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L. DELAVENNA ET AL

2,180,668

PROCESS FOR THE ELECTROLYTIC PREPARATION OF OXYCHLORINE SALTS

Filed Feb. 13, 1936

2 Sheets-Sheet 1

*Fig. 1*

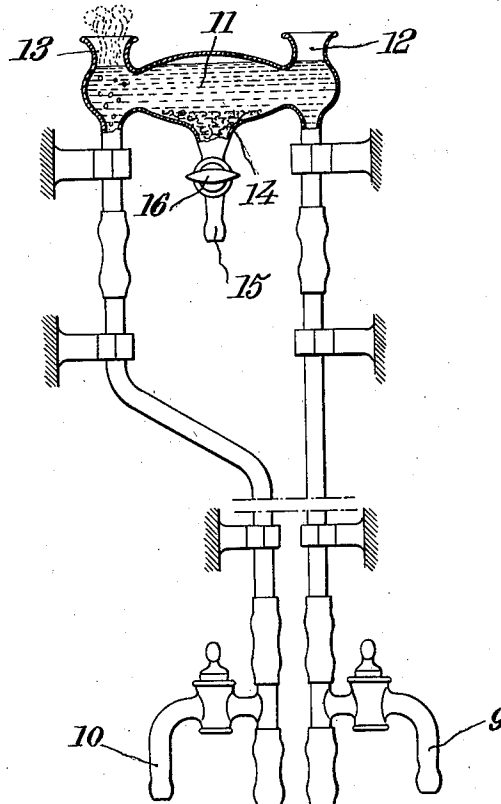
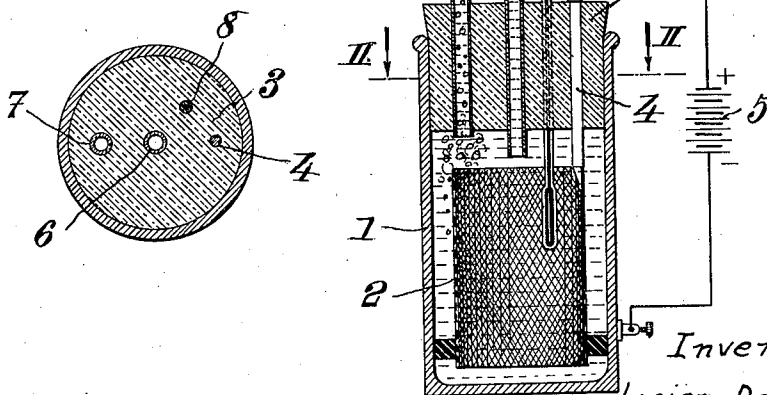


*Fig. 2*



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2 Sheets-Sheet 2

*Fig. 3.*

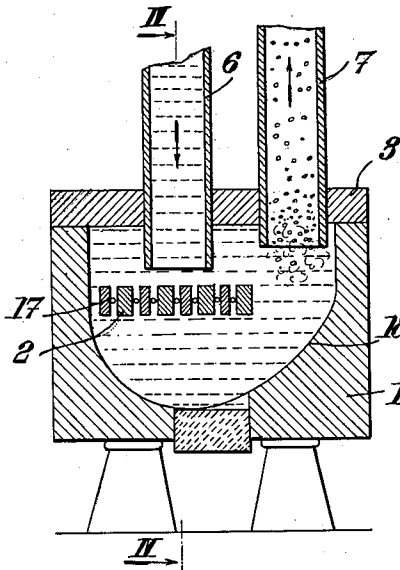


*Fig. 4.*

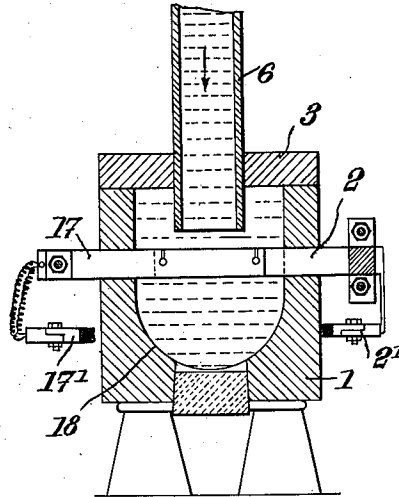


*Fig. 5.*

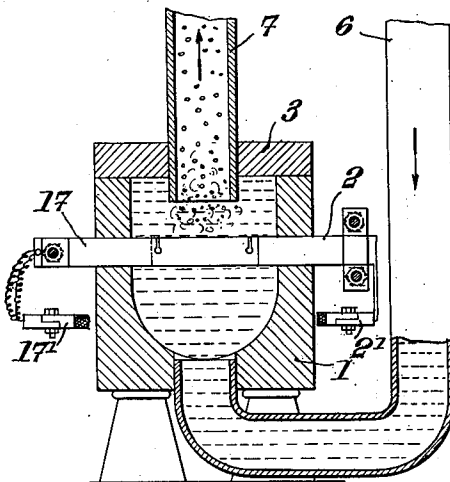
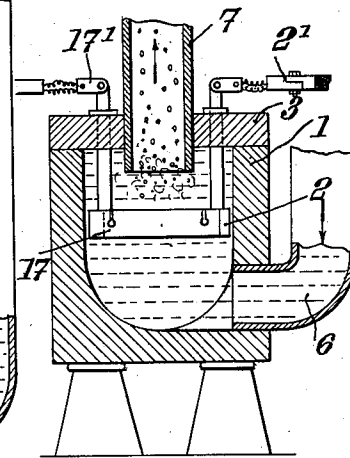


*Fig. 6.*



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## UNITED STATES PATENT OFFICE

2,180,668

## PROCESS FOR THE ELECTROLYTIC PREPARATION OF OXYCHLORINE SALTS

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5 Claims. (Cl. 204—60)

This invention relates to processes and apparatus for the electrolytic treatment of chemical compounds, acids, salts, persalts, etc., and more particularly, but not exclusively, processes and apparatus for the electrolysis of chlorine salts such as aqueous solutions of alkaline or alkali earth or other chlorides.

It is an object of this invention to so provide these processes and apparatus that they give a practically quantitative yield as a result of the electrolytic treatment, and that the deleterious polarisation action is practically eliminated. A further object, more particularly in the case of the electrolytic treatment of chlorine salts, is to so provide the processes and apparatus that all liberations of harmful gases or formation of explosive gases is avoided.

Finally, it is an object of the invention to so provide these processes and apparatus that it is possible to employ a high density current in the electrolysis.

The invention, as far as it relates to processes of the kind indicated above, consists chiefly in submitting a liquid, preferably saturated, to a continuous electrolytic treatment, while the liquid is maintained in circulation and under pressure.

The invention, as far as it relates to the apparatus mentioned above, consists in providing at least one electrolytic cell into which two upwardly-directed tubes open, these tubes being connected together at their upper ends with a communicating conduit in such manner as to form a continuous circuit for the liquid to be treated, and on the other hand to create the desired pressure in the electrolytic cell. The said communicating conduit may be provided in such a way that it includes apertures for the liberation of the gases, for example hydrogen, produced by electrolysis and for the supply of fresh materials, etc., the products formed being collected and raised to a suitable point in the circuit.

The electrolytic treatment may be carried out at low temperature by exposing at least a part of the apparatus employed to a cooling action.

Moreover, and particularly in cases where chlorine salts, such as sodium chloride, are treated with a view to the preparation of the corresponding chlorate, there may be added, under pressure, to the liquid to be treated, a saturated solution of the salt to be treated, this solution containing traces at least of hydrochloric acid. The addition of the saturated solution will be carried out in a continuous or

intermittent manner and preferably at the temperature of the electrolytic action.

The process may be so carried out that auto-precipitation of the salt produced thereby is effected by lowering the temperature of a supersaturated solution of the liquid obtained by electrolysis.

A further feature of the invention consists in so providing the apparatus with an electrolytic cell or vessel, that the anodes of the latter (which are preferably of graphite) are in the path of the electrolyte fed in through a supply conduit, and in giving to the bottom of the cell or vessel such a shape that the fluid current, after having undergone the effects of electrolysis is directed towards the discharge conduit or vice versa.

A still further feature of the invention comprises the inclusion of means for the filtration of the products of electrolysis in the apparatus, these means being adapted to collect the impurities involved.

The invention provides for further modifications of the processes and apparatuses as outlined above, and these modifications will be apparent from the accompanying description.

The accompanying drawings illustrate, by way of example only, embodiments of the apparatus according to this invention.

Figures 1 and 2 show, in axial vertical section and in transverse section along II—II of Fig. 1 respectively, an apparatus constructed in accordance with the invention.

Figures 3 and 4 illustrate, in axial vertical section and in transverse section along IV—IV of Fig. 3 respectively, a part of an apparatus constructed in accordance with a modification of the invention.

Figures 5 and 6 are views similar to that in Fig. 4 but illustrating further embodiments of this invention.

In what follows, reference will be made to these drawings and to a process for the electrolytic treatment of an aqueous solution of an alkaline chloride (or an alkali-earth chloride), such an alkaline chloride being, for instance, sodium chloride, but it must be pointed out that this description (as the drawings) is only to be regarded in the light of an example, since the invention includes any variation or modification of the apparatus or process described which falls within the scope of the appended claims.

Hitherto the electrolytic treatment of salt solution has been carried out by introducing the

solution into a plurality of cells and then subjecting it, in a state of rest, to the action of an electric current. Such a procedure, it can be ascertained, results in a limitation of the quantitative yield by a considerable proportion, owing to the electrolytic reduction phenomena, due to nascent hydrogen, which are produced in spite of the addition of catalysts such as sodium chromate, sodium bichromate, etc. Moreover, the abundant liberation of harmful gases, particularly chlorine, occasions considerable annoyance.

In accordance with this invention an almost complete suppression of electrolytic reduction is effected by constantly and very rapidly removing and evacuating the hydrogen upon its formation and by continually circulating the electrolytic liquid under a pressure which is preferably practically constant.

Moreover the process is carried out with a solution maintained permanently saturated by the addition thereto, when necessary, of the desired quantities of the crystallized salt to be electrolytically decomposed.

Preferably a high density electric current is used for the electrolysis, and the latter is carried out at low temperature by cooling, in a suitable manner, the apparatus used or the material to be treated, for example by circulating cooling brine.

As a result of the circulation under pressure of the alkaline (or alkali earth) chloride solution, the atomic chlorine, produced at the anode by the electrolytic action, is carried along and immediately forms, in the first stage, the hypochlorite and then the corresponding chlorate without any liberation of gaseous chlorine and without danger of explosion of the explosive gases which would otherwise be produced.

Moreover there may be produced by the continuous circulation under pressure and in a continuous manner, crystalline alkaline (or alkali earth) chlorate, and this may be extracted from the apparatus at a suitable point in the circuit, this chlorate being produced continually by the precipitation from the crystalline alkaline chlorine salt introduced into the said circuit.

Chemical analyses of the treated substances and the products obtained from this process indicate an almost quantitative yield in comparison with the ampere-hours used.

Referring now to Figs. 1 and 2 of the drawings, the electrolytic cell comprises a metallic vessel 1, for example of steel, forming the cathode and connected to the negative pole of the electric current source 5.

The anode of the electrolytic device is constituted by a cage 2, e. g., of platinum wire, and is so disposed in the vessel 1 that it takes up a convenient position with respect to the latter. The vessel 1 is sealed in a fluid-tight manner by a cover or plug 3 fixed to the cathode 1 in any suitable manner so as to provide the electrolytic cell as a closed space with walls resistant to the pressure which is visualized in accordance with the present invention. A thermometer 8 and the conducting member 4 which connects the anode 2 to the positive pole of the electricity source 5 (which preferably provides a working current of high density), both pass through the cover or plug 3. A large tube 6, for example of glass or other suitable material, also passes through the plug or the like 3, and its lower end projects from the bottom face of the latter into the electrolytic vessel, while accommodation is provided in the plug 3

for a second tube 7, also of glass or other suitable material, the lower end of the tube 7 being flush with the bottom face of plug 3. It will be understood that each of tubes 6 and 7 might be replaced by a battery of tubes of suitable material, the latter having the same function as the single tubes, while tubes 6 and 7 themselves might either have the same diameter or different diameters.

Each of tubes 6 and 7 is extended upwardly over a suitable distance, corresponding to the static pressure or to the charge which is anticipated, and at a convenient point in each of these tubes there may advantageously be provided a sampling tap 9 or 10.

The upper ends of tubes 6 and 7 communicate with each other through a conduit 11, open to the atmosphere by means of orifices 12 and 13 of suitably chosen section, orifice 12 being disposed above the central tube 6 and orifice 13 above the tube 7. At its central and lower portions the said circuit 11 forms a kind of basin 14 with a fitting 15 closed by a control member 16, this basin being adapted to collect the chlorate formed by the electrolytic treatment and the closable fitting 15 serving to tap off the substances formed, which tapping off may be carried out when desired and at will or by means of an automatically or intermittently operating closure member.

At the commencement of the electrolytic treatment of an aqueous solution of sodium chloride, for example, for the purpose of producing sodium chlorate, the apparatus, which is fluid-tight, is filled with a saturated NaCl solution. This advantageously has added thereto crystalline sodium bichromate or a similar compound. The liquid is introduced through orifice 12 and/or 13 until there is a suitable quantity in the conduit 11. Thus there is formed a continuous circuit comprising the vessel 1, tubes 6 and 7 and connecting conduit 11, and there is obtained in the vessel 1 a liquid pressure depending on the charge of liquid above it, i. e. upon the height chosen for the tubes 6 and 7.

Advantageously the apparatus is submitted to cooling during the treatment, either by the circulation of brine inside a lagged metallic heat exchange device wound externally around the tubes 6 and 7, by external cooling of the cathode vessel 1 in a bath of freezing water stirred by a motor driven agitator, or by any other suitable refrigerating means.

When the apparatus is connected up to the source 5 of electrical energy, the electrolytic process begins and there is automatically produced a circulation of the liquid under the action of the gases formed by this treatment and particularly by the hydrogen liberated, and this liquid movement entrains the liquid in tube 7, re-entry of the liquid into vessel 1 taking place through the tube 6. Atomic chlorine, produced at the anode, is carried along by the circulation of liquid under pressure and at once forms the hypochlorite and then the chlorate of the alkali or alkaline earth under treatment. It will be found that there is no harmful liberation of chlorine or danger of explosion through the formation of explosive gases.

The salt, which is produced continuously, is deposited in the basin 14, since there is at that point a convenient lowering of temperature on account of the external cooling to which the basin is subjected, and a breaking-down of the equilibrium of the solution by the addition of

fresh sodium chloride through the orifices 12 and 13 takes place. On the other hand the hydrogen resulting from the reaction and which constitutes the chief active agent in producing the circulation of the liquid, escapes freely through orifices 12 and 13, whereby the electrolytic reduction effects are simultaneously eliminated.

The volume of the treated solution may be maintained constant by the addition of crystallised NaCl or brine, or by introducing water through orifice 12 or 13, the choice of water or sodium chloride for this addition being, of course, determined by the particular state of equilibrium of the constituents of the solution treated at the time when the addition is made.

By proceeding as indicated above, a relatively high proportion of active chlorine is retained in the process as compared with that hitherto retained and there is also obtained a practically quantitative yield in proportion to the current used. Moreover there is obtained directly, by an action which is continuous at will, crystalline and refined sodium chlorate, without the intermediary of the usual dechlorination, concentration and finally crystallisation operations. The chlorate, owing to this particular method of production, is very pure.

By eliminating the use of sodium bichromate there is also obtained an increased retention of active chlorine but the total yield is somewhat decreased in quantity. Moreover there is no liberation of gaseous chlorine through the orifices 12 and 13 in this process.

It is important that all gaseous hydrogen can be integrally and rapidly removed from the electrolytic cell before the re-entry of the liquid into said cell. Consequently the dimensions of the tubes or batteries of tubes 6 and 7 should so be calculated as to allow for the pressure and circulation, which are essential features of the process of this invention, according to the size of the basin or of the vessel 1 and according to the intensity of the current used for the electrolysis.

There are shown in Figs. 3 to 6 several modifications of the electrolytic cell such as has been described above. In the latter case the electrolytic vessel 1 is made of cement, concrete, ceramic material or any other agglomerated material. Orifices are provided in the cover 3 of the vessel and are adapted to accommodate at least one feed channel 6 and at least one discharge conduit 7. The anode 2 is constituted by bars of a conducting material, for example graphite. These bars are connected by a common lateral connection 2' to the positive side of the current source and alternate with the conductor plates constituting the cathode 17 and are connected by the common lateral connection 17' to the negative side of the same current source. In the example according to Figs. 3 and 4 (as opposed to that shown in Figs. 1 and 2) the feed conduit 6 is arranged out of line with the centre of the vessel, and the electrolysing members 2 and 17 are arranged symmetrically with respect to the mouth of this conduit. Moreover the bottom 18 of the vessel 1 is provided of an asymmetric shape, such that the liquid after it has undergone the electrolytic treatment is directed towards the opening of the discharge conduit 7. This is effected by extending the bottom of the vessel by means of a curved wall to the opening of conduit 7. The positions of conduits (or batteries of conduits) 6 and 7 might, of course, be

reversed, the discharge conduit 7 then being arranged over the electrolysing members 2 and 17.

In the example illustrated in Fig. 5 the conduit 6 supplying the liquid to be treated opens into the bottom of the vessel 1, with respect to the electrolysing members 2 and 17, and the conduit 7 is arranged above the central portion of said electrolysing members. In this way the circulation of the liquid and gases through the apparatus takes place without any dead space or dead angle being left in the vessel 1.

In the example according to Fig. 6 the supply conduit 6 discharges laterally into the vessel 1 below the electrolysing member 2 and 17, while the discharge conduit 7 is arranged in the same way as in Fig. 5. In the present case however, the connections 2' and 17' pass through the cover 3 so that the latter forms the sole support for the assembly of electrodes.

Filtering devices, for example a filter formed in some way by an amalgamation of the salts (chlorates) which are to be produced, may be annexed to the apparatus described. Such a filter or its equivalent may be arranged at a suitable point in the discharge conduit 7 or in by-pass with this conduit, in such manner that it can, as required, collect every trace of material caused by mechanical wear or tear, or like substances, especially graphite, which may be in suspension in the circulating liquid and which may contaminate the chlorate obtained by precipitation. It should be remarked that the graphite which is produced by the breaking down of the electrodes is not, as in the case of the electrolytic apparatus at present employed, in the so-called colloidal state, which tends to give the liquid a greenish-black colour, but conveniently in the form of separate grains in suspension or floating in the liquid so that they can be very easily removed by filtration. By employing such filtering means not only are the impurities and the broken-down particles of graphite removed but sodium chlorate in pure condition and free from leach-brine is directly obtained in a continuous manner.

In the foregoing the use of the process and the apparatus according to the invention has been considered, by way of example, in regard to the electrolytic preparation of a chlorate, such as sodium chlorate, starting with a solution of the corresponding chloride.

Starting with a chloride, the same process and apparatus may be employed in the preparation of the corresponding hypochlorite, for example sodium hypochlorite. As indicated above, the formation of the hypochlorite is an intermediate stage in the electrolytic treatment of the chloride for the purpose of obtaining the chlorate, and this intermediate formation takes place in growing amounts before the chlorate is obtained in any considerable quantity. Thus it is sufficient to remove the hypochlorite in a continuous manner as soon as the quantity formed reaches the proportions of a suitable industrial yield, and this at the same time prevents the transformation of the hypochlorite into the chlorate.

In this application of the process according to the invention, anodes of platinum or graphite adapted to operate at low temperature, the brine being removed continuously when it has attained its maximum content of hypochlorite, while fresh previously cooled brine is introduced continuously into the apparatus in proportions correlated to the volume of liquid removed.

For example, using an anode of graphite, and

if the temperature is kept between  $-3^{\circ}$  and  $0^{\circ}$ , a content of the order of 25 to 28 grams per litre of active chlorine (which corresponds to a content of 52 to 58 grams per litre of hypochlorite) is obtained, at the stage at which the active chlorine produced by the process is actually ex-

In order to obtain the hypochlorite, cooling may be effected by means of a circulation of cooled brine, not only externally of the conduit or conduits 6 and 7, but also in the serpentine current produced in vessel 1 or inside said conduits.

According to a further embodiment of the invention the apparatus may, in the example under consideration, be fed with a brine solution saturated with sodium chloride for the purpose of obtaining the corresponding chlorate. This brine is preferably at the temperature at which electrolytic treatment is carried out, and is conditioned by traces of hydrochloric acid or contains a suitable quantity of this acid. Thus with the addition of hydrochloric acid at the rate of 1 cub. cm./hour per ampere-hour, and using a pressure of the order of 400 grams per square centimeter of water and with the HCl at a concentration of over 30 cub. cms. of the solution at  $22^{\circ}$  Bé. in 100 cub. cms. of the added liquid, no liberation of chlorine is observed.

The liquid so constituted is introduced in a continuous or intermittent manner and under pressure (for example under charge and through the intermediary of a pump) into the apparatus in such a way that the latter is always suitably supplied with the substances which have to be electrolytically decomposed. This introduction of the liquid preferably takes place on a level with the electrolysing members and advantageously into the supply conduit 6 through a valve device, although it must be realised that its introduction is by no means restricted to this particular method. It should be noted that the hydrochloric acid participates in the same way as the sodium chloride in the electrolytic decomposition and contributes efficaciously in the formation of the required chlorate. If the process is carried out in the manner indicated, an almost quantitative Faraday yield is obtained without liberation of chlorine, and equally well at low temperature operation as at ordinary temperature using a platinum anode.

Experience has shown that a graphite anode, used as indicated above, also gives an increased yield, the increase being of the order of 90%, without any liberation of chlorine and without danger of explosion, at ordinary temperatures.

It should be noted that it has already been proposed in the manufacture of sodium chlorate to add dilute hydrochloric acid continuously or intermittently to an electrolyte comprising a sodium chloride brine. In the existing apparatuses, which do not operate under pressure and with continuous circulation, this addition of HCl has the great drawback that it decomposes the hypochlorite while giving rise to a considerable liberation of chlorine.

Referring again to the present invention, the liquid circulating in the apparatus should always be kept saturated with sodium chloride. The equilibrium of the constituents in the liquid may be destroyed not only by the addition of sodium chloride—if desired, together with hydrochloric acid—but also by lowering the temperature of the liquid in circulation, which after the supersaturation stage has been passed causes an auto-

precipitation. Moreover the super-saturation might also be destroyed by the addition of a small quantity of sodium chlorate, for example as fine crystals. At regular or irregular intervals the apparatus may thus be cleared in some suitable way of a large amount of crystalline sodium chlorate in a very fine and very pure condition, so that there is obtained directly by simple drying and without washing a product containing sodium chloride impurities only in infinitely small amounts, viz., of the order of 0.5%.

The treatment as explained above may advantageously be applied to all processes of electrolysis of chemical compounds such as salt solutions, more particularly for example, aqueous solutions, whatever be the desired products. Other examples of processes to which the invention is suited are:

(a) The electrolytic oxidation of mineral or organic chemical compounds, or the formation of the oxides of any metal, including the oxides soluble in alkalis, in the case where liquid is always neutral, of sub-acetates, chlorides, sulphates, chromates, etc., in the case where a salt is to be precipitated and in the case where another salt should be added, the acid radicle of which is adapted to form a soluble product by interaction with the metal of the anode.

(b) The electrolytic reduction of mineral or organic compounds.

Finally, and more particularly, the invention is applicable to galvanic deposition, by the concomitant use of pressure and circulation independent of whether the circulation takes place naturally under the influence of electrolytic phenomena or is produced artificially, maintained or decreased by any suitable means and causing the prevention of the deleterious effect of the hydrogen, and thus provides dense galvanic deposition, with any requisite current density, of metals such as copper, zinc, nickel, cadmium, chromium. In these cases also there is no liberation of harmful gases (as for example would otherwise be the case in the galvanic deposition of chromium).

What we claim is:

1. A method of producing chlorates of alkali and alkaline earth metals and hydrogen by electrolysis from the corresponding chlorides in aqueous solution, comprising circulating the electrolyte along a single path, under the action of the hydrogen developed by the electrolysis, between a closed and diaphragmless electrolytic cell and a vessel positioned at a level above the cell sufficient to produce a pressure in the cell of about 400 grams per square centimeter, maintaining the electrolyte saturated by constant addition thereto, in said vessel, of said chloride in crystalline form, collecting the chlorate in said vessel, and permitting the escape of the hydrogen at the upper part of said vessel.

2. A method as claimed in claim 1, wherein a solution of the chloride salt, containing traces of hydrochloric acid, is added to the circulating electrolyte.

3. A method as claimed in claim 1, wherein a solution of the chloride salt, containing traces of hydrochloric acid, is added under pressure in the electrolytic cell to the circulating electrolyte.

4. A method of producing oxychlorine salts of the alkali and alkaline earth metals by electrolysis from the corresponding chlorides in aqueous solution, comprising circulating the electrolyte along a single path, under the action of the hydrogen developed by the electrolysis, be-

tween a closed and diaphragmless electrolytic cell and a vessel positioned at a level above the cell sufficient to produce a pressure in the cell of about 400 grams per square centimeter, maintaining the electrolyte saturated by constant addition thereto, in said vessel, of said chlorides in crystalline form, removing the oxychlorine salts formed, and permitting the escape of the hydrogen at the upper part of said vessel.

5. A method of producing hypochlorites of alkali and alkaline earth metals and hydrogen by electrolysis from the corresponding chlorides in aqueous solution, comprising circulating the elec-

trolyte along a single path, under the action of the hydrogen developed by the electrolysis, between a closed and diaphragmless electrolytic cell and a vessel positioned at a level above the cell sufficient to produce a pressure in the cell of about 400 grams per square centimeter, maintaining the electrolyte saturated by constant addition thereto, in said vessel, of said chlorides in crystalline form, removing the hypochlorite, and permitting the escape of the hydrogen at the upper part of said vessel.

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