

Aug. 16, 1966

C. R. CAMPBELL ETAL
PRODUCT SEPARATION AND RECOVERY IN
ADIPONITRILE MANUFACTURE

3,267,131

Filed April 27, 1964

3 Sheets-Sheet 1

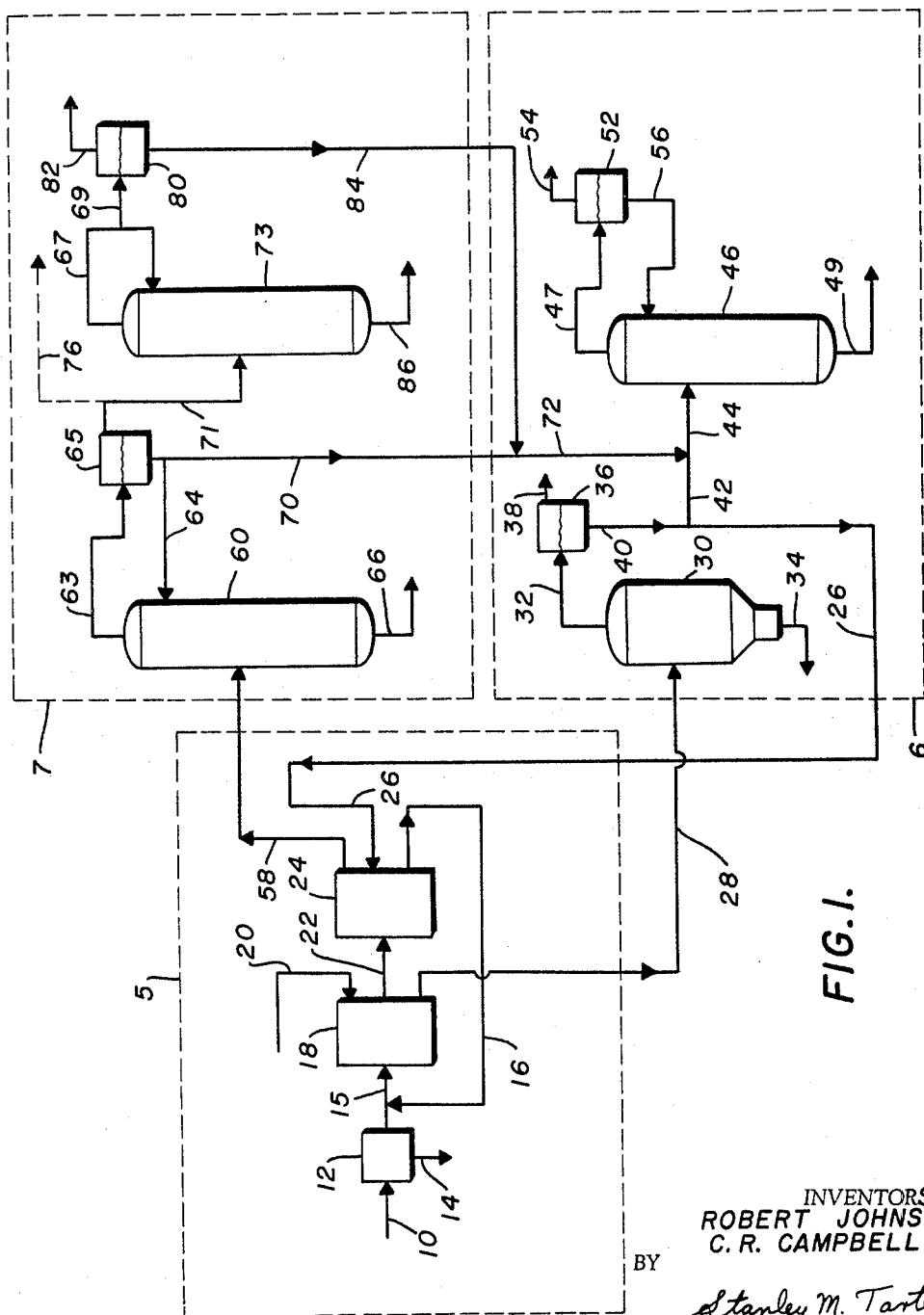


FIG. 1.

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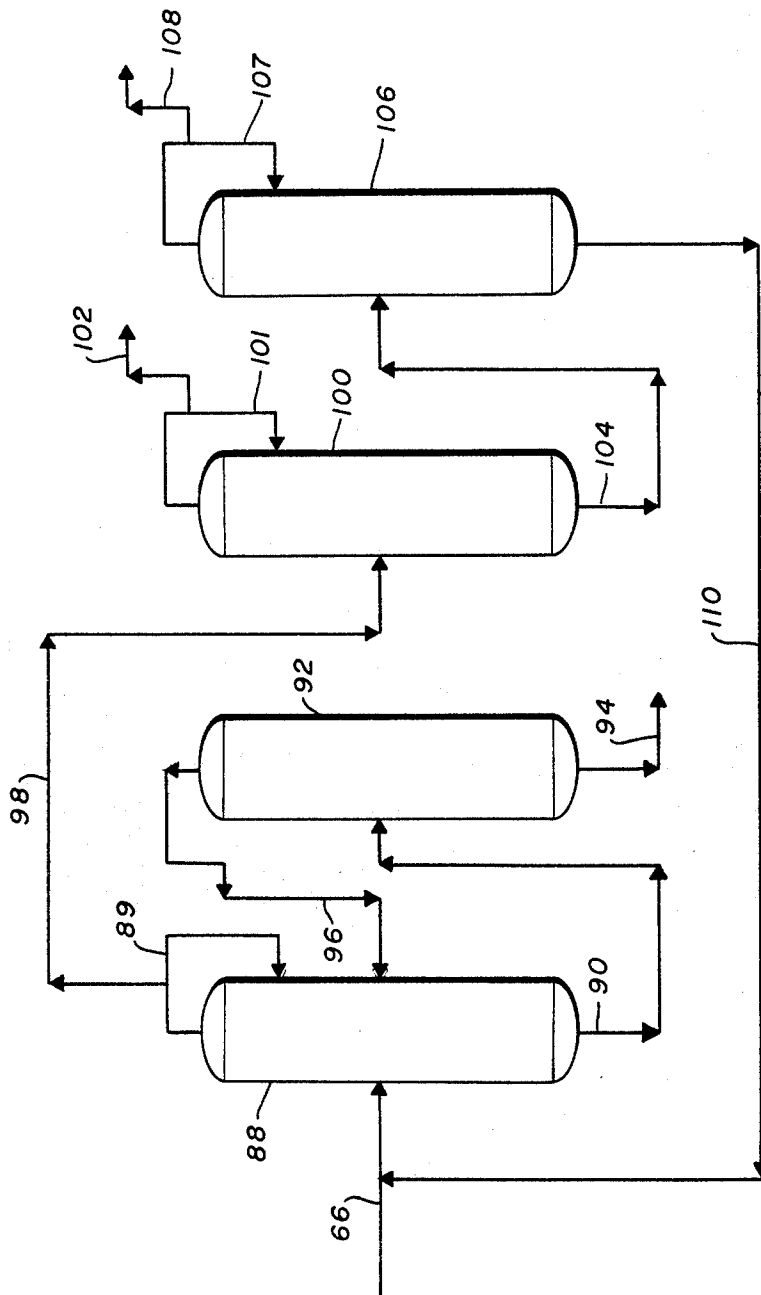


FIG. 2.

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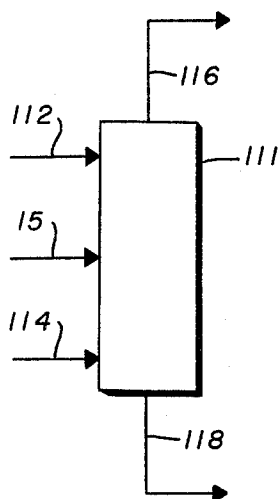


FIG. 3.

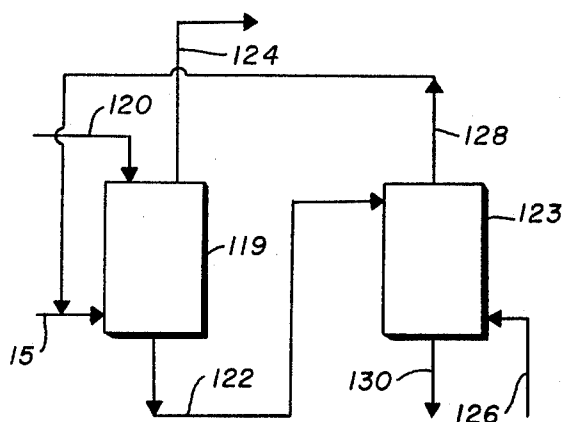


FIG. 4.

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PRODUCT SEPARATION AND RECOVERY IN ADIPONITRILE MANUFACTURE

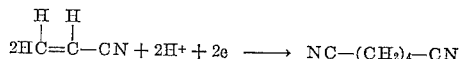
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11 Claims. (Cl. 260-465.8)

The present invention relates to the separation and recovery of various components in the cathode effluent from the electrolytic manufacture of adiponitrile. More particularly, it relates to a process for the separation and recovery of acrylonitrile, adiponitrile and quaternary ammonium salt contained in the cathode effluent from the electrohydrodimerization of acrylonitrile to adiponitrile.

It is known that adiponitrile can be produced by the electrohydrodimerization of acrylonitrile. The reaction takes place in the cathode compartment of a multi-compartmented electrolytic cell. In the anode compartment an aqueous solution of a strong mineral acid, such as sulfuric acid, continuously circulates. For best results the anode compartment is separated from the cathode compartment by a cation exchange membrane. An aqueous solution of acrylonitrile and an electrolyte circulates continuously through the cathode compartment. As current passes from electrode to electrode through the conducting solutions and membrane, some of the acrylonitrile is converted to adiponitrile according to the following reaction:



The adiponitrile forms at the cathode and is withdrawn in the cathode effluent along with reaction by-products that may include propionitrile, bis-cyanoethylether, hydroxypropionitrile and other, high boiling materials.

Quaternary ammonium salts are effectively employed as electrolytes in the electrohydrodimerization of acrylonitrile to adiponitrile. Among such salts are tetramethylammonium salts of benzoic, ethylbenzene sulfonic, toluene sulfonic, xylene sulfonic and benzene sulfonic acids; triethylmethylammonium salts of toluene sulfonic acid; and benzyltrimethylammonium salts of sulfuric and benzene sulfonic acids.

It is necessary for the economic operation of the electrohydrodimerization process to provide a method for recovering unconverted acrylonitrile and electrolyte for reuse in the electrohydrodimerization cell. Furthermore, a method must be provided for separating, recovering and refining the desired reaction product, namely adiponitrile.

Therefore, an object of this invention is to provide a method for selective separation and recovery of unconverted acrylonitrile, adiponitrile, and electrolyte contained in the cathode effluent from the electrohydrodimerization of acrylonitrile to adiponitrile.

A further object is the provision of a method for refining electrolytically produced adiponitrile to the purity demanded for use as an intermediate material in the production of nylon.

Other objects will become apparent from the herein-after detailed description.

The above objects are generally achieved in the provision of a process comprising three major steps. Cathode effluent is first extracted with both water and acrylonitrile. This extraction produces both an acrylonitrile phase containing substantially all of the adiponitrile in the cathode effluent and an aqueous phase containing substantially all of the quaternary ammonium salt in the cathode effluent. The aqueous phase is then passed to an evaporation zone wherein some water and most acrylonitrile solubilized therein is removed, thereby con-

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centrating the quaternary ammonium salt solution. The acrylonitrile phase containing substantially all of the adiponitrile is fractionally distilled to remove substantially all of the adiponitrile therefrom.

FIGURE 1 is a simplified flow diagram illustrating a process for the separation and recovery of acrylonitrile, adiponitrile and quaternary ammonium salt from the cathode effluent in the electrohydrodimerization of acrylonitrile to adiponitrile.

FIGURE 2 is a simplified flow diagram of a distillation train employed to refine crude adiponitrile to a high degree of purity.

FIGURE 3 is a simplified flow diagram illustrating another embodiment of the process.

FIGURE 4 is a simplified flow diagram illustrating a still further embodiment of the process.

Extraction may be performed using customary equipment. For example, extraction may take place in packed towers, with countercurrent phase flow; in a series of mixer and decanter vessels; or in those extractors employing centrifugal force in phase separation.

Catholyte, i.e. cathode effluent, composition can and usually does vary to a certain degree. In the table set out next below an example of a typical catholyte composition is shown.

Component:	Weight percent
Acrylonitrile	16
Adiponitrile and by-products	16
Water	31
Quaternary ammonium salt	37

To further describe the invention reference should now be made to FIGURE 1. It must be emphasized that this is a block-flow diagram. No attempt will be made to describe in detail each piece of equipment or unit operation employed as an integral part of the process.

As will be noted from FIGURE 1 the separation and recovery process is divided into three major zones, as shown by the dotted lines: extraction zone 5, evaporation zone 6, and distillation zone 7. This detailed description is for one embodiment of the invention. Other embodiments will be described hereinafter.

Cathode effluent in line 10 is first filtered by filter 12. Solids filtered from the cathode effluent are drawn off through line 14 and discarded. Filtrate is fed to the first extractor 18 through line 15. Before entering extractor 18 the filtrate in line 15 is diluted with an aqueous phase recycle stream flowed through line 16 from aqueous extractor 24. Additional water thereto, if required, may also be added. Acrylonitrile supplied via extractant feed line 20 is contacted with the diluted filtrate of line 15 in extractor 18. The acrylonitrile phase containing adiponitrile is fed from extractor 18 through line 22 to water extractor 24 to therein substantially remove quaternary ammonium salt. The aqueous extractant stream in line 26 may be recycled from evaporation zone 6, or pure water may be employed. Recycle stream in line 26 from evaporation zone 6 is an aqueous solution comprised of water and some dissolved acrylonitrile.

The aqueous phase containing quaternary ammonium salt is fed from extractor 18 by line 28 to evaporator 30.

Conditions of temperature and pressure in evaporator 30 are so controlled as to produce a tails in line 34 having a salt composition of about 45-75 weight percent. Head pressure in the evaporator can range from 200 mm. of Hg to above atmospheric. Base temperature can be in the order of about 70-150° C. Make in line 32 from evaporator 30 is condensed and fed to decanter 36. In decanter 36 a phase separation into an acrylonitrile and an aqueous phase takes place. The acrylonitrile phase is withdrawn from decanter 36 by line 38 and the aqueous phase is withdrawn through line 40. Acrylonitrile phase effluent

in line 38 is primarily acrylonitrile with a minor quantity of water therein. This phase is suitable for use in the acrylonitrile extraction of zone 5 or as a feed material for the cell itself. Aqueous phase effluent in line 40 is withdrawn from decanter 36. Thereafter a portion of the aqueous phase in line 40 is taken off in line 42 and the other portion recycled through line 26 to water extractor 24. Aqueous phase effluent in line 40 may be completely recycled in line 26. In general, however, only a portion of the aqueous phase effluent in line 40 is needed as recycle for extraction. Line 42 is joined by line 72 to form the total acrylonitrile recovery feed in line 44. Line 72 represents the flow of aqueous solution containing minor quantities of acrylonitrile from distillation zone 7. Acrylonitrile recovery column 46 produces a make contained in line 47 of acrylonitrile and water and a tails of waste water withdrawn by line 49. Make in line 47 is condensed and fed to decanter 52 which separates the make into an acrylonitrile phase effluent in line 54 and an aqueous phase effluent in line 56. Aqueous phase effluent in line 56, containing some acrylonitrile, is fed back to column 46 for further acrylonitrile recovery. Acrylonitrile recovery column 46 can be operated at atmospheric pressure and a base temperature of 100° C.; however, operating conditions may vary when such is thought necessary.

The order of evaporator and acrylonitrile recovery column in zone 6 can be reversed so that acrylonitrile is recovered from the distillation column make. The tails from this distillation is then evaporated to form a make of waste water and a tails of quaternary ammonium salt solution.

The acrylonitrile phase in line 58 from extraction zone 5, specifically extractor 24, is fed to acrylonitrile recovery column 60. Column 60 produces a make drawn off by line 63 which has as major components therein acrylonitrile, propionitrile and water. Make in line 63 is condensed and decanted in decanter 65 to produce an acrylonitrile phase effluent flowed through lines 71 or 76 depending on whether or not removal of propionitrile therefrom is desired. A portion of the aqueous phase from decanter 65 is refluxed to column 60 by line 64. Aqueous phase effluent in line 70 is fed to acrylonitrile recovery column 46 in evaporation zone 6. When it is preferred to remove propionitrile from the acrylonitrile phase of decanter 65, this phase is fed in line 71 to propionitrile recovery column 73 having reflux system 67. In propionitrile recovery column 73 the feed in line 71 is separated into a make in line 69 of acrylonitrile and water and a tails in line 86 of propionitrile. Make in line 69 is condensed and fed to decanter 80 where a separation into an acrylonitrile phase withdrawn in line 82 and an aqueous phase withdrawn in line 84 takes place. Effluent in line 82 can be reused as either the extraction solvent in extractor 18 or as feed for the electrohydrodimerization process. Both aqueous effluents in lines 70 and 84 are joined to form the stream in line 72 which is fed to acrylonitrile recovery column 46 in evaporation zone 6.

Crude adiponitrile tails 66 contains adiponitrile, bis-cyanoethylether, hydroxypropionitrile, traces of quaternary ammonium salt and some miscellaneous high boiling materials. The extraction system can be operated so that the amount of quaternary ammonium salt in the tails from column 60 is less than 0.1 percent. When the quantity of quaternary ammonium salt remaining in the tails stream of line 66 is too great, it can be water washed to reduce the salt content.

Temperature and pressure of acrylonitrile stripping column 60 are not extremely critical. Atmospheric pressure and temperatures from 170 to 225° C. are considered as acceptable. Propionitrile column 73 is normally operated at substantially atmospheric pressure with the head pressure depending upon the water concentration in the feed. Operating reflux ratio in column 73 is determined by the

level of acrylonitrile that is to be allowed to remain in the tails in line 86.

An acrylonitrile polymerization inhibitor is usually fed into the reflux of those columns that have acrylonitrile as a major component therein. When this practice is not followed, undesired fouling of column trays or packing may result. P-aminophenol, or the like, is acceptable for use as a polymerization inhibitor at levels from 5 to 300 p.p.m.

Crude adiponitrile must be refined before it can be used in the manufacture of hexamethylenediamine for making nylon. Adiponitrile for use in nylon production must have a high degree of purity. When this is not true, fouling of the nitrile hydrogenation catalyst and poor quality nylon may result.

Therefore, crude adiponitrile tails in line 66 is fed to the distillation train outline in FIGURE 2. Column 88 having reflux system 89 and stripper 92 are operated together for the removal of bis-cyanoethylether and other high boiling impurities. Bis-cyanoethylether can be effectively separated from adiponitrile by fractional distillation; but when collected as a high boiling residue, it tends to thermally decompose to acrylonitrile and hydroxypropionitrile. For this reason the distillation to remove the ether is performed first. High boiler removal column 88 tails in line 90 composed of bis-cyanoethylether, some other high boilers and adiponitrile are fed to adiponitrile stripper 92, where the bis-cyanoethylether and high boiling impurities are removed as waste tails by line 94. Adiponitrile is stripped out as make in line 96 and returned to column 88 as a second feed stream. Make in line 98 from column 88 having adiponitrile, hydroxypropionitrile, and the acrylonitrile generated in column 88 and stripper 92 is fed to low boiler removal column 100 having reflux system 101 where acrylonitrile and hydroxypropionitrile are removed as waste make in line 102. It has been determined that hydroxypropylamine, an objectionable impurity, is very difficult to remove from hexamethylenediamine by distillation. Therefore, it is important to effectively remove its precursor, hydroxypropionitrile, before hydrogenating adiponitrile to hexamethylenediamine. Low boiler removal column 100 must be operated so as to keep hydroxypropionitrile concentration in the tails of line 104 to a very low level. Tails in line 104 are fed to adiponitrile refining column 106 having reflux system 107 wherein refined adiponitrile is distilled overhead as the make in line 108. High boiling impurities containing some adiponitrile are recycled through line 110 to high boiler removal column 88.

Operating conditions in the distillation train are set by the level of purity desired in the recovered adiponitrile. However, it must be kept in mind that at elevated temperatures adiponitrile decomposes. Adiponitrile is distilled in three columns of the four-column train; therefore, only low boiler removal column 100 can be operated at a head pressure exceeding 25 mm. of Hg. Preferably, all distillation columns should be operated at or near 10 mm. of Hg. This distillation train can produce a product having greater than 99.1 weight percent adiponitrile therein.

Another embodiment of the invention is illustrated by FIGURE 3. This figure illustrates a variation in the extraction procedure.

With reference to FIGURE 3, cathode effluent 15, numbered as in FIGURE 1, is fed to extraction zone 111. Water flows into the zone at the top portion thereof by way of line 112. Line 114 feeds acrylonitrile into the zone at the bottom portion thereof. As catholyte comes into extracting contact with the rising acrylonitrile adiponitrile and reaction by-products are extracted therefrom. After water enters the zone it moves downwardly extracting quaternary ammonium salt from the acrylonitrile phase as it so moves. It must be understood that this extraction takes place in a multistage extraction procedure, thus providing for substantially complete extraction of both adiponitrile and quaternary ammonium salt. Line 116

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has contained therein the substantially quaternary ammonium salt free, adiponitrile containing acrylonitrile phase. This line leads to adiponitrile stripping zone 60 as represented in FIGURE 1. Thereafter the procedure for separation and purification of adiponitrile is the same as that process described in conjunction with FIGURES 1 and 2. Line 118 carries the substantially adiponitrile free, quaternary ammonium salt containing aqueous phase to evaporation zone 30 as shown in FIGURE 1. Thereafter the process is the same as represented in FIGURE 1.

FIGURE 4 represents a still further embodiment of the invention. Cathode effluent 15 enters water extraction zone 119 at the bottom portion thereof. Water is fed to this zone at the top portion thereof through line 120 countercurrently with respect to acrylonitrile in the cathode effluent and emits via line 122. An acrylonitrile phase containing substantially all of the adiponitrile and reaction by-products and substantially free of quaternary ammonium salt exits from the top of the zone. This acrylonitrile phase is fed via line 124 to fractional distillation zone 60 as shown in FIGURE 1. The aqueous phase in line 122 is fed to acrylonitrile extractor 123 at the top portion thereof. Acrylonitrile is fed via line 126 to extraction zone 123 in a countercurrent fashion with respect to the aqueous phase in line 122. The acrylonitrile phase containing substantially all of the adiponitrile and to the cathode effluent feed stream in line 15. The aqueous phase is withdrawn from the bottom portion of zone 123 via line 130 and fed to evaporator 30 as shown in FIGURE 1. It must be noted that, as in FIGURE 3, the process is the same as shown in FIGURE 1 except for the extraction step.

Hereinafter are examples further describing the process. These examples are intended to be illustrative and are not meant to limit the invention in any way.

EXAMPLE I

This example describes a laboratory process employing the basic process of the present invention.

A 57 pound sample of catholyte having the composition shown next below was collected.

Composition of catholyte

Component:	Percent composition by weight
Tetramethylammonium toluene sulfonate	38.04
Water	31.36
Acrylonitrile	14.51
Propionitrile	0.43
Hydroxypropionitrile	0.07
Adiponitrile	14.69
Bis-cyanoethylether	0.26
Miscellaneous high boilers	0.64

The above described catholyte was filtered and diluted with 8.8 pounds of water. Diluted catholyte was fed to a 10 gallon mixing settling tank where six liters of acrylonitrile were added with stirring. After thorough mixing, the acrylonitrile and aqueous phases were allowed to separate. The lower, aqueous, layer was decanted and extracted four more times, employing six liters of acrylonitrile per extraction. The aqueous residue was then thoroughly stripped of acrylonitrile by fractional distillation and concentrated by evaporation to obtain 30.2 pounds of recovered quaternary ammonium salt suitable for recycle to the electrohydrodimerization cell. This solution is described next below.

Composition of recycle solution

Component:	Percent composition by weight
Tetramethylammonium toluene sulfonate	63.35
Water	35.23
Acrylonitrile	0.74
Hydroxypropionitrile	0.04
Adiponitrile	0.64

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The combined upper layers from the acrylonitrile extraction were then washed twice with two liters of water. The water layers were in turn backwashed with fresh acrylonitrile and discarded. The acrylonitrile phases were then combined and evaporated in a small continuous evaporator at 400 mm. of Hg and 110–115° C. The make containing water, acrylonitrile and propionitrile was condensed and decanted. The upper layer was saved for atmospheric fractionation to remove propionitrile and recover acrylonitrile. A tails or residue of 7.8 pounds of crude adiponitrile having the composition described next below was collected.

Crude adiponitrile composition

Component:	Percent composition by weight
Adiponitrile	92.59
Hydroxypropionitrile	0.42
Bis-cyanoethylether	2.01
Miscellaneous high boilers	4.98

A charge of 757 grams of crude adiponitrile having the above composition was fractionated in a glass-packed column at 10 mm. of Hg head pressure. A forecut of 15.1 grams was recovered. Then a heartcut boiling at 154–155° C. was obtained at a reflux ratio of 3:1 leaving a residue of 79.6 grams. Each fraction is described below.

Fraction	Component	Percent Composition By Weight
Forecut	Hydroxypropionitrile	14.94
	Other low boilers ¹	5.69
	Adiponitrile	79.37
Heartcut	Hydroxypropionitrile	0.03
	Other low boilers ²	0.116
	Adiponitrile	99.85
	Bis-cyanoethylether	0.004
Residue	Adiponitrile	28.26
	Bis-cyanoethylether	15.45
	High boilers ³	56.29

¹ Other low boiling impurities are principally traces of methylglutaronitrile, succinonitrile and water.

³ High boilers are primarily 2-cyanoethyladiponitrile.

EXAMPLE II

With reference to FIGURES 1 and 2 this example describes in detail a process for achieving the stated objects of this invention. The composition of the cathode effluent to be processed is shown next below.

Composition of catholyte

Component:	Percent composition by weight
Tetramethylammonium toluene sulfonate (TMATS)	39.86
Water	28.45
Acrylonitrile (AN)	15.82
Propionitrile (PN)	0.79
Hydroxypropionitrile (HOPN) ¹	0.21
Adiponitrile (ADN)	13.54
Bis-cyanoethylether (BCE)	0.55
High boilers ²	0.78

¹ And other impurities of similar boiling point.

² Primarily 4-cyanosuberonitrile.

The catholyte is filtered in filter 12 and mixed with the aqueous effluent from water extractor 24 and introduced into the top of AN extractor 18. Recovered AN is introduced into the bottom of the AN extractor 18 for the extraction of ADN and synthesis by-products from the electrolyte. The AN extractor overhead stream is pumped through line 22 into the bottom of the water extractor 24. A portion of the aqueous make from TMATS evaporator 30 is introduced into TMATS extractor 24, via line 26, to remove residual traces of TMATS from the AN extract. The aqueous phase, substantially freed of ADN and by-products, is pumped through line 28 to TMATS evaporator 30.

The overhead from the TMATS extractor is fed through line 58 to the AN stripper 60. The AN stripper is a

packed column operating at atmospheric pressure with a head temperature of approximately 90° C. and a base temperature of 210° C. Tails having the following composition are withdrawn from the column as dry crude ADN.

Composition of dry crude ADN

Component:	Percent composition by weight
Water -----	0.80
AN -----	0.23
HOPN -----	0.67
ADN -----	90.00
BCE -----	3.04
High boilers -----	5.25

The make from AN stripper 60 is condensed and flows to decanter 65 where an aqueous phase and an AN phase separate. A portion of the lower layer is returned via line 63 to the AN stripper as reflux. The balance of the lower layer flows through line 70 to the AN recovery column. The AN layer from decanter 65 containing 2.5 weight percent H₂O and approximately 4 weight percent PN is pumped through line 71 to PN purge column 73. This column is a packed fractionation column operated at atmospheric pressure with a head temperature of approximately 75° C., a base temperature of approximately 95° C. and a reflux ratio of 4:1. PN is purged from the bottom of this still in the tails stream. Recovered AN is taken overhead and is removed via line 82 to recycle AN storage.

Evaporator 30 is operated at a pressure of 300 mm. of Hg. AN and excess water are removed from the salt which is evaporated to a base temperature of 87° C. Aqueous salt solution is removed as evaporator bottoms through line 34 for recycle to the electrolytic cells. The composition of the recycle TMATS solution is as follows:

Composition of recycle salt

Component:	Percent composition by weight
TMATS -----	74.1
Water -----	24.7
HOPN -----	0.2
ADN -----	1.0

The make from the TMATS evaporator is condensed and flows via line 32 to decanter 36. The upper layer, which is primarily AN, is removed via line 38 to AN storage. The lower layer flows via line 40 to the AN recovery column. A portion of this flow is diverted via line 26 for use as TMATS extractor solvent. The lower layer from the AN stripper decanter also flows to the AN recovery column via lines 70 and 44. The feed to this column contains approximately 8 weight percent AN. The AN recovery column is a packed fractionating column operated at atmospheric pressure. Waste water is withdrawn as tails from this column at a base temperature of 105° C. and is purged through line 49. The vapors from this column are condensed and flow via line 47 to decanter 52. All of the lower layer from this decanter is returned as reflux through line 56. The upper AN layer containing 1 weight percent PN and 2.5 weight percent H₂O is removed via line 54 to recycle AN storage.

Dry crude ADN is fed into the lower third of the high boiler removal column 88 by line 66. This fractionating column is operated at a head pressure of 15 mm. of Hg, a base temperature of 210° C., and a reflux ratio of 0.5:1. The tails from this column are fed via line 90 to ADN stripper 92. The ADN stripper is a simple evaporator operated at a pressure of 5 mm. of Hg and a temperature of 215° C. without reflux. Tails in line 94 from column 92 contain 4.56 weight percent ADN and are purged to waste. The make from the column is returned via line 96 to the high boiler removal column. The make from column 88 is then pumped via line 98 to the low boiler removal column 100.

Low boiler removal column 100 is a packed column operated at a head pressure of 15 mm. of Hg, a reflux ratio of 7:1, and a base temperature of 210° C. Low boiling impurities, containing 25 weight percent ADN, are purged overhead through line 102. The tails from this column are pumped through line 104 to the ADN refining column 106.

The ADN refining column is operated at a head pressure of 15 mm. of Hg and a reflux ratio of 0.7:1. Tails are withdrawn from this column and recycled via line 110 to the high boiler removal column. The make from the ADN refining column is refined ADN of suitable quality for hydrogenation to hexamethylenediamine and is pumped to storage via line 108.

The economic utilization of the electrohydrodimerization of acrylonitrile to adiponitrile process requires a method for the efficient separation and recovery of the various components in the catholyte employed in this reaction. The instant process provides such a method. Unexpended acrylonitrile is recovered from the catholyte and may be recycled to the electrohydrodimerization cell. The electrolyte, quaternary ammonium salt, can be efficiently and economically recovered for reuse in the cell. Finally, the process provides a method for the recovery and purification of the end product of the electrohydrodimerization, adiponitrile. Without such a separation and recovery system economical operation of the electrohydrodimerization process might not be possible.

We claim:

1. A method for the selective separation of adiponitrile and quaternary ammonium salt contained in the cathode effluent from the electrohydrodimerization of acrylonitrile to adiponitrile comprising diluting said effluent with acrylonitrile and water to provide an acrylonitrile phase and an aqueous phase while extracting said acrylonitrile phase in countercurrent multistage fashion with said water and extracting said aqueous phase in countercurrent multistage fashion with said acrylonitrile to produce an aqueous extract phase containing quaternary ammonium salt substantially free of reaction products and to produce an acrylonitrile extract phase substantially containing the reaction products and substantially free of quaternary ammonium salt.

2. A method for the selective separation of adiponitrile and quaternary ammonium salt contained in the cathode effluent from the electrohydrodimerization of acrylonitrile to adiponitrile comprising centrally feeding said effluent into an extraction zone having a top and a bottom while feeding acrylonitrile into the bottom portion of said zone and feeding water into the top portion of said zone thereby producing an aqueous extract phase containing quaternary ammonium salt substantially free of reaction products at the bottom of said zone and to produce at the top of said zone an acrylonitrile extract phase substantially containing the reaction products and substantially free of quaternary ammonium salt.

3. A method for the selective separation of adiponitrile and quaternary ammonium salt contained in the aqueous cathode effluent from the electrohydrodimerization of acrylonitrile to adiponitrile comprising the steps of:

(a) in a first zone contacting said cathode effluent in extracting relationship with water to produce an acrylonitrile extract phase substantially containing the reaction products and substantially free of quaternary ammonium salt and an aqueous phase;

(b) in a second zone contacting said aqueous phase in extracting relationship with acrylonitrile to produce an acrylonitrile extract phase and an aqueous phase containing quaternary ammonium salt substantially free of reaction products; and

(c) recycling the acrylonitrile extract phase of step (b) to said first zone.

4. A method for the selective separation of adiponitrile and quaternary ammonium salt contained in the aqueous

cathode effluent from the electrohydrodimerization of acrylonitrile to adiponitrile comprising the steps of:

- (a) in a first zone contacting said cathode effluent in extracting relationship with water to produce an acrylonitrile extract phase substantially containing the reaction products and substantially free of quaternary ammonium salt and an aqueous phase;
- (b) in a second zone contacting said aqueous phase in extracting relationship with acrylonitrile to produce an acrylonitrile extract phase and an aqueous phase containing quaternary ammonium salt substantially free of reaction products;
- (c) recycling the acrylonitrile extract phase of step (b) to said first zone;
- (d) flowing the aqueous phase of step (b) to a zone having evaporating conditions therein thus producing a make comprised of water and acrylonitrile and a tails comprised of quaternary ammonium salt solution; and
- (e) flowing the acrylonitrile phase of step (a) to a fractional distillation zone to therein produce a make comprised of acrylonitrile, water and by-products and a tails comprised of crude adiponitrile.

5. A method for the selective separation of adiponitrile and quaternary ammonium salt contained in the aqueous cathode effluent from the electrohydrodimerization of acrylonitrile to adiponitrile comprising the steps of:

- (a) in a first zone contacting said cathode effluent in extracting relationship with acrylonitrile to produce an acrylonitrile extract phase and an aqueous extract phase containing quaternary ammonium salt substantially free of reaction products; and
- (b) in a second zone contacting said acrylonitrile extract phase in extracting relationship with water thus producing an acrylonitrile extract phase substantially containing the reaction products and substantially free of quaternary ammonium salt.

6. A method for the selective separation and recovery of adiponitrile and quaternary ammonium salt contained in the aqueous cathode effluent from the electrohydrodimerization of acrylonitrile to adiponitrile comprising the steps of:

- (a) in a first zone contacting said cathode effluent in extracting relationship with acrylonitrile to produce an acrylonitrile extract phase and an aqueous extract phase containing quaternary ammonium salt substantially free of reaction products;
- (b) in a second zone contacting said acrylonitrile extract phase in extracting relationship with water thus producing an acrylonitrile extract phase substantially containing the reaction products substantially free of quaternary ammonium salt;
- (c) flowing the aqueous phase of step (a) to a zone having evaporating conditions therein to produce a make comprised of vaporous water and acrylonitrile and a tails comprised of quaternary ammonium salt solution; and
- (d) flowing the acrylonitrile phase of step (b) to a fractional distillation zone to therein produce a make comprised of acrylonitrile, water and by-products and a tails comprised of crude adiponitrile.

7. A method for the selective separation and recovery of acrylonitrile, adiponitrile and quaternary ammonium salt contained in the aqueous cathode effluent from the electrohydrodimerization of acrylonitrile to adiponitrile comprising the steps of:

- (a) in a first zone contacting said cathode effluent in extracting relationship with acrylonitrile to produce an acrylonitrile phase and an aqueous phase;
- (b) in a second zone contacting said acrylonitrile phase in extracting relationship with water thus producing an acrylonitrile phase and an aqueous phase;
- (c) flowing the aqueous phase of step (a) to a zone having evaporating conditions therein to produce a

make comprised of vaporous water and acrylonitrile and a tails comprised of an aqueous quaternary ammonium salt solution;

- (d) condensing the vaporous make of step (c) thus producing an aqueous phase and an acrylonitrile phase;
- (e) separating the aqueous and acrylonitrile phases of step (d);
- (f) recycling a portion of the aqueous phase of step (d) to the water extraction zone of step (b);
- (g) feeding the remainder of the aqueous phase of step (d) to an acrylonitrile recovery zone to therein produce a vaporous make comprised of acrylonitrile and water and a tails comprised of waste water;
- (h) condensing the make of step (g) thereby producing an acrylonitrile phase and an aqueous phase;
- (i) separating the aqueous and acrylonitrile phases of step (h) and returning the aqueous phase to the acrylonitrile recovery zone of step (g); and
- (j) flowing the acrylonitrile phase of step (b) to a fractional distillation zone to therein produce a make comprised of acrylonitrile, water and by-products and a tails comprised of crude adiponitrile.

8. The process of claim 7 wherein the evaporation zone has a base temperature of 70–150° C. and a head pressure of from 200 mm. of Hg to above atmospheric pressure.

9. A method for the selective separation and recovery of acrylonitrile, adiponitrile and quaternary ammonium salt contained in the cathode effluent from the electrohydrodimerization of acrylonitrile to adiponitrile comprising the steps of:

- (a) in a first zone contacting said cathode effluent in extracting relationship with acrylonitrile to produce an acrylonitrile phase and an aqueous phase;
- (b) in a second zone contacting said acrylonitrile phase in extracting relationship with water thus producing an acrylonitrile phase and an aqueous phase;
- (c) flowing the acrylonitrile phase of step (b) to a fractional distillation zone to therein produce a make comprised of acrylonitrile, water and reaction by-products and a tails comprised of crude adiponitrile;
- (d) condensing the make of step (c) thereby producing an acrylonitrile phase and an aqueous phase;
- (e) separating the acrylonitrile and aqueous phases of step (d);
- (f) feeding the aqueous phase of step (d) to an acrylonitrile recovery zone; and
- (g) flowing the aqueous phase of step (a) to an evaporation zone to therein produce a make comprised of acrylonitrile and water and a tails comprised of an aqueous quaternary ammonium salt solution.

10. A method for the selective separation and recovery of acrylonitrile, adiponitrile and quaternary ammonium salt contained in the aqueous cathode effluent from the electrohydrodimerization of acrylonitrile to adiponitrile comprising the steps of:

- (a) in a first zone contacting said cathode effluent in extracting relationship with acrylonitrile to produce an acrylonitrile phase and an aqueous phase;
- (b) in a second zone contacting said acrylonitrile phase in extracting relationship with water thus producing an acrylonitrile phase and an aqueous phase;
- (c) feeding the acrylonitrile phase of step (b) to a fractional distillation zone to therein produce a make comprised of acrylonitrile, water and by-products and a tails comprised of crude adiponitrile;
- (d) flowing said crude adiponitrile to a distillation train to therein refine it to a high degree of purity;
- (e) condensing the make of step (c) thus producing an acrylonitrile and an aqueous phase;
- (f) separating the acrylonitrile and aqueous phase of step (e);
- (g) feeding the acrylonitrile phase of step (e) to a propionitrile purge zone to therein produce a tails

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comprised of propionitrile and a make comprised of acrylonitrile and water;

(h) condensing the make of step (g) thereby producing an acrylonitrile and an aqueous phase;

(i) separating the phases of step (h);

(j) feeding the aqueous phase of step (h) to an acrylonitrile recovery zone; and

(k) flowing the aqueous phase of step (a) to an evaporation zone to therein produce a make comprised of acrylonitrile and water and a tails comprised of aqueous quaternary ammonium salt solution.

11. A method for the selective separation and recovery of acrylonitrile, adiponitrile and quaternary ammonium salt contained in the aqueous cathode effluent from the electrohydrodimerization of acrylonitrile to adiponitrile comprising the steps of:

(a) in a first zone contacting said cathode effluent in extracting relationship with acrylonitrile to produce an acrylonitrile phase and an aqueous phase;

(b) in a second zone contacting said acrylonitrile phase in extracting relationship with water thus producing an acrylonitrile and an aqueous phase;

(c) feeding the aqueous phase of step (a) to an evaporation zone having a temperature of 110–125° C. and a head pressure of 400–700 mm. of Hg thus producing a make comprised of vaporous water and acrylonitrile and a tails comprised of an aqueous quaternary ammonium salt solution, said solution having a salt concentration of 45–75 percent based on the weight of solution;

(d) condensing the vaporous make of step (c) thus producing an aqueous and an acrylonitrile phase;

(e) separating the aqueous phase of step (d) from the acrylonitrile phase;

(f) recycling a portion of the aqueous phase of step (e) to the extraction zone of step (b);

(g) feeding the remainder of the aqueous phase of step (e) to an acrylonitrile recovery zone having a temperature of about 100° C. and substantially atmospheric pressure therein thus producing a vapor-

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ous make comprised of acrylonitrile and water and tails comprised of waste water;

(h) condensing the make of step (g) thereby producing both an acrylonitrile and an aqueous phase;

(i) decanting the phases of step (h) thereby separating the aqueous phase from the acrylonitrile phase and recycling this aqueous phase to the acrylonitrile recovery zone of step (g) for further removal of acrylonitrile;

(j) flowing the acrylonitrile phase of step (a) to an acrylonitrile stripping zone operated at 170–225° C. and about atmospheric pressure to therein produce a vaporous make comprised of acrylonitrile, water and by-products and a tails comprised of crude adiponitrile;

(k) flowing said tails of of crude adiponitrile to a distillation train to therein refine crude adiponitrile to a high degree of purity;

(l) condensing the vaporous make of step (j) thereby producing an acrylonitrile and an aqueous phase;

(m) decanting the phases of step (l) thus separating the acrylonitrile phase from the aqueous phase;

(n) refluxing a portion of the aqueous phase of step (m) to said acrylonitrile stripping zone and feeding the remainder to the acrylonitrile recovery zone of step (g);

(o) feeding the acrylonitrile phase of step (l) to a propionitrile purge zone to therein produce a waste tails comprised of propionitrile, and a vaporous make comprised of acrylonitrile and water;

(p) condensing the vaporous make of step (o) thereby producing an acrylonitrile and an aqueous phase;

(q) decanting the phases of step (p) thereby separating them; and

(r) feeding the aqueous phase of step (p) to the acrylonitrile recovery zone of step (j) for the removal therein of acrylonitrile.

No references cited.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,267,131

August 16, 1966

Charles R. Campbell et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 26, strike out "containing substantially all of the adiponitrile and" and insert instead -- emits from zone 123 via line 128 and is recycled --.

Signed and sealed this 1st day of August 1967.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents