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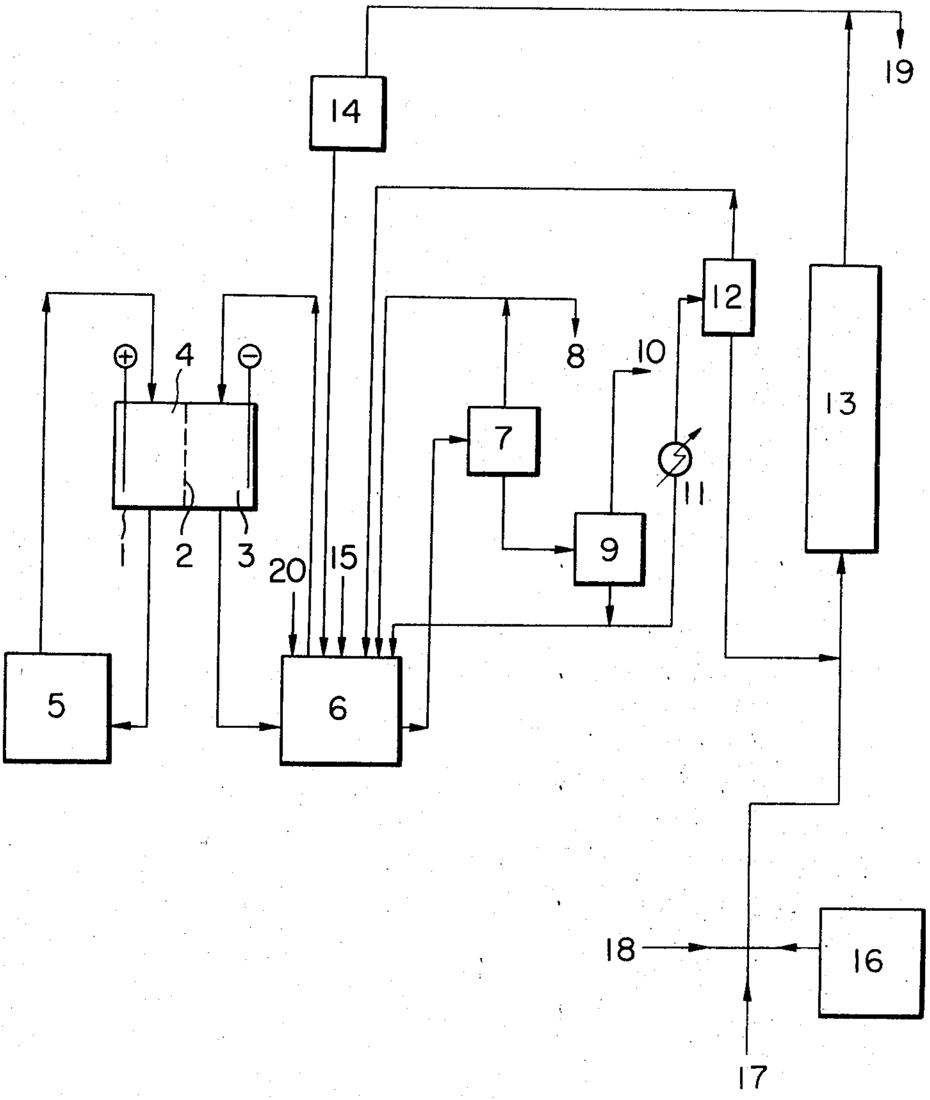

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PROCESS FOR HYDRODIMERIZING ACRYLONITRILE

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ABSTRACT OF THE DISCLOSURE

In the process for hydrodimerizing acrylonitrile, the improvement which comprises contacting an electrolyte effluent containing an electrolytic supporting salt, acrylonitrile, adiponitrile and electrode reaction-impairing materials with a cation exchange resin, thereby removing the electrode-reaction impairing materials by adsorption on the resin and circulating the solution having passed through the ion exchange resin into the electrolytic cell for reuse in the electrolysis while conducting the electrolysis.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to hydrodimerization of acrylonitrile wherein the electrolytic process is carried out while passing the electrolyte effluent through a cation exchange resin and returning the resulting effluent containing the electrolytic supporting salt back to the catholyte tank.

(2) Description of the prior art

Various methods are known of the production of adiponitrile by hydrodimerization of acrylonitrile as follows:

There are disclosed in U.S. Pat. Nos. 3,193,477, 3,193,480 and 3,193,481 the use of a homogeneous solution as the electrolyte and in Belgian Pat. Nos. 699,926, 699,928 and 684,436 the use of an emulsion as the electrolyte.

Separation and recovery of adiponitrile from the electrolytes obtained by these electrolytic processes are described in U.S. Pat. No. 3,267,131 and Belgian Pat. No. 706,573. As the electrolyte are used a homogeneous solution in the former and an emulsion in the latter.

Removal of the substances which impair the electrode reaction in the hydodimerization of acrylonitrile are known in publications such as U.S. Pat. No. 3,335,162, Belgian Pat. No. 681,980, Dutch Pat. No. 6,515,510 and Belgian Pat. No. 716,095.

In these methods, however, one disadvantage is that continuous operation over 1000 hours is associated with progressive reduction in the yield of adiponitrile with elapse of time which results on the whole in low yield of adiponitrile.

SUMMARY OF THE INVENTION

It is an object of this invention to provide a method for preventing reduction in the yield of adiponitrile during hydrodimerization of acrylonitrile when operated for a prolonged period of time. Other objects will be apparent hereinbelow.

These objects may be achieved by adsorbing electrode reaction-impairing materials formed and accumulated during hydrodimerization of acrylonitrile when operated for a long period of time upon a cation exchange resin and eliminating the substances out of the electrolysis system, thereby preventing by-production of propionitrile and formation of agglutinates on the surface of the cathode promoted by the presence of these substances and resulting in reduction of the formation rate of adiponitrile with elapse of time.

After an extensive investigation of the cause for the reduction in the yield of adiponitrile we have found that mainly responsible for it are by-products formed and accumulated in the system during the electrolysis when carried out for a long period of time including ammonia, cyanoethylated products thereof, decomposition products of the electrolytic supporting salt, 1-imino-2-cyanocyclopentane, amines formed by reduction of nitriles, carboxylic acids formed by hydrolysis of nitriles, polymers of acrylonitrile and degenerated products thereof and polymers of adiponitrile and degenerated products thereof and metals.

As a result of the foregoing investigation and discovery we have devised an important improvement in the process wherein a cation exchange resin can be used for adsorbing the aforementioned electrode reaction-impairing substances to eliminate the same out of the system.

The method according to the present invention can be applied to any of the electrolyte taking place in any known electrolytic processes and solutions obtained in the course of the separation and the recovery of adiponitrile from the electrolyte.

By carrying out the method of the invention it has become feasible to maintain a high yield of adiponitrile through stable operation over a prolonged period of time.

DESCRIPTION OF THE INVENTION

Electrode reaction-impairing materials as referred to herein include ammonia, cyanoethylated products thereof such as hydroxy propionitrile and bis-cyanoethyl ether, 1-imino-2-cyanocyclopentane, decomposition products of the electrolytic supporting salt such as trialkyl amine, amines formed by reduction of nitriles, organic carboxylic acids formed by hydrolysis of nitriles, polymers of acrylontrile and degenerated products thereof, and polymers of adiponitrile and modified products thereof, which are accumulated in the system, as well as metals dissolved out and accumulated in the electrolyte. The presence of these materials results in reduction in the yield of adiponitrile and formation of agglutinates on the surface of the cathode which further promote reduction in the yield of adiponitrile.

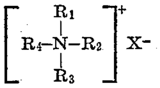
The method of the present invention is applied to any electrolytes, i.e., in emulsion, in aqueous layer which was obtained by settling emulsion into oily and aqueous layers, in homogeneous solution, in aqueous layer which was obtained by separating a homogeneous solution into two layers by the addition of water and acrylontrile to a homogeneous solution and solutions which were obtained by removing acrylonitrile from aforementioned liquids.

If desired, the treatment according to the invention may be carried out after removal not only of acrylonitrile but also of adiponitrile, propionitrile and the like from the electrolyte by such means as solvent extraction. The hydrolysis of the nitrile occurring during the treatment can be effectively prevented by removing acrylonitrile, adiponitrile, propionitrile and the like from the electrolyte prior to the treatment thereof with ion exchange resin.

Concentration of the electrode reaction-impairing materials in the electrolyte is indicated by the amount of alkali required for titration of the electrolyte from pH 7 to pH 11. High yield of adiponitrile over a long period of time is continuously achieved by carrying out the electrolysis while maintaining the concentration of the electrode reaction-impairing material below 20 milliequivalents per liter electrolyte, preferably below 15 milliequivalents per liter.

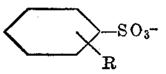
The cation exchange resin is an exchange resin widely used for general purposes of adsorption, purification and separation, which has a characteristic of receiving the cation in a liquid phase while releasing another cation by itself. The cation exchange resin is broadly classified into the strongly acidic cation exchange resin and the weakly acidic cation exchange resin. Representative of the former are methacrylate-divinylbenzene resin and phenolcarboxresin having sulfonic group. Representative of the latter are methacrylate-divinylbenzene resin and phenolcarboxylate resin containing carboxylic group and phenolic group as the exchange group. Although any of these resins can be used in the present invention in which the resin may be either in hydrogen form or in the cation form of the electrolytic supporting salt used, the latter is preferred. Use of a weakly acidic resin can enhance selectivity of the electrode reaction-impairing materials toward the resin thereby to enable the highly efficient adsorption of said material on the resin. Weakly acid cation exchange resin having the cation of the supporting salt as exchange group promotes exchange between the electrode reaction-impairing materials and the cation of the supporting salt and adsorption of the former on the resin thereby further improving efficiency in the adsorption.

As the electrolytic supporting salts are generally used are alkali metal salts and electrolyte salts represented by the general formula:



$$\left[\begin{array}{c} R_1 \\ | \\ R_4{-}N{-}R_2 \\ | \\ R_3 \end{array}\right]^+ X^-$$

wherein R_1 through R_4 are alkyl containing from 1 to 4, preferably from 2 to 3 carbon atoms and as X^- may be used sulfate ion, alkylsulfate ion, arylsulfonate ion of the general formula



wherein R is alkyl containing from 0 to 2 carbon atoms such as p-toluenesulfonate and besides other anions forming an electrolytic supporting salt known to be effective for electrolytic hydrodimerization of acrylonitrile such as halogen ion, nitrate ion and phosphate ion. Carboxylate(s) is excluded from the category of anions cited above. Among these supporting salts are most suitable quaternary ammonium salts, which lead to a high yield of adiponitrile.

Preferable pH of the electrolyte in electrolytic hydrodimerization of acrylonitrile is between 3 and 10. Below pH 3 the hydrolysis of nitriles and dissolution of metals will occur whereas above pH 10 hydrolysis of nitriles and formation of bis-cyanoethyl ether will be associated.

Quantity of the liquid to be placed under purification is desired to be as much as possible so far as it is economically acceptable and in general the treatment is conducted with the amount in the range from 0.1 to 20 ml./a. hr. Amount of the resin to be used is from 0.0002 to 1 ml./a. hr. in terms of the resin of H-form. When the cation exchange resin used is in H-form the treated liquid is passed in an amount more than the breakthrough exchange capacity of the resin with respect to the cation of the electrolytic supporting salt. If the cation exchange resin used has cation of the supporting salt as an exchanging group, there is of course no limitation as to the lower limit of the amount of the liquor to be passed.

As the electrode reaction-impairing materials tend to be more easily adsorbed on the cation exchange resin than the cation of the supporting salt at pH below 10, the materials contained in the electrolyte that is passed through a cation exchange resin are selectively adsorbed on said resin, whereas most of the cation of the supporting salt can be recovered as the effluent flowed out. Therefore, separation of the electrode reaction-impairing materials and the cation of the supporting salt can be achieved by conducting the electrolysis while returning treated effluent to the catholyte tank.

It is sometimes required to effect further separation of a small amount of the cation of the electrolytic supporting salt adsorbed on the resin and the electrode reaction-impairing materials. Efficient separation is achieved by the following treatment:

Regeneration of the cation exchange resin which has cation of the electrolytic supporting salt and the electrode reaction-impairing materials as adsorbed on it with an acid is carried out in an ion-exchange chromatographic manner, by which the former cation is eluted earlier and the latter material later thereby both being separated.

The separation may also be effected by means of a multi-stage ion exchange using two or more ion exchange columns arranged in a cascade system, each column containing ion exchange resin of cation form of the supporting salt. The catholyte effluent is first passed through the first column containing the ion exchange resin. Then an acid is passed through said column to desorb said materials to give an outflow enriched with said materials. Then this outflow is passed through the second column, which is subsequently regenerated with an acid giving an outflow more enriched with said materials. Thus, the outflow discharged from each column is then passed through next column and grows more and more concentrated with said materials, and less and less concentrated with cations of said supporting salts, finally giving an outflow which has carried off as much said impairing materials as possible. The last one containing a large amount of said impairing material being discarded.

The electrolytic supporting salt may also be recovered by extracting the electrode reaction-impairing materials from said outflow with an organic solvent to eliminate the same out of the system. The salt may also be recovered by dialysis thereby removing the electrode reaction-impairing materials.

The electrolyte used for electrolytic hydrodimerization of acrylonitrile may be either in solution or in emulsion containing acrylonitrile and an electrolytic supporting salt and the method of this invention can be applied independently of said supporting salt and concentration of acrylonitrile in the electrolyte. The electrolyte may contain by-products other than acrylonitrile, and/or an emulsifier, polymerization inhibitor and other additives necessary for effectively conducting the electrolysis.

As the cathode is preferably employed one with a high hydrogen overvoltage and usually lead, mercury, zinc, carbon or cadmium, or alloys thereof. It is preferable to use as an anode any with a high corrosion resistance such as lead, lead oxide alloy, lead peroxide, platinum, carbon or titanium or alloys thereof.

The diaphragm may be of any of those materials as a porcelain plate, a parchment paper, a cation exchange membrane and an amphoteric membrane. It is also possible to conduct the electrolysis in an undivided cell.

Though, in a divided cell provided with a diaphragm, any anolyte may be employed, those which do not hamper the corrosion-resistance of anode nor adversely affect the hydrodimerization reaction and are cheap are preferably selected. Particularly preferable is, therefore, sulfuric acid.

It is critical that the electrolytic cell is designed in such a way as being capable of carrying out the electrolysis while stirring or circulating the electrolyte. The electrolysis temperature is preferably below 70° C. The current density is preferably so high that no evolution of hydrogen gas occurs, and generally below 50 a./100 cm.^{2}. Adjustment of pH changing as the electrolysis progresses to a desired value can be conducted by addition of an appropriate acid which is not conflicting with the supporting salt.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

An embodiment of this invention is described hereinafter with reference to a typical flow sheet, but the invention is not intended to be limited to the process as indicated in the flow sheet.

In the flow sheet, the electrolyzer **1**, in which electrolytic hydrodimerization of acrylonitrile is carried out for the production of adiponitrile, consists of two chambers, the cathode chamber **3** and the anode chamber **4** partitioned by a cation exchange diaphragm **2**. Through the anode chamber **4** is circulated an anolyte sent from the anolyte tank **5**, whereas through the cathode cell **3** is circulated a catholyte passed from the catholyte chamber **6**.

The catholyte is a solution or an emulsion containing acrylonitrile, adiponitrile, an electrolytic supporting salt and other additives.

The catholyte in the catholyte tank **6** is in portions sent to the acrylonitrile stripper **7**, where the acrylonitrile is recovered and returned to the catholyte tank **6** and the water condensed and separated from the acrylonitrile is led to the outlet **8**. The catholyte in the acrylonitrile stripper **7** from which acrylonitrile and water have been removed is settled for separation in the decanter **9**, from which the oily layer mainly composed of adiponitrile is passed through the outlet **10** to the adiponitrile purification step (not shown). On the other hand, the aqueous layer is recovered through the bottom of the decanter **9** into the catholyte tank **6**. A portion of said aqueous solution is cooled in the cooler **11** and continuously or intermittently drawn out. The treated solution is stored in the decanter **12**. The aqueous layer is passed to the cation exchange resin column **13** in the form of cation of the electrolytic supporting salt. The effluent is stored in the tank **14** and continuously or intermittently returned to the catholyte tank **6**. pH of the catholyte in the tank **6** is adjusted, as occasion demands, using an acid or an alkali corresponding to the type of hydroxide of the supporting salt.

The cation exchange resin, which, upon contact with the catholyte, adsorbs the undesirable electrode reaction-impairing materials as mentioned above, is subjected to regeneration, i.e., desorption of the cations with an aqueous sulfuric acid in the tank **16**, followed by washing with water introduced from the nozzle **17**. An aqueous hydroxide solution of the electrolytic supporting salt introduced from the nozzle **18** is passed to convert the form of the resin to the form of cation of the supporting salt. In case of a strongly acidic exchange resin, an aqueous solution of the supporting salt may be employed. In the flow sheet **20** is the pipe for filling up acrylonitrile consumed by the conversion to adiponitrile and **19** is the outlet for the washing water of the ion exchange column and the regenerated liquid. Pipe **15** is provided for introducing an aqueous solution of hydroxide of the electrolytic supporting salt or an appropriate acid to adjust pH of the catholyte.

Although a batchwise ion-exchange apparatus is used in the flow sheet as a cation exchange resin apparatus, operation using a continuous ion-exchange apparatus is also involved within the scope of the invention.

This invention is described in more details in the following examples:

EXAMPLE 1

An electrolyzer provided with an anode chamber and a cathode cell both being in a size 10 cm. in width x 10 cm. in length and 1 mm. in thickness and a partitioning cation exchange diaphragm 1 mm. in thickness placed between a cathode of lead alloy containing 6% antimony with an effective area of cathode surface 10 cm. in width x 10 cm. in length and an anode of lead alloy containing 0.3% silver and 6% antimony with the same area was used as an experimental equipment shown in the accompanied drawing flow sheet. Through the anode chamber was circulated 2 N sulfuric acid at a flow rate of 200 cm./sec. and through the cathode chamber was circulated a catholyte, which was an emulsion of pH 7 containing in 8:2 volume ratio an aqueous phase consisting of 2% acrylonitrile, 79.75% water, 10% tetraethyl ammonium sulfate, 0.05% emulsifier and by-products mainly composed of 0.2% 2-cyanoethyladiponitrile and an oily layer consisting of 70% adiponitrile, 20% acrylonitrile, 5% water, 2% trimer and 3% electrolytic by-products mainly composed of propionitrile at the same flow rate. Electrolysis was conducted at a liquid temperature of 50° C. and an electric current of 20 a.

The catholyte was 3000 ml. in total amount and was treated using the equipment as shown in the accompanied drawing flow sheet, wherein electrolytic reaction was carried out while passing the catholyte at a flow rate of 10 ml./hr. through an ion exchange resin column of 30 cm. in length x 2.5 cm.^{2} in sectional area filled with 50 ml. of a cation exchange resin Amberlite IRC–84 of tetraethylammonium form. Alkali titration of the aqueous phase of the electrolyte from pH 7 to pH 11 was constantly held at 4 milliequivalents/l. The results of the electrolysis are shown in Table 1.

TABLE 1

Operation time (hr.)	Yield on the basis of acrylonitrile consumed	
	Adiponitrile	Propionitrile
100	93	5.2
1,000	93	4.8

The resin after the use during operation for 1000 hr. was regenerated by passing 0.1 N sulfuric acid at SV=1. From the effluents in an amount of 360 ml. from the beginning was recovered 92% of the tetraethylammonium ion which had been adsorbed to the resin, 37 milliequivalents and the effluents afterwards contained the electrode reaction-impairing materials. Thus, the ion-exchange chromatography resulted in separation of tetraethylammonium and the electrode reaction-impairing materials.

Reference Example 1

For reference, electrolysis was carried out in such a way as shown in the accompanied drawing flow sheet except that no purification of the catholyte was made with 13 through 19 eliminated. Other experimental conditions were the same as in Example 1. The results are shown in Table 2. Alkali titration of the aqueous layer of the electrolyte during following 1000 hours' operation was 35 milliequivalents/l.

TABLE 2

Operation time (hr.)	Yield on the basis of acrylonitrile consumed	
	Adiponitrile	Propionitrile
100	92	5.5
1,000	75	20.3

Example 2

An electrolysis was made under the same conditions as in Example 1 except that the catholyte was drawn out from the catholyte tank **6** directly into the decanter **12** without passing through the acrylonitrile stripper **7** and the decanter **9** for removal of acrylonitrile thereby directly treating the aqueous phase of the catholyte containing acrylonitrile with the cation exchange resin and pH of the catholyte was 8. Results are shown in Table 3. Alkali titration of the aqueous phase of the electrolyte from pH 7 to 11 was held at 4.5 milliequivalents/l.

TABLE 3

Operation time (hr.)	Yield on the basis of acrylonitrile consumed	
	Adiponitrile	Propionitrile
100	93	4.8
1,000	92	5.1

Example 3

An electrolysis was made under the same conditions as in Example 1 except that the catholyte tank **6** was connected to the ion exchange column **13** without passing through the acrylonitrile stripper **7** and the decanters **9** and **12** and pH of the catholyte was 5. Alkali titration of the electrolyte from pH 7 to 11 was 3.5 milliequivalents/l.

TABLE 4

Operation time (hr.)	Yield on the basis of acrylonitrile consumed	
	Adiponitrile	Propionitrile
100	90	6.0
1,000	91	5.9

Example 4

An electrolysis was made using the same electrolyzer as in Example 1, the catholyte used being a homogeneous solution composed of 35% tetramethylammonium p-toluenesulfonate, 15% acrylonitrile, 15% adiponitrile and 35% water, with an electric current of 20 A. at 50° C. While conducting the electrolysis, the solution in the catholyte tank was drawn out in portions, followed by addtion of 1 part of acrylonitrile and 2 parts of water to 1 part of the catholyte to separate the solution into oily and aqueous layers. The aqueous layer was treated in the same way as in Example 1 for purification. Alkali titration of the electrolyte from pH 7 to 11 was held at 5 milliequivalents/l. Results of the experiment conducted under the conditions cited above are shown in Table 5.

TABLE 5

Operation time (hr.)	Yield on the basis of acrylonitrile consumed	
	Adiponitrile	Propionitrile
100	89	5.8
1,000	88	6.0

Reference Example 2

An electrolysis was made under the same conditions as in Example 4 except that the catholyte was not subjected to resin treatment. Results are shown in Table 6.

TABLE 6

Operation time (hr.)	Yield on the basis of acrylonitrile consumed	
	Adiponitrile	Propionitrile
100	80	15.0
1,000	72	21.2

Alkali titration of the electrolyte after 1000 hours' operation from pH 7 to 11 was 35 milliequivalents/l.

Example 5

An electrolysis was made under the same conditions as in Example 4 except that pH of the catholyte was 6, the electrolytic supporting salt was 35% solution of tributylethylammonium ethylsulfate, and the catholyte in homogeneous solution drawn out from the catholyte tank **6** was treated as it was using the cation exchange resin of tributylethylammonium form without passing through the acrylonitrile stripper **7** and the decanters **9** and **12**. Results are shown in Table 7. Alkali titration of the electrolyte from pH 7 to 11 was held at 4.5 milliequivalents/l.

TABLE 7

Operation time (hr.)	Yield on the basis of acrylonitrile consumed	
	Adiponitrile	Propionitrile
100	89	6.0
1,000	88	6.1

Example 6

An electrolysis was made under the same conditions as in Example 1 except that 80 ml. of a strongly acid cation exchange resin of sulfonate type Amberlite 200 in tetraethylammonium form were used in place of the weakly acid cation exchange resin. Alkali titration of the aqueous layer of the electrolyte from pH 7 to 11 was held at 4 milliequivalents/l.

TABLE 8—Results of the electrolysis

Operation time (hr.)	Yield on the basis of acrylonitrile consumed	
	Adiponitrile	Propionitrile
100	90	5.1
1,000	93	4.9

Example 7

An electrolysis was made under the same conditions as in Example 1 except that 50 ml. of a weakly acidic cation exchange resin (Amberlite IRC–84; trade name) of hydrogen form was used as it was and pH was 9. Results are shown in Table 9. Alkali titration of the electrolyte from pH 7 to 11 was 4 milliequivalents/l.

TABLE 9

Operation time (hr.)	Yield on the basis of acrylonitrile consumed	
	Adiponitrile	Propionitrile
100	91	5.2
1,000	92	5.1

Example 8

One hundred l. of the catholyte obtained in Reference Example 1 after 1000 hours' operation were passed through 2 l. of cation exchange resin Amberlite IRC–84 of tetraethylammonium form in a column 2 m. in length x 10 cm.^{2} in sectional area. Then, 0.1 N sulfuric acid was passed at SV–2 for regeneration. From the first fraction in an amount of 15 l. from the beginning was recovered 1770 milliequivalents, i.e., 315 g. as tetraethylammonium sulfate, corresponding to 95% of the tetraethylammonium ion remaining on the resin. The second fraction afterwards contained the electrode reaction-impairing materials. Thus, the separation of tetraethylammonium and the electrode reaction-impairing materials was feasible by the chromatography. The first fraction in an amount of 15 l. was distillated, concentrated and subjected to electrolysis using an electrolyte of the same composition as in Example 1. pH of the electrolyte was 4. Results are shown in Table 10. Alkali titration of the aqueous phase of the electrolyte at the start of electrolysis from pH 7 to 11 was below 4.0 milliequivalents/l.

TABLE 10

Operation time (hr.)	Yield on the basis of acrylonitrile consumed	
	Adiponitrile	Propionitrile
100	92	5.1
1,000	93	4.8

Reference Example 3

The second fraction in an amount of 6 l. from the regeneration in Example 8 was concentrated to recover 60 g. of tetraethylammonium sulfate. An electrolysis was made following adjustment of the composition of electrolyte under the same conditions as in Reference Example 1. Results are shown in Table 11, which indicates that efficient separation of the electrode reaction-impairing materials by chromatographic concentration was achieved in Example 8.

TABLE 11

Operation time (hr.)	Yield on the basis of acrylonitrile consumed	
	Adiponitrile	Propionitrile
20	40	43

Example 9

Forty liters of the catholyte obtained in 1000 hours of operation in the Reference Example 1 were passed through the first column packed with 2 l. of a weakly acidic cation exchange resin Amberlite IRC–84 of tetraethylammonium form. The resin was regenerated with 2.2 l. of 1 N sulfuric acid and then washed with 1.8 l. of purging water 4 l. of the effluent being regenerated. Composition of the outflow is as follows:

Outflow from the first column: 4.0 l.
$[(C_2H_5)_4N]_2SO_4$: 1564 meq.
H_2SO_4: 344 meq.
Electrode reaction-impairing materials: 356 meq.

The outflow was then passed through the second column packed with 1.1 l. of a weakly acidic cation exchange resin Amberlite IRC–84 for regeneration in the same way as with the first column.

Outflow from the second column: 2.2 l.
$[(C_2H_5)_4N]_2SO_4$: 390
H_2SO_4: 120
Electrode reaction-impairing materials: 349

The outflow was further passed through the third column packed with 0.6 l. of the resin, which was then regenerated in the same way as above to give the following outflow.

Outflow from the third column: 1.2 l.
$[(C_2H_5)_4N]_2SO_4$: 110
H_2SO_4: 65
Electrode reaction-impairing materials: 343

The outflow was eliminated out of the system. As shown, removal of the electrode reaction-impairing materials by concentration by the use of a multi-stage ion exchange treatment was feasible.

Example 10

The same outflow as from the first column in Example 9, 7.5 l., was concentrated by distillation to a concentration of tetraethylammonium sulfate of about 50%. One liter of the resulting liquor was subjected to continuous extraction using 1 l. of 1,2-dichloroethane for 24 hours to extract the electrode reaction-impairing materials into the 1,2-dichloroethane layer. From the purified aqueous solution was removed 1,2-dichloroethane by distillation followed by electrolysis under the same conditions as in Example 1. Results are shown in Table 12. Titration of the aqueous phase of the electrolyte at the start of electrolysis from pH 7 to 11 was 4 milliequivalents/l.

TABLE 12

Operation time (hr.)	Yield on the basis of acrylonitrile consumed	
	Adiponitrile	Propionitrile
100	90	5.9
1,000	91	6.0

Example 11

Five liters of the same liquid as one discharged from the first column in Example 9 were treated with a dialytic diaphragm made of bundles of nylon yarns which had been immersed in formic acid to selectively pass tetraethylammonium sulfate for separation of the electrode reaction-impairing materials. Recovery of tetraethylammonium sulfate was at 70%. The resulting liquid was subjected to electrolysis in the same way as in Example 1. Results are shown in Table 13. Alkali titration at the beginning of electrolysis from pH 7 to 11 was 6 milliequivalents/l.

TABLE 13

Operation time (hr.)	Yield on the basis of acrylonitrile consumed	
	Adiponitrile	Propionitrile
100	91	6.0
1,000	89	6.3

8 l. of the same outflow as one discharged from the regeneration step of the first column in Example 9 was concentrated to 3 l. The resulting liquid was used as the anolyte in the electrolysis using the same electrolyzer as in Example 1 except that 3 l. of 2 N sulfuric acid were used as the catholyte and iron was used as the cathode, at a flow rate of 50 cm./sec. with an electric current of 50 A. at a temperature of 50° C. for 10 hours. Tetraethylammonium ion transferred into the catholyte was 2.3 equivalents.

An electrolysis was made using the resulting catholyte under the same conditions as in Example 1. Titration of the aqueous phase of the electrolyte at the start of electrolysis from pH 7 to 11 was 5 milliequivalents/l. Results of the electrolysis are shown in Table 14.

TABLE 14

Operation time (hr.)	Yield on the basis of acrylonitrile consumed	
	Adiponitrile	Propionitrile
100	90	5.1
1,000	89	5.2

Example 14

Five liters of the catholyte obtained after 1000 hours of operation in Reference Example 1 were passed through 100 ml. of a weakly acidic cation exchange resin of tetraethylammonium form at SV=1. Then, 1.1 l. of 0.1 N sulfuric acid was passed at SV=2 for regeneration. Then, 1.1 l. of 0.1 N aqueous solution of tetraethylammonium hydroxide was passed at SV=2 to convert the resin to the tetraethylammonium form. The procedures for regeneration and adsorption were repeated 20 times. The liquid obtained after the 20th purification was used for electrolysis under the same conditions as in Example 1. Results of the electrolysis are shown in Table 15. Alkali titration of the aqueous phase of the electrolyte at the beginning of electrolysis was 4 milliequivalents/l.

TABLE 15

Operation time (hr.)	Yield on the basis of acrylonitrile consumed	
	Adiponitrile	Propionitrile
100	92	5.4
1,000	93	5.5

Example 14

An experiment was made in the same way as in Example 1 except that, in place of partition between the anode and the cathode and use of liquids of different compositions as the anolyte and catholyte in Example 1, no diaphragm was placed between the anode and the cathode and 10% sodium acid phosphate and 1% tetraethylammonium acid phosphate were used as the electrolytic supporting salt. Results are shown in Table 16.

TABLE 16

Operation time (hr.)	Yield on the basis of acrylonitrile consumed	
	Adiponitrile	Propionitrile
100	73	19
400	72	19

Reference Example 4

An electrolysis was made under the same conditions as in Example 14 except that no resin treatment was applied to the electrolyte. Results are shown in Table 17.

TABLE 17

Operation time (hr.)	Yield on the basis of acrylonitrile consumed	
	Adiponitrile	Propionitrile
100	67	22
400	40	50

Example 15

An electrolysis was made under the same conditions as in Example 1 except that the electrolytic supporting salt was 20% sodium sulfate and the resin of sodium form was used. Results are shown in Table 18.

TABLE 18

Operation time (hr.)	Yield on the basis of acrylonitrile consumed	
	Adiponitrile	Propionitrile
100	63	32
500	62	33

Reference Example 5

An electrolysis was made under the same conditions as in Example 15 except that no resin treatment was applied to the electrolyte. Results are shown in Table 19.

TABLE 19

Operation time (hr.)	Yield on the basis of acrylonitrile consumed	
	Adiponitrile	Propionitrile
100	60	36
500	55	40

We claim:

1. In the process for hydrodimerizing acrylonitrile, the improvement which comprises contacting an electrolyte effluent containing an electrolysis-supporting salt, acrylonitrile, adiponitrile and electrode reaction-impairing materials with a cation exchange resin, thereby removing the electrode-reaction impairing materials by adsorpton on the resin and circulating the solution having passed through the ion exchange resin into the electrolytic cell for reuse in the electrolysis while conducting the electrolysis.

2. Method according to claim **1** wherein the electrolyte effluent is an emulsion.

3. Method according to claim **2** wherein said emulsion is separated into oily and aqueous layers and the aqueous layer alone is contacted with the cation exchange resin.

4. Method according to claim **1** wherein the electrolyte is a homogeneous solution.

5. Method according to claim **4** wherein acrylonitrile and water are added to said homogeneous solution to separate into aqueous and oily layers and the aqueous layer alone is contacted with the cation exchange resin.

6. Method according to claim **1** wherein contact with the cation exchange resin is carried out following removal of acrylonitrile from the electrolyte effluent or the aqueous layer separated therefrom to be contacted with the cation exchange resin.

7. Method according to claim **1** wherein concentration of said electrode reaction-imparting materials in said electrolyte or in said aqueous phase is below 15 milliequivalents/l. in terms of the amount of alkali required for titration from pH 7 to 11.

8. Method according to claim **1** wherein said ion exchange resin is a weakly acidic cation exchange resin.

9. Method according to claim **1** wherein said weakly acidic cation exchange resin is in the form of cation of said supporting salt.

10. Method according to claim **1** wherein said supporting salt is a quaternary ammonium salt.

11. Method according to claim **10** wherein the amount of said electrolyte or said aqueous layer to be contacted with the cation exchange resin is above the exchange capacity of said resin.

12. Method according to claim **1** wherein said ion exchange resin is of H-form.

13. Method according to claim **1** wherein the electrode reaction-imparting materials and the cation of the supporting salt adsorbed on the resin are separated by ion exchange chromatography, the earlier effluent containing the cation of the supporting salt is recycled to the electrolytic cell and the later effluent containing the electrode reaction-impairing materials is eliminated out of the system.

14. Method according to claim **1** wherein the cation exchange resin with the electrode reaction-impairing materials and the cation of said supporting salt adsorbed is regenerated with an acid, the passage of a portion or the whole of the regeneration liquid through a cation exchange resin and the regeneration thereof with acid are repeated once or more and the regeneration liquid thus purified is recycled to the electric cell for use in electrolysis.

15. Method according to claim **1** wherein the cation exchange resin loaded with the electrode reaction-impairing materials and the cation of said supporting salt is regenerated with an acid, a portion or the whole of the resulting outflow is extracted with an organic solvent to transfer the electrode reaction-impairing materials into the organic phase and the outflow thus purified is recycled to the electrolytic cell for use in the electrolysis.

16. Method according to claim **1** wherein the cation exchange resin loaded with the electrode reaction-impairing materials and the cation of the supporting salt is regenerated with an acid, a portion or the whole of the resulting outflow is dialyzed by means of a diaphragm which selectively passes the cation of the supporting salt only and then the effluent thus enriched with the cation of the supporting salt is recycled to the electrolytic cell.

17. Method according to claim **1** wherein the cation exchange resin loaded with the electrode reaction-impairing materials and the cation of the supporting salt is regenerated with an acid, a portion or the whole of the resulting outflow is electrodialyzed and the resulting catholyte enriched with the cation of the supporting salt is recycled to the electrolytic cell.

18. Method according to claim **1** wherein the amount of electrolyte to be treated is from 0.1 to 20 ml./a. hr.

19. Method according to claim **1** wherein pH of the electrolyte is from 3 to 10.

20. Method according to claim **1** wherein the amount of the resin used is from 0.0002 to 1 ml./a. hr. in terms of the resin of hydrogen form.

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F. C. EDMUNDSON, Primary Examiner

U.S. Cl. X.R.

204—237

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,682,793 Dated August 8, 1972

Inventor(s) Maomi Seko et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 3, line 6

"methacrylate-divinylbenzene resin and phenolcarbox-" should read -- polystyrene-divinylbenzene resin and phenolsulfonate --.

Col. 8, line 8

Under Adiponitrile, "90" should be -- 91 --.

Col. 8, line 32

"SV-2" should be -- SV=2 --.

Col. 11, line 33

"adsorpton" should be -- adsorption --.

Signed and sealed this 9th day of January 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents