

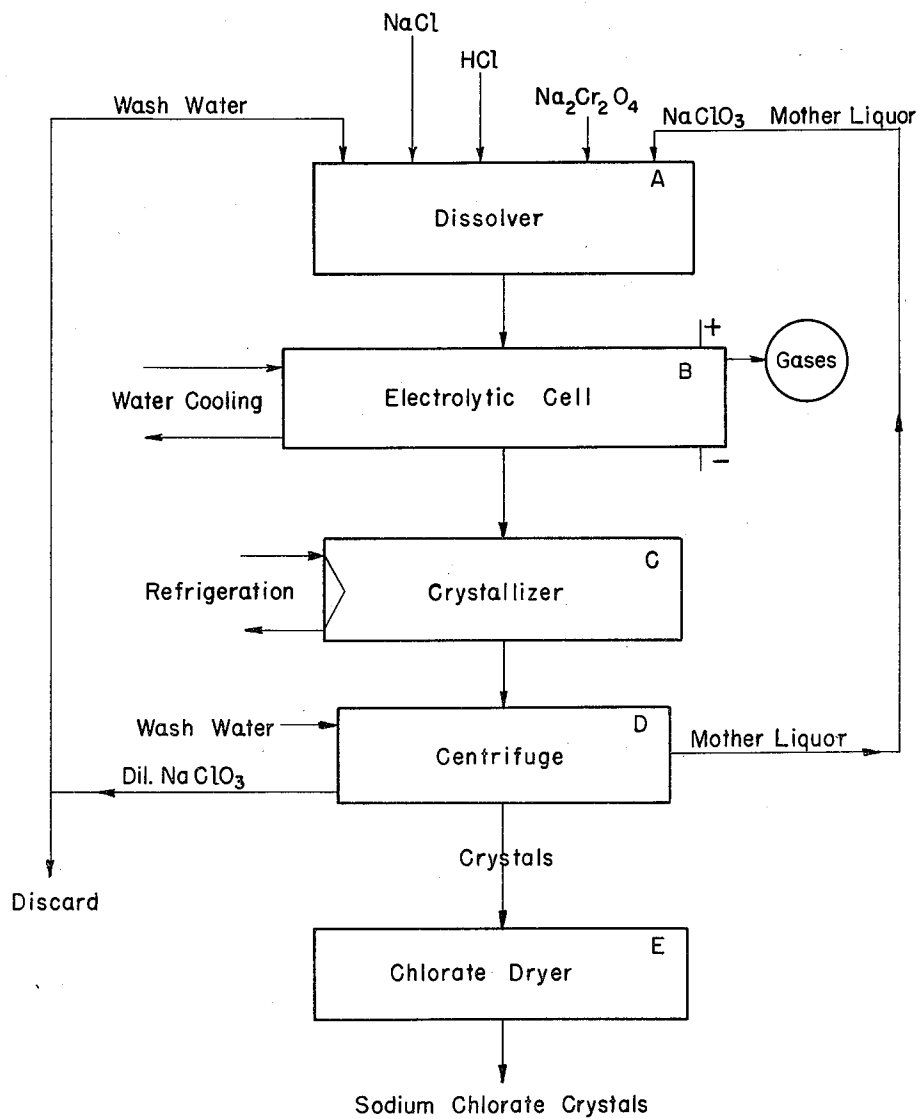
June 13, 1950

J. C. SCHUMACHER

2,511,516

PROCESS FOR MAKING SODIUM CHLORATE

Filed Oct. 31, 1945



INVENTOR

JOSEPH C. SCHUMACHER

BY *Z. R. Hartmann*

ATTORNEY

UNITED STATES PATENT OFFICE

2,511,516

PROCESS FOR MAKING SODIUM CHLORATE

Joseph C. Schumacher, Los Angeles, Calif., assignor to Western Electrochemical Company, Los Angeles, Calif., a corporation of Nevada

Application October 31, 1945, Serial No. 625,856

5 Claims. (Cl. 204—95)

1

This invention relates to a process for manufacturing sodium chlorate.

One object of the invention is to provide an improved continuous electrolytic process for making sodium chlorate. Other objects are to provide for the continuous maintenance of the composition and condition of the electrolyte for maximum energy efficiency and capacity in producing sodium chlorate; to provide for a circulating liquid of high chloride and high chlorate concentration through the electrolytic cell; and to provide for the production of sodium chlorate of high purity at an economical cost.

These and other objects are attained by my invention which will now be described in detail, reference being made to the accompanying drawing diagrammatically representing the steps and flow of material in my process.

In general the process involves the electrolysis of an aqueous solution of sodium chloride in an electrolytic cell having graphite anodes and steel cathodes, the electrolyte being continuously circulated into and out of the electrolytic cells with continuous removal of excess sodium chlorate and continuous replenishment of sodium chloride while the liquid is outside the cell. Referring to the diagram, solid sodium chloride is dissolved in the dissolver A in the aqueous mother liquor produced in the later step D of the process. Water, hydrochloric acid, and sodium chromate or dichromate are also added, the hydrochloric acid being introduced to control the pH value of the electrolyte and the sodium dichromate being used to promote the oxidation reactions within the electrolytic cell in accordance with the usual practice in making chlorate electrolytically. The solution from the dissolver A is pumped continuously into an electrolytic cell B where it is electrolyzed between graphite anodes and steel cathodes, the latter conveniently being the walls of the container and the steel pipe water cooling coils within the cell. The effluent from the electrolytic cell, now containing additional sodium chlorate formed in the electrolytic process as the liquid flows through the cell, is passed through a refrigerated continuous crystallizer C, where crystals of sodium chlorate are precipitated, the slurry being then passed into a centrifuge D, which is conveniently of the continuous feed and discharge type, which separates the mother liquor from the solid crystals. The centrifuged sodium chlorate crystals may be water washed if this is desired for greater purity in the product, the wash liquor being collected separately from the mother liquor in order to avoid undue dilution of the lat-

2

ter and at least a portion being returned to the dissolver to supply make-up water lost in the process. The crystals of sodium chlorate, after centrifuging are delivered to a drier E, where the solid sodium chlorate is heated to dry it. The mother liquor from the centrifuge D is pumped back to the dissolver A where it is replenished with sodium chloride and recycled through the electrolytic cell as above described. The gases, chlorine, hydrogen, oxygen, carbon dioxide, and water vapor which are produced in the electrolytic cell are withdrawn from the system.

I have discovered that unusual efficiency and long continuous operation of the process above described can be attained by maintaining a relatively high concentration of both sodium chloride and sodium chlorate in the electrolyte. Considering the sodium chloride constituent in the electrolyte, I have found that the concentration of this should be maintained at not less than about 90 grams to one liter of electrolyte, but may be greater than this concentration up to a nearly saturated solution, but should be enough below saturation to avoid the possibility of precipitation of solid sodium chloride from the electrolyte at any low temperature which may be encountered in the circulatory path of the electrolyte in the process above described.

In my preferred method of operation, the lowest temperature encountered is in the sodium chlorate precipitation step where about 0° C. is a preferred operating temperature. Under this operating condition I have found that a concentration of sodium chloride as high as 100 grams per liter does not precipitate sodium chloride even in the presence of the saturation amount of sodium chlorate in the solution. Since the temperature of cooling to precipitate excess sodium chlorate is not critical at 0° C. but is selected to give the optimum operation in this and other steps of the process, it may vary as much as 10° C. in either direction with corresponding changes in the permissible limit of sodium chloride concentration in the influent electrolyte. Considering the sodium chlorate constituent in the electrolyte, I have found that the concentration of this should be maintained at about 400 grams per liter or more throughout the circulatory system. The upper limit of concentration of sodium chlorate is that concentration which at the temperature of operation in the electrolytic cell will still remain in solution (not precipitate as solid) in the electrolytic cell; or, in other words, slightly less than a saturated solution of sodium chlorate in the electrolyte at the temperature within the

3

cell. Under the preferred operation conditions of my process, the electrolytic cell temperature is maintained at about 45° C., and is continuously circulated through the cell, with the influent liquid having a chlorate content of about 400 grams sodium chlorate per liter, increasing in chlorate content on its flow between the electrodes and through the cell. The added chlorate in the effluent liquor from the electrolytic cell is precipitated in my process by cooling the effluent, and separating out the sodium chlorate crystals, and then recirculating through the electrolytic cell the warmed up mother liquid (saturated as to sodium chlorate at the said cooling temperature), after making it up to a high sodium chloride content. When the influent liquid to the electrolytic cell is of about this concentration, the effluent from the electrolytic cell will, because of the electrochemical reactions, contain a higher concentration of sodium chlorate and a correspondingly lower concentration of sodium chloride, depending upon the amount of oxidation of chloride to chlorate which has taken place in the passage of the electrolyte through the cell, and this in turn being dependent upon the time required for the electrolyte to pass through the cell unit and upon the energy input. As a typical example, using a narrow, elongated electrolytic cell such as that described in my copending application, Ser. No. 625,858, in which the electrolyte passes through the cell at the rate of about 60 gallons per hour, the cell drawing 2500 amperes per hour at 3.0 to 3.5 volts, with graphite anode current density of 30 amperes per square foot and steel cathode density of about 50 amperes per square foot, the effluent liquor at about 45° C. temperature, contains about 560 grams per liter of sodium chlorate with 92 grams per liter of sodium chloride. When this cell effluent is cooled to about 0° C. as in the crystallizer C of the diagram, about one-fourth of the sodium chlorate crystallizes out and may be separated from the liquid, as in a centrifuge, leaving a mother liquor containing about 100 grams per liter of sodium chloride with about 425 grams per liter of sodium chlorate. This mother liquor is then replenished with sodium chloride to a concentration of about 175 grams per liter, as in the dissolver A in the diagram, and this liquid is again passed through the electrolytic cell. In this illustrative example, the sodium dichromate was maintained at about 3 to 4 grams per liter of electrolyte, and the pH was maintained at about 6.1 by the required addition of hydrochloric acid solution to the influent cell liquid. Greater efficiency results when concentrated sodium chlorate solutions are passed into the cell, and when a high current density at the anodes is used. Also the high chlorate content of the effluent from the cells permits crystallizing out the excess sodium chlorate by cooling.

The continuous flow of the electrolyte through the electrolytic cell provides a means of controlling the temperature of the electrolytic reaction, too high a temperature resulting in a decrease in the life of the anodes, and in excessive gassing, and too low a temperature resulting in a marked decrease in the rate of formation of the chlorate. The avoidance of local high temperatures gives maximum life to the anodes because their disintegration is slower, and of a uniform nature. The continuous flow of electrolyte through the electrolytic cell also permits the necessary close control of the pH value of the electrolyte which has been found to be at an optimum in the range from 6.0 to 6.2, this being most important in getting efficient production of chlorate in the elec-

4

trolytic reaction, and at the same time suppressing the secondary reactions, particularly those causing the evolution of gases such as oxygen, chlorine, and hydrogen.

Because of the continuous circulation of the electrolyte around the electrodes in going through the cell from the entrance point to the discharge point, substantially constant conditions of electrolysis are maintained, and therefore optimum current density, electrolyte composition, and temperature, may be employed, which is not possible with a stagnant electrolyte.

The use of the continuous circulation system for the electrolyte and the resultant uniform conditions in the system, also permits the use of ordinary mild steel vessels, pipe lines, etc., whereas much more expensive nickel or chrome nickel alloys would be required if the system were operated at a higher temperature or if a discontinuous process of electrolysis were used, or if the effluent required evaporative concentration in order to separate the constituents.

The circulation of a relatively high concentration of sodium chlorate through the electrolytic cell has the great advantage that it permits the removal of the added sodium chlorate produced in that passage through the cell by the simple expedient of cooling the effluent so that sodium chlorate crystallizes out and the maintenance of a high chloride concentration in the influent of the cell is necessary to provide the constituents for the formation of the additional chlorate in the passage through the cell.

I claim:

1. In a process for making sodium chlorate by the electrolysis under normal atmospheric pressures and at a temperature of about 45° C., of an aqueous solution containing sodium chloride and a small amount of sodium chromate, the steps consisting of continuously withdrawing electrolyte from an electrolytic cell, continuously passing into the said electrolytic cell an electrolyte consisting of the mother liquor from said withdrawn electrolyte after cooling to remove the excess sodium chlorate and containing not less than 75 grams per liter of sodium chloride along with not less than about 400 grams of sodium chlorate per liter, said electrolyte having a pH value of about 6.1, and electrolyzing the said circulating electrolyte between immersed carbon and iron electrodes under current density and voltage conditions adapted to produce additional sodium chlorate.

2. In a process for making sodium chlorate by the electrolysis under normal atmospheric pressures and at a temperature of about 45° C., of an aqueous solution containing sodium chloride and a small amount of sodium chromate, the steps consisting of continuously withdrawing electrolyte from an electrolytic cell, continuously passing into the said electrolytic cell an electrolyte consisting of the mother liquor from said withdrawn electrolyte after cooling to remove the excess sodium chlorate and containing a substantially saturating amount of sodium chloride along with sodium chlorate in concentration not less than about 400 grams per liter, said electrolyte having a pH value of about 6.1, and electrolyzing the said circulating electrolyte between immersed carbon and iron electrodes under current density and voltage conditions adapted to produce additional sodium chlorate.

3. In a process for making sodium chlorate by the electrolysis under normal atmospheric pressures and at a temperature of about 45° C., of an

5

aqueous solution containing sodium chloride and a small amount of sodium chromate, the steps comprising continuously withdrawing electrolyte from an electrolytic cell, continuously passing into the said electrolytic cell an electrolyte consisting of the mother liquor from said withdrawn electrolyte after cooling to remove the excess sodium chlorate and containing about 175 grams per liter of sodium chloride along with sodium chlorate in concentration not less than about 400 grams per liter, said electrolyte having a pH value of about 6.1, and electrolyzing the said circulating electrolyte between immersed carbon and iron electrodes under current density and voltage conditions adapted to produce additional sodium chlorate.

4. In a process for making sodium chlorate by the electrolysis under normal atmospheric pressures and at a temperature of about 45° C., of an aqueous solution containing sodium chloride and a small amount of sodium chromate, the steps consisting of continuously withdrawing electrolyte from an electrolytic cell, continuously passing into the said electrolytic cell an electrolyte consisting of the mother liquor from said withdrawn electrolyte after cooling to remove the excess sodium chlorate and containing a substantially saturating amount of sodium chloride along with sodium chlorate in concentration not less than that which would yield a solution saturated with respect to sodium chlorate in the electrolyte if cooled to a temperature of about 0° C., said electrolyte having a pH value of about 6.1, electrolyzing the said circulating electrolyte between immersed carbon and iron electrodes under current density and voltage conditions adapted to produce additional sodium chlorate, precipitating out the additional sodium chlorate by cooling the withdrawn effluent electrolyte, separating the precipitated sodium chlorate from the mother liquor, restoring the sodium chloride content of said liquor to an approximately saturated solution, and continuously returning the restored mother liquor to the electrolytic cell.

5. In a process for making sodium chlorate by

6

the electrolysis under normal atmospheric pressures and at a temperature of about 45° C., of an aqueous solution containing sodium chloride and a small amount of sodium chromate, the steps consisting of continuously withdrawing electrolyte from an electrolytic cell, continuously passing into the said electrolytic cell an electrolyte consisting of the mother liquor from said withdrawn electrolyte after cooling to remove the excess sodium chlorate and containing a substantially saturating amount of sodium chloride along with sodium chlorate in concentration not less than about 400 grams per liter, said influent electrolyte having a pH value of about 6.1, electrolyzing the said circulating electrolyte between immersed carbon and iron electrodes to produce additional sodium chlorate, cooling said effluent electrolyte to precipitate out said additional sodium chlorate, adding sodium chloride to restore the influent electrolyte to its original condition, and returning it to the electrolytic cell.

JOSEPH C. SCHUMACHER.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
693,035	Lederlin	Feb. 11, 1902
727,813	Lederlin	May 12, 1903
732,753	Lederlin	July 7, 1903
802,205	Gibbs	Oct. 17, 1905
1,023,545	Bates et al.	Apr. 16, 1912
1,143,586	Laib	June 15, 1915
2,180,668	Delavenna et al.	Nov. 21, 1939

OTHER REFERENCES

- Chemical and Metallurgical Engineering, No. 12, vol. 45, Dec. 1938, pages 692-696.
 The Principles of Applied Electrochemistry, A. J. Allmand, 1912, pages 340, 341.
 Principles of Applied Electrochemistry, Allmand et al. 1924, pages 388-391.