May 26, 1931. E. B. HIGGINS 1,806,801

ELECTROLYTIC PRODUCTION OF STERILIZING AGENTS, GERMICIDES, AND THE LIKE

Filed Jan. 16, 1929

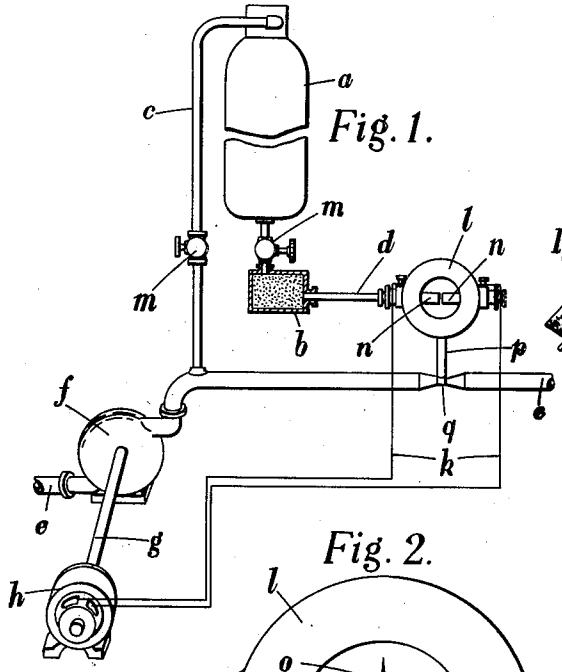


Fig. 1.

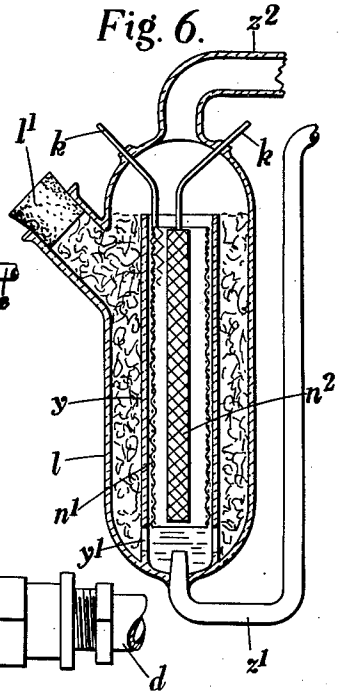


Fig. 6.

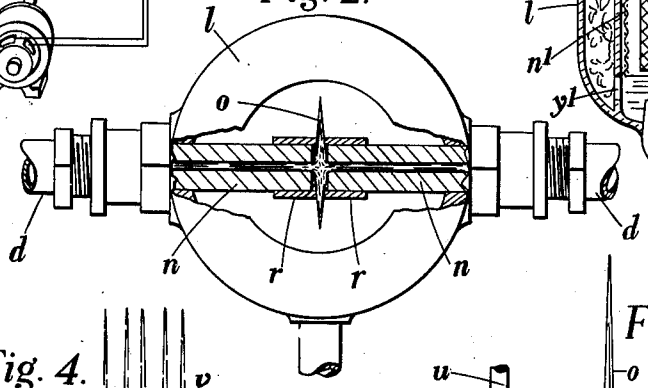


Fig. 2.

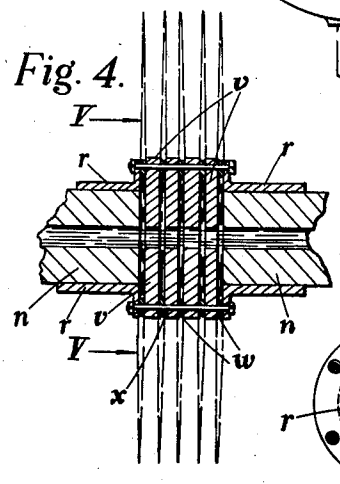


Fig. 4.

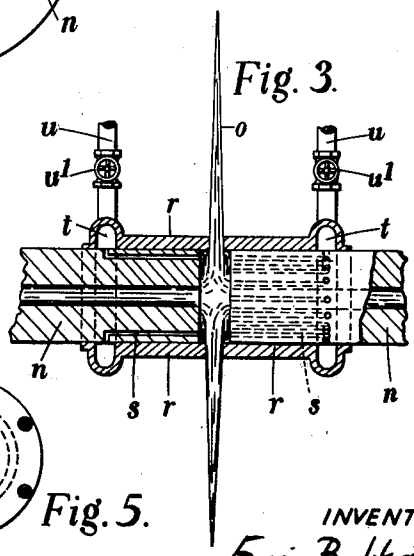


Fig. 3.

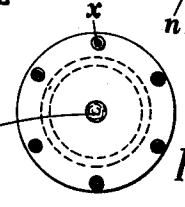


Fig. 5.

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UNITED STATES PATENT OFFICE

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ELECTROLYTIC PRODUCTION OF STERILIZING AGENTS, GERMICIDES, AND THE LIKE

Application filed January 16, 1929, Serial No. 332,842, and in Great Britain February 6, 1928.

This invention relates to the manufacture of sterilizing agents, germicides and the like by an electrolytic process, and more particularly to the electrolytic manufacture of chloramines.

As set forth in the specification of British Patent No. 22,280 of 1912, electrolysis of sodium chloride solution may be carried out by means of impinging jets in such a way that the products of the electrolysis are immediately removed from the sphere of action. The use of impinging jets, however, postulates streams of conductive liquid of relatively small cross-sectional area, with the result that currents of only relatively small values can be caused to flow. It is primarily the object of the present invention to enable chloramines to be produced cheaply and easily, but also to enable relatively large current densities in the electrodes to be used in the electrolytic production of chloramines while still enabling the products of the reaction to flow away from the sphere of action.

According to the present invention monochloramine or di-chloramine or both is prepared by the electrolysis of an alkali chloride to which an ammonium salt has been added. It is found that some ammonium salts, for example, ammonium chloride are soluble in common salt brine, and such a solution may conveniently be used as the electrolyte in carrying out the novel process. In one method which is found to be convenient two or more electrodes are arranged so that the space between them is extremely small relatively to the cross-section of either electrode, and the electrolyte is arranged to flow from one or both electrodes. The result is that between them there is a continuous body of electrolyte having a length in the direction of current flow very small compared with the cross-sectional area offered to the current flow. The net result is that the resistance of the path in the electrolyte is rendered very small indeed, so that large currents can be caused to flow and a relatively large output obtained. Good results can be obtained by causing the electrolyte to flow through the anode and to impinge upon the opposite face of the cathode, for then there is a tendency for the electrolyte continuously to flush the surface of the cathode. On the other hand, however, the electrolyte can be caused to flow through the cathode, but when making chloramines this method is found less beneficial. The best results, however, of all are obtained by causing the electrolytes to flow through both electrodes and to meet in the space between them, and then to flow out radially by arranging insulating sleeves around the two electrodes to project beyond their front faces. This outflowing stream of liquid may actually form a liquid diaphragm having most of the properties of a porous diaphragm, but, of course, of much lower resistance. In such a case the two electrodes may be formed with small return passages or bores apart from the main flow passages for the electrolyte, and bodies formed actually on the surfaces of the electrodes may be forced back through these additional passages and may be suitably collected. On the other hand, in an apparatus which is particularly applicable to the production of gaseous mixtures containing chloramines, the electrodes may be immersed in the electrolyte and may be spaced closely together and have a large surface area, being, for example, formed of metal gauze. Gas such as air is bubbled through the space between the electrodes and the resulting mixture of chloramines, with the gas may be employed, for example, in the treatment of flour.

In order that the invention may be clearly understood and readily carried into effect, some forms of apparatus in accordance therewith will be described by way of example with reference to the accompanying drawings, wherein:—

Figure 1 is a diagrammatic view showing a complete electrolytic plant for dealing with a water supply in accordance with the invention;

Figure 2 is a side view of the electrolytic vessel and its electrodes to an enlarged scale;

Figure 3 is a central section of a modified arrangement of the electrodes;

Figure 4 is a similar view of yet another arrangement;

Figure 5 shows a cross-section of the same on the line V—V of Figure 4, and

Figure 6 shows diagrammatically a form of electrolytic cell which may be employed in the formation of a gaseous mixture containing chloramine.

In Figure 1 the vessel *a* contains solid common salt and the vessel *b* contains an ammonium salt such as ammonium chloride in the solid condition. A proportion of the crude water flows through the branch pipe *c* into the vessel *a* to produce the common salt brine, and the latter is conducted through the ammonium chloride in the vessel *b*. It is found that common salt brine in these circumstances will actually dissolve some ammonium salts; for example, the solubility of ammonium chloride in common salt solution is about 15 per cent, but that of ammonium alum is considerably less. In any case, the solution leaving the vessel *b* through the pipe *d* has taken up sufficient of the ammonium chloride to serve as the electrolyte to produce chloramine. As a matter of fact, if the rate of flow is such that excess of ammonium salt is taken up, the chloramine produced will be largely or wholly di-chloramine, but either the monochloramine or the di-chloramine can be produced wholly or in excess by judicious selection of the ratio between the effective amount of chlorine produced during the electrolysis and the amount of the ammonium salt employed. In fact, the most desirable ratios between the effective chlorine produced and the ammonium salt are precisely as set forth in the specification of United States Patent No. 1,590,372, issued to Charles Henry Hasler Harold.

The main water pipe is shown at *e*, and the water flows through a device *f*, which as illustrated is a rotary pump on a shaft *g*, for pumping the water through the pipe *e*. Nevertheless, if the crude water is under pressure, the pump *f* may be replaced by a water motor, such as a turbine. In that case, the shaft *g* may be driven from the turbine, but as shown in Figure 1, the prime mover for driving the shaft *g* is not illustrated. The shaft *g* also carries the armature of a small electric generator *h* capable of generating relatively large currents at low voltage to be supplied through the conductors *k* to the electrolytic cell *l*.

It is preferred, as shown, to take off the branch pipe *c* on the outlet side of the pump *f*, but, of course, if desired it may be taken off from the inlet side of the pump *f*. The rate of flow of water in the branch pipes *c* and *d* and the proportion of the total water which flows through them is controlled by valves *m*.

The electrolytic cell or bath *l* consists of a small cylindrical vessel, preferably of insulating material, with the electrodes *n* projecting inwardly from opposite sides. Their surfaces must be parallel to one another and their axes coincident in order to obtain a symmetrical flow of liquid. One or both of the electrodes may be adjustable, and they may be brought together so that there is a gap between them of, for example, only 0.2 millimeters in length. Both electrodes may have a diameter of 1 centimeter, so that the inter-electrode gap is very small relatively to the diameter of the electrodes.

As shown in Figure 1, the solution through the pipe *d* only passes through the left-hand electrode, but in Figure 2 provision is made for allowing it to flow in through both electrodes *n*. As described above, the electrolyte is common salt brine containing a certain amount of ammonium salt, such as ammonium chloride.

The electrolyte in the arrangement shown in Figure 1 is ejected from the front end of the left-hand electrode *n*, striking immediately the face of the opposite electrode and being distributed in all directions from the gap between the electrodes. In Figure 2, of course, the two jets meet in the middle and a symmetrical distribution of the outflowing electrolyte, as indicated at *o*, is the result. The electrolyte may collect at the bottom of the vessel *l*, flowing out through a pipe *p* which admits it direct to the crude water pipe *e* at the point *q*, where the pipe *e* is formed with a contraction. The outflowing electrolyte contains the chloramine which is therefore supplied direct to the crude water, which it immediately sterilizes. There is, therefore, illustrated in Figure 1 a self-contained plant producing a sterilizing agent on the spot for treating the crude water. Of course, the point at which the electrolytic bath is situated and the point *q* at which the formed products are admitted to the crude water may obviously be a considerable distance from the pump *f* and the electric generator *h*. Although the latter generates at a small voltage a relatively large current, in fact the current is actually small because the electrolytic bath *l* is only of small capacity, so that the current can be led through the conductors *k*, which can be of considerable length. The amount of solution flowing through the branch pipes *c*, *d* may be automatically controlled in any known manner in accordance with the amount of crude water flowing, but as the amount of solution is quite small relatively to the amount of crude water, it is not usually found necessary.

The new process is found to yield a very satisfactory output of the sterilizing bodies; for example, with quite small electrodes, that is to say, circular electrodes having a diameter of 1 centimeter, with their forward ends spaced 0.2 millimeters apart, saturated brine containing about 2 per cent by weight of ammonium salts, was caused to flow through at the rate of 47 cubic centimeters per minute. The current employed was a total current of 7 amperes, and the yield was 0.84 grams of

effective chlorine per ampere hour. The chlorine was obtained almost wholly in the form of one or both of the chloramines, but with a relatively small proportion of free chlorine. As another example, with the same electrodes, and the same spacing, saturated common salt brine was caused to flow through at a rate of 69 cubic centimeters per minute and the total current was from 7.5 amperes up to 9 amperes. In this case the yield was about 1 gram of effective chlorine per ampere hour. In both these cases, the voltage required between the electrodes was of the order of 6 volts.

In the form of construction shown to an enlarged scale in Figure 2, the electrolyte flows through both electrodes n, entering by pipes d. The faces of the electrodes n are parallel and may, for example, be spaced apart by a distance of five-thousandths of an inch. The electrodes are cylindrical, and near their tips have sleeves r of resistance insulating material, each of which extends beyond its electrode n so that between the sleeves r there is an annular gap which may, for example, be two-thousandths of an inch. The electrolyte thus meets in the gap between the electrodes and forms a continuous liquid diaphragm of disc shape, as shown at o, and escapes continually through the gap between the ends of the sleeves r. Chlorine is formed on the surface of one of the electrodes n, and in the presence of ammonium salts is converted into chloramine, while caustic soda and hydrogen are formed on the other.

Yet a further development of the form of electrodes shown in Figure 2 is illustrated in Figure 3, where again the electrodes are seen at n, the sleeves at r, and the liquid diaphragm discharged between the ends of the sleeves at o. It will be noted that in each of the electrodes fine passages s are formed which at the rear open into annular ducts t formed in the rear ends of the sleeves r. The products, that is to say, chloramine or chlorine or both and caustic soda, collect in these ducts as they are formed on the extreme surface of the electrodes, and are forced back by the pressure of the liquid electrolyte, and the products may be conducted off from the ducts t through valve-controlled pipes u. All of these products may pass off in this way, or their passage may be obstructed by partly or wholly closing the valves u', in which case part or all of the products will pass off with the excess electrolyte, escaping from the gap between the sleeves r.

In the arrangement shown in Figures 4 and 5, a number of electrodes are interposed between the extreme positive and negative electrodes n. These additional electrodes consist of discs v, and therefore form a number of narrow gaps in the electrolyte in series. Each intermediate electrode v is a positive electrode on one face and a negative electrode on the other face. It will be seen that the sleeves r are illustrated as flanged, and the intermediate electrodes v is a positive electrode on one face and a negative electrode on the other face. It will be seen that the sleeves r are illustrated as flanged, and the intermediate electrodes v are shown as bolted between the flanges with intermediate spacing rings w, by means of small bolts x of insulating material. Such an arrangement has very considerable practical importance, for under many existing conditions it is more convenient to pass a relatively small current through a number of gaps between such electrodes at a voltage which is the sum of those across the consequent pairs of electrodes rather than to supply a multiple of the current at a corresponding fraction of the total voltage. It will be noted that in this arrangement the electrolyte enters through both electrodes n and issues in the form of a number of thin discs, passing through the free spaces between consecutive electrodes. Of course, if the electrolyte is to be passed in at one end only, the opposite electrolyte n will have no passage at all or will have its passage entirely closed.

In Fig. 6, the electrolytic cell l is of earthenware, glass or other refractory material and has an internal upwardly tubular member y with aperture y' at the foot affording access from the outside to the inside of the member y. The electrodes are in the form of two concentric cylinders n', n^2 of metal gauze placed relatively closely together and each having a large surface area. The current is led to them through the conductors k. The common salt brine fills the vessel to the upper edge of the member y and crystals of ammonium salt are introduced through a mouth normally closed by a stopper l'. The sodium chloride is not used up during the reaction so to make the action continuous it is only necessary to introduce crystals of the ammonium salt from time to time.

The result of the electrolysis is that chloramine is liberated at the anode n' and hydrogen at the cathode n^2 and if air or other gas introduced through the tube z' is bubbled through the electrolyte, it carries off the products of the electrolysis with it through the outlet pipe z^2. As an alternative, the cathode n^2 may be enclosed in a porous pot and the hydrogen taken off separately. In order to make it possible to work with high current densities, the whole cell may be immersed in water in order to provide adequate cooling.

The invention is not limited to the production of chloramines in the manner described. For example, other sources of ammonia than those mentioned can be used. For example, di-ammonium hydrogen-phosphate gives particularly good results. Further, although the method described consists in mixing an

ammonium salt, for example, ammonium chloride, with an alkali halide such as sodium chloride, which mixture is electrolyzed, as an alternative, gaseous ammonia may be mixed with the alkali salt and electrolyzed; or again, the alkali halide may be electrolyzed and the electrodes submerged in an ammonium salt or a solution of ammonia may be allowed to drip on to the electrodes.

Finally, of course, one method of applying the invention to a plant directly associated with a crude water supply has been described, in which case the proportion of sterilizing body added to the water may be controlled by varying the current flowing through the electrolytic bath. As an alternative, however, the actual electrodes may be submerged in the main water stream to be treated, in which case the sterilizing body or bodies is, of course, formed actually in situ. However, the products may be obtained in such a concentration that they can be used at any time. The products obtained from the process, which, as will be appreciated, in one case consists in the excess electrolyte, for example sodium chloride and ammonium chloride containing the chloramine produced, or in other cases may be the chloramine itself removed from the electrolyte by volatilization, for example by blowing air through the same, can be stored for some time, particularly in a vessel protected from heat and bright sunlight. It is preferred, however, to employ the products within a short time after their production. Apart from the sterilization of water, the products may be used as antiseptics and germicides in general practice.

I claim:—

1. A method of producing chloramine which consists in electrolyzing an alkali chloride in the presence of a soluble ammonium salt.

2. A method of producing chloramine which consists in electrolyzing a solution of an ammonium salt in common salt brine.

3. A method of producing a chloramine which consists in electrolyzing an alkali chloride in the presence of a soluble ammonium salt and bubbling a carrier gas through the electrolyte to take off the chloramine liberated.

4. A method of producing a gaseous mixture containing chloramine which consists in electrolyzing an alkali chloride in the presence of a soluble ammonium salt and bubbling air through the electrolyte to take off the chloramine liberated.

5. A method of producing a gaseous mixture containing chloramine which consists in electrolyzing a solution of an ammonium salt in common salt brine and bubbling air through said solution.

In witness whereof I hereunto subscribe my name this 3rd day of January, 1929.

ERIC BERKELEY HIGGINS.