N° 13,452 A.D. 1915

(*Under International Convention.*)

Date claimed for Patent under Patents and Designs Act, 1907, being date of first Foreign Application (in the United States), ... *5th May, 1915*

Date of Application (in the United Kingdom), 21st Sept., 1915

At the expiration of twelve months from the date of the first Foreign Application, the provision of Section 91 (3) (a) of the Patents and Designs Act, 1907, as to inspection of Specification, became operative

Accepted, 21st Nov., 1916

COMPLETE SPECIFICATION.

Improved Manufacture of Chlorates of Alkali Metals.

I, Arthur Edward Gibbs, Chemist, of Wayne, in the County of Wayne, State of Pennsylvania, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

My present invention is designed to provide a simple and highly efficient method of producing chlorates.

The electrolytic part of my present method takes place in a cell such as is used for the production of alkali and chlorine. The chlorine is removed from the anode compartment and combined with alkali outside of the cell. Some or all of the chlorate and chloride formed from this combination is returned to the anode compartment of the cell and is allowed to pass through to the cathode compartment when it again becomes strongly alkaline and is ready to absorb more chlorine, thereby increasing its chlorate content. The chlorate is separated as hereinafter described.

In the accompanying drawing I have illustrated diagrammatically, one apparatus for carrying out my invention; namely, an electrolytic cell 2, such as is used for the production of caustic alkali and chlorine and which may be of the mercury, diaphragm or other type. I find, however, that the type of cell described in Specifications Nos. 27,830 of 1907 and 28,147 of 1908, is particularly efficient for this work by reason of the large space for anode liquor as compared with the volume occupied by the anodes. Furthermore, the diaphragm used in this cell prevents contamination of the chlorate with carbonaceous matter resulting from breaking down or disintegration of the anodes. I have accordingly illustrated a cell of this type at 2 in the accompanying drawing, which is a diagrammatic view of one form of apparatus suitable for

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carrying out the invention. 3 designates the anodes, 4 the perforated sheet metal cathode and 5 the diaphragm. 6 is the elevated cup connected with the interior of the anode chamber by the feed pipe 7.

The outlet pipe 8 from the cathode compartment of the cell leads through a suitable pump 9 into a tank 10 provided with a suitable agitator 11. The tank 10 has an overflow connection at 12 into a settling tank 13. The tank 10 is also preferably provided with a bottom draw-off 14, and the tank 13 is shown as having a similar bottom draw-off 15. The upper portion of the settling tank is connected by a pipe 16 with the upper portion of an absorption tower 17. 18 is an off-take connection from said tower leading to an exhaust fan at 19. The tower 17 discharges at the bottom into a solution tank 20 which is connected by a pipe 20*a* with another solution tank 20*b* having a syphon connection 21 with the feed cup 6. 22 is an overflow pipe for the cup 6 leading into a tank 23 which is connected back to the tank 20*b* through a pump 24 and pipe 25. 26 is a pipe leading from the top of the anode chamber of the cell 2 into the lower portion of the tower 17.

When sodium chlorate is the product desired, the method may be started and carried out as follows:—

A solution of sodium chloride is supplied to the feed cup 6 from whence it passes into the anode compartment of the cell 2 and is electrolysed. The caustic or cathode liquor is drawn from the cathode compartment of the cell by means of the pump 9 and flows into the tank 10, from which it overflows into the tank 13, and thence to the tower 17. In passing through this tower it meets an ascending current of chlorine gas delivered from the pipe 26 from the anode compartment. Hypochlorite of soda is formed and this is converted into chlorate by the excess of chlorine which exists near the bottom of the tower. If the conversion to chlorate is not otherwise complete, artificial heat may be supplied in any suitable manner. In the event of any unconverted hypochlorite passing into the tank 20*b* and thence to the cell 2, it is immediately oxidized in the anode compartment of the cell. The overflow from the feed cup 6 falls into the tank 23 and is returned by the pump 24 to the tank 20*b*. During the operation sodium chloride is supplied to the tank 10 to keep the solution saturated to as high a degree as is practicable with that salt. After the liquors have circulated through the system a number of times, the chlorate gradually increases in amount and the liquor is then removed and concentrated for the recovery of the chlorate. The salt which separates out can be returned to the system.

The alkaline liquor coming from the cathode compartment of the cell contains, in solution, sodium chloride, sodium chlorate, caustic soda and some carbonate of soda. The electrolyte in its passage through the cell has been depleted of some of its sodium chloride and this loss is made up by the addition of more sodium chloride to the tank 10, as before described. A convenient way of getting this sodium chloride into the solution is by means of the agitator 11. The grade of salt usually employed for this work does not dissolve to a clear solution. It also usually contains some calcium, and magnesium salts. This is precipitated in the tank 10 by the caustic and carbonated alkali. Some of this sediment or precipitate settles out at the bottom of the tank 10 and the remainder passes on to tank 13, in which it settles. These precipitates are drawn off at 14 and 15.

The precipitation of the lime or magnesia salts, which are usually present in the chloride salts, added to the tank 10, is at the expense of some of the caustic or carbonated alkali present in this tank. The result of this, together with the removal of the chlorate from the solution at the bottom of the tanks 10 and 13 is a deficiency of the alkali with respect to the chlorine produced in the cell, so that there is a sufficient excess of chlorine present in the absorption tower 17 to effect the conversion of hypochlorites to chlorates in said tower. If a pure chloride should be added in the tank 10, the excess of chlorine would be maintained by withdrawing some alkaline liquor at either 14 or 15.

Potassium chlorate can be conveniently made by using a potassium chloride electrolyte, or a mixture of potassium and sodium chloride in solution, or by adding potassium chloride to the sodium chloride electrolyte above described. Double decomposition between the sodium chlorate and potassium chloride takes place and the less soluble potassium chlorate separates out.

The chlorate of potash may be removed either at 14 or 15. It is in the form of a sludge, and may then be purified in any usual way, as by placing it in a centrifuge to separate the caustic liquor from the chlorate and from the insoluble mud precipitated from the commercial chloride which is added at this point. The sludge can then be purified by re-dissolving, settling and crystallizing or concentrating by well known methods. While drawing the sludge off at 14, connections may be made so that the liquid from pump 9 will go direct to tank 13. Similarly, when the sludge is drawn off at 15, the liquid may be passed directly from the tank 13 to the tower 17 by any suitable connection. The operations for either chlorate of soda or chlorate of potassium are generally similar, except that in the case of the former, it being very soluble, does not crystallize in the vessels 10 or 13, but must be drawn off and concentrated. The sodium chloride which separates out first can be returned to the system. By circulating the liquor through the cell a number of times, the proportion of chlorate to chloride is greatly increased, and the solution going to the concentrators can thus be made to contain more chlorate than chloride. As the reaction between caustic and chlorine to produce chlorate is such that five molecules of chloride are produced to one molecule of chlorate, this feature is of great importance. The necessity of handling a large amount of chloride for a small production of chlorate has caused the commercial abandonment of many other methods which have been tried.

It is obvious that many changes can be made in the apparatus used and in the details of the method described, without departing from the spirit and scope of my invention, as defined in the appended claims. Thus, instead of one absorption tower, several may be employed, and the chlorate may be removed from the liquor at any desirable point in the system.

If it is desirable to use the strong chlorine produced in the cell for purposes other than chlorate such as for making liquid chlorine, I can replace the amount so used with chlorine from another source or produced by chemical means. But whatever the source of the alkali and chlorine, I prefer to supply these to the system outside of the cell in such proportions that the chlorine is in excess, the chlorate and chloride thus produced being returned to the electrolytic cell. If a mercury or gravity type of cell is used, I prefer to filter or thoroughly settle the liquors containing the chlorate, in order to avoid the danger caused by the presence of carbonaceous matter in the chlorate. If a cell is used with a mercury cathode, some or all of the solution containing chlorate and chloride is allowed to pass to the cathode compartment, preferably from the anode compartment, where it is decomposed by the sodium in the mercury, forming caustic soda and hydrogen, the chlorate being substantially unaltered.

Some of the advantages resulting from my invention are as follows:—

The operation can be carried out at a temperature considerably in excess of 40° C. without causing undue corrosion of the electrodes.

As the conductivity of wet electrolytes increases with the increase of temperature, the cell can be run at a lower voltage at the higher temperature. The addition to the electrolyte of chronic acid or its salts can be dispensed with, if desired. Power efficiency exceeding fifty-two *per cent.* of the theoretical efficiency can be obtained, assuming the decomposition voltage of sodium chloride to be 2.02 volts.

When carbon or graphite anodes are used in connection with a diaphragm cell, contamination of the chlorate with carbonaceous matter is prevented. The grinding of chlorate is attended with considerable danger; and this danger is greatly increased if carbonaceous matter is present. The diaphragm being an excellent filter removes from the system all of the carbon or graphite which disintegrates from the electrodes.

The removal of the chlorate from the electrolyte is accomplished without disengaging or losing chlorine and without discomfort to the workmen. This is because the chlorate is removed from the system at a point between the electrolysing apparatus and the absorption chamber where there is no chlorine present and the strong alkaline liquor is free from odor or corrosive action on iron.

The solution containing chlorate being strongly alkaline and substantially free from hypochlorite, entails less expense for apparatus and the problem of handling, cooling, heating and concentrating these liquors is simplified to a considerable extent.

The use of an alkali chlorine cell makes negligible the loss of efficiency caused by the reducing action of the hydrogen, the chlorate subjected to the action of nascent hydrogen being always in the cathode compartment and strongly alkaline. Chlorate is not reduced to any appreciable extent by nascent hydrogen if the solution is alkaline.

The loss of efficiency which occurs in chlorate cells with secondary electrodes, due to the jumping of the current around some of the electrodes, is avoided in my improved method.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that I am aware of Specifications No. 6417/1887 and No. 2987/1902 and I do not claim anything claimed therein, but what I claim is:—

1. A process of making a chlorate salt, which consists in electrolysing a chloride solution, bringing the alkaline liquor from the cathode compartment of the electrolysing apparatus into contact with an excess of chlorine, outside of the anode and cathode compartments of said apparatus, returning the chlorate-containing solution to the said apparatus, and removing chlorate from the alkali liquor at a point between the electrolysing apparatus and the absorption chamber.

2. A process as claimed in Claim 1, in which a fresh supply of chloride is mixed with the solution during the repeated operations.

3. A process of making a chlorate salt as claimed in Claim 1, in which the quantity of the produced alkali passing to the combining chamber is diminished relatively to the amount of chlorine, to thereby maintain an excess of chlorine in the combining chamber.

4. A process of making a chlorate salt, consisting in electrolyzing a chloride solution to produce chlorine and an alkali, discharging the alkali solution from the cathode compartment of the electrolyzing apparatus and the chlorine from the anode compartment of the electrolyzing apparatus, adding fresh chloride to the alkali solution, and then bringing the solution into contact with the chlorine to produce a chlorate liquor.

5. A process of making a chlorate salt, as claimed in Claim 1 in which a diaphragm cell having carbon or graphite anodes is used for electrolyzing the chloride solution.

6. A process of making a chlorate salt, which consists in electrolyzing a solution containing both a chloride and a chlorate, the major portion of the chlorate passing to the cathode compartment of the electrolyzing apparatus without change, and the chloride being electrolyzed therein to form chlorine and a caustic alkali, conducting the chlorine to an absorption chamber, adding fresh chloride to the alkaline solution discharged from the cathode compartment of the electrolyzing apparatus, and then bringing the alkaline liquor

into contact with the chlorine, and removing chlorate from the system at a point between the electrolyzing apparatus and the absorption chamber.

7. The process of making a chlorate salt substantially as described with reference to the accompanying drawings.

Dated this 21st day of September, 1915.

BOULT, WADE & TENNANT,
111 & 112, Hatton Garden, London, E.C.,
Chartered Patent Agents.

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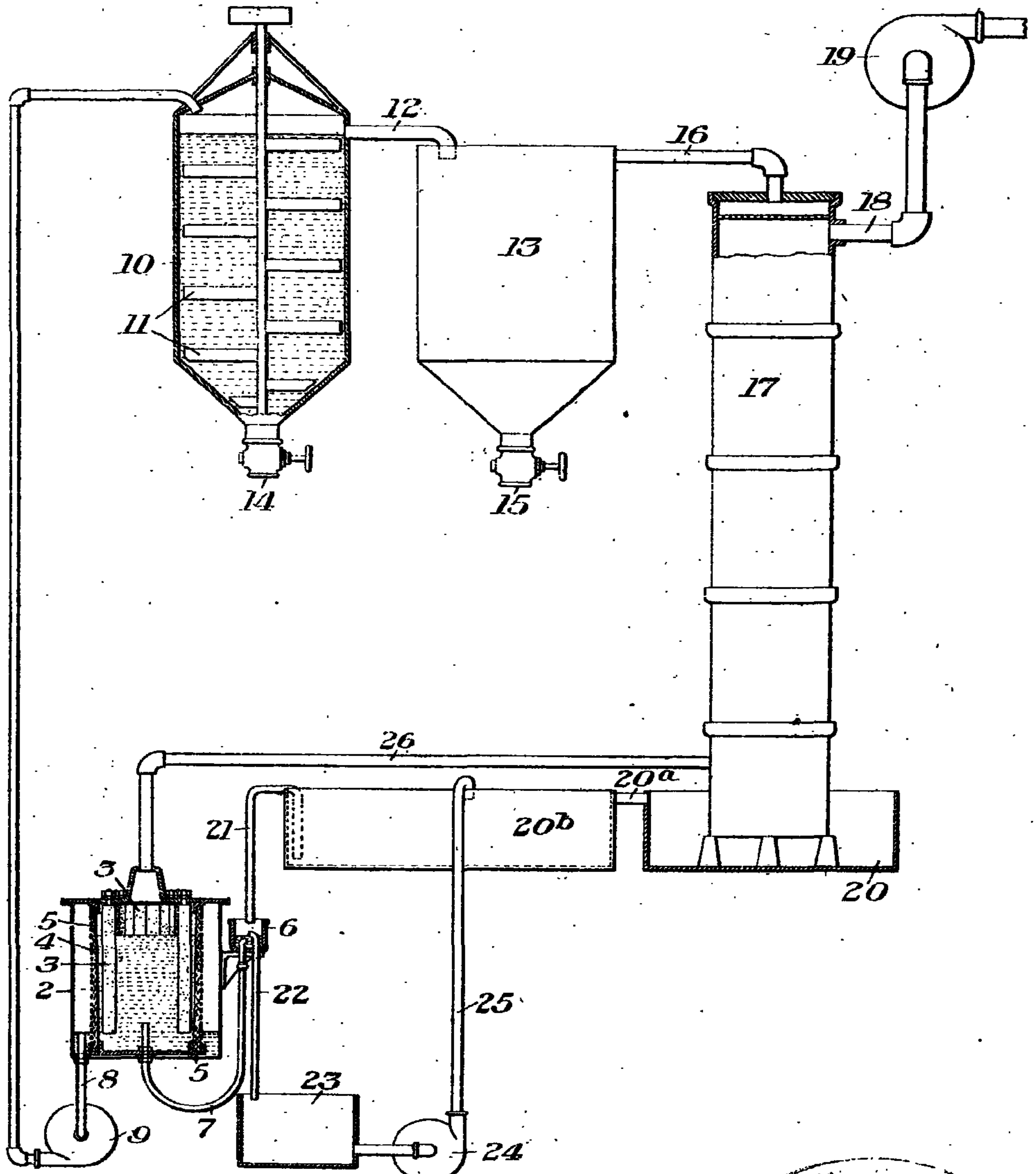
GIBBS' COMPLETE SPECIFICATION. (1 SHEET)

[This Drawing is a reproduction of the Original on a reduced scale]



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