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ELECTROLYSIS OF AMMONIUM CHLORIDE

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This invention relates to the electrolysis of ammonium chloride for the recovery or production of chlorine or ammonia or both.

While ammonium chloride in aqueous solution is easily decomposed by electrolytic action, the process is not commonly employed on account of the great danger from the tendency of ammonia and chlorine to react and form the highly explosive compound nitrogen trichloride. It is also a rather expensive raw material to employ for the production of chlorine, under ordinary circumstances, and this fact alone would tend to disqualify it for commercial chlorine production even if the process of electrolytic decomposition were not so dangerous. We have found certain conditions under which chlorine or ammonia, or both of these materials, may be electrolytically produced from aqueous solutions of ammonium chloride, without the formation of the explosive nitrogen trichloride. At the same time, our discovery opens the way to the economical use of this material for the electrolytic production of chlorine.

While we have mentioned the formation of nitrogen trichloride by the reaction of chlorine on ammonia, there are other objectionable products which would often be formed in the electrolysis of aqueous ammonium chloride solutions, for example, the mono and dichloramines and nitrogen. Our discovery also makes it possible to avoid the formation of these products.

The underlying principle on which the invention is based resides in the electrolysis of aqueous ammonium chloride solutions in the presence of chlorides of alkali metal and alkaline earths which we find inhibit the production of nitrogen trichloride, and such products as nitrogen and chloramines. Under proper conditions, the electrolyte, containing ammonium chloride and one or more chlorides of alkali metal or alkaline earths, can be electrolyzed to produce ammonia and chlorine from the ammonium chloride without substantially reducing the content of the other chlorides. It is, however, important that the other chlorides be present in substantial quantities, for example, one-third chemical equivalent of the ammonium chloride, if the full advantages of the invention are to be obtained. Preferably, the ratio of the other metal chloride to ammonium chloride, on the basis of chemical equivalents, is at least 1-1, that is to say, the other chloride should at least equal and may even exceed the ammonium chloride in terms of chemical equivalents. The total concentration of the electrolyte may be, for example, between 25% and

30% solids. The temperature in the electrolyte should not be below 35° C., and it should preferably be maintained around 60 to 65° C., although as high as 90° C. is not at all harmful. The anode current density in a 26% aqueous solution of ammonium chloride and sodium chloride, for example, at 65° C., may be maintained at from 100 to 150 amperes per square foot, under which conditions, with suitable electrodes and cell construction, the decomposition efficiency of the ammonium chloride may amount to from 75 to 90% of the theoretical, the efficiency approaching the higher figure as the percentage of the sodium chloride approaches or exceeds that of the ammonium chloride.

It is important in electrolyzing the mixed solutions to have the anode compartment as small as can conveniently be arranged in an electrolytic cell. Any of the well-known types of electrolytic cells, such as used for the electrolysis of sodium chloride, may be employed, for example, a diaphragm cell, a cell of the bell-jar type, or a mercury cell. If the diaphragm cell is used, asbestos paper is used as the diaphragm. The cathode may be of perforated iron or of any other conducting material which is inert to sodium and ammonium chlorides as well as hydroxides. The anode may be of the usual carbon, graphite or magnetite composition. If a mercury cell is used, the cathode should be dipped into the mercury and the cathode chamber should be sufficiently large to take care of the large volume necessitated by mercury and ammonium amalgam. The voltage required in, for example, the Vorce type of diaphragm cell about four feet high and two feet in diameter, is between 3 and 5 volts, at about 1200 amperes current. This voltage, as well as the amperage, will vary somewhat, depending upon the concentration and the temperature of the electrolyte, the resistance and polarizations. The current density may be kept between, for example, 100 and 150 amperes per square foot of anode surface in a 26% aqueous solution containing chemical equivalents of sodium chloride and ammonium chloride. The flow of electrolyte may be maintained between, say, 15 and 20 liters per hour, and the temperature at about 60° C. The rate of flow with respect to the current density should be so adjusted as to keep the ammonium chloride concentration in the effluent from the cell as low as possible.

Under the conditions recited, nearly two parts by weight of chlorine are produced for each part of ammonia. The purity of the chlorine produced is generally over 96%, and the remaining solu-

tion contains very little ammonium chloride. The sodium chloride remains approximately constant, and hence the regeneration of the solution to be returned to the cell may be principally accomplished by the addition of ammonium chloride, although some addition of sodium chloride may be required to keep the composition of the electrolyte entering the cell in cyclic operation approximately constant.

10 Instead of passing a mixed solution of ammonium chloride and sodium chloride through the cell, the two solutions of ammonium chloride and sodium chloride respectively, at about 25% concentration, may be separately passed through the anode and cathode compartments, that is to say, the solution of ammonium chloride may be passed through the anode compartment and the solution of sodium chloride through the cathode compartment. The operating conditions may in other respects be similar to those employed when the mixed solution is used.

The electrolysis of the mixed solution of sodium chloride and ammonium chloride is especially advantageous when introduced as a step in the ammonia soda process. In the ammonia soda process, the ammonium chloride liquor, from which the ammonia is to be recovered for use again in the production of sodium bicarbonate, contains substantial quantities of sodium chloride. The composition of this liquor commonly runs from 17 to 18% ammonium chloride, and 7 to 8% sodium chloride. By employing the process of our present invention in the ammonia soda process, the ammonia is returned to the system for reaction with carbon dioxide and sodium chloride, and the chlorine is recovered as a valuable by-product, where heretofore the chlorine has been discharged from the system usually in the form of calcium chloride, for which there is no large market. The economy of the process of this invention is, therefore, particularly marked when the process is employed in conjunction with the production of soda by the ammonia soda process. The invention may thus be regarded as offering an improvement in the ammonia soda process. The electrolyte coming from the decomposition cell has been largely depleted of its ammonium chloride content, and to a much less extent of its sodium chloride. Since the liquor from the ammonia soda process is much higher in ammonium chloride than in sodium chloride, the regeneration of the spent electrolyte by the addition of suitable quantities of the liquor from the ammonia soda process offers an economical method for the continuous electrolytic production of chlorine from ammonium chloride without the danger of forming nitrogen trichloride and substitution products thereof, while at the same time restoring to the soda process the ammonia which heretofore has usually been recov-

ered at the expense of converting the chlorine into the relatively much cheaper by-product, calcium chloride.

We claim:

1. The method of producing substantially pure chlorine and recovering ammonia in good yield from aqueous ammonium chloride solutions, which comprises passing an electrolyzing current through an electrolytic cell having an aqueous electrolyte containing ammonium and sodium chlorides, the concentration of the sodium chloride being at least equal to that of the ammonium chloride, thereby discharging the ammonium ions from the catholyte containing chlorides of ammonium and sodium and discharging chlorine ions from the anolyte containing sodium chloride and any residual ammonium chloride.

2. The method of producing substantially pure chlorine and recovering ammonia in good yield from aqueous ammonium chloride solutions, which comprises passing an electrolyzing current through an electrolytic cell having an aqueous electrolyte containing ammonium chloride and a chloride selected from the group consisting of alkali metal chlorides and alkaline earth metal chlorides at a concentration at least one third of an equivalent of the ammonium chloride, thereby discharging ammonium ions from the catholyte containing chloride of ammonium and the chloride selected from the group consisting of alkali metal chlorides and alkaline earth metal chlorides, and discharging chlorine from the anolyte containing the chloride selected from the group consisting of alkali metal chlorides and alkaline earth metal chlorides and any residual ammonium chloride.

3. The method of producing substantially pure chlorine and recovering ammonia in good yield from aqueous ammonium chloride solutions, which comprises passing an electrolyzing current through an electrolytic cell having an aqueous electrolyte containing ammonium chloride and a chloride selected from the group consisting of alkali metal chlorides and alkaline earth metal chlorides at a concentration at least one third of an equivalent of the ammonium chloride, while maintaining the temperature in the neighborhood of 60 to 65° C., thereby discharging ammonium ions from the catholyte containing chloride of ammonium and the chloride selected from the group consisting of alkali metal chlorides and alkaline earth metal chlorides, and discharging chlorine from the anolyte containing the chloride selected from the group consisting of alkali metal chlorides and alkaline earth metal chlorides and any residual ammonium chloride.

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