

THE ELECTRICAL PREPARATION OF SODIUM HYPOCHLORITE.
A SIMPLE METHOD OF PREPARING AN EFFICIENT GENERAL
ANTISEPTIC.

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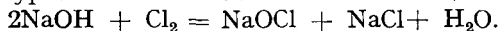
Royal Army Medical Corps.

DURING the summer of 1942, some local shortage of issue antiseptics was experienced and it was decided to devise, if possible, a cheap and trouble-free method of preparing a substitute which could be applied by any Medical Officer in his own M.I. Room. The choice fell on sodium hypochlorite which presents the following advantages:—

- (i) It is non-irritant and may be used at full strength if required.
- (ii) As prepared below, it is sufficiently stable to keep for a considerable length of time.
- (iii) It is a powerful bactericidal agent, its action being due to the liberation of chlorine and nascent oxygen.
- (iv) The starting point of the process, common salt, is always procurable.

The essential principles underlying the method are well known and a theoretical description of the reaction may be found in any standard chemical textbook. It has been applied commercially for some years, there being several electrolytic hypochlorite solutions for sale in the open market, mostly of excellent quality. The method to be described, however, demonstrates how easily the reaction may be carried out with a minimum requirement of equipment and the product obtained is similar to commercial preparations in its antiseptic properties whilst its cost is negligible.

Theory.—Common salt solution is electrolysed. Sodium is liberated at the cathode (–), and chlorine at the anode (+). The sodium reacts immediately with water to form caustic soda, free hydrogen being evolved, and the chlorine interacts with the caustic soda to form sodium hypochlorite. Thus:—



It will be seen that one molecule of NaCl is regenerated for each molecule of NaOCl formed.

This represents the process under ideal conditions but, in practice, the percentage yield of hypochlorite is relatively small and a number of side reactions take place resulting in the formation of other compounds, the most important of which is sodium chlorate. These by-products, however, do not impair but tend rather to improve the antiseptic action since they are all powerful oxidizing agents.

In evolving the method employed, it was decided from the commencement to standardize three factors: (a) The source of electricity; (b) the time of electrolysis; (c) the volume of solution used.

The reason for this is the aim at producing the highest yield of hypochlorite for the maximum economy in electrical energy required and time spent. In the final series of experiments two concentrations of salt solution were employed—10 per cent and 15 per cent. These were found to give the best results under the prevalent experimental conditions. It is left to the individual worker to choose his own concentrations and temperatures. These factors will shortly be discussed.

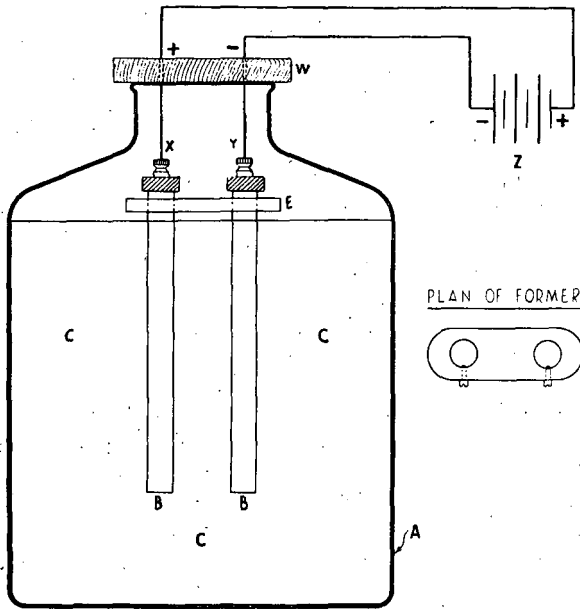
DETAILS OF THE PROCESS.

(1) *The Container.*—This should be of glass or some other inert insulator. Metal is unsuitable since it takes part in the reaction and is corroded. The writer utilizes a two-gallon glass cask such as those used for storing sulphuric acid and distilled water. The internal diameter of the neck must not be less than 2 inches (fig. 1).

(2) *The Electrodes.*—Carbon rods are used. Those employed are obtained from exhausted telephone dry batteries and measure 7 to 8 inches in length and $\frac{1}{2}$ inch in diameter.

(These particular rods came from old Italian telephone cells.) Some care must be exercised in separating the carbon from the body of the cell since it is easily broken. The best method is to saw longitudinally through the cell so that the line of the cut lies just external to the rod which may then be withdrawn with ease. These rods have a brass cap at one end and to this is soldered a small terminal; the metal below the contact gap of the terminal is then painted with shellac or some other protective varnish. Unless this is done the solder will be rapidly attacked by chlorine and converted into a putty-like paste of chlorides which have a high electrical resistance and cut down the current available for electrolysis.

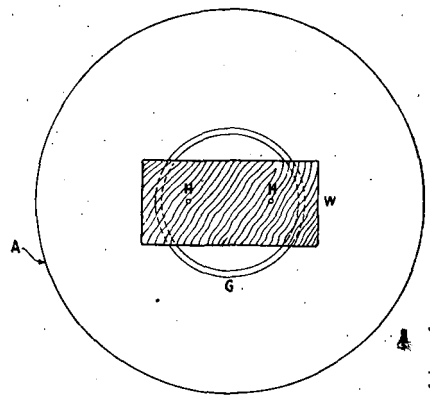
It is found in practice that the anode disintegrates and finely powdered carbon is deposited on the floor of the container. This disintegration is relatively slow, however, and, with care, an anode will be useful for up to 20 gallons of solution.



- A GLASS CONTAINER
- B B CARBON RODS WITH BRASS CAPS (SHADED)
- C SALINE SOLUTION
- XY CONNECTING WIRES
- Z 6 VOLT 125 AMP HR. BATTERY
- W WOODEN PLATE THROUGH WHICH WIRES PASS

FIG. 1.

PLAN OF SUPPORTING PLATE FOR WIRES



- G TOP OF GLASS CONTAINER
- W WOODEN PLATE
- H H HOLES THROUGH WHICH CONNECTING WIRES PASS. THESE HOLES MUST BE SUFFICIENTLY SMALL TO ENSURE THAT THE WIRE WILL BE A FAIRLY TIGHT FIT AND WILL STAND THE WEIGHT OF THE RODS WITHOUT SLIPPING THE DEPTH OF THE ELECTRODES IS ADJUSTED BY PUSHING IN OR WITHDRAWING THE WIRES. THE HOLES SHOULD BE FAIRLY CLOSE TOGETHER, BUT NOT SO CLOSE THAT THE ELECTRODES TOUCH EACH OTHER.
- E EBONITE FORMER FOR RODS

FIG. 2.

The cathode slowly acquires a deposit of an insoluble white substance—probably lime from the water—and, as this is a poor conductor, it is necessary periodically to clean this electrode with an abrasive—a few minutes work—after which it is wiped, washed and ready for use. A small vulcanite former is used to maintain the carbons at a constant parallel distance of $\frac{1}{8}$ inch. This is fixed up as shown in fig. 2. It is not absolutely necessary but ensures a relatively constant current and prevents the electrodes from shorting. The connecting wires pass through a piece of wood placed across the top of the vessel. The rods are immersed to within $\frac{1}{2}$ inch of the former.

(3) *Battery*.—The best battery for the purpose is the 125 amp. hour, 6 volt, accumulator which is issued for radio use. These batteries are easy to obtain since they are issued to all

units and their recharging is carried out by the unit charging plant. No resistance need be employed since the current supplied without reduction is most suitable. A fresh battery is desirable for every two gallons and in any case not more than four gallons should be electrolysed from one charge.

(4) *The Salt Solution.*—Better results are obtained with 15 per cent than with 10 per cent NaCl. Ordinary coarse issue salt is used, dissolved in the minimum volume of warm water, and made up to the required volume and temperature by the addition of more water. Filtration is not necessary since the solution rapidly clears itself during electrolysis. The amount of NaCl required for 15 per cent in 2 gallons is fairly accurately measured by filling a deep 6 inch drinking bowl (as issued to troops) with salt well heaped up above the level of the rim. The weight of salt contained is then about 3 pounds.

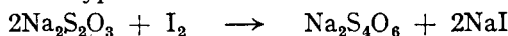
RESULTS.

The first series of experiments was conducted with rising concentrations of 5, 10, 15 and 20 per cent of NaCl. It was found that 5 per cent gave too low a yield and that 20 per cent did not give a yield sufficiently greater than that of 10 per cent and 15 per cent to justify the extra outlay of salt. The method of estimation of hypochlorite content is as follows:—

To 25 c.c. of the solution are added 15 c.c. of 10 per cent potassium iodide. This liberates free iodine which colours the liquid dark brown. A few drops of dilute HCl are then added and the resultant solution is titrated against 0.1 normal sodium thiosulphate (hypo). When the brown has changed to light yellow, indicating that the reaction is nearing completion, a few drops of starch solution are added and the black starch iodide so formed is an efficient indicator of the end point since the colour is totally discharged when neutralization of the iodine is complete.

The reactions involved are:—

- (a) The displacement of free iodine from KI by the available chlorine in the solution.
- (b) The interaction of hypo and free iodine:—



To calculate available chlorine:—

Let X = the number of c.c. of 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ required to neutralize 25 c.c. of hypochlorite solution.

Then

$$\frac{X}{25} \times 0.1 \times 35.5 = \text{grams/litre of available chlorine.}$$

e.g.:—

25 c.c. of hypochlorite solution + 15 c.c. of 10 per cent KI = 24.0 c.c. of 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$.

Therefore the solution contains

$$\frac{24}{25} \times 0.1 \times 35.5 \text{ grams/litre of chlorine.}$$

$$= 3.408 \text{ grams/litre.}$$

$$= 0.341 \text{ per cent chlorine.}$$

To convert this figure into percentage of NaOCl the calculation is modified slightly.

$$\frac{24}{25} \times 0.1 \times 74.5 = 7.15 \text{ grams NaOCl/litre.}$$

$$= 0.715 \text{ per cent NaOCl.}$$

The actual figures obtained are tabulated below.

TABLE I.

Percentage of salt solution used	Commen- cing Temp. °F.	Temp. at end of Elec- trolysis °F.	Current in amperes	Percentage yield at 1st analysis		Interval days	Percentage yield at 2nd analysis		Fractional Deteriora- tion	Average daily Deteriora- tion	
				As Chlorine	As Sodium Hypo- chlorite		As Chlorine	As Sodium Hypo- chlorite			
Atmospheric Temperature 60°-70° F.	1st Series	5	65	67	4.2	0.06	0.13	Not performed			
		10	65	68	4.6	0.14	0.31	"			
		15	65	70	4.9	0.14	0.31	"			
		20	60	70	6.5	0.16	0.35	"			
	10	100	88	5.2	0.20	0.42	75 d's.	0.17	0.36	15%	0.2%
	10	113	94	4.9	0.15	0.30	Not performed				
	10	122	114	8.25	0.45	0.95	21 d's.	0.44	0.92	2.2%	0.105%
	10	113	114	8.0	0.36	0.74	18 d's.	0.22	0.46	39%	0.22%
	10	100	107	7.8	0.30	0.63	14 d's.	0.23	0.48	23.3%	1.6%
	15	100	117	8.7	0.55	1.2	58 d's.	0.42	0.89	23.6%	0.41%
	15	113	116	8.7	0.48	1.01	Not performed				
	Atmospheric Temperature 75°-90° F.	2nd Series	15	122	120	9.2	0.53	1.12	"		
10			100	108	8.0	0.32	0.66	"			
10			113	115	7.0	0.21	0.45	"			
10			122	116	8.2	0.35	0.75	"			
15		100	110	8.7	0.47	1.0	31 d's.	0.20	0.42	57.4%	1.85%
15		113	116	8.2	0.39	0.82	Not performed				
10		100	120	9.0	0.37	0.78	7 d's.	0.29	0.62	21.6%	3.1%
10		113	122	8.2	0.25	0.52	3 d's.	0.20	0.43	20.0%	6.6%
10		122	126	8.8	0.29	0.62	"	0.22	0.46	24.0%	8.0%
15		100	113	9.4	0.43	0.89	"	0.36	0.76	16.3%	5.4%
15		113	115	8.8	0.40	0.84	"	0.39	0.82	2.5%	0.83%
15		122	120	8.8	0.47	1.0	"	0.37	0.77	21.2%	7.06%

Battery : 6 volt, 125 ampere hours. Amount of saline : 2 gallons. Time of electrolysis : 5 hours.

EVALUATION OF RESULTS.

A glance at the above table will show two outstanding features :—

- (i) A considerable variation in yields ; (ii) a wide variation in deterioration rates.

The investigation of the causes of these variations necessitates the consideration of several variable factors involved in the production of the solution.

Temperature.—It is pointed out by most textbooks that the yield of hypochlorite increases up to 77° F. after which it decreases, with the subsequent formation of higher percentages of the chlorate and perchlorate. It was considered, therefore, that a fair assessment of the effect of temperature variation could be obtained by using (a) a starting temperature of between 60° and 70° F. ; (b) (in the second series) temperatures of 100°, 113° and 122° F., the concentrations used to be 10 per cent and 15 per cent.

In no cases was it attempted to produce increments in yield by altering either the voltage (and therefore current) or the time of electrolysis. It cannot, therefore, be denied that carrying the electrolysis nearer to completion for, say, twenty-four or even thirty-six hours at room temperature or the utilization of 12 instead of 6 volts for the same time may produce better results than those tabulated. Either factor, however, immediately introduces added difficulties—the necessary extra supervision and the extra battery—each a possible source of trouble to the M.O. The temptation to include this aspect was therefore resisted for the time being although, for use in larger formations such as hospitals and C.C.S.s, there seems no reason why further experiments should not be conducted on these lines. With the higher starting temperatures the current—an important deciding factor in the amount of chlorine liberated—was much higher. Although a more rapid breakdown of hypochlorite was expected this was not found in practice so excessive as to be uneconomical and it was finally decided that, for the purposes required, it was in fact more suitable to use a temperature of 100° F.

The atmospheric temperature was found to exert a marked influence. The reaction is exothermic. When the atmospheric temperature is between 60° and 70° F. and the commencing temperature of the solution is 100° to 122° F there is (roughly) a balance set up between heat gained and heat lost and yields are good. When, however, the atmospheric temperature rises above 75° F. (see table) the heat accumulates and the solution temperature rises excessively. This diminishes the yield. It is recommended, therefore that, under the latter conditions, the preparation be commenced at room temperature.

It is also found that, when the higher atmospheric temperatures are encountered, the stability of the hypochlorite is impaired so that deterioration is usually more rapid. It is not known exactly how much this is due to the rise in temperature of the solution during the experiment and to what extent it is due to the alterations of pH ; the latter is important but, since it was not possible to estimate it during the course of the investigation, the relation of pH alteration to temperature rise was not determined.

On the other hand, a reference to sample (5) in the table shows that the minute deterioration on an average of 2 per cent daily over a period of seventy-five days bears no relation to the variation in atmospheric temperature, since this sample was kept from February to May, 1943. It does emerge, however, that the stability of samples prepared during the cool season very markedly exceeds that of those prepared during the warm season and this is an important point to be considered with regard to storage. The presence of traces of magnesium salts in the solution has also a stabilizing effect. A more complete investigation on these lines will be carried out later.

Current.—Diminution in current by 50 per cent caused a diminution in yield of 66 per cent (approx.) for a similar atmospheric temperature. The factors of importance in this respect are :—

- (i) The efficiency of the electrical connections with the liability of the chlorine-saturated spray from the solution to attack the metal of the electrodes. It was found that careful cleaning of the latter was necessary at the commencement of each experiment. A further

useful precaution is to smear a small quantity of vaseline over the outside of the terminal once the connexions are completed.

(ii) The diameter of the anode. After 20 gallons of solution have been electrolysed the diameter of the anode is about $\frac{1}{4}$ inch. This decrease in area of electrical surface exposed reduces the current very considerably and necessitates renewal of the anode. It has been suggested that a non-corrodable stainless steel electrode might be utilized as an anode but this has not yet been tried; in any case, since the carbons cost nothing, it seems a needless expense.

PREPARING THE SOLUTION FOR USE AND ITS STORAGE.

After the completion of electrolysis rough filtration through cotton wool is all that is necessary. Light hastens deterioration and the hypochlorite should be stored in clear bottles in a dark cupboard or in brown glass bottles or store jars in daylight. Since it is not expected that M.O.s will prepare more than is necessary for a week or so the question of storage is not of paramount importance.

USES OF HYPOCHLORITE.

It is to be emphasized that the finished product consists of a solution of sodium hypochlorite and hypertonic saline. Furthermore, the reagent must not be confused with the various chemically prepared hypochlorite solutions such as Eusol, Dakin's solution, etc., which differ from it in the following respects:—

- (a) They contain large quantities of alkali and have an irritant action.
- (b) They are most unstable and it is impossible to predict the hypochlorite content in any given sample within quite wide limits.
- (c) They are incidentally much more expensive to prepare.

The variety of uses to which the solution may be turned are exemplified below:—

(1) It is of great value in both the prophylactic and therapeutic treatment of wounds. The maximum permissible percentage of sodium hypochlorite for the actual continued treatment of open wounds is 0.2 per cent; higher concentrations are irritant. It will thus be seen that a standard of dilution of 1 : 5 conforms sufficiently accurately with this requirement. For the immediate treatment of foul smelling wounds or grossly contaminated fresh wounds it may be used for a limited time at full strength. Burns respond extremely well to irrigation with the diluted solution.

(2) General disinfection, e.g. sterilization of water supplies, eating utensils, glassware and rubber instruments. The Cookhouse and N.A.A.F.I. of the camp where the writer is quartered draw a regular ration of hypochlorite which is used to sterilize the men's eating utensils and drinking glasses after use.

When it is proposed to sterilize water the routine Horrocks' test must first be carried out, substituting drops of full strength hypochlorite for the W.S.P. solution. The number of the cup which first exhibits a blue colour on the addition of starch cadmium iodide indicator is multiplied by three to give the number of drops of hypochlorite required to sterilize one pint of water.

(3) Blood clot is dissolved by hypochlorite. The solution is utilized in the cleansing of blood transfusion apparatus.

(4) As a deodorant and for air sterilization it is very valuable. For this purpose it is used in the form of an air spray around and on the bandages of foul wounds.

(5) Dysidrosis and athlete's foot, so common in the tropics and sub-tropics during the summer months, are markedly improved by footbaths of a 1 : 20 dilution.

Although it has been pointed out that for continued use on wounds the solution should not be employed in a stronger concentration than 1 : 5, the limits imposed on dilution are considerably more elastic. It has been used with success in as high a dilution as 1 : 50. For wounds, however, the dilution should not be so great as to render the residual saline (about

13.5 per cent) hypertonic ; for this type of therapy, therefore, it is never diluted more than 1 : 10, thus maintaining a hypertonic saline solution throughout.

There are almost no antiseptic uses in hospital or M.I. Room work where hypochlorite cannot be utilized whereas many antiseptics available under Service conditions (especially the cresols) are quite unsuitable for the purposes for which hypochlorite is employed. It has occurred to the writer that a considerable saving in shipping space and expense could be effected by the widespread adoption of a method such as that outlined above so that an antiseptic may be prepared in the place where it is required.

SUMMARY.

- (1) A method of electrical preparation of sodium hypochlorite suitable for active service conditions is described.
- (2) The mode of analysis is outlined and results tabulated.
- (3) Effects are shown of variation in current, temperature and size of electrodes.
- (4) The uses of hypochlorite are discussed.

I am greatly indebted to Dr. Wadie Tedros of the Faculty of Chemistry, Fuad I, University, for his helpful suggestions and assistance in the many analyses necessary ; to Major Pulvertaft, R.A.M.C., for constructive criticism of the text and to my M.I. Room staff for their collaboration in the preparation of samples.