Cholestol reaction, 85
Choline, 7
Cloth oils, 704
Coast cod oil, 476
Cocceric acid, 64
Coccerin, 15
Cocceryl alcohol, 76
Cocceryl coccerate, 15
Cochineal wax, 15, 45, 76
Cochin oil, 538
Cocoa butter, 527
Cocoa nut oil, 537
nut oleine, 541
nut stearine, 541
Cod liver oil, 475
liver oil dégras, 702
Cod oil, 475
Coffee berry oil, 465
Cohesion figures, 274
Cold test, 136, 713
Colophony, 234
Colouring matters in butter, 614
matters in soap, 772
Colour of fats, 319
Colour reactions, 313
Colza oil, 399
Congealing points of oils, 259
Consistency, 102
Constant acid value, 206
ether value, 206
saponification value, 206
Constituents of fat and waxes, 24-86
Copper, detection of, in fats, 98
Coprah oil, 537
Copraol, 528
Corn oil, 372
Corroine, 695, 704
Cotton seed foots, 692
seed oil, 375
seed oil, blown, 734

Cotton seed oil, detection in lard, 580
seed oil, detection in tallow, 597
seed oil group, 366
seed oil rubber substitute, 743
seed stearine (acid), 692
seed stearine (fat), 506
seed wax, 649
Coula oil, 5
Crab wood oil, 509
Cresylic acid in soap, 783
Critical temperature of dissolution, 122, 276
Crotonic acid, 176
Croton oil, 414
Crotonoleic acid, 26, 414
Cryoscopic method of testing butter, 630
Curcas oil, 416
Curcuma, detection of, in butter, 614

Dame's violet oil, 363
Daturic acid, 47
Dégras, 693
former, 699
Diacetylglycid, 678
Diagometer, 121
Dibasic acids, 72
Dicerotin, 3
Dierucin, 2, 191
Diglycerides, 2, 190
determination of, 190
Dihydroxyasellic acid, 70
Dihydroxybehenic acid, 71
p-Dihydroxybehenic acid, 71
Dihydroxyheptadecylic acid, 70
Dihydroxyjecoleic acid, 70
Dihydroxylated acids, 69
Dihydroxypalmitic acid, 70
Dihydroxystearic acid, 66, 70, 141
Dihydroxystearidic acid, 70
Dihydroxystearo-sulphuric acid, 65
Dihydroxytiglic acid, 69
Dika oil, 533
Dimelissin, 3
Diricinoleic acid, 65
Distearin, 3
Distillation glycerin, 805
stearine, 755
Distilled glycerin, 786, 802
grease, 691
grease, analysis of, 820
grease oleine, 691
grease stearine, 691, 755
grease stearine in tallow, 597
oleine, 746
stearine, 196, 755
Doeglic acid, 58
Doegling oil, 278
Dog fat, 551
Dolphin oil, 278, 495
Domestic cat fat, 551
duck fat, 551
Driers, 737
Drying of fatty acids, 180
oils, 10
oils, description of, 336-366
Drying oils, general characters, 279
Dutch butter, 678
Dynamite glycerin, 802

Earthnut oil, 441
Edible fats, 678
oils, 684
Egg oil, 503
Elæomargaric acid, 60
Elæostearic acid, 60
Elaïdic acid, 57
Elaïdin, 5
test, 280
Elaïne, 765
Electrical conductivity, 121, 275
Elk fat, 551
Emulsion wool oils, 709
Erucic acid, 59
Erucin, 5
Ethal, 74
Ethane series of alcohols, 73
Ethereal oils in fats, 90
oils in soap, 772
Ether value, 154
Examples, 811
Extraction apparatus, 66

Fallow buck fat, 551
Fat, definition of, 1
determination of, 90
estimation of water in, 88
nature of, 1, 2
preparation of, for analysis, 92
Fat, badger, 551
beef marrow, 586
blackcock, 551
bone, 587
butter, 601
chamois, 551
chicken, 551
dog, 551
domestic cat, 332, 551
domestic duck, 332, 551
elk, 551
fallow buck, 551
fox, 551
goose, 559
hare, 555
horse, 552
horse marrow, 555
human, 562
milk, 601
pigeon, 551
pine marten, 551
polecat, 551
rabbit, 557
roebuck, 551
sawarri, 521
stag, 641
starling, 551
turkey, 551
ucuhuba, 544
wild boar, 332, 564
wild cat, 332, 551
wild duck, 332, 551

Fat, wild goose, 332, 561
wild olive, 550
wild rabbit, 332, 558
wool, 686
Fats, animal, 550
edible, 678
properties of, 8
saponification of, 18
solid, 506
synthetical, 676
unsaponifiable matter in, 6
vegetable, 506
waste, 687
Fatty acids (*see* Acids), 26-72
acids, acetyl values of, 164
acids, acid values of, 150
acids, action on indicators, 31
acids, boiling points of, 30
acids, determination of, 182
acids, drying of, 180
acids, free, determination of, 182, 183
acids, free, in fats, 7
acids, free, in waxes, 16
acids, insoluble, 31
acids, insoluble, determination of, 180, 191
acids, insoluble, preparation of, 100
acids, liquid, 108, 149
acids, melting points of, 27
acids, non-volatile, 30
acids, non-volatile, examination of, 196
acids, properties of, 27
acids, salts of, 33
acids, saturated, 149
acids, solid, 192
acids, solidifying point of (titer test), 133
acids, solubility of, 30
acids, soluble, 30, 31
acids, viscosity of, 33
acids, volatile, 30, 154
Fatty oils, 1, 718
oils, as lubricants, 718
oils, properties of, 8
Fin-back oil, 492
Fir seed oil, 358
Fish oils, 278, 469
Fish stearine, 475
Fish tallow, 472, 475
Flash point, 715
point of mineral oils, 717
Fluorescence, 226, 722
Formalin, 616
Formic acid, 527
Fox fat, 551
Fractional crystallisation, 140
distillation, 144
Free fatty acids, *see* Fatty acids
Freezing point of oils, 135
Freezing mixtures, 135
Fuller's grease, 693

Gaduine, 481
Gaïdic acid, 53
Galam butter, 513
Galena oils, 726
Galipot, 235
Garden cress oil, 397
rocket oil, 363
German sesamé oil, 367
Getah wax, 649
Gingili oil, 385
Glycerides, 1, 2, 336-642
Glycerin, chemically pure, 786
commercial, 786
crude, 805
crude, distillation, 805
crude, saponification, 805
crude, soap lye, 805
crystallised, 786
distilled, 802
dynamite, 802
in soap, 782
in spent lyes, 809
refined, 786
Glycerol, 77
determination of, by oxidation processes, 208
determination of, by the acetin process, 213, 806
determination of, by titration with caustic potash, 208
determination of, in chemically pure glycerin, 790
determination of, in crude glycerin, 806
determination of, in dynamite glycerin, 802
Glycerolphosphoric acid, 7
Glyceroxides, 79
Glyceryl stearate, 2
Glycolic series of alcohols, 76
Glycyl ethers, 2, 80
arsenite, 80
trinitrate, 80
Goa butter, 531
Goat's tallow, 598
Gold chloride test for cotton seed oil, 384
Goose fat, 559
Grape seed oil, 418
Grease, brown, 686
distilled, 690, 820
fuller's 693
lubricating, 726
recovered, 686, 816
wool, 686
Yorkshire, 687, 816
Gutzeit's test, 789

Haddock liver oil, 485, 489
Hake liver oil, 485
Hare fat, 555
Hazelnut oil, 449
Heat of bromination test, 300
Hedge mustard oil, 399
Hehner value, 160
value of fatty oils, 306
value of solid fats, 328
Hemp seed oil, 348
Henbane seed oil, 365
Herring oil, 485
Hexahydroxystearic acid, 72

Hirschsohn's test for cotton seed oil, 384
Horse fat, 552
Horse marrow fat, 555
Horses' foot oil, 501
Hübl iodine value, 170
Human fat, 562
Humpback oil, 492
Hyænic acid, 50
Hydrocarbons, 217
Hydrolysis of fats, 18
  of soap, 35
  of waxes, 22
Hydrostatic balance, 125
Hydroxy(lated) acids, 63, 64, 68
  acids, determination of, 204
Hydroxyoleic acid, 55
Hydroxystearic acid, 68
Hypogæic acid, 53

Ignition point, 717
Illipé oil, 8, 511
Indian laurel oil, 365
Indicators in fat analysis, 31
Inner anhydrides, 206
Inner iodine value, 195, 312
Insect wax, 672
Insoluble fatty acids, 31, 191
Iodine, action on fats, 14
  in cod liver oil, 487
  value, 167, 170
  value of liquid fatty acids, 312
  value of oils and liquid waxes, 307
  value of solid fats, 329
Iron in fats, 99
Isanic acid, 63
Isano oil, 362
Isobutylacetic acid, 43
Isoceryl alcohol, 75
Isocetic acid, 45
Isocholesterol, 85
  detection of, in unsaponifiable matter, 231
Isocholesteryl acetate, 85
  benzoate, 85
  stearate, 16
Isodihydroxybehenic acid, 71
Isoerucic acid, 60
Isoglycerol, 83
Isolinolenic acid, 62
Isolinusic acid, 72, 141
Isooleic acid, 57
Isoricinoleic acid, 65
Isotrihydroxystearic acid, 71
Isovaleric acid, 43

Jambo oil, 413
Japanese wood oil, 345
Japan fish oil, 472
Japan wax, 546
  wax, detection in beeswax, 659, 666
Jaw oils, 496, 498
Jecoleic acid, 59
Jecoric acid, 62,

Kapok oil, 375
Kitchen grease, 686
Kokum butter, 531
Köttstorfer value, 151

Labiche test for cotton seed oil, 384
Lacmoïd, 33
Lactine, 528, 541, 682
Lactones, 206
Lallemantia oil, 347
Lanoceric acid, 67
Lanolin alcohol, 76
Lanoline, 689
Lanopalmic acid, 63
Lard, 563
  oil, 584
  stearine, 584
  substitutes, 682
Laurel oil, 509
  nut oil, 509
Laureol, 541
Lauric acid, 44
Laurin, 4
Laurostearin, 4
Lead acetate test for cotton seed oil, 384
Lead, detection of, in fats, 98
  estimation of, in fats, 98
  plaster, 785
  powder, 231
Lecithin, 7, 97
  in butter, 604
Liebermann-Storch reaction, 226
Lignoceric acid, 49
Lime, in fats, 97
  saponification, 745
  soaps in bone fat, 749
Linolenic acid, 62
Linoleum, 741
Linolic acid, 60, 144, 202
Linoxyn, 61, 288, 337
Linseed cake, 675
  oil, 336
  oil, adulteration of, 343
  oil, boiled, 735
  oil rubber substitutes, 743
  oil varnishes, 739
Linusic acid, 72, 141
Lipochromes, 85, 315
Liquid fatty acids, 141, 192
  determination of, 202
Liquid waxes, 277, 643
Lithographic varnishes, 739
Litmus, 33
Livache test, 285
Liver oils, 278, 469, 474
Lubricating oils, 712
Lycopodic acid, 54

Macassar oil, 520
Mace butter, 523
Madia oil, 360
Mafura tallow, 521
Magma, 693
Mahwah butter, 511
Maize oil, 372
Malabar tallow, 549

Mangosteen oil, 531
Margaric acid, 47
Margarine, 591, 678
Margarine oil, 591
Marine animal oils, 468, 469
Marine soaps, 45
Maumené test, 291
Medullic acid, 587
Melissic acid, 50
Melissin, 5
Melissyl alcohol, 75
Melting point, determination of, 130
  point of fats and waxes, 323
  point of fatty acids, 27
  point of mixed fatty acids from oils and liquid waxes, 260
  point of mixed fatty acids from solid fats and waxes, 325
Menhaden oil, 470
Metallic soaps, 41, 785
Methylated spirit, 19
  purification of, 20
Methylorange, 31
Microscopic examination, 121
Milk fat, 601
Millet oil acid, 61
Milliau test for cotton seed oil, 383
Mineral oil, 224
Mineral oils as lubricants, 719
Mkanyi fat, 526
Mocaya oil, 534
Moëllon, 694
Mohamba oil, 363
Molecular weight of fatty acids, 184, 188
Monocerotin, 3
Monoglycerides, 2
Monohydroxylated acids, 68
Monomelissin, 3
Monostearin, 2
Moringic acid, 26
Morrhuic acid, 481
Morrhuine, 481
Mowrah seed oil, 511
Mucilage, 692
Mutton tallow, 598
Myricin, 15, 661
Myricyl alcohol, 75
  palmitate, 15
Myristic acid, 45
Myristin, 4
Myrtle wax, 542

Neat's foot oil, 504
Neoline, 710
Neutral fat, determination of, 182
  fat in soaps, 779
Neutral fats, 2
Niger seed oil, 354
Nitric acid, action on fats, 13
Nitric acid test for cotton seed oil, 381
Nitroglycerin, 80, 803
Nitrous acid, action on fat, 13
  acid in elaïdin test, 280
Non-drying oils, 279, 426
Non-saturated fatty acids, 192
Nucoline, 541
Nutmeg butter, 523
Nut oil, 350

Oba oil, 533
Occurrence of fatty acids, 26
Ocotilla wax, 649
Octodecyl acetate, 74
  alcohol, 74
  palmitate, 15
Ocuba wax, 649
Oil, acorn, 434
  almond, 435
  apricot kernel, 428
  arachis, 441
  arctic sperm, 278, 647
  basswood, 393
  beechnut, 393
  beeswax, 657
  ben, 467
  black, 693
  black fish, 495
  black mustard, 407
  bottlenose, 278, 647
  Brazil nut, 395
  cabbage seed, 265
  Californian nutmeg, 441
  cameline, 367
  candle nut, 362
  carapa, 509
  castor, 420
  celosia, 365
  Ceylon, 538
  chaulmoogra, 508
  cherry kernel, 426
  cherry laurel, 428
  coast cod, 475
  Cochin, 538
  cocoa nut, 537
  cod, 475
  cod liver, 475
  coffee berry, 465
  colza, 399
  coprah, 537
  corn, 372
  cotton seed, 375
  coula, 5
  crab wood, 509
  croton, 414
  curcas, 416
  dame's violet, 365
  dika, 533
  doegling, 278
  dolphin, 278, 492
  earthnut, 441
  egg, 503
  fin-back, 492
  fir seed, 358
  garden cress, 397
  garden rocket, 363
  German sesamé, 367
  gingili, 385
  grape seed, 418
  haddock liver, 485, 489
  hake liver, 485

Oil, hazelnut, 449
hedge mustard, 399
hemp seed, 348
henbane seed, 365
herring, 485
horses' foot, 501
humpback, 492
illipé, 8, 511
Indian laurel, 365
isano, 362
jambo, 413
Japanese wood, 345
Japan fish, 472
kapok, 375
lallemantia, 347
lard, 584
laurel, 509
laurel nut, 509
linseed, 336
macassar, 520
madia, 360
maize, 372
mangosteen, 531
margarine, 591
menhaden, 470
mocaya, 534
mohamba, 363
mowrah seed, 511
neat's foot, 504
niger seed, 354
nut, 350
oba, 533
olive, 451
olive kernel, 464
palm, 517
palm nut, 535
peach kernel, 432
peanut, 441
pine nut, 358
pistachio, 449
plum kernel, 430
poonseed, 509
poppy seed, 352
porpoise, 497
pumpkin seed, 371
purging nut, 416
radish seed, 411
rape, 399
ravison, 273, 336, 401
ray liver, 485
rice, 447
salmon, 470
sanguinella, 440
sardine, 472
seal, 490
secale, 468
seek, 693
sesamé, 385
shark liver, 485, 487, 489
sheep's foot, 499
skate liver, 485, 489
sod, 693
soja bean, 369
sperm, 278, 643
sprat, 485
Oil, strophantus seed, 467
sunflower, 356
tallow, 591
tea seed, 447
teel, 385
tobacco seed, 366
ungnadia, 466
ungueko, 362
walnut, 350
wax, 352
weld seed, 366
whale, 492
wheat meal, 434
white mustard, 409
Oil cakes, 673
nuts, 544
thickener, 56, 720, 785
thickener in lubricating oils, 720
Oils, animal, 468-505
base, 13, 733
blown, 13, 733
blubber, 277, 490
burning, 685
cloth, 704
drying, 10, 277, 336-366
drying properties of, 277, 279
edible, 684
fatty, 718
fish, 277, 278, 470
galena, 726
liver, 277, 474
lubricating, 712
marine animal, 469
mineral, 225, 719
nature of, 1
non-drying, 426
non-drying, properties of, 10, 277
oxidised, 13, 733
paint, 685
plumbago, 726
resin, 225, 721
salad, 684
semi-drying, 366
tar, 225
terrestrial animal, 499
thickened, 733
turkey-red, 726
vegetable, 336-468
vulcanised, 742
wool, 704
Oleaginous seeds, 673
Oleic acid, 54
acid, commercial, 765
acid, conversion into candle material, 747
acid, determination of, 192, 197, 201
acid, determination of, in press cakes, 753
Olein, 5
Oleine, 745
cotton foots, 692
distilled, 746
distilled grease, 691
saponification, 746
saponified, 746
wool fat, 691

Oleine wool oil, 704
Oelodistearin, 3
Oleomargarine, 591, 681
Oleo-palmito-butyrate, 3
Oleo-refractometer, 119
  in analysis of butter, 623
  in analysis of lard, 578
  in analysis of oleine, 769
  in analysis of olive oil, 459
Oleostearine, 576
Olive oil, 451
  kernel oil, 464
  oil grease, 451
Opium wax, 15, 649
Optical methods of examination, 261
Organoleptic methods, 252
Oxidation of unsaturated fatty acids, 68
Oxidised oils, 13, 733
Oxygen absorption test, 285
Oxyoelic acid, 61
Ozokerit, 763

Paint oils, 685
Palmitic acid, 46
  acid, determination of, 199, 201
  acid, separation from oleic acid, 196
Palmitin, 4
Palmitolic acid, 60
Palm oil, 517
  nut oil, 535
  nut oleine, 537
  oil grease, 520
  wax, 649
Paraffin scale, 759
  wax, 757
  wax candles, 757
  wax, detection in unsaponifiable matter, 232
Para-oleic acid, 57
Pattern test, 275
Peach kernel oil, 432
Peanut oil, 441
Pentadecylic acid, 76
Pentaricinoleic acid, 728
Phenolphthalein, 32
Phospho-molybdic acid, 316
Phosphoric acid as reagent, 278, 316
Phosphorus in fats, 7, 97
Phulwara butter, 511
Physetoleic acid, 53
Physical methods of examining fatty oils and liquid waxes, 253, 254-276
Physical methods of examining solid fats and waxes, 320
Physical properties of oils, fats, and waxes, 102-136
Phytosterol, 86
  detection of, in oils, 317
  in palm oil, 319
  in unsaponifiable matter, 231
Picnometer, 125
Pigeon fat, 551
Pimaric acid, 235
Pinates, 237
Pine marten fat, 551
Pine nut oil, 358
Piney tallow, 549
Pistachio oil, 449
Pitch, from distilled grease, 692
  from stearine, 755
  from wool fat, 692
Plumbago oils, 726
Plum kernel oil, 430
Polarimetric examination, 120
  examination of oils, 267
  examination of resin oils, 228
Polarisation microscope, 121
Polecat fat, 551
Polyglycerols, 788, 809
Polyricinoleic acids, 65
Poonseed oil, 509
Poppy seed oil, 352
  seed oil rubber substitute, 743
Porpoise oil, 497
Potash soaps, 769
Poutet's test, 280
Premier jus, 591
Psyllostearyl alcohol, 76
Pumpkin seed oil, 371
Purging nut oil, 416

Qualitative examination of fats, 138
Qualitative reactions, 313
Quantitative analysis of fats, 147
Quantitative reactions, 147

Rabbit fat, 557
Radish seed oil, 411
Rambutan tallow, 49, 526
Rancidity, 11
Rape oil, 399
  oil, blown, 734
  oil group, 397
  oil rubber substitute, 743
  oil stearine, 190
Rapic acid, 58
Ravison oil, 273, 336, 401
Ray liver oil, 485
Recovered black oil, 693
  grease, 686
Red oil, 766
Refractive indices of fats, 262
  indices of oils, 333
Refractive power of fats, 113
Refractometer, 114-119
Refractometric examination of oils, 261-267
Reichert's distillation process, 155
Reichert value, 154
Reichert-Meissl value, 154
  values of oils and liquid fats, 306
  values of solid fats, 329
Renard's test for arachis oil, 445
  test for resin oil, 227
Residues from distillation of glycerin, 809
Resin, 234
  detection of, 238
  determination of, 239
  oil in lubricating oils, 721
  oils, 225-228
  soaps, 237, 779

Resin spirit, 225
Resinates, 237, 785
Rice oil, 447
Ricinelaïdic acid, 65
Ricinic acid, 66
Ricinisoleic acid, 64
Ricinoleic acid, 64
Ricinolein, 5
Ricinoleo-sulphuric acid, 65
Roebuck fat, 551
Rotation of polarised light, 120
Rubber substitutes, 742

Saffron in butter, 615
Salad oils, 684
Salicylic acid in butter, 616
Salmon oil, 470
Salts of fatty acids, 33
Sampling of fats, 87
Sanguinella oil, 440
Saponification, 18-23
  equivalent, 152, 306
  glycerin, 805
  oleine, 746
  stearine, 755
  technical, 745
  technical, by means of acids, 746
  technical, by means of lime, 745
  technical, by means of water, 746
  value, 151
  values of ethers, 154
  values of fatty oils, 303, 304
  values of glycerides, 153
  values of liquid waxes, 303
  values of solid fats, 329
  values of waxes, 154, 329
Saponified oleine, 745
  stearine, 755
Sardine oil, 472
Sativic acid, 72, 141
Saturated acids, 42
  acids, determination of, 192
  acids, examination of, 140
Sawarri fat, 521
Scale, *see* Paraffin scale
Seal oil, 490
  oil, blown, 743
  oil dégras, 702
Seeds, oleaginous, 673
Seek oil, 693
Semi-drying oils, 366
Sesamé oil, 385
Sesamin, 389
Shark liver oil, 485, 487, 489
  liver oil dégras, 702
Shea butter, 513
Sheep's foot oil, 499
Ship's fat, 686
Skate liver oil, 485, 489
Skin grease, 686
Soap, carbolic, 783
  curd, 770
  dry, 785
  hard, 39, 769
  hydrolysis of, 35
Soap, insoluble, 785
  medicated, 773
  metallic, 41, 785
  milled, 771
  potash, 39
  soda, 39
  soft, 39, 769
  superfatted, 779
  textile, 784
  toilet, 771
  transparent, 773
Soap powders, 785
Soaps, 33, 769
Sod oil, 693
Soja bean oil, 369
Solid fats, 506
  lubricants, 726
  oleic acid, 57
  saturated acids, 140
  unsaponifiable substances, 229
  waxes, 649
Solidifying points, determination of, 130
  points of fats and waxes, 323
  points of fatty acids from fats and waxes, 325
  points of mixed fatty acids, 260
  points of oils, 259
Solubility of fatty acids, 30
  of oils as a means of identification, 269
  of solid fats, 328
Soluble castor oil, 13, 733
Soluble fatty acids, 31, 191
  neoline, 710
Soxhlet's extractor, 90
Specific gravities of fats and waxes, 320
  gravities of oils, 254-258
Specific gravity, determination of, 123
Specific temperature reaction, 296
Spectroscopic examination, 113, 261
Spermaceti, 669
  candles, 756
Sperm candles, 756
  oil, 278, 647
  oil, blown, 734
Sprat oil, 485
Stag fat, 641
Stannic chloride as reagent, 227
Starch, detection of, 89
Starling fat, 551
Stearate, amyl, 4
  glycyl, 2
Stearates, 48
Stearic acid, 47
  acid, commercial, 745
  acid, determination of, 198, 201
  acid, separation from oleic acid, 192, 196
Stearin, 4
Stearine, 745
  candles, 745
  distilled, 691, 755
  distilled grease, 691, 755
  from cotton seed foots, 692
  pitch, 755
Stearolactone, 69
  determination of, 206

Stearolactone in candle material, 747
Stearolic acid, 60
Strophantus seed oil, 467
Suberic acid, 73
Sugar in soaps, 783
Sulphocarbon oils, 451, 463
Sulpholeates, 732
Sulphostearic acid, 747
Sulphur, action on fats, 14
  detection of, in fats, 95
  determination of, in fats, 93
Sulphur chloride test, 282
  chloride in examination of lard, 582
  chloride thermal test, 298
Sulphuric acid, action on fats, 13
  acid colour test, 315
  acid Maumené test, 291
  acid saponification, 746
Sunflower oil, 356
Sweet oils, 684
Sylvic acid, 236

Tallow, 591
  beef, 592
  Borneo, 533
  Chinese, 515
  goat's, 598
  mafura, 521
  Malabar, 549
  mutton, 598
  piney, 549
  rambutan, 49, 526
  veal, *see* Veal tallow
  vegetable, 515
Tallow candles, 745
  oil, 591
  stearine, 591
  titer, 749
Tangkallah fat, 44
Tariric acid, 61
Tar oils, 225-229
Tea seed oil, 447
Teel oil, 385
Temperature reaction, 291
Terebenthene number, 228
Terrestrial animal oils, 468, 499
Tetrahydroxystearic acid, 72
Textile soaps, 784
Theobromic acid, 527
Therapic acid, 63
Thermal tests, 291, 333
  tests with bromine, 300
  tests with sulphuric acid, 291
  tests with sulphur chloride, 298
Thermelæometer, 294
Thermo-regulator, 93
Thermostat, 93
Thickened oils, 733
Tiglic acid, 53
Tigliceric acid, 67
Titer test, 133
  test of mixed fatty acids, 327
Tobacco seed oil, 366
Tournant oil, 451, 464
  oil, analysis of, 811
Train oil, 277, 469, 492
Triacetin, 3, 26, 677
Triacetyldiglycerol, 678
Triarachin, 5
Tribrassidin, 5
Tributyrin, 3
Tricerotin, 5
Trielaidin, 5
Trierucin, 5
Triglycerides, 3
Trihydroxystearic acid, 71
Triisovalerin, 4
Trilaurin, 4
Trimelissin, 5
Trimyristin, 4
Triolein, 5
Tripalmitin, 4
Triricinolein, 5
Tristearin, 3
Turkey-red oil, 464
Turkey-red oils, 726, 727
  oils, detection of iron in, 99

Ucuhuba fat, 544
Ultimate analysis of fats, 137
Umbellulic acid, 27, 44, 508
Ungnadia oil, 466
Ungueko oil, 362
Unsaponifiable, definition of, 217
  detection of, 217
  determination of, 146, 218, 222
  examination of, 224
  in fats, 6
  in waxes, 17
  substances, liquid, 224
  substances, solid, 229

Valenta's test for resin oils, 228
  test for fatty oils, 270
Valerin, 4
Varnishes, lithographic, 739
  wax, 651
Veal tallow, 273, 328, 578
Vegaline, 682
Vegetable butter, 541, 682
  fats, 506
  oils, 336-468
  oils, distinction between, and animal oils, 317
  tallow, 515
  waxes, 649
Vegetaline, 541
Viscosimeter, 105-112
Viscosimetric examination, 268
Viscosity, 103
  of fatty acids, 33
Volatile fatty acids, 30, 191
  fatty acids, examination of, 139
Vulcanised oils, 742

Walnut oil, 350
Washing powders, 785
Waste fats, 687
Water—estimation in fats, 88
Wax, candles, 755

Wax, definition of, 1
oil, 352
quantitative examination of, 147
saponification value of, 154
solidifying points of, 323
Wax, bees, 655
carnaüba, 649
Chinese, 672
cochineal, 15, 45, 76
cotton seed, 649
getah, 649
insect, 672
Japan, 546
myrtle, 542
ocotilla, 649
ocuba, 649
opium, 15, 649
palm, 649
varnishes, 651
wool, 651
Waxes, animal, 651
chemical constitution of, 14
liquid, 277, 643
properties of, 17
saponification of, 22
Waxes, solid, 649
vegetable, 649
Weld seed oil, 366
Whale oil, 492
oil dégras, 702
Wheat-meal oil, 434
White mustard oil, 409
White substitutes, 742
Wild boar fat, 564
cat fat, 551
duck fat, 551
goose fat, 561
olive fat, 550
rabbit fat, 558
Wool fat, 651, 687
grease, 651, 687
grease in soaps, 779
oils, 704
wax, 651

Yorkshire grease, 687

Zinc chloride, product of action of, on oleic acid, 812

THE END

WELLCOME LIBRARY INSTITUTE

Printed by R. & R. Clark, Limited, *Edinburgh.*

JOHN M'NEIL AND CO.

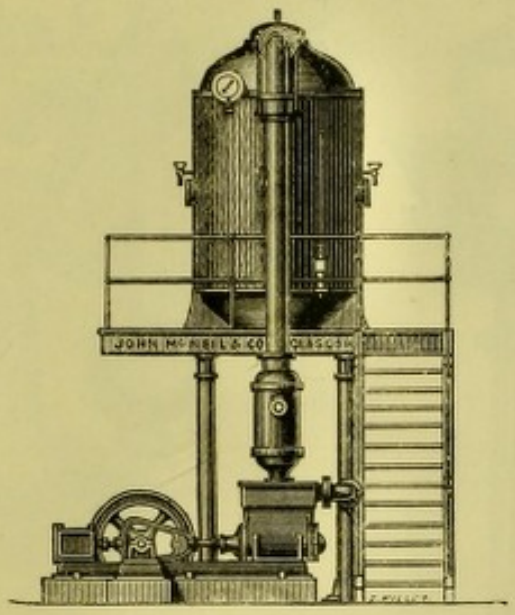
(Formerly AITKEN, M'NEIL AND CO.)

Engineers.

GLASGOW.—Colonial Iron Works, Govan. *Telegrams.*—"Colonial," Glasgow.

LONDON.—35 Queen Victoria Street, E.C. *Telegrams.*—"Idustria," London.

Sugar and Rice Machinery.



PATENT EVAPORATOR.

Multiple Effet Evaporators.

SOAP, CANDLE, OIL REFINING,

AND

CHEMICAL PLANTS.

GLYCERINE RECOVERY,

AND

GLYCERINE REFINING PLANTS.

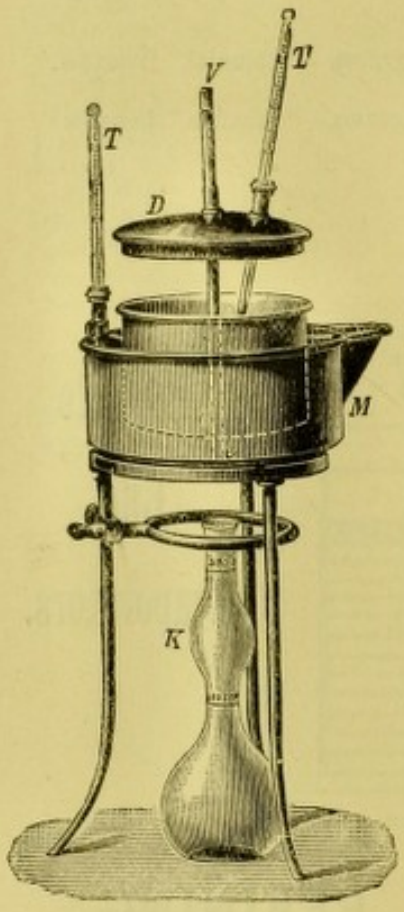
JOHN J. GRIFFIN & SONS, Ltd.

MANUFACTURERS OF

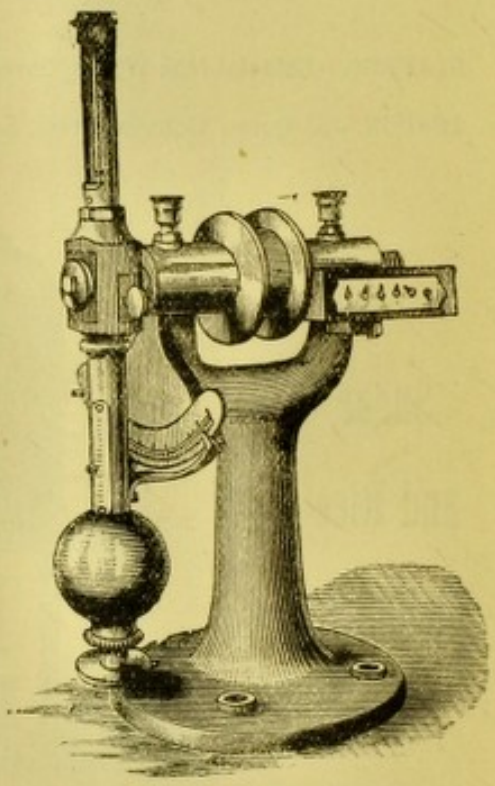
CHEMICAL AND PHILOSOPHICAL APPARATUS.

All requirements for the investigation of the properties of Oils, Fats, etc.

Viscometers. **Oil Testers.**



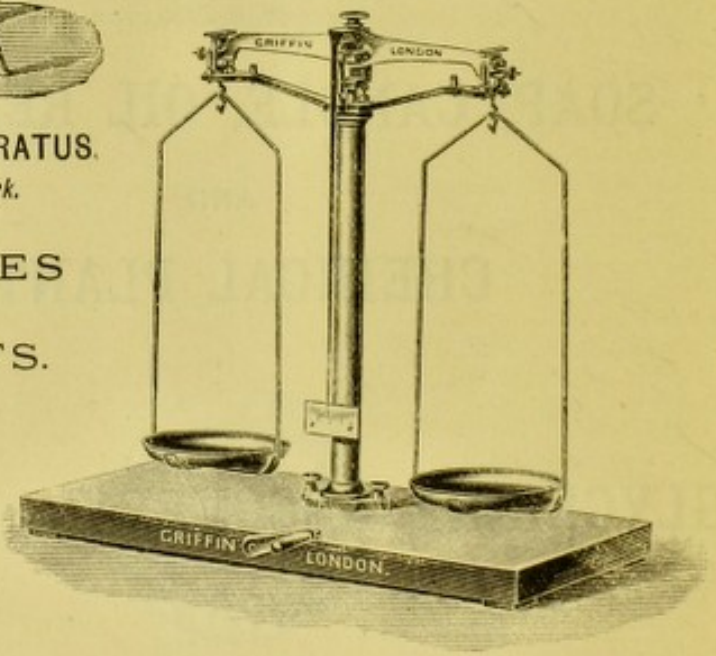
FLASH-TEST APPARATUS.



CHEMICAL APPARATUS.
For General Work.

BALANCES
AND
WEIGHTS.

MILK TESTERS
AND
MILK TUBES.



CATALOGUES
upon Application.

22 Garrick Street, London, W.C.

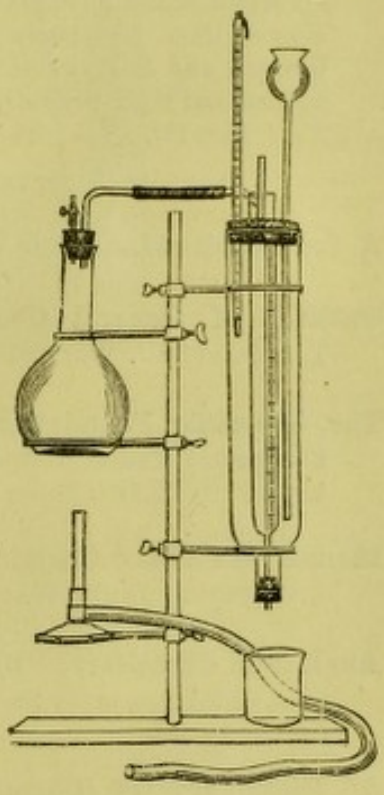
APPARATUS FOR
COMMERCIAL ANALYSIS
OF
OILS, FATS, ETC.

FOR VISCOSITY—

Viscosity Apparatus, as figured, complete with burner, or spirit lamp if preferred, and two thermometers, £1 : 7 : 6.

Simpler form, with one thermometer, and without arrangement for heating, 10s. 6d.

Redwood's Viscosity Apparatus, standardised for the determination of the viscosity of lubricating oils, £4 : 10s.



FOR SPECIFIC GRAVITY—

Set of Six Hydrometers, ranging from 700/1000, having 50 degrees on each spindle, in leather case, 15s. ; or 1s. 6d. each.

For the more accurate determination of Specific Gravity—

Specific Gravity Balances, £1 : 10s. and £3 : 3s.

Bath for taking Specific Gravity at temperatures up to 212° F., 7s. 6d.

FOR FLASH POINT—

Open Test Apparatus, for heavy mineral oils, etc., complete with accurate thermometer to 600° F., burner and stand, 15s.

Closed Test Apparatus, for heavy mineral oils, etc., complete with accurate thermometer to 600° F., £3 : 3s.

Abel's Petroleum Test Apparatus, as recommended by the Board of Trade ; Petroleum Act, 1879 ; complete in mahogany case with fittings, £5 : 5s.

Board of Trade fee for stamping, 5s. extra.

When ordering, please state if required for use with gas or oil.

FOR QUANTITATIVE DETERMINATION—

Soxhlet's and other Apparatus, Separators, etc. For prices, etc., see our Catalogue.

ILLUSTRATED PRICE LISTS FREE.

FREDERICK JACKSON & CO.,

LABORATORY FURNISHERS,

14 Cross Street, Manchester.

MACMILLAN AND CO.'S

TEXT-BOOKS FOR ADVANCED STUDENTS.

BY SIR H. E. ROSCOE AND THE LATE PROFESSOR SCHORLEMMER.

A Treatise on Chemistry. By Sir H. E. ROSCOE, F.R.S., and C. SCHORLEMMER, F.R.S., Professor of Chemistry in Owens College, Manchester. Vol. I. The Non-Metallic Elements. New Edition, completely revised by Sir H. E. ROSCOE, assisted by Drs. H. E. COLMAN and A. HARDEN. With illustrations and a Portrait of Dalton engraved by C. H. JEENS. 8vo. 21s. Vol. II. The Metals. New Edition, completely revised by Sir H. E. ROSCOE, assisted by Drs. H. G. COLMAN and A. HARDEN. 31s. 6d. Vol. III. The Chemistry of the Hydrocarbons and their Derivatives, or Organic Chemistry. Part I. 21s. Part II. 21s. Part III. 18s. Part IV. 21s. Part V. 18s. Part VI. 21s.

A Text-Book of Inorganic Chemistry. By Professor IRA REMSEN. 8vo. 16s.

Outlines of General Chemistry. By Professor WILHELM OSTWALD. Translated by J. WALKER, D.Sc., Ph.D. 8vo. 10s. net.

The Scientific Foundations of Analytical Chemistry treated in an Elementary Manner. By WILHELM OSTWALD, Ph.D. Translated by GEORGE M'GOWAN, Ph.D. Crown 8vo. 5s. net.

Manual of Physico-Chemical Measurements. By Professor W. OSTWALD. Translated by JAMES WALKER, D.Sc., Ph.D. Illustrated. 8vo. 7s. net.

Analytical Chemistry. By A. MENSCHUTKIN. Translated from the third German Edition, under the supervision of the Author, by JAMES LOCKE. Medium 8vo. 17s. net.

A Dictionary of Chemical Solubilities, Inorganic. By ARTHUR MESSINGER COMEY, Ph.D. Demy 8vo. 15s. net.

Systematic Survey of the Organic Matters. By Drs. G. SCHULTZ and P. JULIUS. Translated and Edited, with extensive additions, by ARTHUR G. GREEN, F.I.C., F.C.S., Examiner in Coal Tar Products to the City and Guilds of London Institute. Imperial 8vo. 21s. net.

Popular Astronomy. By SIMON NEWCOMB, LL.D., Professor U.S. Naval Observatory. With 112 Engravings and five Maps of the Stars. Medium 8vo. 18s.

A Text-Book of the Principles of Physics. By ALFRED DANIELL, M.A. Second Edition. Medium 8vo. 21s.

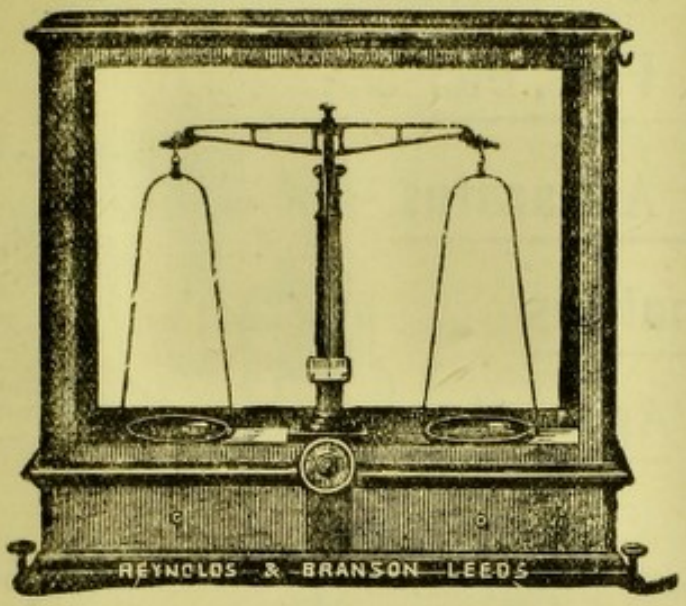
The Theory of Heat. By THOMAS PRESTON, M.A. With Illustrations, 8vo. 17s. net.

Applied Mechanics. By JAMES H. COTTERILL, F.R.S., Professor of Applied Mechanics in the Royal Naval College, Greenwich. Second Edition, revised. Medium 8vo. 18s.

MACMILLAN AND CO., LTD., LONDON.

REYNOLDS & BRANSON'S

TECHNICAL BALANCES.



"**Phœnix**" **Short Beam Balance**, specially designed to meet the requirements of Analysts who require a sensitive instrument for technical work, to carry 100 grammes, sensitive to ½ milligramme ($\frac{1}{130}$ grain), graduated beam for use with rider, polished walnut case, levelling screws, and plumb line. Price **£2 : 12 : 6.**

With drawer for weights, as figure. Price **£2 : 17 : 6.**

Ditto, with agate bearings throughout (unaffected by steam and acid vapours) as figure. Price **£3 : 5s.**

"**Phœnix**" **Balance.** Best improved Dutch pattern, with extra hook for taking specific gravity, on polished wood base, 12 inch beam, loose best gilt pans to carry 250 grammes, sensitive to one milligramme ; *Agate bearings.* **£2.**

Ditto, with steel bearings—

To carry 50 grms.	100 grms.	250 grms.
25s. 6d.	**28s. 6d.**	**32s.**

Weights.—Nickel-plated, 50 grammes down to ·001 gramme, suitable for above balances, **8s.** Best quality, gold plated, **27s. 6d.**

Balances for Research and highly Technical Work, see

ILLUSTRATED AND PRICED CATALOGUE OF

CHEMICAL AND PHYSICAL APPARATUS, ETC.

Ninth Edition, greatly enlarged, pp. 332.

PRICE LIST OF

PURE CHEMICALS AND RE-AGENTS,

For Chemical Analysis, etc. *Post Free.*

Also Catalogues of the following apparatus :—

Microscopes and Accessories. Opera, Marine, and Field Glasses.
Photographic Apparatus.
Electrical and Galvanic Apparatus.
Mercurial and Aneroid Barometers and Thermometers.
Optical and Dissolving View Lanterns. Compressed Oxygen.
Lantern Slides for Sale and Hire.
Spectacles and Eyeglasses, etc., of all kinds.

ESTIMATES GIVEN FOR FITTING LABORATORIES.

14 Commercial Street, Leeds.

CHEMICAL APPARATUS

of every description for the Analysis of

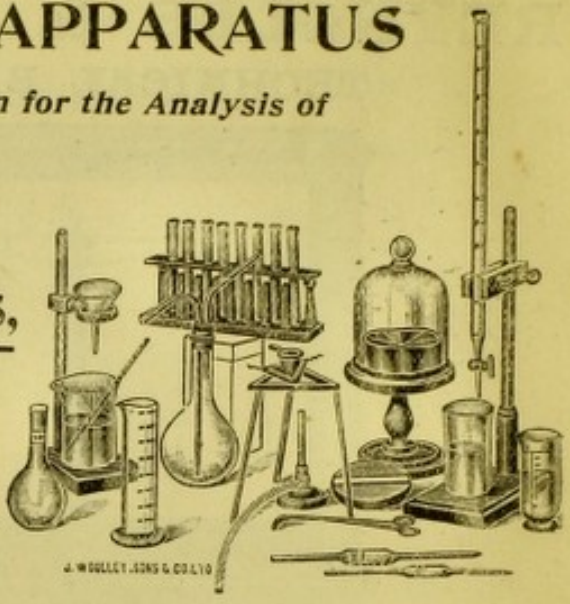
Oils, Fats, etc.

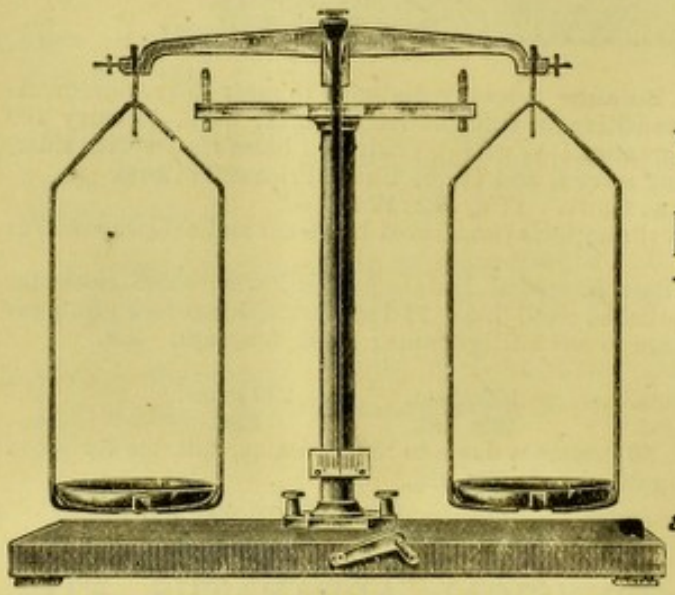
Assay Apparatus,

Gas Analysis

Apparatus

etc., etc.





BALANCES
and
WEIGHTS by
Becker,
Kuhlmann,
Oertling,

and all the principal Makers.

BACTERIOLOGICAL APPARATUS, MICROSCOPES,
AND ACCESSORIES.

JAMES WOOLLEY, SONS & CO., Ltd.

Manufacturers, Importers, and Dealers in every description of

CHEMICAL AND SCIENTIFIC APPARATUS,

Victoria Bridge, MANCHESTER.

ILLUSTRATED AND DESCRIPTIVE CATALOGUES
Free on Application.