

Electrolytically produced fluids containing hypochlorites, their manufacture, and the rationale and chemistry of the process for securing stability / by Frederick W. Alexander.

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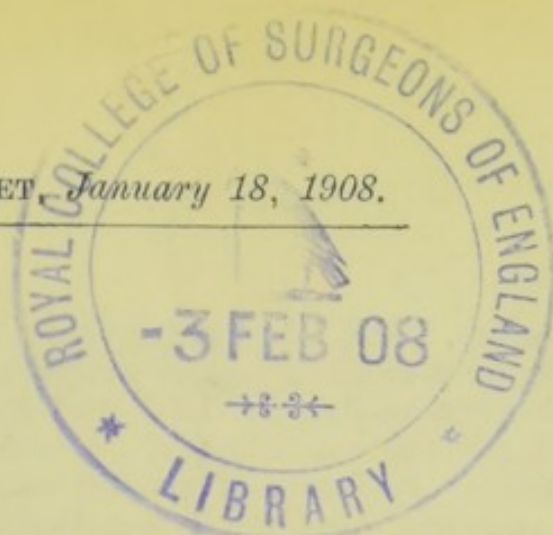
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ELECTROLYTICALLY PRODUCED FLUIDS
CONTAINING HYPOCHLORITES,
THEIR MANUFACTURE, AND THE
RATIONALE AND CHEMISTRY
OF THE PROCESS FOR
SECURING STABILITY.

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OF POPLAR.

IN the metropolitan borough of Poplar the Hermite process of making an electrolytic disinfecting fluid has been in operation for a period of nearly two years. The fluid has been made throughout at an average strength of from 4·2 to 4·8 grammes or more of available chlorine per litre and by appropriate treatment has been rendered exceedingly stable, thereby enabling it practically to maintain an undiminished strength for months, and even extending to years, as samples taken and kept since the installation of the plant prove. Owing to the evanescence of the chlorine great difficulty was experienced at first in rendering the fluid stable. I was occasioned much anxiety, as the process that I had recommended and which had been adopted by my council was not giving the satisfactory results that I had anticipated and had been led to hope for. I had been assured, and in turn had assured my council, before adopting the process, that the fluid could be rendered quite stable by the addition of certain chemicals,

In September, 1905, I had given to me a note relative to the bases formerly used to render stable the fluid made by the Hermite process—namely, lime and caustic soda. Neither of the processes was adopted. I had ascertained that by merely adding a solution of caustic soda to the fluid it would produce stability, but such I found on experiment would not bring about the desired effect, for fluid made at 4·8 grammes of available chlorine per litre began to degenerate immediately it left the electrolyzers and in a very few hours only gave a test of 2·0 grammes of available chlorine per litre and continued to diminish in strength. Then, after the addition of caustic soda, the carboy was necessarily shaken for some minutes, but shaking a carboy of 150 pounds weight by hand was, of course, a most difficult operation. Better results, however, were certainly obtained by half filling the carboy. It was observed that upon the addition of caustic soda to the electrolytic fluid a white precipitate was formed which immediately fell to the bottom of the carboy. The precipitate was, of course, hydroxide of magnesium and the shaking of the carboy caused this insoluble and not easily diffusible compound to be distributed throughout the fluid and to give it a milky appearance, and it was found that the more milky in appearance the fluid became the more stable was the fluid rendered. The white precipitate ultimately settled at the bottom of the carboy and the fluid became quite clear. Having arrived at this point, and in order to secure the desired full amount of chlorine in the fluid from the moment it leaves the electrolyzers, arrangements were made to drop the solution of caustic soda into the carboys and to stir whilst they were being filled, and by another simple mechanical arrangement the hydroxide of magnesium and the electrolytic fluid were mixed well together by stirring the mixture in the carboys immediately after the process of filling. For my present purpose I need not further describe this arrangement and the apparatus for mixing. Careful thought and experiments have explained to me the rationale of this process and my explanation will possibly throw some light upon the whole process of the electrolytic production of hypochlorites.

To understand the process of making the fluid stable one must first comprehend what is common knowledge respecting the electrical action within the electrolyzers and to find out if there be any point which has been previously overlooked. I venture to say that my observations and experi-

ments have demonstrated there *is* a point and this the crucial one, the discovery of which has been most gratifying and which I consider well worth all the trouble I have taken in this direction. The Hermite process adopted at Poplar, which no doubt will give a key to all other processes, has been described as follows :—

(a) When a solution of a mixture of magnesium chloride and sodium chloride is submitted to the action of an electric current of the proper strength in a special apparatus called an electrolyser, the magnesium chloride is decomposed by the electric current, as also is the water. Nascent chlorine and nascent oxygen or ozone are formed at the positive pole. These two bodies immediately combine and form an oxygenated compound of chlorine, unstable, but of great oxidising power. This chlorine compound is soluble in the liquid in which it is formed. The hydrogen produced by the decomposition of the water and the magnesium are set free at the negative pole, the latter decomposing the water and producing magnesium hydrate, of which part combines with the chlorine compound set free, and the rest remains in suspension in the tank.

The sodium chloride acts as a conductor for the electric current.

The solution of the chlorine compound obtained by this method has only a slight smell of chlorine, it is nearly neutral. Its strength can be easily tested by the usual arsenious acid test.—Extract from a pamphlet upon Sanitation by Electricity—Hermite System.

Or again :—

(b) The principle of this process is passing a current of electricity through sea water, or if sea water is not handy, a solution of magnesium and sodium chlorides; a portion of these chlorides is converted into hypochlorite, a substance which disinfects, deodorises, and bleaches similarly to the active ingredient of bleaching powder—calcium hypochlorite. The change from chloride to hypochlorite takes place almost entirely with the magnesium salt—yielding magnesium hypochlorite $Mg(ClO)_2$. It is found, however, that in the electrolyzers and tanks a white deposit takes place, consisting of magnesium oxide combined with water, viz., magnesium hydrate, showing that the magnesium hypochlorite has decomposed, forming magnesium hydrate, which precipitates, leaving hypochlorous acid in solution. The action may take place as follows: $Mg(ClO)_2 + 2H_2O = Mg(HO)_2 + 2HClO$. The amount of oxidising power is expressed by the quantity of available chlorine in grammes per litre, the usual working strengths being from 0.5 to 1.0 gramme per litre of solution.—From a paper read before the British Association by J. Napier, F.C.S., F.I.C., borough and county analyst, Ipswich.

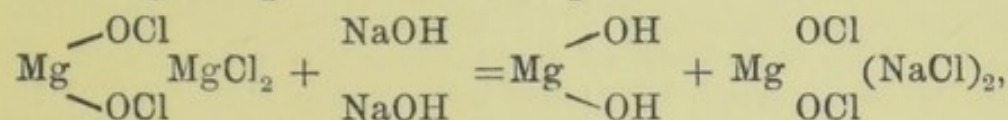
Now is this chemical expression right? I venture to suggest that it is not, for the reason that the major portion of the white deposit in the electrolyzers is an oxychloride of magnesium ($MgCl(OCl)$) and the formation and accumulation of this deposit is the *bête noire* of the process. I have explained in another place how difficulties of working the

electrolysers on account of this formation of oxychloride of magnesium are at present surmounted. No doubt there is a limited quantity of hydroxide of magnesium in the deposit but not much. I have caused an analysis to be made of the deposit. NaCl is not acted upon to any extent, if any at all, but carries the current to the $MgCl_2$, and there is formed, according to the above description (*a*), magnesium hypochlorite in solution and magnesium hydrate in suspension; and, according to description (*b*), hypochlorous acid in solution and magnesium hydroxide in suspension; but nothing is said in either instance about the deposit of oxychloride of magnesium.

Now I venture to suggest, and I think it can be proved, that there are in the electrolysers in solution both hypochlorite of magnesium and hypochlorous acid. What really must occur during the electrolytic process is that hydroxide of magnesium is certainly formed at the negative pole and unstable compounds of oxygen and chlorine at the positive pole and the hydroxide of magnesium endeavours to combine with these unstable compounds of oxygen and chlorine. Some of it no doubt does do so, but a large portion, possibly half, for reasons which will be given further on, is prevented from doing so by the formation of the oxychloride of magnesium or there may not be sufficient hydroxide of magnesium formed to combine with all the unstable compounds of oxygen and chlorine, so that clearly what one has to do to render the fluid stable is either to assist the process by the addition of hydroxide of magnesium whilst the electrolysis is taking place or to complete the process afterwards by the addition of hydroxide of magnesium after the fluid has left the electrolysers or to combine both methods. It must be remembered that hypochlorite of magnesium is stable for practical purposes when kept in non-actinic bottles and stoppered with paraffined corks or kept away from the light, but hypochlorous acid is very unstable even in the dark.

In Poplar there is added and kept stirred within the fluid to be electrolysed a small quantity of hydroxide of magnesium the object of which is obvious—namely, to assist in picking up the unstable compounds of oxygen and chlorine formed at the positive pole. Now, if the heaped-up deposit in the electrolysers and which deposit lies closely against the positive pole were hydroxide of magnesium, where would be the necessity to add this compound? It speaks for itself that the deposit is not hydroxide of magnesium but magnesium oxychloride. Now for a step further. When

sodium hydroxide is added to the electrolysed solution the following change is said to take place :—



the magnesium sodium double salt being considerably more stable than the corresponding magnesium one.

This may be so, but I venture to say that the double magnesium sodium salt is not formed and here I would call attention to the fact that the hydroxide of magnesium falls to the bottom as mentioned in the first part of this paper and the fluid will not remain stable unless it be rendered milky throughout, either by shaking or stirring, which in other words means that the hydroxide of magnesium, which is extremely insoluble and not diffusible, must, in order to fix the unstable and evanescent compounds of oxygen and chlorine—that is to say, to preserve the strength of the fluid—be brought into immediate and absolute contact with such compounds by making the fluid milky throughout, then the hydroxide of magnesium having done its work, the surplus sinks to the bottom of the carboy. In order to make hydroxide of magnesium soluble it requires 5000 parts of water at 15.5° and 36,000 parts at 100°. Will the addition and stirring of hydroxide of magnesium in the electrolytic fluid answer the same purpose? Yes, certainly it will, and I find it will answer much better than the addition of sodium hydroxide for a reason I will presently state; therefore, it cannot be that a magnesium sodium double salt is formed when magnesium hydroxide is added instead of the sodium hydroxide. Hydroxide of magnesium has no action upon the already formed hypochlorite of magnesium, hence it must be the unstable compounds of chlorine and oxygen present in conjunction with the hydroxide of magnesium which effect the result aforementioned. To pursue the case further I have added and stirred into a filling carboy oxide of magnesium in place of hydroxide of magnesium and have rendered the fluid quite stable and obtained the same results, and in this instance no double magnesium sodium salt could have been formed, and oxide of magnesium will not act upon hypochlorite of magnesium. Carbonate of magnesium I have found up to the present not satisfactory as the unstable compounds of oxygen and chlorine in the strength of solution manufactured will not displace carbonic acid.

The following experiment which I have carried out is, no doubt, interesting and assists my contention. Electrolytic fluid was being made at 4·818 grammes of available chlorine per litre, $\frac{1}{2}$ lb. carbonate of magnesium was placed into the specially constructed 15 gallon carboy, and the electrolytic fluid as it came direct from the electrolyzers was allowed to run into the carboy and during the time of filling kept well stirred with the carbonate of magnesium, of course making a very milky fluid, and when this carboy was filled a final stir was given by means of the geared stirrer. Into another 15 gallon carboy $\frac{1}{2}$ lb. of oxide of magnesium was placed and a similar process as mentioned above in the case of the carbonate was carried out. In due course the fluids cleared themselves and sediment formed. The electrolytic fluid, as mentioned above, was being made at 4·818 grammes of available chlorine per litre and within 24 hours the fluid with the carbonate of magnesium gave a test result of 2·741 grammes of available chlorine per litre, but the one containing the oxide of magnesium remained at 4·818 grammes per litre.

Fluid made at 4·818 grammes per litre and mixed with carbonate of magnesium—

At expiration of 24 hours gave 2·741 grammes per litre.

“	48	“	“	2·064	“	“
“	72	“	“	1·870	“	“
“	96	“	“	1·691	“	“
“	120	“	“	1·590	“	“
“	168	“	“	1·500	“	“
“	192	“	“	1·472	“	“
“	216	“	“	1·394	“	“
“	37 days	“	“	0·963	“	“*

* After continued testings and exposures.

And fluid made with oxide of magnesium and made at 4·818 grammes per litre—

At expiration of 24 hours gave 4·818 grammes per litre.

“	48	“	“	4·818	“	“
“	72	“	“	4·818	“	“
“	96	“	“	4·818	“	“
“	120	“	“	4·818	“	“
“	168	“	“	4·676	“	“
“	192	“	“	4·676	“	“
“	216	“	“	4·676	“	“
“	37 days	“	“	4·416	“	“*

* After continued testings and exposures.

This no doubt shows that there were 2.741 grammes of available chlorine per litre due to hypochlorite of magnesium and 2.077 grammes of available chlorine were due to hypochlorous acid or other unstable compounds of oxygen and chlorine. The fluid upon standing in the carboy in which the oxide of magnesium was stirred gave an alkaline reaction and the fluid upon standing in the carboy with carbonate of magnesium added gave a faintly acid reaction. This clearly proves that hypochlorous acid or the other unstable compounds of oxygen and chlorine are not strong enough in the strength of the manufactured solution to displace the carbonic acid from the carbonate of magnesium but readily combine with the oxide of magnesium and the fluid becomes also alkaline. The continued dropping in strength of the available chlorine in the carboy with the insoluble carbonate of magnesium is undoubtedly due to the exceedingly unstable hypochlorous acid or other unstable compounds of oxygen and chlorine which lose some chlorine in the first state, the remainder being converted into hydrochloric acid which then slowly but steadily acts upon the hypochlorite of magnesium.

It is obvious that the stable solutions of electrolytically made hypochlorite of magnesium are preferable to those of sodium and potassium or even calcium, because for fixing purposes there would have to be used hydroxide of the metals of the alkalis which are extremely caustic, alkaline, and very soluble, and where varying strengths of electrolytic fluid containing the hypochlorites of sodium and potassium are produced one may add too much or too little of the hydroxides of the alkalis. The hydroxide of the alkaline earth calcium may also be used as stated in the first portion of this article, but when the extremely insoluble hydroxide or oxide of magnesium is added and stirred in the manner described one can add and stir in any quantity but only the necessary amount will be absorbed. Besides, the alkalinity of the hydroxide of magnesium can only be observed by placing a small portion in the moist state upon test paper which clearly shows as well as its insolubility that it is not a strong alkali. By very simple means the hydroxide or the oxide of magnesium can be added to the fluid in the electrolyser and kept stirred in it immediately it has passed over the last weir, thereby securing the full amount of chlorine. I think it is common knowledge that metallic hypochlorites of the alkali metals and alkaline earths may be obtained in the pure state by neutralising hypochlorous

acid with certain metallic hydroxides of the alkali metals and alkaline earth groups, but to obtain hypochlorite of magnesium by means of the hydroxide or oxide of magnesium even upon a small scale, to say nothing of the large quantity manufactured in Poplar, is not common experience and knowledge.

I particularly desire, in conclusion, to state that throughout my experience in the production and improvement of the electrolytic disinfecting fluid I have had no desire to pose as a chemist. I have been much interested in the Hermite process since the publication of the report of "THE LANCET Commission" in the year 1894, and since the plant has been working in Poplar for the last two years I have given close observation and continued attention to the process, in the course of which I have not hesitated to avail myself of the valued knowledge and experience in these matters of M. Hermite, the chemical knowledge of Dr. W. R. Hodgkinson of the Military Academy, Woolwich, Dr. J. Gordon Parker of the Herald's Institute, Bermondsey, and Mr. Albert E. Parkes, analyst for Stepney, to all of whom I am much indebted for the success achieved in the undertaking.

Public Health Office, Bow-road, E.