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PROCESS OF PREPARING ALUMINUM CHLORHYDROXIDES
AND ALUMINUM HYDROXIDE

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This invention relates to a process of preparing aluminum chlorohydroxides, particularly Al₃(OH)₄Cl₃, the 5% basic salt, by electrolysis of aluminum chloride, and to an apparatus for carrying out this process.

The electrolysis of aluminum chloride to produce aluminum chlorohydroxide Al₃(OH)₄Cl₃ is described in U.S. Patent No. 2,392,531. An aqueous solution of aluminum chloride is subjected to electrolysis in a diaphragm cell in which catholyte and anolyte are kept in separate compartments. In the course of this process, hydrogen is liberated at the cathode and chlorine at the anode. The reaction is quantitative, so far as the electrolysis of aluminum chloride is concerned. The yield of aluminum chlorohydroxide is not good, however, because of the loss of chlorine at the anode. In order to make the process practical commercially, it is necessary to recover this chlorine, but this is rather difficult to do, and there is also the problem of its contamination with other materials. Consequently, the electrolytic production of aluminum chlorohydroxide has never been fully satisfactory.

In accordance with the instant invention, a process of preparing aluminum chlorohydroxides and aluminum hydroxide by electrolysis of aluminum chloride as the catholyte is provided wherein the loss of chlorine at the anode is prevented by reaction of such chloride ion as migrates from the cathode compartment with aluminum oxide before it reaches the anode compartment, regenerating aluminum chloride, which can be recirculated to the cathode compartment for conversion to aluminum chlorohydroxide. The reactions which take place in this electrolysis can be summarized as follows, using the 5% basic salt as illustrative.

In cathode compartment:

\[ \text{I.} \quad 5\text{H}_2\text{O} + 2\text{HCl}^+ + \text{SO}_4^{2-} \rightarrow 2\text{Al}_3(\text{OH})_4\text{Cl}_3 + 5\text{OH}^- \]

In compartment adjacent cathode compartment:

\[ \text{II.} \quad 2\text{AlCl}_3 + 6\text{OH}^- \rightarrow 2\text{Al}_3(\text{OH})_4\text{Cl}_3 + 3\text{Cl}^- \]

In anode compartment:

\[ \text{III.} \quad 2\text{Al}_3(\text{OH})_4\text{Cl}_3 + 6\text{HC}_2\text{O} + 2\text{AlCl}_3 + 3\text{H}_2\text{O} \]

This invention proceeds down the series from No. 1 to No. 6, as the ultimate product, and can be followed by observing the pH of the reaction mixture, which ranges from about 1 at the start to about 4.4 at No. 5, the other aluminum chlorohydroxides being intermediate, and the aluminum hydroxide is formed as a precipitate at the end stage of the electrolysis. Hence, any desired aluminum chlorohydroxide can be prepared simply by stopping the electrolysis at the pH value corresponding to the desired chlorohydroxide.

The anolyte plays no role in these reactions, and preferably is kept isolated therefrom so that chloride ion cannot migrate into it.

It is apparent from the above scheme that one mole of hydrogen chloride is consumed for every mole of Al₃(OH)₄Cl₃ produced. Hence, to start the reaction initially it is necessary to have hydrogen chloride present in the aluminum oxide compartment, at least in the proportion of one mole of hydrogen chloride for every mole of aluminum chlorohydroxide Al₃(OH)₄Cl₃ produced. If other aluminum chlorohydroxides are desired, such as the ⅚ basic salt Al₂(OH)₃Cl₄ or the ⅓ basic salt Al(OH)₃Cl₃, the amount of hydrogen chloride will be increased accordingly. The overall effect of the process, therefore, as shown, is to convert water, aluminum oxide and hydrogen chloride into aluminum chlorohydroxide, hydrogen and oxygen.

The process of the invention can be carried out continuously or semicontinuously or batchwise in an electrolyte cell having three compartments, a cathode compartment, an anode compartment, and a third compartment intermediate these two compartments. The type of cell contemplated is shown in cross-section in the FIGURE.

The cathode compartment 1 is equipped with a cathode 2 of material which is not attacked by aqueous aluminum chloride solution, such as carbon. The anode compartment 3 is equipped with an anode 4 of acid-resistant material such as platinum. The anode and cathode compartments are separated from the intermediate compartment 5 by diaphragms 6 and 7, which permit the passage of ions required for carrying out the reactions of the invention in their respective compartments, and preferably prevent passage of all others.

In operation, the catholyte, aqueous aluminum chloride solution, is placed in the cathode compartment, and the anolyte, an aqueous acid whose anion is not discharged as a gas at the anode, such as sulfuric acid, is put in the anode compartment. An aqueous slurry of aluminum oxide containing as much hydrogen chloride as is required to start the reaction is put in the intermediate compartment 5. Then the electrolysis is begun.

In the cathode compartment, hydrogen gas is discharged at the cathode, leaving behind OH⁻ ion, and resulting in the formation of Al₃(OH)₄Cl₃ in the catholyte, where n represents the proportion of OH⁻ ion in the product, and can range from 1 to 6. When n is 6, the product is aluminum hydroxide. Chloride ion from the cathode compartment and hydrogen ion from the anode compartment migrate into the intermediate compartment, and there react with aluminum oxide in accordance with reaction III above to form aluminum chlorohydroxide. The conditions are so adjusted that a minimum of chloride ion migrates from the intermediate compartment into the anode compartment, inasmuch as chloride ion in the anolyte could be discharged at the anode to form chlorine gas, reducing the yield.

While diaphragms of any of the types commonly employed in diaphragm cells can be used between the various compartments in this cell, it is preferred that the diaphragm between the anode compartment and the intermediate compartment be of cation-perselective material which will not pass chlorine ion. This excludes chloride ion entirely from the anode compartment. A variety of cation-perselective membrane material useful as diaphragms in electrolytic cells is known to those in the art. Such permselective membranes are in general to those of
two types. One type is in the form of sheets, or films formed wholly of the cation-perselective material, such as are described, for example, in U.S. Patents Nos. 2,636,851 to Judi et al., 2,702,272 to Kasper, 2,730,768, 2,731,408, 2,731,411, 2,752,202 to Clarke, 2,805,196 to Roebersen et al., and 2,858,264 and 2,867,573 to De Jouy. These membranes can be formed directly from monomeric or unpolymerized reactive ingredients, polymerizing them under conditions such that the desired film is formed. The reactive ingredients may include the functional cation-exchange groups, or such groups may be incorporated in the film after its formation by appropriate reaction procedures, all of which are well known in the art. Suitable acidic functional groups linked to the matrix include SO₃H and COOH groups, the former being preferred because of its high dissociation constant. Typical polymeric matrices to which such functional groups are linked include polystyrene, phenol-aldehyde resins, polystyrene-divinyl benzene copolymers, resorcinol-aldehyde polymers, copolymers of divinyl benzene with acrylic acid, copolymers of divinyl benzene with maleic anhydride, copolymers of divinyl benzene with acrylonitrile, copolymers of divinyl benzene and methacrylic acid, cellulose derivatives such as regenerated cellulose, ethyl cellulose and polyvinyl alcohol, and like polymers containing free hydroxyl groups, reacted with sulfonating agents, and polyethylene reacted with chlorosulfonic acids or other sulfonating agents. Examples of such membranes will be found in the patents referred to.

The cation-exchange resins which can be employed in either of these types of films include the sulfonated phenol-aldehyde resins described in U.S. Patents Nos. 2,184,943, 2,195,196, 2,284,539, 2,228,258, 2,228,159, 2,228,160, 2,230,641, 2,259,455, 2,285,750, 2,319,959 and 2,361,754, the sulfonated cross-linked polymers of styrene described in U.S. Patent No. 2,366,007, and the carboxylic resins described in Patents Nos. 2,340,110 and 2,340,111.

Porous diaphragms of other materials can be used, such as porous bonded mats or mats of nonwoven chemically resistant fibers, such as glass, asbestos, alundum, nylon and polycrylonitrile fibers. Perforated plates and microporous corrosion-resistant metal and synthetic resin membranes also can be employed.

The reaction temperatures are not critical. The formation of aluminum chlorohydrate in the cathode compartment is favored by electrolysis at a temperature above about 70 °C. At lower temperatures, there is a tendency to form hydrochloric acid, which may precipitate out. The upper temperature limit is determined by the boiling point of the catholyte, and is usually approximately 100 °C.

The reaction of aluminum oxide with chloride ion or hydrogen chloride to form aluminum chloride in the intermediate compartment proceeds at elevated temperatures, above about 70 °C. Thus the reaction proceeds with good efficiency at the temperatures applied in the cathode compartment.

Chloride ion migration from the intermediate compartment into the anode compartment is less at low temperatures, and it is accordingly preferred that the anode compartment be kept at room temperature or below, or at least as close to room temperature as is convenient. Ion-perselective membranes tend to lose their efficiency in barring passage of ions as temperature increases, and this is an additional reason for maintaining the anolyte at as low a temperature as possible.

The desired temperature gradient from the cathode compartment to the anode compartment can be achieved by interposing cooling coils in the intermediate compartment adjacent the diaphragm separating the intermediate and anode compartments. The diaphragm would be on the anode side of the cooling coils. Other ways of achieving temperature gradients are known to the art, and are disclosed in the literature on diaphragm type cells, inasmuch as this problem is encountered in other processes.

3. The concentration of aluminum chloride in the catholyte can be modified as desired, according to the particular aluminum chlorohydrate that is desired. Solutions of aluminum chloride ranging from about 5 to about 25% AlCl₃ are satisfactory. Usually, the maximum concentration of aluminum chloride that can be obtained without too high a viscosity is used, because this avoids the necessity of concentrating the anolyte solution, since the aluminum chlorohydrate is ordinarily sold as a 50% aqueous solution.

The concentration of aluminum oxide in the slurry in the intermediate compartment will be determined by the aluminum chloride concentration and the amount of migration of chloride ion from the catholyte into that compartment. More aluminum oxide may be required per mole of aluminum chloride when the % basic salt is produced, for example, because more chloride ion is available to migrate into the intermediate compartment. However, it is also possible in a semicontinuous or continuous process to adjust for different concentrations of aluminum chloride and aluminum oxide simply by modifying the rate of removal of the liquor from these compartments to correspond to the amounts of aluminum chlorohydrate and aluminum chloride, respectively, that are formed therein.

The amount of acid required in the anode compartment is simply enough to permit efficient electrolysis. An 0.5 to 10% solution of a strong acid, such as sulfuric acid, is quite satisfactory. A somewhat greater concentration of a weaker acid, such as phosphoric acid, may be necessary because of the lesser ionization of the acid to achieve the same current efficiency as is obtained at these sulfuric acid concentrations.

The following examples in the opinion of the inventor represent the best embodiments of this invention:

**Example 1**

A diaphragm cell was employed in this run, of the type shown in FIGURE 1. The diaphragms separating the cathode and anode compartments from the intermediate compartment were made of porous aluminum sheet. 195 g. (0.3 mole) of a 24° Baumé solution of aluminum chloride was placed in the cathode compartment, which was equipped with a carbon cathode. A slurry of 30 g. of aluminum oxide and 5 ml. of hydrogen chloride (2.17 g. chloride) in 50 ml. of water was put in the intermediate compartment, and 150 ml. of 10% aqueous sulfuric acid solution was put in the anode compartment, which was equipped with a platinum anode. The aluminum oxide slurry was prepared by mixing the water and hydrogen chloride, and bringing the resulting solution to a boil, after which the aluminum oxide was added.

The catholyte was brought to a temperature of 94 to 98 °C., and the current then turned on. A current of 2 amperes was applied for 4.5 hours. 8.5 volts was required at first. After one hour, this had dropped to 6 volts. The current was then changed to 1 amperes for 0.5 hour, at the end of which time the pH of the catholyte was 3.25. The current was continued at 1 amper for three hours, after which the voltage had dropped to 4, and the pH was 4.2.

135.6 g. of catholyte were obtained, having an aluminum content of 2.79%, and a chlorine content of 1.85%.

Thus, the aluminum:chloride ratio Al/Cl was 1.98. The ratio for Al₂(OH)₃Cl is 2, showing that the product was quite pure.

The liquor in the intermediate compartment showed that 15.2 g. of aluminum oxide was dissolved. The aluminum content was 1.27% and the chloride content 4.14%. Thus, the Al/Cl ratio was 0.39. This ratio for AlCl₃ is 0.33, showing a very significant conversion of aluminum oxide to aluminum chloride.

The anolyte liquor weighed 131 g., and contained 0.05% aluminum and 0.116% chlorine.
Example 2

The electrolytic cell employed in this run was the same as used in Example 1. 390 g. (0.6 mole) of a 24° Baumé solution of aluminum chloride was placed in the cathode compartment. A slurry, prepared as set forth in Example 1, of 40 g. of aluminum oxide and 5 ml. of concentrated hydrochloric acid (2.17 g. of chlorine) in 500 ml. of water was placed in the intermediate compartment. 150 ml. of a 10% aqueous sulfuric acid solution was placed in the anode compartment.

The electrolysis was conducted for a total of 22.75 amperes hours at a temperature of 95 to 96° C. in the cathode compartment. The first seven hours were at a current of 3 amperes. At the end of this time, the pH was 3.3, and the voltage 6.2. The current was reduced to 1.5 amperes at 0.75 hour at 6 volts and to 1 amperes for 0.25 hour at 5 volts. The pH then was 3.75. The current was stopped after an additional 0.42 hour at 1 amper and 6 volts. The pH then was 4.35.

150.5 g. of catholyte were recovered, containing 4% aluminum and 2.62% chlorine. This corresponded to an Al/Cℓ ratio of 2.005, substantially pure Al₂(OH)₄Cl. Analysis of the slurry in the intermediate compartment showed that 21.2 g. of aluminum oxide had reacted. The aluminum content was 2.79%, and the chlorine content 9.34%, giving an Al/Cℓ ratio of corresponding very closely to the theoretical ratio of AlCl₃, which is 0.33. The SO₄²⁻ content was 2.12%.

315.7 g. of anolyte was recovered, containing 0.37% aluminum and 1.14% chlorine.

Example 3

The diaphragm cell similar to that described in FIGURE 1 was employed to prepare an aluminum chlorohydrxide having an Al/Cℓ ratio of 2.06, essentially pure Al₂(OH)₄Cl. The diaphragm separating the cathode and intermediate compartment was made of ¾ inch medium porosity aluminum sheet. The diaphragm separating the anode and intermediate compartments was a sheet of cation exchange membrane of the sulfonated polystyrene type, comprising particles of sulfonated polystyrene bonded together with an inert resin binder. The resin is available commercially under the trade name Permütit Q, and the membrane is sold under the trade designation Permütit 3142. In place of this membrane, equally good results are obtained employing the strongly acid sulfonated copolymer of styrene and divinyl benzene prepared in sheet form in accordance with Example 4 of Patent No. 2,635,851.

In the cathode compartment containing a graphite electrode was placed 780 g. (1.20 moles) of 24° Baumé aluminum chloride solution. The intermediate compartment was filled with a slurry of 200 g. of hydrated alumina (130 g. Al₂O₃), 50 ml. of concentrated hydrochloric acid (21.7 g. chlorine, and about 9 liters of water). Into the anode compartment containing a platinum electrode was placed 9.3 liters of 0.95% sulfuric acid solution. The catholyte was brought to a temperature of 95° C. and the current then turned on. The temperature was maintained at from 95 to 105° C. in the cathode compartment, 79 to 81° C. in the intermediate compartment and 30 to 33° C. in the anode compartment. A current of 3 amperes was applied over a period of 31.5 hours, at which point a coating of aluminum oxide was detected on the cathode, and the pH of the catholyte was 4.2.

The catholyte was filtered, and yielded 388 g. of aluminum and 4.20% chlorine, the atomic Al/Cℓ ratio being 2.06. The intermediate compartment yielded 105.0 g. of liquor, containing 55% aluminum and 1.19% chlorine, showing that 72 g. of aluminum chloride was formed during the reaction.

Example 4

The electrolytic cell in this example shown in FIGURE 1 was employed to prepare an aluminum chlorohydrxide of approximately the composition Al₂(OH)₄Cl₃, i.e., a mixture of some Al₂(OH)₃Cl with, mostly, Al₂(OH)₄Cl₂.

The cathode compartment contained 780 g. (1.20 moles) of a 24° Baumé aluminum chloride solution. The intermediate compartment contained a slurry of 200 g. of hydrated alumina (130 g. Al₂O₃), 100 ml. of concentrated hydrochloric acid (43.4 g. of chlorine) and 9 liters of water. The anode compartment contained 9 liters of 0.59% sulfuric acid solution. The catholyte was brought to a temperature of 95° C. and held at 95 to 100° C. for the duration of the run. During this period, the intermediate compartment temperature was held within the range from 82 to 85° C., and the anode compartment at within the range from 33 to 36° C.

A current of 3 amperes was applied as soon as the catholyte had been brought to 95° C., and the current was continued for 19.5 hours, at the end of which time the pH of the catholyte had risen to 3.3. The catholyte was clarified by filtration, and yielded 331 g. of product assaying 7.09% aluminum and 6.42% chlorine, for an atomic Al/Cℓ ratio of 1.45.

The intermediate compartment yielded 12,000 g. of liquor assaying 0.104% aluminum and 1.01% chlorine, showing that 39.4 g. of aluminum chloride was produced.

Example 5

The electrolytic cell used in Example 1 was employed to prepare an aluminum chlorohydrxide having the approximate composition Al₂(OH)₄Cl₃.

Into the cathode compartment was placed 780 g. (1.2 mole) of a 24° Baumé aluminum chloride solution. The intermediate compartment was filled with a slurry of 200 g. of hydrated alumina (130 g. Al₂O₃), 150 ml. of concentrated hydrochloric acid (65.1 g. of chlorine) and 9 liters of water. The anode compartment contained 9 liters of 0.59% sulfuric acid solution. The catholyte was brought to 95° C. and held at from 95 to 100° C. throughout the electrolysis. The intermediate compartment was held at 93 to 85° C., and the anolyte at 33 to 35° C. during the run.

The current was turned on as soon as the catholyte had reached 95° C., and was applied over a period of 15.25 hours, at which point the pH of the catholyte had reached 2.7. The catholyte was clarified by filtration, and 458 g. of product recovered, assaying 6.00% aluminum and 10.9% chlorine, indicating an Al/Cℓ ratio of 0.72. 30.6 g. of aluminum chloride was produced in the intermediate compartment.

Claim:

1. In the process for preparing aluminum chlorohydrxides and aluminum hydroxide from aluminum chloride by electrolitically an aqueous solution of aluminum chloride as catholyte to liberate hydrogen at the cathode, and form aluminum chlorohydrxides in the catholyte, the improvement which comprises contacting chloride ions migrating towards the anode with aluminum oxide to form aluminum chloride.

2. A process for preparing aluminum chlorohydrxides and aluminum hydroxide from aluminum chloride, which comprises electrolitically in a compartmented cell an aqueous solution of aluminum chloride as catholyte, thereby liberating hydrogen and forming aluminum chlorohydrxides and aluminum hydroxide in the catholyte, containing chloride ions migrating towards the anode, with aluminum oxide to form aluminum chloride.

3. A process in accordance with claim 2 in which the proportions of aluminum chloride and the conditions during electrolysis are so adjusted as to produce principally aluminum chlorohydrxide Al₂(OH)₃Cl₂.

4. A process in accordance with claim 2 in which the proportions of aluminum chloride and the conditions during electrolysis are so adjusted as to produce principally aluminum dichlorohydrxide Al₂(OH)₂Cl₄.

5. A process in accordance with claim 2 in which the proportions of aluminum chloride and the conditions dur-
ing electrolysis are so adjusted as to produce principally aluminum tetrachlorhydroxide $\text{Al}_2(\text{OH})_2\text{Cl}_4$.

6. A process in accordance with claim 2 in which the catholyte is held at a temperature within the range from at least 70° C. up to the boiling point of the catholyte.

7. A process in accordance with claim 2 in which the anolyte is an aqueous solution of an inorganic acid whose anion is not discharged as a gas at the anode.

8. A process in accordance with claim 7 in which the acid is sulfuric acid.

9. A process for continuously producing aluminum chlorhydroxides and aluminum hydroxide from aluminum chloride in a compartmented cell having cathode, anode and intermediate compartments, which comprises electrolyzing an aqueous solution of aluminum chloride as catholyte, thereby liberating hydrogen and forming aluminum chlorhydroxide and aluminum hydroxide in the catholyte, reacting chloride ion which migrates into an intermediate compartment of the cell with aluminum oxide to form aluminum chloride, continuously withdrawing catholyte and recovering aluminum chlorhydroxides therefrom, continuously supplying aluminum oxide and hydrogen chloride to the intermediate compartment, and continuously withdrawing aluminum chloride from the intermediate compartment and recirculating this to the cathode compartment.

References Cited in the file of this patent

UNITED STATES PATENTS

2,176,343 Howard Oct. 17, 1939
2,392,531 Huehn et al. Jan. 8, 1946
2,921,005 Bodamer Jan. 12, 1960
2,967,806 Osborne et al. Jan. 10, 1961

OTHER REFERENCES