POLYMERIC IMPURITY REMOVAL FROM AN AQUEOUS QUATERNARY AMMONIUM SALT SOLUTION

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This invention relates to removing certain organic impurities from an aqueous solution of a hydrotypic quaternary ammonium salt.

Adiponitrile can be produced by electrohydrodimerizing acrylonitrile. The electrohydrodimerization is carried out in an electrode cell having an anode chamber and a cathode chamber separated by an ion exchange resin. Acrylonitrile is dissolved in an aqueous quaternary ammonium salt solution. This solution, i.e., catholyte, is then continuously circulated through the cathode compartment while a dilute acid solution, i.e., anolyte, is circulated through the anode compartment. An electrical potential is established between the anode and cathode sufficient to produce a unidirectional current flow. Thus acrylonitrile is reductively dimerized to adiponitrile at the cathode.

The catholyte is then extracted with acrylonitrile to remove adiponitrile plus a small quantity of certain by-products, e.g., propionitrile, bis-cyanoethyl ether, hydroxypropionitrile, etc. The acrylonitrile plus other products is in turn water-washed to remove any dissolved quaternary ammonium salt. The aqueous quaternary ammonium salt raffinate from the acrylonitrile extraction plus any aqueous quaternary ammonium salt solution obtained from water-washing the acrylonitrile extract are evaporated to the proper quaternary ammonium salt concentration before the quaternary ammonium salt solution is returned to the catholyte circulating system.

The salt employed in the electrohydrodimerization of acrylonitrile to adiponitrile must serve two functions: one, the salt must conduct electrical current and, two, it must act to dissolve acrylonitrile in the aqueous solution of salt, i.e., the salt must be hydrotypic. Quaternary ammonium salts have been found to be admirably suited for such purposes. Included among the suitable quaternary ammonium salts are, generally, tetraalkylammonium sulfates, tetraalkylammonium aryl sulfonates, and tetraalkylammonium alkyl sulfates. Two specifically useful salts are tetramethylammonium toluene sulfonate and tetraethylammonium ethyl sulfate.

Under the described evaporation and recycle procedure a given batch of quaternary ammonium salt is repeatedly reused. For efficient cell operation the quaternary ammonium salt solution must be kept substantially free of impurities. One impurity formed in the electrohydrodimerization process is polyacrylonitrile. Most of this material is removable by ordinary filtration or like processes for removing solids from liquids. Nevertheless, small quantities of polyacrylonitrile partially hydrolyze to produce a polymer having sufficient carboxylate groups to make it readily soluble in quaternary ammonium salt solution. In one sample of aqueous quaternary ammonium salt which had been recycled 25 times partially hydrolyzed polyacrylonitrile was found to be present at a level of about 0.1 percent based on the solution weight.

Even this extremely small quantity deposits on the cell cathode by fouling same and substantially reducing the electrohydrodimerization yield. On analysis it was determined that the major portion of the material fouling the cathode consisted of deposited polyacrylonitrile plus small quantities of quaternary ammonium salt.

It is a general object of this invention to eliminate or substantially reduce cathode fouling in a cell used in the electrohydrodimerization of acrylonitrile to adiponitrile.

A further object is to substantially remove organic impurities, especially polyacrylonitrile, from an aqueous solution of quaternary ammonium salt.

A still further object is to improve, by reducing all cathode fouling, the product yield in the electrohydrodimerization of acrylonitrile to adiponitrile.

Other objects will become apparent upon reading the following descriptive material.

In general, the above objects are achieved by providing a process wherein the above noted partially hydrolyzed polyacrylonitrile is removed from an aqueous solution of a hydrotypic quaternary ammonium salt by means of a procedure including precipitating the polyacrylonitrile by adjusting the salt concentration of the solution to not more than about 55 weight percent and adjusting the pH of the aqueous solution to not more than about 7.

This precipitated material is then separated from the aqueous salt solution.

To achieve proper polyacrylonitrile precipitation requires that the treated quaternary ammonium salt solution have a concentration of not more than about 55 weight percent and a pH of not more than about 7, i.e., be neutral or acidic. There are various ways to achieve these conditions, depending upon the initial condition of the solution, of course. When the solution is already acidic but the concentration is more than about 55 weight percent then it is only necessary to decrease the salt concentration to achieve the proper precipitating conditions. When both concentration and pH are above the maximum limits then it is necessary to lower the salt concentration, i.e., dilute the solution, and to put sufficient acid in the solution to make it acidic.

The order in which the concentration adjustment and pH adjustment takes place may vary. The solution can be made acidic then have the concentration adjusted or the concentration can be adjusted, then the solution can be made acidic. When the salt concentration is greater than about 55 percent weight and the pH is greater than 7, i.e., alkaline, the solution can be simultaneously diluted and acidified with a proper quantity of an aqueous acid solution.

The most effective precipitation occurs when the pH is not more than about 7 and the salt concentration is not more than about 40 weight percent.

The preferred acids used to acidify the salt solution, because it is desirable not to contaminate the electrolyte with extraneous acids, are those whose anion corresponds to the anion of the quaternary ammonium salt being treated, for instance, when tetraethylammonium ethyl sulfate is the salt the acid should be ethyl sulfurous acid.

The procedure can be performed in batch form or it can be performed upon a continuous stream. The methods for separating the precipitated material from the salt solution include filtering, centrifuging, and other like processes well known to persons skilled in the art.

The examples below are set out to more fully illustrate the invention. It is not intended that the examples limit the invention in any manner whatsoever.

Example 1

A quantity of tetramethylammonium toluene sulfonate that had been recycled 25 times through the electrolytic cell employed to electrohydrodimerize acrylonitrile to adiponitrile was so concentrated by a series of concentration and crystallization procedures until the level of organic impurities present in the aqueous salt was approximately equivalent to that quantity of organic impurities that would have been present if the salt had been recycled about 150 times. This salt, having a large quantity
of organic impurities therein, was then employed as the supporting electrolyte in the catholyte used in electrohydrodimerizing acrylonitrile to adiponitrile. The catholyte included 25 weight percent acrylonitrile (45.9 weight percent tetramethylammonium toluene sulfonate, and 29.1 weight percent water. The pH was 9.0.

Upon conclusion of this test, which lasted for six hours, using highly contaminated electrolyte the catholyte was extracted with acrylonitrile to recover the adiponitrile and other like organic products. The remaining tetramethylammonium toluene sulfonate solution was adjusted to a salt concentration of 12 weight percent and the pH was adjusted to about 1 with p-toluene sulfonic acid. Immediately a precipitate appeared. This precipitate was then filtered from the salt solution and was determined to be about 0.8 weight percent of the salt solution based on the dry salt.

The diluted salt solution from which the partially hydrolyzed polyacrylonitrile had been removed was reconstituted and had the pH readjusted, and had enough acrylonitrile added thereto to produce a catholyte substantially equivalent to that described above, i.e., the pH was adjusted to about 9.0 with tetramethylammonium hydroxide, acrylonitrile concentration to about 25 weight percent, tetramethylammonium toluene sulfonate concentration to about 45.9 weight percent and about 29.1 weight percent of the catholyte was water. This catholyte was used in the same cell as was the contaminated electrolyte and was run for the same period of time, six hours. Upon analysis of the acrylonitrile extracted product of electrohydrodimerization the results shown in Table I were obtained. All amounts are given as weight percent based on the total product weight.

**TABLE 1**

<table>
<thead>
<tr>
<th>Products Obtained</th>
<th>Contaminated Salt</th>
<th>Purified Salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adiponitrile</td>
<td>72.33</td>
<td>83.05</td>
</tr>
<tr>
<td>Propionitrile</td>
<td>9.74</td>
<td>9.46</td>
</tr>
<tr>
<td>Bis-cyanoethyleth</td>
<td>13.60</td>
<td>2.62</td>
</tr>
<tr>
<td>Hydroxypropionitrile</td>
<td>0.97</td>
<td>0.44</td>
</tr>
<tr>
<td>Other high boiling impurities</td>
<td>3.56</td>
<td>4.44</td>
</tr>
</tbody>
</table>

1 Principally 2-cyanoethylpropionitrile.

From the results in Table I, it is quite apparent that the production of the desired product, adiponitrile, is substantially increased by removal of the partially hydrolyzed polyacrylonitrile produced in the electrohydrodimerization process.

**Example II**

A sample of catholyte which had been extracted, evaporated, and recycled more than 100 times was obtained. The catholyte contained as an electrolyte 85 weight percent tetramethylammonium salt sulfonate in water. The sample was divided into three portions, each of which was diluted to 50 weight percent salt. The pH of two portions was adjusted to 8.0 and the other was adjusted to 7.0. Table 2 summarizes the results. The quantity of polymer removed is based on the amount of dry salt present in the solution.

**TABLE 2—COMPARATIVE POLYMER REMOVAL RESULTS**

<table>
<thead>
<tr>
<th>Salt concentration, weight percent</th>
<th>pH</th>
<th>Amount of polymer removed, weight percent based on dry salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>7.0</td>
<td>0.4</td>
</tr>
<tr>
<td>50</td>
<td>8.0</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>50</td>
<td>8.0</td>
<td>&lt;0.05</td>
</tr>
</tbody>
</table>

Thus, it is clear that once the pH of the diluted salt becomes greater than 7.0 polymer removal becomes negligible. However, as can be seen from Example I, best results are obtained when the salt concentration and pH are lower than set out in this example.

It can be readily seen that the primary advantage of this invention is the significant improvement in adiponitrile yield. A second advantage is the increased useful life span of a particular cathode, i.e., the cathode becomes fouled at a much slower rate when the electrolyte is substantially free of organic impurities such as polyacrylonitrile, thus increasing the periods between cathode cleanings.

Although the invention has been described by reference to particular embodiments and examples, it is evident that many other embodiments and variations would be apparent to those skilled in the art to which the invention pertains. Therefore, the invention should be broadly construed and should only be limited to the reasonable scope of the appended claims.

What is claimed is:

1. A process for removing partially hydrolyzed polyacrylonitrile from an aqueous solution of a hydrotrropic quaternary ammonium salt comprising, in combination, the steps of:

   (a) precipitating said polyacrylonitrile by adjusting the salt concentration of said solution to not more than about 55 weight percent and adjusting the pH of said solution to not more than about 7;

   (b) separating said polyacrylonitrile from said solution.

2. The process of claim 1 wherein the hydrotrropic quaternary ammonium salt is a tetraalkylammonium ary1 sulfonate.

3. The process of claim 1 wherein the hydrotrropic quaternary ammonium salt is a tetraalkylammonium alkyl sulfate.

4. A process for removing partially hydrolyzed polyacrylonitrile from an aqueous salt solution of a hydrotrropic quaternary ammonium salt comprising, in combination, the steps of:

   (a) precipitating said polyacrylonitrile by sequentially:

   (1) adding sufficient water to said aqueous solution to adjust the salt concentration thereof to not more than about 40 weight percent,

   (2) acidifying said aqueous solution to adjust the pH thereof to not more than about 7; and

   (b) separating said polyacrylonitrile from said aqueous salt solution.

5. A process for removing partially hydrolyzed polyacrylonitrile from an aqueous salt solution of a hydrotrropic quaternary ammonium salt comprising, in combination, the steps of:

   (a) precipitating said polyacrylonitrile by sequentially:

   (1) acidifying said aqueous solution to adjust the pH thereof to not more than about 7,

   (2) adding sufficient water to said aqueous salt solution having a pH of not more than about 7 to adjust the salt concentration thereof to not more than about 40 weight percent; and

   (b) separating said polyacrylonitrile from said aqueous solution.

6. A process for removing partially hydrolyzed polyacrylonitrile from an aqueous solution of a hydrotrropic quaternary ammonium salt selected from the group consisting of tetraalkylammonium alkyl sulfates and tetraalkylammonium ary1 sulfonates used as a supporting electrolyte in a process for electrohydrodimerizing acrylonitrile to adiponitrile comprising, in combination, the steps of:

   (a) precipitating said partially hydrolyzed polyacrylonitrile by adjusting the salt concentration of said solution to not more than about 40 weight percent and adjusting the pH of said solution to not more than about 7; and
5. (b) separating said polyacrylonitrile from said aqueous solution.

7. The process of claim 6 wherein the hydrotropic quaternary ammonium salt is tetraethylammonium ethyl sulfate.

8. The process of claim 6 wherein the hydrotropic quaternary ammonium salt is tetramethylammonium toluene sulfonate.

References Cited
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CHARLES B. PARKER, Primary Examiner.
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