

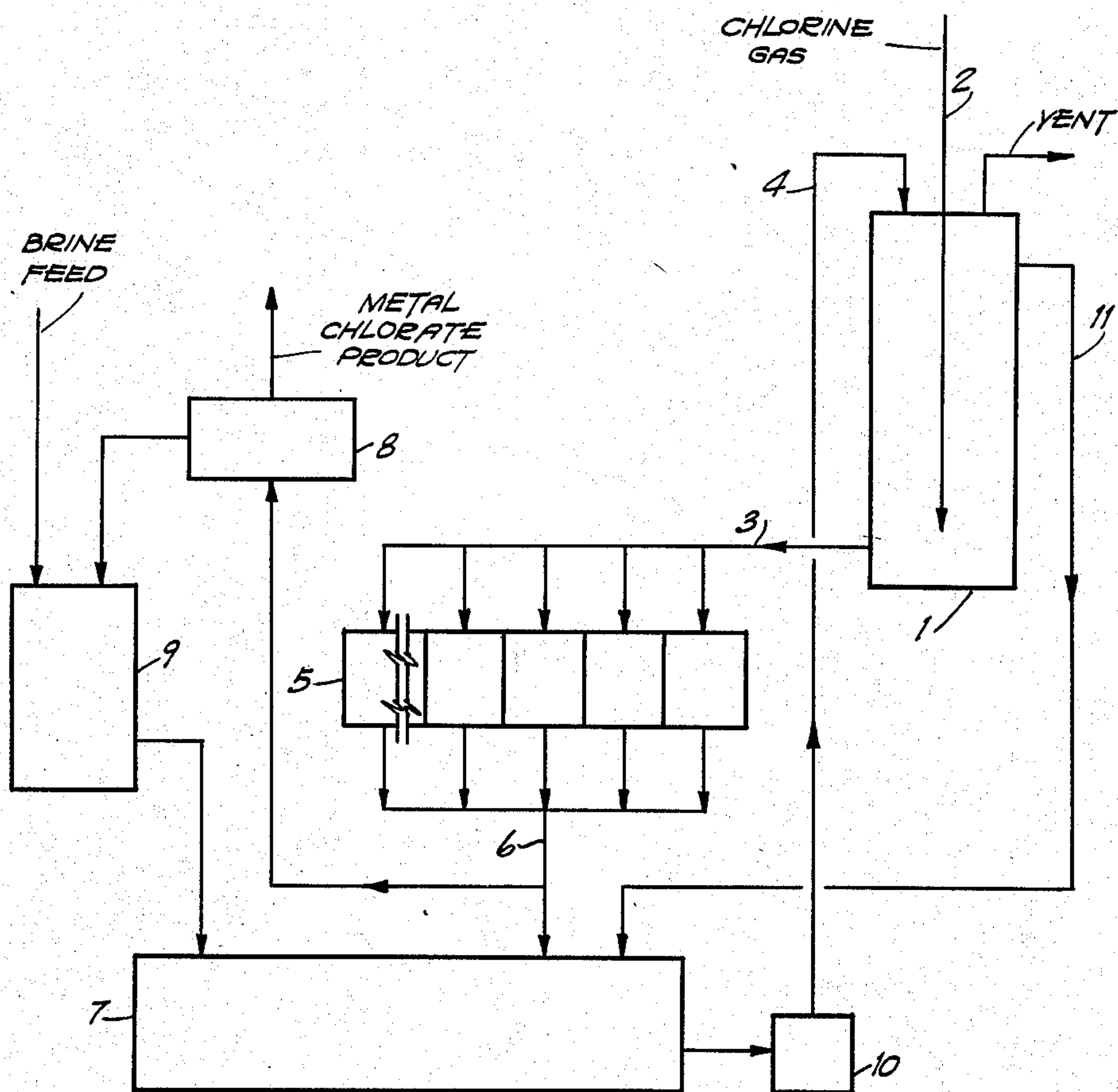
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ELECTROLYTIC PRODUCTION OF CHLORATES

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ELECTROLYTIC PRODUCTION OF
CHLORATES

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5 Claims. (Cl. 204—95)

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This invention relates to improvements in the production of alkali metal chlorates by electrolytic methods.

The improvements of this invention are particularly applicable to the electrolytic process for the manufacture of metal chlorates as described in the copending application for United States Letters Patent of Arthur E. Gibbs, Serial No. 674,627, filed on June 5, 1946 (now abandoned). This process involves the use of gaseous chlorine for the acidification of electrolytes used in the electrolytic production of metal chlorates. Among the advantages of this invention are included the increase in the concentration of hypochlorous acid caused by the reaction of chlorine with hydroxyl ions resulting in the acceleration of the formation of chlorates by reaction between said hypochlorous acid and hypochlorite ions, and the conversion of chromate to dichromate ions, by which proper acidity in the cell is maintained, without the necessity of adding hydrochloric acid to the cell liquor.

In carrying out the process of the Gibbs application, there are various procedures by which chlorine may be introduced into the cell liquor. For example, the chlorine may be introduced into the discharge side of a cell feed pump or into the tank used for making up the electrolyte after the chlorine separation stage. Many of these methods, however, introduce difficulties in practice. For example, in employing some of the possible methods of introducing chlorine, it has been found advisable to use an excess of chlorine in order to get the desired effect, and this excess chlorine is later expelled from the cell liquor into the cell room, causing a health hazard.

We have now discovered a simple and effective method and means for introducing chlorine into the electrolyte of such processes that avoids these difficulties. Our new method and apparatus for introducing chlorine are based on the discovery that, when chlorine is used to control acidity in chlorate cell liquor, it is particularly advantageous, in order to make effective use of the chlorine and minimize the health hazard, to provide a "seasoning" period for the chlorine-treated cell liquor before sending it on to the cells. We have thus found it desirable to "season" the chlorine-treated cell liquor for at least 5 minutes after it has first been contacted with chlorine before sending it on to the cell.

According to a preferred embodiment of my invention the cell electrolyte, after passing through the chlorate separation stage and having been made up to the appropriate composi-

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tion by addition of alkali chloride, is introduced in any convenient manner into a chlorinating tower designed so that the depth of electrolyte becomes a predominate feature. An inlet for gaseous chlorine and an outlet for the acidified electrolyte are provided near the bottom of this tower. This procedure and apparatus have the important advantage of permitting the above-indicated time interval to elapse after the cell liquor has first been treated with chlorine and before it is sent on to the cells. This apparatus also has the advantage of causing the gaseous chlorine to pass through a substantial body of electrolyte, whereby it is completely absorbed, and hence there is no wastage of chlorine. The electrolyte outlet, being located near the bottom of the tower, has the advantage of utilizing the pressure resulting from the extreme height of the electrolyte to cause the electrolyte to flow from the tower through connecting lines and into the cells. This eliminates the necessity of feed pumps and the corrosion and other problems inherent thereto. A further advantage is that the reactions initiated by the chlorine have sufficient time to be completed and hence when the electrolyte is introduced into the cells there is no release of gaseous chlorine to the cell room. A still further advantage of our invention is that the possibility of the electrolyte backing into the chlorine inlet or containers is minimized.

The process and apparatus of our invention are illustrated in the accompanying drawing, which forms a part of our application. The drawing is both a flow sheet of our preferred process and a diagrammatic representation of our preferred apparatus.

In the drawing the reference numeral 1 indicates a cylindrical shaped tower which may, for example, be about 21 feet in height and 2 feet inside diameter, fitted with a chlorine inlet 2 opening near the bottom and an electrolyte outlet 3 also near the bottom. The top of the tower is also provided with a vent for spent gas.

The electrolyte enters the chlorinating tower at 4 and is almost immediately subjected to the action of gaseous chlorine rising in the tower. The acidified electrolyte leaves the chlorinating tower at 3, after an average stay in the tower of at least 5 minutes, and flows thence into the electrolytic cells 5. The conduit 6 communicates with a storage tank 7 and also the apparatus used for chlorate separation 8. The liquor from 8 runs into a make-up tank 9 where alkali metal chloride is added. The electrolyte then passes into 7 and is forced by pump 10 into the chlori-

nating tower 1. The chlorinating tower also has an overflow line 11 to return excess electrolyte to the storage tank 7. We prefer to add the electrolyte into the top of the tower as shown in the diagram, so that, as the electrolyte flows down towards the outlet it is subjected to increasing concentrations of gaseous chlorine which is rising in the tower countercurrent to the flow of electrolyte. This method of adding electrolyte completely eliminates any stagnation of electrolyte which might otherwise be present in the tower.

In a typical operation involving production of sodium chlorate by electrolysis of sodium chloride in aqueous solution, the cell electrolyte contains both the sodium chloride starting material and some sodium chlorate product from previous operation. The electrolyte also contains a small amount of sodium dichromate as a buffer material to maintain the desired pH of 6.7 to 6.9 in the cells. For example, in a typical electrolyte there may be 150 grams sodium chloride per liter, 350 grams sodium chlorate, and 5 grams sodium dichromate. As electrolysis goes on and the sodium chloride is converted to sodium chlorate, the pH of the cell liquor tends to rise. However, in the presence of sodium dichromate the alkaline materials tending to raise the cell liquor pH react with the dichromate, convert it to chromate, and the cell pH is thus at least partially stabilized.

In order to maintain proper pH, cell liquor, in which a substantial part of the original dichromate has thus been converted to chromate, is being constantly withdrawn from the cells at a pH of about 6.9 and is constantly being replaced by cell liquor of pH about 5.8 to 6 in which the chromate has been at least in part reconverted to dichromate by action of gaseous chlorine. During this recirculating, some sodium chlorate is also removed from the cell liquor, as product, and the cell liquor is fortified with sodium chloride, as pointed out in connection with the drawing.

Since many modifications are possible in the process and apparatus of our invention as above described without departing from the scope of the invention, it is intended that the above description of our invention should be interpreted as illustrative, and the invention is not to be limited except as set forth in the claims which follow:

We claim:

1. In a process for the electrolytic production of an alkali metal chlorate by the electrolysis of an acidic aqueous solution of an alkali metal chloride, employing gaseous chlorine for maintaining proper acidification of the solution, the step that comprises holding the solution for at least five minutes after first contacting the acidic solution with chlorine and before introducing it into the electrolytic cell.

2. The process for production of sodium chlorate that comprises subjecting an acidic sodium chloride solution to electrolysis for electrolytic conversion of the chloride to chlorate, treating the acidic electrolyte with elemental chlorine prior to its introduction into the electrolysis zone,

to counteract the tendency of the electrolyte to diverge from a set range of acid concentration, and holding the treated electrolyte for at least five minutes after first contacting it with chlorine and before introducing it into the electrolytic cell.

3. The process for production of alkali metal chlorate that comprises subjecting an acidic alkali metal chloride solution to electrolysis for electrolytic conversion of the chloride to chlorate, said electrolyte containing also a small amount of dichromate in solution as a buffering agent, treating the acidic electrolyte with elemental chlorine at a point outside the electrolytic cell to counteract divergence of the electrolyte from a set range of acid concentration, and holding the treated electrolyte for at least five minutes after first contacting it with chlorine and before introducing it into the electrolytic cell.

4. The cyclic process for production of sodium chlorate that comprises subjecting a sodium chloride solution of pH 5.8 to 6.9 to electrolysis for electrolytic conversion of the chloride to chlorate, said electrolyte containing also a small amount of dichromate in solution as a buffering agent, withdrawing electrolyte from the cell, separating sodium chlorate therefrom, treating the acidic electrolyte, while outside the cell, with elemental chlorine to counteract the divergence of the electrolyte from the desired value in said pH range, holding the treated electrolyte for at least five minutes after first contacting it with chlorine, and thereafter reintroducing the resulting electrolyte into the cell.

5. The cyclic process for production of sodium chlorate that comprises subjecting a sodium chloride solution of pH not greater than 6.9 to electrolysis for electrolytic conversion of the chloride to chlorate, withdrawing electrolyte from the cell, separating sodium chlorate therefrom, treating the electrolyte of pH not greater than 6.9, while outside the cell, with elemental chlorine, maintaining the electrolyte and chlorine in contact for at least five minutes and until sufficient chlorine has been absorbed and hydrolyzed to lower the pH of the treated electrolyte appreciably, and thereafter reintroducing the treated electrolyte into the cell.

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