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ELECTROLYTIC METHOD OF MANUFACTURING HYDRODIMER OF ACRYLONITRILE

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ABSTRACT OF THE DISCLOSURE

In the manufacture of adiponitrile by electrolyzing in a divided cell the catholyte of an aqueous solution comprising acrylonitrile and a quaternary ammonium sulfate, using sulfuric acid solution as an anolyte, the improvement comprising using a concentration of dissolved acrylonitrile in said catholyte of from 3 to 10% by weight.

This invention relates to a method for the manufacture of adiponitrile, the hydrodimer of acrylonitrile, characterized by electrolyzing a catholyte comprising an aqueous solution of alkyl, aryl or aralkyl quaternary ammonium sulfate and acrylonitrile in a divided cell, employing an anolyte of an aqueous solution of sulfuric acid and the anolyte being separated, by a cation-exchange membrane placed between the cathode compartment and the anode compartment, from the catholyte.

More particularly, it relates to a method for hydrodimerizing acrylonitrile by electrolyzing the catholyte comprising said quaternary ammonium sulfate used as the supporting electrolyte and acrylonitrile, which is characterized by separating a cathode effluent solution into two phases, i.e. aqueous and oil phases by adding acrylonitrile thereto and extracting adiponitrile from the resulting aqeuous solution phase.

Particularly, this invention relates to a method for electrolytically hydrodimerizing acrylonitrile to adiponitrile by using quaternary ammonium sulfate with can alkyl radical having no more than three carbon atoms bonded to nitrogen atom of quaternary ammonium as a supporting electrolyte, and electrolyzing the catholyte in which acrylonitrile is dissolved together with said supporting electrolyte. Thus, the electrolysis of this invention may be carried out advantageously in a high selectivity of adiponitrile even when the acrylonitrile concentration in the catholyte is as low as 3 to 10% by weight. In other words, even if the solubility of acrylonitrile in the catholyte is substantially the same as that in water and the concentration of acrylonitrile in the catholyte is below 10% at normal temperature, a high selectivity of adiponitrile may be obtained according to the method of this invention. This is the point which is essentially different from the processes of conventional hydrodimerization known heretofore.

A conventional method known to the trade is of such principle that an aqueous solution containing such salt as aryl-or alkaryl sulfonate or alkylsulfate of aliphatic amine or heterocyclic amine together with acrylonitrile is contacted with the cathode and electrolyzed to obtain hydrodimerization product of acrylonitrile. Further details of this method are found in U.S. Patents Nos. 3,193,481, 3,193,480 and 3,193,477. Basic invention of these known in the literature is that by increasing the solubility of acrylonitrile by the use of specific supporting salts, high selectivity of adiponitrile may be obtained. Such typical

salts for this method are tetraethylammonium paratoluenesulfonate or tetraethylammonium ethylsulfate. On the other hand, Journal of the Electrochemical Society, vol. 102 (1955), page 239 describes the observation that the electrolysis of the aqueous solution of an olefinic compound, whn electrolyzed with tetraalkyl halide as the supporting electrolyte (which is defined as the salt that keeps discharge potential at the cathode enough negative for electrolysis), produces hydrodimer. The use of tetraalkylammonium halide for the production of hydrodimer of acrylonitrile has been also known from the specification of Belgium Pat. No. 649,625.

The specification of U.S. Patent No. 3,193,481 describes the possible use of tetraethylammonium sulfate as a supporting salt for hydrodimerization of acrylonitrile, however, the use of this salt is restricted for the concentration of acrylonitrile of catholyte to at least 15% as described at column 10 of the specification of U.S. Patent No. 3,193,481. Moreover, as the solubility of acrylonitrile in the catholyte by the use of tetraethylammonium sulfate will never be increased substantially more than that in water in the range of the concentration of tetraethylammonium sulfate less than 60%, the use of tetraethylammonium sulfate as a supporting salt is opposite to the basic idea of said U.S. Patent No. 3,193,481 that the increase of the concentration of acrylonitrile in the catholyte is essentially for the good yield of adiponitrile.

It is an object of this invention to provide a novel method for the manufacture of adiponitrile by electrolytically hydrodimerizing acrylonitrile.

Further objects and appending features of this invention will become apparent as the description of this specification proceeds.

According to the present invention there is provided a novel method for electrolytically hydrodimerizing acrylonitrile to produce adiponitrile efficiently and economically in a good stability.

This invention is essentially different from said conventionally known methods in that it conducts electrolysis by using as the catholyte the aqueous solution containing alkyl, aryl and/or alkaryl quaternary ammonium sulfate and acrylonitrile, and the concentration of acrylonitrile is substantially less than the solubility of acrylonitrile in water.

The advantages of the method of this invention may be explained more fully in the following:

The first advantage of the method of this invention consists in the use of the supporting electrolyte to facilitate the separation of the mixed solution of adiponitrile and acrylonitrile from the aqueous solution of supporting electrolyte and, as a result, when the effluent solution of the cathode compartment is separated into the supporting electrolyte, adiponitrile, acrylonitrile and water so as to isolate adiponitrile as the product, the recovery of acrylonitrile and the supporting electrolyte can be conducted very easily and re-used as the catholyte components.

By contrast, when tetraethylammonium p-toluenesulfonate or tetraethylammonium ethylsulfate is used as the supporting electrolyte according to the above known literature, acrylonitrile is dissolved to a very high concentration or at any indefinite ratio into the aqueous solution of supporting salt, due to the existence of alkaryl sulfonate ions or alkylsulfate ions as the anion. Thus, since the supporting electrolyte dissolves acrylonitrile to very high solubility in both water and organic substances, it is diffuclt to separate the organic components containing adiponitrile and acrylonitrile (oil phase) from the aqueous solution of supporting electrolyte (aqueous phase). Moreover, even if the oil phase is separated from the water phase, the supporting electrolyte is contained in

a considerably high concentration in the oil phase, and also adiponitrile and acrylonitrile is left in the aqueous phase. Thus, it is very difficult to isolate adiponitrile efficiently from the oil phase. In addition, when adiponitrile and acrylonitrile are separated from the oil phase, the oil phase solution containing supporting the electrolyte must be subjected to fractional distillation, therefore, the yield of adiponitrile is low. Besides, such operation involves decomposition of expensive supporting electrolyte and loss of the electrolyte at the bottom of the distillator. Also, at the time of recovering the supporting electrolyte from the aqueous phase after the process of extraction by adding acrylonitrile, the fact that adiponitrile or acrylonitrile is contained in the aqueous phase at a relatively high concentration complicates the process of separating the supporting electrolyte and reduces the efficiency for the recovery of the supporting electrolyte.

However, because this invention uses said tetraammonium sulfate as the supporting electrolyte, the solubility of acrylonitrile and adiponitrile in the aqueous solution of the supporting electrolyte is substantially same as that in water and much lower than that of acrylonitrile using the supporting electrolyte of U.S. Patents Nos. 3,193,481, 3,193,480 and 3,193,477. Because of this lower solubility of acrylonitrile, the quaternary ammonium sulfate of this invention is convenient for the separation of the oil phase from the aqueous phase in the effluent of the cathode compartment. Compared with quaternary ammonium aryl or alkaryl sulfonate or alkylsulfate used as the supporting electrolyte in the conventional known methods, the supporting electrolyte of this invention has such characteristics that it is very easy to separate the oil phase of adiponitrile and acrylonitrile containing substantially negligible amount of supporting electrolyte from the aqueous phase composed of the aqueous solution of mainly supporting salt and having a low adiponitrile content. The isolation of the ingredients in the oil phase and the aqueous phase is generally accomplished by conventional separation or extraction method, such as cooling, heating and fractional distillation or the solvent extraction by use of either organic or inorganic solvent. In any form of such separating operation, because the supporting electrolyte of this invention has little affinity and low solubility with and in the organic components, it is easy to separate the organic components from the cathode effluent solution.

The second advantage of this invention consists in the fact that because quaternary ammonium sulfate is used in the catholyte, sulfuric acid solution as the anolyte and the electrolysis is conducted in a divided cell separated by cation-exchange membrane placed between the cathode compartment and the anode compartment, the anions which can migrate from the cathode compartment to the anode compartment are sulfate ions which are identical with the anions existing from the beginning of the operation in the anode compartment. Therefore, even if the constituents of the anode compartment pass through the membrane due to the migration by electric current or diffusion, no difficulty such as erosion of anode occurs. If, as in the case of the conventional known method, quaternary ammonium halide is used as the supporting electrolyte in the catholyte, the chloride ion pass through the cation exchange membrane, produces halogen at the anode and consequently corrodes the anode, impeding its industrial application. Similarly, when tetraethylammonium p-toluenesulfonate is used as a supporting salt as in the method of U.S. Patent No. 3,193,481, p-toluenesulfonate ions move from the cathode compartment to the anode compartment and discharge at the anode. Anode is usually made of lead, lead alloy, or platinum, and particularly lead alloy for industrial purposes. The lead alloy is corroded by the discharge of halide ion and sulfonic acid ion, whereas no such corrosion takes place at all where sulfate ion discharges at the anode.

The third advantage of this invention consists in the fact that because the process for manufacturing quaternary ammonium sulfate is simple, and the supporting electrolyte of this invention can be manufactured less expensively than the conventional known tetraethylammonium p-toluenesulfonate. Moreover, the rate of the Hoffman decomposition reaction of quaternary ammonium sulfate is less than that of the conventional salt such as quaternary ammonium arylsulfonate or quaternary ammonium alkylsulfate, if the alkyl groups of quaternary ammonium salt is same.

The fourth advantage of this invention consists in the fact that adiponitrile can be manufactured in a high yield from acrylonitrile without having a substantial yield of propionitrile even when the acrylonitrile concentration in the electrolyte is below 10%, especially if quaternary ammonium sulfate in which alkyl radical having a small number of carbon atoms, particularly not more than three carbon atoms is bonded to nitrogen atom, is used as the supporting electrolyte. Because in this case solubility of acrylonitrile in the electrolyte never is increased more than that in water in the concentration of salt less than 60%. The reason for this is explained as follows: generally, the best yield of adiponitrile is obtained in the suitable range of C/C_S, preferably from 0.4 to 1, wherein C_S is the solubility of acrylonitrile in the electrolyte, and C is the concentration of acrylonitrile in the electrolyte. In this invention, C/C_S can be easily adjusted because the C_S using quaternary ammonium sulfate is smaller than 10%. On the contrary, according to such methods as described in U.S. Patent No. 3,193,477 and U.S. Patent No. 3,193,481, however, because the solubility of acrylonitrile in the electrolyte C_S is high and, as a result, the ratio of acrylonitrile concentration (C) to the solubility (C_S) becomes too small, and therefore, in such form of electrolysis, the selectivity of adiponitrile is reduced with the increasing deviation from the suitable value of ratio (C/C_S) for the same acrylonitrile concentration.

The fifth advantage of this invention consists in the fact that the high stability against the decomposition of the supporting electrolyte can be utilized for heating the catholyte and other solutions originating therefrom to high temperatures for the purpose of isolating adiponitrile.

The sixth advantage of this invention consists in the fact that the high specific conductivity of the supporting electrolyte serves to reduce the consumption of electricity involved in the manufacture of hydrodimer. For example, a solution composed of 30% of tetraethylammonium sulfate, the supporting electrolyte used for this invention, 8% of acrylonitrile and 62% of water has a specific resistance of 26Ω cm. at 25° C., whereas a mixed solution of 30% (corresponding to the concentration of the previous solution) of tetraethylammonium p-toluenesulfonate, which is a quaternary ammonium salt used by the conventional known methods and which has the same alkyl group, 8% of acrylonitrile, and 62% of water has a specific resistance of 62Ω cm. at 25° C. The high specific conductivity of the supporting electrolyte of this invention can be explained by reasoning that cations of this invention occurring from the dissociation of the supporting electrolyte have substantially the same conductivity as those of the conventional known supporting electrolyte whereas anions of this invention are sulfate ion, which are smaller in dimensions and consequently higher in mobility than p-toluenesulfonate ions or alkylsulfate ion of the conventional known method.

Especially, as the seventh advantage of this invention, the cell resistance is reduced remarkably and the selectivity of adiponitrile is increased when the electrolysis is carried out by using a quaternary ammonium sulfate having an alkyl group of not more than three carbon atoms, with the concentration of this suppotring salt in the electrolyte fixed below 40%. The reason is that the aqueous solution of quaternary ammonium salt of this invention shows its minimum specific resistance in the salt concen-

tration range of from 20 to 40% by weight. In the higher concentration range of supporting salt, the specific conductivity is lowered which increases the unit power consumption for the manufacture of adiponitrile and also increases the solubility of acrylonitrile, therefore, the production of adiponitrile cannot be accomplished in a good yield and consequently the purpose of this invention cannot be achieved unless the concentration of acrylonitrile should be increased to a suitable range of C/C_S. Such adjustment increases the power consumption again.

As described above, the method of this invention is effective in that the hydrodimerization of acrylonitrile can be accomplished in a substantially high yield with small power consumption, and that the dimerization can be conducted while preventing the formation of propionitrile and harmful side reaction at the anode. Further, in this invention the process of separating the product and the raw material can be simplified and recovery of the supporting electrolyte is simplified.

According to this invention, the catholyte is a solution which contains a quaternary ammonium sulfate, acrylonitrile, and water, with the concentration of acrylonitrile ranging from 3 to 60% by weight, that of water corresponding to 10 to 90% of the total weight of the catholyte, and that of quaternary ammonium sulfate in the range of from 1 to 60%. Generally, with the increasing number of carbon atoms in the group bonded to the nitrogen of quaternary ammonium sulfate, the solubility of acrylonitrile in the catholyte is increased. For example, acrylonitrile is dissolved by about 8% by weight in the catholyte at 25° C. which contains 0 to 60% of tetraethylammonium sulfate. In the aqueous solution of more than 20% of tetrabutylammonium sulfate, acrylonitrile can be dissolved to form homogeneous solution at whatever concentration desired at 25° C.

In view of separating adiponitrile formed by electrolysis from a cathode compartment effluent, it is advantageous to use a quaternary ammonium salt of high affinity with water but comparatively less affinity with adiponitrile and acrylonitrile. It is, therefore, advantageous to employ a quaternary ammonium compound such as tetramethylammonium sulfate or tetraethylammonium sulfate with a radical having less carbon atom bonded to nitrogen. In conducting electrolysis using quaternary ammonium salt of comparatively less affinity with adiponitrile and acrylonitrile as stated above, it is easy to obtain a solution of adiponitrile containing less amount of supporting electrolyte by extracting the cathode compartment effluent with an organic solvent. For example, in the actual operation of electrolysis the effluent of cathode compartment is received in a tank outside the electrolytic cell and the lower layer is drawn from the bottom of said tank to circulate to a cathode compartment while feeding acrylonitrile to said tank or a cathode compartment effluent. By doing so, the adiponitrile in the cathode compartment effluent is extracted with acrylonitrile added, and in the tank there are produced an oil layer consisting of adiponitrile and acrylonitrile as an upper layer and an aqueous layer mostly composed of the supporting electrolyte and water together with decreased concentration of adiponitrile due to extraction by acrylonitrile as a lower layer. When this lower layer is supplied to the cathode compartment and the electrolysis is continued, the adiponitrile formed by electrolysis is extracted by acrylonitrile and separated in the upper layer of the tank. It is possible in this invention to obtain with ease the product containing less supporting electrolyte by drawing off the upper layer alone.

Use of a quaternary ammonium salt of this invention will not cause a substantial increase of solubility of acrylonitrile beyond the solubility of acrylonitrile in water.

Especially, in a special method wherein a quaternary ammonium salt having alkyl group of less than three carbon atoms is used, the solubility of acrylonitrile in the electrolyte is not substantially increased due to the addition of supporting salt beyond that in the water, and C/C_S, representing a ratio of the concentration of acrylonitrile in the catholyte for electrolysis C to a solubility of acrylonitrile in the electrolyte C_S, is easily adjusted to a suitable value near to 1, as compared with the case using a supporting electrolyte which substantially increase a solubility of acrylonitrile beyond that in the water.

Generally, in the electrodimerization, as C/C_S is in a suitable range near to 1, so a selectivity of acrylonitrile to adiponitrile is higher. Therefore, when a supporting electrolyte of quaternary ammonium sulfate of less solubility of acrylonitrile, having an alkyl group of less than three carbon atom is used, the selectivity of acrylonitrile to adiponitrile is high.

In the case where a part of the acrylonitrile in the electrolyte is replaced by adiponitrile, it is particularly advantageous because of less formation of oligomer of acrylonitrile such as trimer, tetramer, etc. The reason is that it is possible to adjust the amount of acrylonitrile on the electrode surface and prevent a formation of oligomer in an advantageous way because adiponitrile dissolves in the electroylte in the same performance as that of acrylonitrile and the solubility of the mixture of acrylonitrile and adiponitrile makes almost no change in terms of the value of weight percentage even if a part of the acrylonitrile is replaced by adiponitrile.

The special quaternary ammonimum salt having an alkyl group of not more than three carbon atoms bonded to nitrogen, one of the optimum conditions of the present invention, is explained in detail as follows.

In case such aqueous solution of quaternary ammonium salt is used, minimum point of the specific resistivity of the electroylte is found with the increase of the concentration of salt while keeping the content of acrylonitrile constant. As an example, a specific resistivity of supporting electrolyte solution and a solubility of acrylonitrile is illustrated hereinbelow. Following tables show the relation of the specific resistivity of aqueous solution of supporting electroylte vs. the concentration of said salt and solubility of acrylonitrile in the aqueous solution at the definite concentration of salt. Even if the relation of the specific resistivity of aqueous electrolyte containing specific amount of acrylonitrile is plotted against the concentration of supporting salt, the concentration of the supporting salt which corresponds to the minimum value of resistivity of the said electrolyte is not substantially changed.

TABLE 1

Specific resistivity of tetraethylammonium sulfate aqueous solution (25° C.)

Salt concentration (percent weight):	Specific resistivity (Ω-cm)
10	39
20	26
30	22
40	25
50	39
60	72

Solubility of acrylonitrile in 30% (weight) tetraethyl sulfate aqueous solution

Percent (weight):	°C.
8.0	40
6.0	20

Similarly, conventional electrolyte has the same tendency as shown in Table 2.

TABLE 2

Specific resistivity of aqueous solution of tetraethylammonium p-toluenesulfonate.

Salt concentration (percent weight):	Specific resistivity (Ω-cm)
10	96
20	65
30	59
40	58
50	64
60	88

Solubility of acrylonitrile in 35% (weight) solution

Percent (weight):

	° C.
20	40
15.5	20

As evident from the above, when an electrolysis is especially conducted by using a supporting electrolyte of quaternary ammonium cation having an alkyl group of not more than three carbon atoms bonded to the nitrogen, and having sulfate as an anion, solubility of acrylonitrile is about 10% in a range of salt concentration from 0 to ity. This value shows substantially no increase of acrylonitrile solubility as compared with the solubility of acrylonitrile in water, 7.35% (weight) at 20° C., 7.9% (weight) at 40° C., and 9% (weight) at 60° C.

Generally, electrolysis in such special conditions facilitates the formation of acrylonitrile oligomer (e.g. hydrotrimer and hydrotetramer of acrylonitrile) as the concentration of acrylonitrile approaches near saturation. Furthermore, a lower concentration of acrylonitrile than saturation causes the formation of hydrogen gas, and leads to the formation of undesirable by-product propionitrile. Therefore, the optimum point for an effective preparation of adiponitrile by using quaternary ammonium having an alkyl group of not more than three carbon atoms, may be influenced by acrylonitrile concentration, current density agitating condition on anode surface, temperature, etc., but generally the optimum condition is in the range of about 3 to 10% acrylonitrile concentration, if the concentration of supporting salt is defined to cover a lower range than the concentration corresponding to the minimum specific resistivity of the electrolyte.

The temperature of electrolysis in the present invention can be at any degree up to the boiling point of acrylonitrile, preferably in the range of 0–80° C. for better adjustment of solution and operation. The higher the temperature, the greater the solubility of acrylonitrile. The temperature of the electrolysis, so long as it stays in the aforesaid range, usually has no great influence upon the current efficiency and utilization of monomer for preparation of hydrodimer, but a higher temperature causes less electrolytic cell resistance and less power consumption.

Sometimes it is desirable to add a solvent to the anolyte for the purpose of improving the current efficiency in the formation of hydrodimer or the selectivity of acrylonitrile at the cathode, or for the purpose of improving or controlling the solubility of acrylonitrile into the catholyte.

It is sometimes desirable to add to the catholyte such solvents as acetonitrile, propionitrile, dioxane, dimethylformamide, dimethylsulfoxide, trimethylamine, dimethylamine and other amines which are all solvents of high polarity. It is also sometimes effective to add solvents, which are electron acceptors. For the purpose of preventing polymer formation other than the hydrodimer in the cathode, it is desirable to add a polymerization inhibitor thereto and, at the same time, remove oxygen from acrylonitrile and/or the catholyte.

Among the salts which can be employed according to the invention, quaternary ammonium sulfates are generally suitable. Such salts can be alkyl quaternary ammonium salts, quaternary ammonium salts having alkyl and aralkyl groups, quaternary ammonium salts having aryl and/or alkyl groups, heterocyclic quaternary ammonium salts and alkylalkanol quaternary ammonium salts. Of the above quaternary ammonium compounds having alkyl groups, those having methyl, ethyl, butyl, and/or propyl groups bonded to the nitrogen atom are the most convenient to use. Compounds of quaternary ammonium having the phenyl group and the naphthyl group, are representative salts having aryl groups bonded to a nitrogen atom, and salts having the benzyl group and the methylbenzyl group are representative of the salts having aralkyl groups bonded to nitrogen. Typical of these quaternary ammonium compounds are

tetramethylammonium sulfate,
tetraethylammonium sulfate,
trimethylethylammonium sulfate,
triethylmethylammonium sulfate,
tetrapropylammonium sulfate,
tetrabutylammonium sulfate,
trimethylethylammonium sulfate,
methylpyridinium sulfate,
ethylpyridinium sulfate,
trimethylbenzylammonium sulfate,
triethylbenzylammonium sulfate,
trimethylaniline sulfate and
triethylaniline sulfate.

As to the cathode, it is desirable to use an electrode which has high hydrogen overvoltage in order to prevent hydrogen formation at the cathode. Generally, there may be used such metals as copper, lead, tin and mercury or alloys of such metals.

Current density employed for the electrolysis may be in the range of from 1 and 100 amperes/dm.^{2}. As a result of electrolysis, acrylonitrile is converted generally by 70 to 100% into adiponitrile, while a part of it may undergo side reaction for forming propionitrile, oligomer of acrylonitrile (such as hydrotrimer), or biscyanoethyl ether. It is necessary to control the occurrence of these side reactions as far as possible. Of said side reactions, the formation of propionitrile is easy to occur in the cathode compartment solution having a low pH value and in the electrolytic cell wherein the turbulence condition in the cathode compartment is not so strong as the supply enough acrylonitrile to the cathode, and also oligomer is liable to occur when the acrylonitrile concentration is high. Therefore, the concentration of acrylonitrile and the pH of the cathode compartment should be selected so as to minimize the yield of these side reactions. It is necessary, therefore, to maintain the catholyte at such pH that the effluent solution from cathode compartment will have pH in the range of from 2 to 9.5, and it is proper to keep the concentration of acrylonitrile in the catholyte in the order of from 3 to 40%. The side reactions at the cathode are influenced by the pH, monomer concentration, etc., on the surface of the cathode, therefore, it is necessary to make suitable arrangements so that the electrolyte may be sufficiently agitated in the cell and on the surface of the electrode and the concentration gradient of hydroxyl ion and acrylonitrile on the cathode may be reduced sufficiently. To accomplish this purpose, it is suitable to increase the flow velocity in the cathode compartment or to insert a spacer (or separator) within the cathode compartment for creating turbulence flow by the collision of the flow with the spacer, or to use a spacer called "tortuous path" which is so designed that the fluid is passed through narrow channel at a high speed and is caused to create turbulence due to collision against obstacles placed between said channel to half the compartment width. Generally, the flow velocity suitable for this invention is in the range of from 0.1 to 200 cm./second, more desirably from 5 to 100 cm./second.

Sulfuric acid solution is used as an anolyte. The concentration of sulfuric acid can be selected in the range of from 1 to 60%, it is proper generally to select it in the range of from 1 to 20% because the corrosion of anode becomes heavier with the increasing sulfuric acid concentration. As the material of anode, it is suitable to use platinum, nickel, nickel silicide, Duriron, lead, and lead alloys, particularly lead-antimony alloy.

As a cation exchange membrane, the ion-exchange membranes having sulfonic acid groups and carboxyl groups can be used, the most suitable membrane is the sulfonated styrene-divinylbenzene polymer. Such cation exchange membranes can be either homogeneous or heterogeneous. When a cation exchange membrane is placed to separate the anode compartment and the cathode compartment, the membrane selectively transfers

hydrogen ions from the anode compartment to the cathode compartment and, as a consequence, the hydroxy ions produced at the cathode are neutralized quantitatively, permitting the pH of the cathode compartment to be maintained constant. It the electrolysis, the cation exchange membrane is desired to have ideal characteristics as to transfer only hydrogen ions but prevent sulfate ion and other catholyte ingredient like acrylonitrile from migration to anode compartment. In the case of this invention, however, even if anions of the supporting electrolyte in the cathode compartment migrate through the membrane in a small amount and discharge at the anode, they will not induce harmful corrosion of the anode. When the pH of the cathode compartment is changed through insufficient neutralization, required neutralization can be accomplished by adding any kind of acid from outside.

The present invention will be explained in the following examples, however, it should not be constructed that these examples restrict the present invention in any event, since they are given merely by way of illustration:

EXAMPLE 1

The electrolytic cell was used, in which both the anode and cathode were of lead, the anode compartment and cathode compartment was divided by a cation exchange membrane of sulfonated 1 mm. thick divinylbenzene-styrene-butadiene copolymer and the distance between the membrane and the electrode was 1 mm. As an anolyte, 0.5 N sulfuric acid solution was circulated. The catholyte was circulated in the cathode compartment at a flow velocity of 20 cm./sec. and electrolyzed at the temperature of electrolyte of 40° C. The current density was 10 amp./dm.^{2} for both electrode.

During the electrolysis, the effluent of cathode compartment was separated into two phases by adding acrylonitrile to the cathode effluent. When this solution stood for more than few minutes, adiponitrile formed at the cathode was extracted with acrylonitrile as the upper oil phase. The lower phase was recirculated to the cathode compartment. Tetrapropylammonium sulfate was used to support electrolyte in catholyte.

During the electrolysis, the composition of the upper oil phase was 60.7% of adiponitrile, 8% of oligomer, biscyanoethyl ether and propionitrile, 0.4% of supporting electrolyte, 24.6% of acrylonitrile and 6% of water. Also, the composition of the lower phase was 6% of acrylonitrile, 12% of supporting salt, the rest being water and electrolytic products which were mainly adiponitrile and minor part of propionitrile, oligomer, biscyanoethyl ether and etc.

On the basis of the amount of acrylonitrile consumed in this electrolysis, the selectivity of electrolytic reaction was as follows:

Product:	Selectivity, percent
Adiponitrile	88.9
Propionitrile	7.7
Oligomer	3.4
Biscyanoethyl ether	0.1

On the contrary, when the hitherto publicly known tetraethylammonium p-toluenesulfonate was used as supporting salt in lieu of tetrapropylammonium sulfate and this electrolyte was electrolyzed under the same electrolytic conditions as the above, the concentration of supporting salt in the upper phase was 4% and the yield of adiponitrile 83%.

EXAMPLE 2

An electrolytic cell was used, in which both the anode and cathode were of lead, the anode compartment and cathode compartment was divided by cation exchange membrane of sulfonated 1 mm. thick divinylbenzene-styrene-butadiene copolymer and the distance between the membrane and electrode was 1 mm. As an anolyte, 0.5 N sulfuric acid solution was circulated and the catholyte was circulated in the cathode compartment at a flow velocity of 20 cm./sec. and electrolyzed at the temperature of 30° C., the current density was 10 amp./dm.^{2} for both electrodes.

The catholyte in which, as supporting electrolyte, tetraethylammonium sulfate was used, was electrolyzed for two hours while being controlled in the following composition.

Catholyte composition:

Acrylonitrile	percent weight	5.0–6.0
Supporting salt	do	10–9
Electrolytic products and water	do	The rest
pH		4
α-Naphthylamine (inhibitor)	p.p.m.	1,000

The electrolytic products were mainly adiponitrile and minor part of propionitrile, oligomer, biscyanoethyl ether and etc. On the basis of the amount of acrylonitrile consumed in this electrolysis, the selectivity of the electrolytic reaction was as follows:

Product:	Selectivity, percent
Adiponitrile	88.5
Propionitrile	6.4
Oligomer	5.0
Biscyanoethyl ether	0.1

EXAMPLE 3

The same electrolytic cell as in the Example 2 was used except that the lead-antimony anode and cathode were used. The anode compartment is circulated by 5% sulfuric acid, and the catholyte was circulated in the cathode compartment at a flow velocity of 60 cm./sec. and electrolyzed at a temperature of 60° C. The current density was 10 amp./dm.^{2} for both electrodes.

The catholyte in which, as supporting salt, tetramethylammonium sulfate was used, was electrolyzed for two hours while being controlled in the following composition.

Catholyte composition:

Acrylonitrile	percent weight	6.0–7.0
Supporting electrolyte	do	29–30
Electrolytic products and water	do	The rest
pH		8
α-Naphthylamine	p.p.m.	1,000

On the basis of the amount of acrylonitrile consumed in this electrolysis, the selectivity of electrolytic reaction was as follows:

Product:	Selectivity, percent
Adiponitrile	78.0
Propionitrile	16.8
Oligomer	5.0
Biscyanoethyl ether	0.2

EXAMPLE 4

The same electrolytic cell and anolyte as in the Example 2 were used. The catholyte was circulated in the cathode compartment at a flow velocity of 60 cm./sec. and electrolyzed at a temperature of 30° C. The current density was 10 amp./dm.^{2} for both electrodes. The catholyte, in which as a supporting salt diethylethanolbenzylammonium sulfate was used, was electrolyzed for two hours while being controlled in the following composition.

Catholyte composition:

Acrylonitrile	percent weight	6.0–7.0
Supporting electrolyte	do	12–13
Electrolytic product and water	do	The rest
pH		8
α-Naphthylamine	p.p.m.	1,000

On the basis of the amount of acrylonitrile consumed in this electrolysis, the selectivity of electrolytic reaction was as follows:

Product:	Selectivity percent
Adiponitrile	85.0
Propionitrile	6.2
Oligomer	8.5
Biscyanoethyl ether	0.3

EXAMPLE 5

The same electrolytic cell and anolyte as in the Example 2 were used. The catholyte was circulated in the cathode compartment at a flow velocity of 40 cm./sec. and electrolyzed at a temperature of 40° C. The current density was 10 amp./dm.^{2} for both electrodes.

The catholyte, in which as supporting salt methyltriethylammonium sulfate was used and dimethylformamide added as a solvent, was electrolyzed for two hours while being controlled in the following composition.

Catholyte composition:		
Acrylonitrile	percent weight	20
Supporting electrolyte	do	19–20
Dimethylformamide	do	20
Electrolytic products and water	do	The rest
pH		7.2
α-Naphthylamine	p.p.m.	1,000

On the basis of the amount of acrylonitrile consumed in this electrolysis, the selectivity of adiponitrile was 83%. In the above Examples 2–7, the oil phase of adiponitrile was enough low in the content of supporting electrolyte and could be separated and extracted, as in the case of the Example 1 by adding acrylonitrile to the solution at the effluent of cathode compartment.

EXAMPLE 6

An electrolytic cell was used, in which both the anode and cathode are of lead, the anode compartment and cathode compartment are divided by cation exchange membrane of sulfonated 1 mm. thick divinylbenzene-styrene-butadiene copolymer, and the distance between the membrane and electrode was 1 mm. As an anolyte, 2 N sulfuric acid was circulated in the anode compartment. The catholyte was circulated in the cathode compartment at a flow velocity of 20 cm./sec. and electrolyzed at a temperature at 40° C. The current density was 10 amp./dm.^{2} for both electrodes.

The catholyte in which, as supporting salt, tetraethylammonium sulfate was used, was electrolyzed for two hours while being controlled in the following composition.

Catholyte composition:		
Acrylonitrile	percent weight	7.0–5.0
Supporting electrolyte	do	19–21
Electrolytic products and water	do	The rest
pH		4
α-Naphthylamine	p.p.m.	1,000

The electrolytic products were mainly adiponitrile and minor parts of oligomer, biscyanoethyl ether and etc. On the basis of the amount of acrylonitrile consumed in this electrolysis, the selectivity of electrolytic reaction was as follows:

Product:	Selectivity, percent
Adiponitrile	88.9
Propionitrile	7.6
Oligomer	3.4
Biscyanoethyl ether	0.1

What is claimed is:

1. In a method of manufacturing adiponitrile by electrolyzing in a divided cell the catholyte of an aqueous solution comprising acrylonitrile and quaternary ammonium sulfate having at least one radical selected from the group consisting of alkyl, aryl and aralkyl bonded to the nitrogen atom of said quaternary ammonium compound, sulfuric acid solution being used as an anolyte, and the anolyte being separated by a cation exchange membrane from the catholyte, the improvement comprising using a concentration of dissolved acrylonitrile in said catholyte of from 3 to 10% by weight.

2. Method according to claim 1 in which the effluent solution of the cathode compartment of said divided cell is separated into two phases by adding acrylonitrile to said effluent to extract adiponitrile therefrom.

3. Method according to claim 1 in which said quaternary ammonium sulfate has an alkyl radical of not more than three carbon atoms.

4. Method according to claim 1 in which said quaternary ammonium sulfate has at least one alkyl radical of not more than three carbon atoms and the concentration of said salt is kept at lower than that where the specific resistivity of the cathlyte is minimum in relation to the concentration of said salt.

5. Method according to claim 1 in which said quaternary ammonium sulfate is selected from the group consisting of tetramethylammonium sulfate, tetraethylammonium sulfate, trimethylethylammonium sulfate, triethylmethylammonium sulfate and tetrapropylammonium sulfate.

6. Method according to claim 1 in which the sulfate provides solubility of acrylonitrile not higher than that in water and adiponitrile is separated from the effluent solution of cathode compartment.

7. Method according to claim 1 in which the sulfate provides solubility of acrylonitrile in the catholyte substantially less than that in water, acrylonitrile is added to the effluent solution of cathode compartment and adiponitrile is extracted and separated from the upper phase at the phase separation tank outside of the electrolytic cell.

References Cited

UNITED STATES PATENTS

Re. 24,865	9/1960	Juda et al.	204—98
3,193,477	6/1965	Baizer	204—73
3,193,480	6/1965	Baizer et al.	204—73
3,193,481	6/1965	Baizer	204—73
3,267,131	8/1966	Campbell et al.	204—73

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