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PROCESS FOR PRODUCING NITROGEN TRICHLORIDE

Gerrit van der Lee, Deventer, Netherlands, assignor to Naamlooze Vennootschap Industrieele Maatschappij Voorheen Noury & Van Der Land, Deventer, Netherlands, a company of the Netherlands

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The nitrogen chlorine compounds, nitrogen trichloride (NCl_3), dichloramine ($NHCl_2$) and monochloramine (NH_2Cl), may be prepared by electrolysis of aqueous liquids in which ammonium and chloride ions are present. The degree of acidity of the electrolyte determines what nitrogen chlorine compounds are formed by the electrolysis. In such electrolytic preparation of nitrogen trichloride, acid is preferably added to the electrolyte. This acid may be, for example, hydrochloric acid. Chloramines, however, are best formed in very weakly acid, neutral or alkaline solutions. If, for example, a small quantity of ammonia is added to a water solution of ammonium chloride, no nitrogen trichloride is obtained by electrolyzing this liquid, but chloramines are obtained.

In preparing nitrogen trichloride according to the above mentioned electrolytic process, it was now found that the yield of nitrogen trichloride per unit quantity of electricity fluctuated rather strongly depending on the circumstances under which the process was performed. It was further found that the cause of these fluctuations has to be sought in the greater or smaller extent to which side or undesired reactions take place, owing to which the nitrogen trichloride after being formed by the main electrolytic reactions is decomposed by the said side reactions. It is difficult to say exactly what these side reactions are. One may consider, for example, the following chemical equation as representing one of them:

$$NCl_3+NH_4Cl \rightarrow N_2+4HCl$$

It was now found that the side reactions could be limited or reduced to a considerable extent by restricting the contact of the nitrogen trichloride formed with the constituents of the electrolyte. There are various ways or possibilities to reach this effect, which are, however, all based on the same basic principle. In the first place it has appeared that in the electrochemical production of nitrogen trichloride it is of importance to keep the concentration of the ammonium ions in the electrolyte low. Since the yield of nitrogen trichloride in the electrolysis of dilute acid water solutions of ammonium chloride takes place with low yields of nitrogen trichloride per unit quantity of electricity, owing to the decrease in the concentration of the ammonium chloride in the electrolyte, the solution was not to be found by a simple decrease of the ammonium chloride concentration. It appeared however, that the desired result was gained by taking care that in the electrolyte, besides a relatively small quantity of ammonium ions, a proportionally larger quantity of chloride ions was present. To accomplish this end, a part and preferably a greater part of the ammonium chloride was substituted by sodium chloride. Instead of sodium chloride other soluble chlorides may be dissolved in the electrolyte, either separately or in mixtures, for example, chlorides of the alkali metals and of the alkaline earth metals. In this manner the concentration of chloride ions in the electrolyte may be made to greatly exceed the concentration of ammonium ions. Upon the electrolysis of electrolytes prepared in this manner to produce nitrogen trichloride, the said dissolved metal chlorides, which are present in the electrolyte are not converted into volatile constituents, and accordingly remain constantly in the electrolyte and need not be supplemented. According to tests made, more than 95% of the ammonium chloride in the electrolyte may be substituted by another chloride. However, there is not always sense in going so far, since if the electrolyte contains too little ammonium chloride, this material must constantly be supplemented. This objection is experienced to a smaller degree if care is taken to provide for continuous addition of ammonium chloride. This may, for example, take place by mounting in the electrolyzing cell or in a chamber connected therewith or fixed thereon, a vessel reaching into the electrolyte, which vessel is provided with openings in the part that is in contact with the electrolyte. This vessel is filled with ammonium chloride and subsequently closed, excepting that the said openings in contact with the electrolyte are permitted to remain open. The electrolyte that is in constant contact with the solid ammonium chloride remains saturated with it. Since, however, owing to the simultaneous presence of the said other dissolved chloride, the solubility of the ammonium chloride in the electrolyte is reduced, such quantities of ammonium chloride as would be detrimental to the conditions required according to the process of the present invention cannot go into solution in the electrolyte.

It has further appeared that the quantities of acid, such as hydrochloric acid, that must be added to the electrolyte used in the preparation of nitrogen trichloride by the electrolysis of water solutions of ammonium chloride can be reduced by using an electrolyte prepared as above described.

According to the method described above, the contact of the reaction products with the parts of the electrolyte and especially with the ammonium ions is limited, but this limitation of contact can be attained also in another way according to the present invention. If the volume of the electrolyte is limited, and the electrolysis is conducted with a great strength of current in proportion to the volume of the electrolyte, the side reactions take place to a decreased extent. According to the invention electrolyzing cells with a small capacity are used with a high strength of current, or both measures are applied. It was, for example, found that under otherwise equal circumstances a much better yield per unit quantity of electricity was attained in a narrow cylinder with a small volume of liquid than in a large electrolyzing cell in which there was much liquid. In the latter cell, the products formed on the electrodes find an opportunity to diffuse into the parts of the electrolyte that are not in direct contact with the electrodes, and in such diffusion are exposed to decomposition reactions by contact with the parts of the electrolyte which are outside of the zone of electrolytic action. Operating on this same principle, it was also found that a construction of the electrolyzing cell could be used in which the cell consists of two parts separated by a wall provided with openings. In one chamber of said cell, preferably the smaller, the electrodes are mounted surrounded by only a small quantity of electrolyte, while the other part or chamber of the cell serves as a reservoir for the electrolyte.

Finally the decomposition or side reactions may also be reduced in extent by a quick elimination of the nitrogen trichloride from the cell. This measure is carried out in the simplest way by conducting air through the electrolyte during the electrolysis, or by pumping away the volatile reaction products by diminishing the pressure above the electrolyte. Instead of air another gas or mixture of gases may be used. It was found that the use of large quantities of air or gas in the manner described, or the very quick aspiration of the volatile reaction products, offered important advantages and gave better yields per unit quantity of electricity than the application of smaller quantities of air or gas, or the more slow aspiration of the volatile products. Preferably so much air or gas is conducted through the electrolyte during electrolysis that the mixture coming from the cell contains 0.05–2.0 weight percentage of nitrogen trichloride. For the sake of completeness it is stated that the electrolytic cell is preferably operated at a pressure considerably below atmospheric pressure, so that reaction products having an irritating action cannot escape into the atmosphere surrounding the cell.

It is to be understood that the various procedures described above for limiting or eliminating side reactions may not only be used by themselves or individually, but may be combined with each other, so that two or more of the procedures may be combined.

I claim:

1. Process for producing nitrogen trichloride which comprises electrolyzing an aqueous solution of acid reaction containing ammonium and chloride ions, the acidity of said solution being greater than the normal acidity of ammonium chloride dissolved in water, and which solution contains dissolved therein a chloride of a metal selected from the group of metals consisting of the alkali metals and alkaline earth metals, said chloride of a metal being present in sufficient amount to cause the concentration of chloride ions in the said aqueous solution to greatly exceed the concentration of ammonium ions therein.

2. Process for producing nitrogen trichloride which comprises electrolyzing an aqueous solution of acid reaction containing ammonium and chloride ions, the acidity of said solution being greater than the normal acidity of ammonium chloride dissolved in water, said solution containing dissolved therein a chloride of a metal selected from the group of metals consisting of the alkali metals and the alkaline earth metals in sufficient amount to cause the concentration of chloride ions in the said aqueous solution to greatly exceed the concentration of ammonium ions therein, and quickly removing produced nitrogen trichloride from said solution.

3. Process for producing nitrogen trichloride which comprises electrolyzing an aqueous solution of acid reaction containing ammonium and chloride ions, the acidity of said solution being greater than the normal acidity of ammonium chloride dissolved in water, said solution also containing dissolved therein a chloride of a metal selected from the group of metals consisting of the alkali metals and alkaline earth metals in sufficient quantity to depress the concentration of ammonium ions in said solution, the electrolyzing of said solution being conducted with a high current strength while restricting the diffusion of nitrogen trichloride formed to a small body of said solution, and quickly removing produced nitrogen trichloride from said solution.

GERRIT VAN DER LEE.