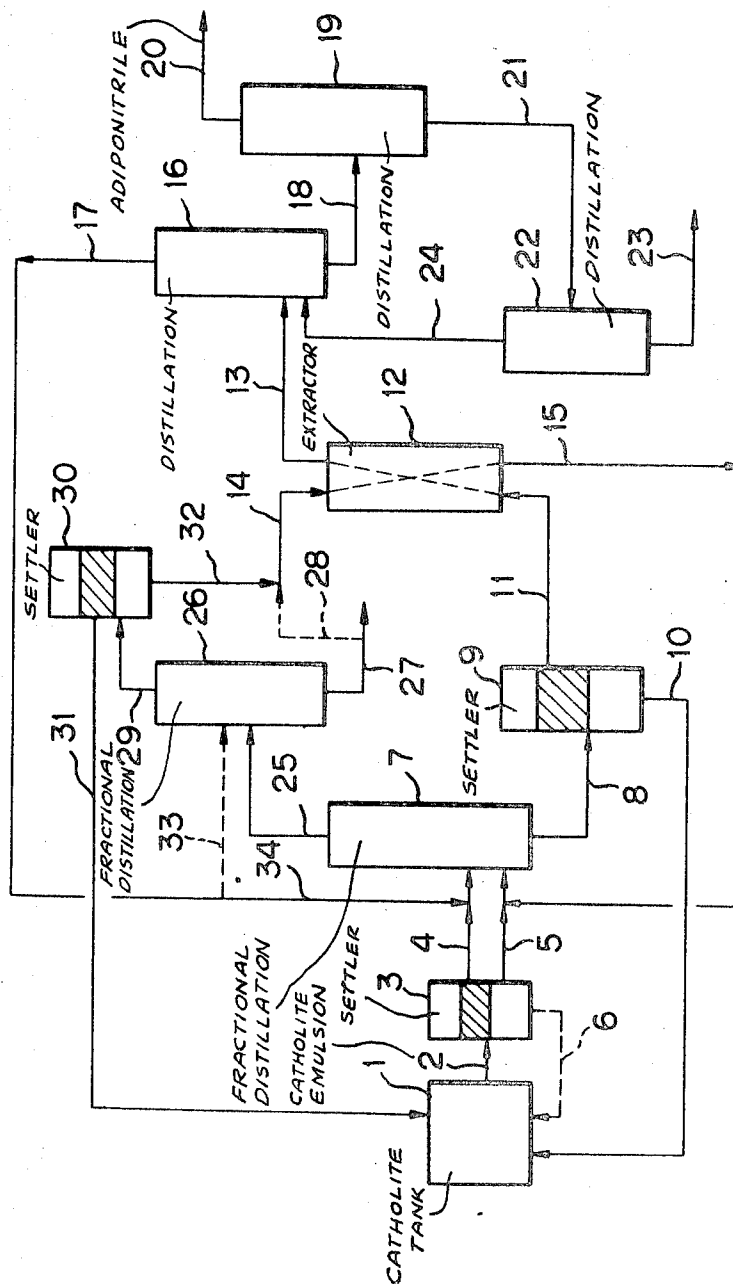


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ELECTROLYTIC HYDRODIMERIZATION BY DIRECTLY
DISTILLING THE CATHOLYTE EMULSION
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INVENTOR.

SHINSAKU OGAWA & SHOICHIRO
BY KUMAZAKI
BURGESS, DINKLAGE & SPRUNG

ATTORNEYS

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PROCESS FOR THE RECOVERY OF ADIPONITRILE FROM AN ELECTROLYTIC HYDRODIMERIZATION BY DIRECTLY DISTILLING THE CATHOLYTE EMULSION**Shinsaku Ogawa and Shoichiro Kumazaki, Yokohamashi, Japan, assignors to Asahi Kasei Kogyo Kabushiki Kaisha, Osaka, Japan**

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20 Claims

ABSTRACT OF THE DISCLOSURE

The recovery of adiponitrile from a catholyte emulsion used in the electrolytic hydrodimerization of acrylonitrile which has an oil phase, a continuous aqueous phase, and a supporting electrolyte salt by distilling a mixture of the oil phase and aqueous phase from the catholyte emulsion to thereby distill off acrylonitrile and water, separating the remaining distillation bottom into an oil phase and aqueous phase and recovering adiponitrile from the separated oil phase. The catholyte emulsion may be directly subjected to the distillation treatment or may first be separated into an oil phase and aqueous phase with the separated oil phase and a portion of the aqueous phase distilled together. The adiponitrile is preferably recovered from the oil phase by distilling off the lower boiling components, and most preferably subjected to an aqueous extraction to remove supporting electrolyte salt prior to this distillation. The adiponitrile may be further purified utilizing a rectifying tower with the bottoms from this tower being recycled through a stripper back to the distillation of the lower boiling components. The distillate from the initial distillation of the oil phase and aqueous phase mixture may be recycled directly or after further treatment including, for example, a propionitrile rectification or such rectification followed by phase separation by cooling.

This invention relates to a process for separating and purifying adiponitrile from a catholyte in the production of adiponitrile by the electrolytic hydrodimerization of acrylonitrile.

It is well known that adiponitrile may be obtained by the electrolytic hydrodimerization of acrylonitrile as disclosed in U.S. Pats. No. 3,193,480 and 3,193,481. Moreover, a process for separating adiponitrile from the catholyte in such processes is described in U.S. Pat. No. 3,193,477 and Dutch Pat. No. 6505391.

In general, the catholyte in the electrolytic hydrodimerization of acrylonitrile consists of propionitrile, adiponitrile, ethylene cyanohydrin, biscyanoethyl ether, acrylonitrile oligomers (mainly 2-cyanoethyl adiponitrile, and the like), which are formed in the electrolysis, water, acrylonitrile, supporting electrolyte salt and other additives. The electrolysis cell used in the hydrodimerization of acrylonitrile is preferably partitioned by a membrane separating the catholyte from the anolyte. However, in general, when an electric current is passed through a cell, there occurs a migration of hydrogen ions from the anolyte to the catholyte, accompanied by a transferring of water into the catholyte. The amount of water transferred is quite considerable, and for example, assuming that the conversion of acrylonitrile to adiponitrile is 100%, the yield of adiponitrile is 54 g./Faraday, whereas the amount of water transferred is as much as 10–50 g./Faraday.

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Thus, in order to carry out the operation continuously for a prolonged period of time while maintaining an optimum composition of the catholyte to afford a good conversion of adiponitrile, it is necessary to separate water, propionitrile, ethylene cyanohydrin and acrylonitrile oligomers by-produced in the electrolysis from the catholyte and discharge them out of the reaction system while recovering the product adiponitrile simultaneously. Also, it is highly desirable that as much as possible of the acrylonitrile, the supporting electrolyte salt and other additives be recovered for reuse.

The relationships between the vapor pressures of these main components to be separated and their boiling points are as follows:

Pressure (mm. Hg).....	760	150	15	5
Acrylonitrile, ° C.....	77.3	33	-----	-----
Propionitrile, ° C.....	97	52	-----	-----
Water, ° C.....	100	61	18	-----
Ethylene cyanohydrin, ° C.....	222	164	110	-----
Adiponitrile, ° C.....	-----	240	168	140
Biscyanoethyl ether, ° C.....	-----	250	178	160
2-cyanoethyl adiponitrile, ° C.....	-----	-----	270	243

Although these respective components may be separable by way of a distillation, there is a relative difficulty in their separation and recovery depending on the type and properties of the electrolyte salts used in the electrolysis and, as a result, there may be caused inconveniences such as disorder in the separation and purification processes, requirement for increased number of rectifying towers and an inevitable degradation in economy.

In the conventional processes known heretofore, such as disclosed in U.S. Pat. No. 3,193,477 and Dutch Pat. No. 6505391, mentioned above, salts having great capability of dissolving acrylonitrile, e.g. arylsulfonates are used as the supporting electrolyte in the catholyte and it has been considered that the desired adiponitrile may not be obtained in a high yield unless the concentration of acrylonitrile in the catholyte is maintained at a high level. Thus, many attempts have been directed heretofore to a process for separating adiponitrile from such solutions.

For this reason, it has been required in the prior art processes known heretofore to separate the catholyte into an oil phase and an aqueous phase by adding acrylonitrile and/or water, and/or organic solvent such as methylene chloride to the catholyte as a first step of separating adiponitrile from the catholyte.

In addition, since the salts having great capability of dissolving acrylonitrile are used as the supporting electrolyte, the oil phase obtained in the above-mentioned first step contains a large amount of the supporting electrolyte. For this reason it has been considered necessary to remove the supporting electrolyte from the oil phase by an extraction with, for example, water as a second step. It has been further considered necessary to separate acrylonitrile and propionitrile from the oil phase now free from the supporting electrolyte by way of a distillation as a third stage.

On the other hand, it has been required to remove water by an evaporation from the aqueous phase obtained in the first stage in a separate, independent process.

In contrast with the above described prior art processes, a process is disclosed in copending U.S. patent application No. 642,321, filed May 31, 1967, which enables the production of adiponitrile in a higher yield as compared with the prior art processes. Unlike these prior art processes in which the catholyte is maintained in the state of a solution, this process described in U.S. application 642,321 utilizes a catholyte maintained in the state of an emulsion consisting of an oil phase mainly comprising

adiponitrile and acrylonitrile and a continuous aqueous phase mainly comprising water and a supporting electrolyte salt with the concentration of the supporting electrolyte salt being less than 30% and with a low concentration of acrylonitrile in both oil and aqueous phases. In this latter process an electrolyte capable of increasing the solubility of acrylonitrile in the catholyte is not required.

It is an object of this invention to provide a novel process for purifying and obtaining adiponitrile with high efficiency from the catholyte in the form of an emulsion.

This and still further objects will become apparent from the following description read in conjunction with the drawing which shows a flowsheet of a preferred embodiment of this invention.

In accordance with the invention the adiponitrile is recovered from the catholyte emulsion used in the electrolytic hydrodimerization of acrylonitrile which emulsion contains an oil phase, a continuous aqueous phase, and a supporting electrolyte salt by distilling a mixture of the oil phase and the aqueous phase obtained from the emulsion to thereby distill off acrylonitrile and water followed by separating the remaining distillation bottom into an oil phase and aqueous phase and recovering adiponitrile from the separated oil phase.

The catholyte emulsion may be directly subjected to the distillation, or may initially be first separated into an oil phase and aqueous phase with the separated oil phase and a portion of the aqueous phase distilled together as a mixture.

In the process of this invention, the incorporation of a third component into the catholyte to separate the same into two phases as required in the prior art processes is unnecessary and the separation of acrylonitrile and adiponitrile and the evaporation of water from the aqueous phase can be accomplished in a single step.

The process in accordance with the invention is applicable for the treatment of any of the catholyte emulsions which may be used in the electrolytic hydrodimerization of acrylonitrile and which contain an oil phase, a continuous aqueous phase, and a supporting electrolyte salt. These emulsions by their very nature and with respect to the hydrodimerization process in which they are used, as described in copending application Ser. No. 642,321, generally have a limited solubility of acrylonitrile and adiponitrile in the aqueous phase of the emulsion, and generally do not contain a material which greatly increases the solubility of the acrylonitrile and adiponitrile in the aqueous phase. These catholytes generally contain sulfates or halides as the supporting electrolyte salt. In general the catholytes preferably have the composition as described in copending application Ser. No. 642,321, and the entire disclosure thereof is incorporated herein by reference.

It is essential in the process of this invention to distill the catholyte consisting of the oil and aqueous phases and separate the resulting bottom into two phases, and the satisfactory operation of the process has close relations with the type and the concentration of the supporting electrolyte used, the degree of the concentration of the bottom and the separating temperature.

Since it is not necessary in the process of this invention to separate the catholyte by incorporating acrylonitrile, water and/or organic solvent such as methylene chloride as in the prior art processes known heretofore, the new process has many advantages including the following:

(1) The number of steps can be reduced and the operation becomes easier.

(2) The acrylonitrile, water, methylene chloride which are incorporated in the catholyte in the prior art processes have to be separated and recovered by the distillation afterwards. However, since this operation is not required in the present process, the amount of liquid to be subjected to the distillation can be greatly reduced.

Since the oil and aqueous phases can be distilled to-

gether in the present process, the following advantages over the prior art processes can be enjoyed:

(1) The rectification for removing acrylonitrile and propionitrile from the oil phase and the rectification for removing water from the aqueous phase can be accomplished in a single rectifying tower. Thus, the number of steps required can be reduced.

(2) Since a large amount of water is distilled together with acrylonitrile in the present process, a sort of steam distillation is effected, thus, acrylonitrile can be removed from the oil phase quite efficiently even at a temperature of the bottom of 100-120° C. under atmospheric pressure. In contrast, if acrylonitrile is to be removed by distilling the oil phase alone as in the prior art processes, the temperature of the bottom should be at 170-225° C. under atmospheric pressure.

(3) In the present process, since the temperature of the bottom may be lowered in the distillation of acrylonitrile and acrylonitrile is distilled together with a large amount of water which functions as a polymerization inhibitor for acrylonitrile, the polymerization of acrylonitrile in the course of the distillation can be prevented easily.

(4) The number of steps in which dangerous acrylonitrile having a high reactivity is dealt with can be reduced and thus the process control becomes easier.

As described above, there are brought about many advantages from the distillation of the catholyte in the form of an emulsion consisting of the oil and aqueous phases.

In the explanation of the present process, the rectifying tower used for distilling the oil and aqueous phases together may be referred to as "acrylonitrile rectifying tower" for convenience hereinafter. The liquid distilled in this tower mainly consists of acrylonitrile, water and propionitrile. However, since it is undesirable that adiponitrile is contained therein, it is desirable to carry out the rectification so that adiponitrile having a higher boiling point may not be distilled.

The acrylonitrile rectifying tower mentioned above may be operated not only under atmospheric pressure, but also under a reduced pressure. The use of a reduced pressure has advantages in that the resulting bottom may be separated into two phases without requiring the cooling thereof and that the undesirable side-reactions such as the hydrolysis of adiponitrile and acrylonitrile may be easily prevented because the temperature of the bottom may be maintained at a low level.

As described above, in the present process the bottom obtained in the acrylonitrile rectifying tower is separated into two phases. In this instance, the bottom may be separated into two phases by allowing the bottom to stand still. However, in general, an efficient separation can be accomplished by cooling the bottom since, by so doing, the concentration of water and the supporting electrolyte dissolved in the oil phase and the concentration of adiponitrile dissolved in the aqueous phase are decreased. The aqueous phase obtained here is recycled to a catholyte tank. The oil phase mainly consists of adiponitrile and water, and contains a part of the supporting electrolyte.

While sufficiently purified adiponitrile can be obtained by rectifying the thus obtained oil phase directly, it may be preferable to further treat the same as hereinafter described.

According to a further feature of the present invention this oil phase is subjected to an extraction with water or a saturated aqueous solution of acrylonitrile containing about 11-7% of acrylonitrile in order to remove supporting electrolyte salt.

According to the known processes as described in Dutch Pat. No. 6505391, the supporting electrolyte is extracted with water from the oil phase before removing acrylonitrile therefrom. On the contrary, in this embodiment of the process of this invention, the supporting electrolyte is extracted with water from the oil phase only after removing acrylonitrile therefrom. This has advantages in that the amount of the oil phase to be treated is decreased

and thus the safety in the operation is increased. The separation can be accomplished easily in the instant extraction since there is little tendency toward emulsification as the oil phase mainly contains adiponitrile. As contrasted to this, when extracting an oil phase containing a large amount of acrylonitrile with water, the separation occurs only with great difficulty due to an emulsifying tendency of the extraction mixture.

It is convenient to carry out the extraction by using a countercurrent multiple extractor, because an oil phase containing no supporting electrolyte can be obtained using only a small amount of water. As the countercurrent multiple extractor there may be preferably employed the conventional equipment such as packed towers, multiple towers, spray towers, mixer settlers, and pulsating towers.

By following the extraction operation, an oil phase containing no supporting electrolyte and an aqueous phase containing supporting electrolyte are obtained. It is convenient to recycle the aqueous phase obtained here to the acrylonitrile rectifying tower explained before.

A further feature of the present invention resides in providing an adiponitrile stripper which serves to recover adiponitrile from the bottom of the adiponitrile rectifying tower described hereinafter and charging the distillate obtained in the said stripper directly to a lower boiling component separator positioned prior to the adiponitrile rectifying tower. This prevents intermixing of ethylene cyanohydrin with the adiponitrile.

The above described oil phase containing no supporting electrolyte and obtained by the extraction according to the present invention consists mainly of adiponitrile, but contains water and a small amount of acrylonitrile as lower boiling components. To remove the latter, the oil phase is supplied to a lower boiling component separator. This separator is operated with a bottom temperature of 100–200° C. and the still pressure of 40–50 mm. Hg. Ethylene cyanohydrin which is produced by the thermal decomposition of biscyanoethyl ether by-produced in the electrolysis is also distilled off. As it is not desirable that adiponitrile is distilled off together therewith, a rectification procedure is recommended.

Though the bottom of the lower boiling component separator mainly consists of adiponitrile, it also contains impurities such as biscyanoethyl ether and oligomers of acrylonitrile (mainly 2-cyanoethyladiponitrile) by-produced in the electrolysis.

It is necessary to rectify adiponitrile from the said bottom if the rectification is to be carried out in a single rectifying tower. The bottom is then mainly composed of 2-cyanoethyladiponitrile and biscyanethyl ether. If the residual amount of adiponitrile in the bottom to be discharged is intended to be, for instance, less than 10%, the bottom should be kept at a temperature higher than 220° C. under a high vacuum below 5 mm Hg. Under such conditions of high temperature and high vacuum, biscyanoethyl ether is decomposed thermally to produce acrylonitrile and ethylene cyanohydrin, which would not be intermixed with the product.

The boiling point of adiponitrile is 180°C. at 25 mm. Hg and 160° C. at 10 mm. Hg. Thus, in order to solve the above problem two towers may be employed, one being a tower for rectifying adiponitrile (the tower referred to hereinafter as an adiponitrile rectifying tower), and the other being an adiponitrile stripper for separating adiponitrile exhaustively from 2-cyanoethyladiponitrile which is a main component of the bottom. The distillate obtained in the adiponitrile stripper is supplied to the above described lower boiling component separator.

Therefore, in the process of this invention, the bottom temperature of the adiponitrile rectifying tower is chosen so as not to distill off ethylene cyanohydrin produced by the thermal decomposition of biscyanoethyl ether from the top of the tower. Consequently, the bottom temperature of the adiponitrile rectifying tower is lower than that

of the adiponitrile stripper, and the bottom is kept at a high adiponitrile content. Such a bottom is supplied to the adiponitrile stripper.

The adiponitrile stripper is kept under such conditions with respect to the degree of vacuum and the temperature of bottom that adiponitrile may be removed from the bottom as completely as possible even when biscyanoethyl ether is decomposed thermally. As a result, the bottom of the adiponitrile stripper thus obtained mainly consists of acrylonitrile oligomers of which the main component is 2-cyanoethyladiponitrile and a small amount of the residual supporting electrolyte. The bottom is discharged while the concentration of adiponitrile therein is maintained at less than about 10%.

In the known process described in Dutch Pat. No. 6505391, since the vapor discharged from an adiponitrile stripper is fed to an adiponitrile rectifying tower, the distillate of the tower is required to be fed to a low boiling component separator to remove ethylene cyanohydrin and the bottom of the separator should be again supplied to the adiponitrile rectifying tower.

On the contrary, the process of the present invention has such advantages as follows:

First, the required number of the rectifying towers is reduced. Since a lesser amount of lower boiling components is mixed in the vapor of the tower rectifying adiponitrile, which is difficultly rectified, the tower can be kept at a high vacuum easily.

As the vapor of the low boiling component separator mainly consists of water and contains less materials such as acrylonitrile which have a lower boiling point and are difficult to condense, the tower can be easily kept at a high vacuum and the lower boiling components can be effectively removed.

A still further feature of the present invention is to feed the vapor of the above-described acrylonitrile rectifying tower to a propionitrile separator and, after rectifying, to remove propionitrile as the bottom together with water.

The vapor of the acrylonitrile rectifying tower mainly consists of acrylonitrile, water, propionitrile and ethylene cyanohydrin. Among these, water, propionitrile and ethylene cyanohydrin accumulate in the catholyte, so that they should be discarded out of the system. It is undesirable to entrain acrylonitrile together with them for it causes a decrease in the overall yield of adiponitrile.

Since acrylonitrile has the lowest boiling point among these, the vapor discharged from the acrylonitrile rectifying tower is fed to a propionitrile separator to separate a bottom mainly consisting of water, propionitrile and ethylene cyanohydrin and containing little acrylonitrile.

On the contrary, in a prior known method wherein, unlike the process of the present invention, the oil phase and the aqueous phase obtained by treating catholyte cannot be distilled together, it is necessary to provide both an acrylonitrile rectifying tower for removing acrylonitrile from the oil phase and a vaporizer for evaporating water from the aqueous phase.

In this case a great majority of propionitrile is transferred to the oil phase and therefore in the prior known process, it is necessary in order to discharge propionitrile and water out of the system, to subject the vapor of the acrylonitrile rectifying tower to a further rectification to separate acrylonitrile from propionitrile, while there is required a rectifying tower to recover acrylonitrile from the vapor discharged from the water vaporizer containing a small amount of acrylonitrile.

Compared with the above described process, the process of the present invention has such advantages as explained below.

As the number of the required rectifying tower is reduced, the cost of construction is saved. Second, the operation can be easily controlled.

The bottom of the propionitrile rectifying tower in the present invention may be discarded, or partially used

as an extracting agent in the countercurrent extractor. The vapor of the tower mainly consists of acrylonitrile and water, and when condensed, it separates into two phases, one mainly consisting of acrylonitrile and the other mainly consisting of water. The phase mainly consisting of acrylonitrile is recycled to a catholyte tank to be reused. The phase consisting mainly of water may be recycled and reused as an extracting agent in the extractor.

Referring to the embodiment shown in the drawing by way of illustration and not limitation:

A catholyte 2 in a catholyte tank 1 is kept so that the oil phase and the aqueous phase exist in an emulsion state. With or without such treatments as heating, centrifugal separating, and filtering for separating the oil phase from the aqueous phase in the catholyte 2, the catholyte is fed to a catholyte separating tank 3. The oil phase 4 and the aqueous phase 5 separated here are combined and charged together to an acrylonitrile rectifying tower 7. At this time, it is preferable to feed back a part of the aqueous phase 6 separated in the said catholyte separating tank 3 to the catholyte tank 1, so that the amount of the solution charged to the acrylonitrile rectifying tower 7 is decreased. However, an important feature of the present invention resides in charging the oil phase and the aqueous phase of the catholyte to an acrylonitrile rectifying tower for treatment together. The catholyte separating tank 3 is thus not necessarily required and the catholyte 2 can be supplied to the acrylonitrile rectifying tower 7 directly.

To the acrylonitrile rectifying tower 7, the extract, i.e. an aqueous phase containing supporting electrolyte 15 obtained in an extractor 12 is further charged. In some cases, a distillate 34 of a lower boiling component separator 16 is also charged.

In the acrylonitrile rectifying tower 7 a bottom 8 is obtained by distilling off vapor 25 from these charged solutions. Rectification is carried out in order that the distilled vapor 25 is mainly composed of acrylonitrile, propionitrile and ethylene cyanohydrin but contains no adiponitrile. The bottom 8 is separated into an oil phase 11 and an aqueous phase 10 in a bottom separator 9 after settling with or without cooling. The aqueous phase 10 is returned to the catholyte tank 1. As the oil phase 11 contains supporting electrolyte, the phase is fed to an extractor 12 to remove it. It is convenient to employ a continuous countercurrent multiple extractor as the extractor 12, and in this case, the oil phase 11 is charged at the bottom of the tower, while water or a part of saturated aqueous solution of acrylonitrile 32 obtained in a cooling separator 30 and/or a part 28 of the bottom 27 of a propionitrile separator 26 are charged as an extracting agent at the top of the tower, and then both solutions are contacted countercurrently. Thus, there are obtained an oil phase 13 free from supporting electrolyte from the top of the tower and an aqueous solution 15 containing supporting electrolyte from the bottom. The aqueous solution 15 containing supporting electrolyte is charged to the acrylonitrile rectifying tower 7.

The oil phase 13 free from supporting electrolyte is charged to a lower boiling component separator 16. To this tower 16, the vapor 24 of an adiponitrile stripper 22 is also charged. In the lower boiling component separator 16, a distillate 17 consisting mainly of water, acrylonitrile and ethylene cyanohydrin is obtained from the top of the tower. It is preferable in the lower boiling component separator 16 to rectify so that the distillate may contain as little as possible adiponitrile. The distillate 17 is recycled as a feed solution 34 to the acrylonitrile rectifying tower or a feed solution 33 to the propionitrile separator 26. Whether the distillate 17 is used as 34 or 33 is mainly decided depending on the amount of adiponitrile contained in the distillate 17. When the adiponitrile content of the distillate 17 is small, it is pref-

erably used as a feed solution to the propionitrile separator.

The bottom 18 of the lower boiling component separator 16 is supplied to the adiponitrile rectifying tower 19. Adiponitrile is distilled from the top of this tower as a product 20. The bottom 21 obtained from the bottom of the tower consists mainly of adiponitrile, biscyanoethyl ether and 2-cyanoethyladiponitrile.

The bottom 21 is fed to an adiponitrile stripper 22. In the adiponitrile stripper 22, it is preferable to discharge the bottom 23 after reducing the content of adiponitrile to less than 10%. The bottom mainly consists of acrylonitrile oligomers (mainly 2-cyanoethyl ether), biscyanoethyl ether and supporting electrolyte which has not been removed in the extractor. The distillate 24 of the adiponitrile stripper 22 is supplied to the lower boiling component separator 16.

The vapor 25 of the acrylonitrile rectifying tower 7 is charged to the propionitrile separator 26. From this tower, a liquid 27 containing mainly water, propionitrile and ethylene cyanohydrin is discharged as a bottom. As it is preferable that the bottom contains as little as possible acrylonitrile, rectification is carried out so as to achieve this effect.

The distilled vapor from the propionitrile separator 26 is condensed by cooling in a cooling separator 30 and separated into an oil phase 31 mainly consisting of acrylonitrile and an aqueous phase 32 mainly consisting of water. The oil phase 31 is circulated to the catholyte tank 1. The aqueous phase 32 is used as an extracting agent in the extractor 12.

The supporting electrolyte in the catholyte used in the process of the present invention should possess an ability of separating the concentrated bottom obtained by distillation of catholyte consisting of the oil and aqueous phases into two phases, and from this aspect, various supporting electrolytes can be used alone or as a mixture, and the degree of concentration of the catholyte and the concentration of the supporting electrolyte in the catholyte may be adequately selected.

As the supporting electrolyte possessing the said property, there may be preferably used mainly sulfates, halides monomethyl sulfates and monoethyl sulfates.

The cation of the said supporting electrolyte is preferably the one possessing a lower discharge potential than that at which acrylonitrile is converted to adiponitrile, such as quaternary ammonium ion, ammonium ion and alkali metal ion.

For keeping the electrolysis at a stable state for a prolonged period of time, it is preferable to add an anion polymerization inhibitor as disclosed in U.S. patent application No. 642,321, or a known inhibitor for radical polymerization of acrylonitrile.

For stabilizing the emulsion of the oil and aqueous phases in the catholyte, there may be added as emulsifying agent animal viscous material, vegetable viscous material and various other synthetic viscous materials.

The concentration of the supporting electrolyte used in the catholyte is preferably less than 30%, since the conductivity of the catholyte generally reaches its maximum in the range of concentration of the supporting electrolyte of 10-30% by weight in the aqueous phase, and since the aqueous phase should be concentrated later. It is possible, however, to use concentration higher than 30%.

The concentration of acrylonitrile in the catholyte and the mixing ratio of the oil phase to the aqueous phase in the catholyte are decided depending on the electrolytic yield of adiponitrile, conductivity of the emulsion and from the standpoint that the amount of acrylonitrile to be treated in the recovering and purifying process should be preferably as small as possible. The optimum values depend on the type of the supporting electrolyte, but in general the acrylonitrile concentration in the oil phase is less than 50%, the acrylonitrile concentration in the

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aqueous phase is less than 5%, and the mixing ratio of the oil phase in the catholyte is less than 50%.

The present invention is more fully explained in the following examples which are given by way of illustration and not limitation.

EXAMPLE 1

An arrangement was used as shown in the drawing. An emulsion consisting of an aqueous phase and the oil phase having the following composition was employed as a catholyte.

Composition of the aqueous phase in the catholyte:		Percent
Acrylonitrile	-----	2.0
Propionitrile	-----	0.2
Ethylene cyanohydrin	-----	Trace
Adiponitrile	-----	5.6
Acrylonitrile oligomer	-----	0.2
Biscyanoethyl ether	-----	Trace
Water	-----	74.0
Supporting electrolyte:		Percent
Tetraethylammonium sulfate	-----	16.0
Hexamethylenediamine sulfate	-----	2.0
pH 4		
Composition of the oil phase in the catholyte:		Percent
Acrylonitrile	-----	23.2
Propionitrile	-----	2.1
Ethylene cyanohydrin	-----	Trace
Adiponitrile	-----	65.3
Acrylonitrile oligomer	-----	2.7
Biscyanoethyl ether	-----	0.2
Water	-----	6
Supporting electrolyte:		Percent
Tetraethylammonium sulfate	-----	0.3
Hexamethylenediamine sulfate	-----	0.2

The catholyte was composed of the above described aqueous phase and oil phase in a ratio of 75:25 by weight. A part of the catholyte was removed and separated into two layers after settling in the catholyte separator 3. 3 parts of the said oil phase and 1 part of the said aqueous phase were mixed and charged to the acrylonitrile rectifying tower.

The bottom of acrylonitrile rectifying tower 7 was kept at a temperature of 110° C. under atmospheric pressure. The bottom was removed, cooled to 30° C. and separated by settling into the oil phase and the aqueous phase having the following compositions.

Composition of the oil phase:		Percent
Acrylonitrile	-----	0.1
Propionitrile	-----	Trace
Ethylene cyanohydrin	-----	Do.
Adiponitrile	-----	90.7
Acrylonitrile oligomer	-----	3.9
Biscyanoethyl ether	-----	0.2
Water	-----	3.8
Supporting electrolyte	-----	1.2
Composition of the aqueous phase:		
Acrylonitrile	-----	Trace
Propionitrile	-----	Do.
Ethylene cyanohydrin	-----	Do.
Acrylonitrile oligomer	-----	Do.
Biscyanoethyl ether	-----	Do.
Adiponitrile	-----	3.0
Water	-----	53
Supporting electrolyte	-----	44

The aqueous phase was returned to the catholyte tank and the oil phase was charged to the packed counter-current continuous extractor 12 at the bottom thereof, and from the top of the extractor the saturated aqueous solution of acrylonitrile 32 obtained in the cooling separator 30 was charged as an extracting agent.

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The amount of the extracting agent charged was 1/3 of the amount of the oil phase charged.

An oil phase of the following composition which contains little supporting electrolyte was obtained from the top of the extractor:

	Percent
Acrylonitrile	----- 1.9
Propionitrile	----- Trace
Ethylene cyanohydrin	----- Do.
Adiponitrile oligomer	----- 3.8
Biscyanoethyl ether	----- 0.2
Water	----- 3.9
Supporting electrolyte	----- 0.02
Adiponitrile	----- 90.2

The oil phase was rectified in the lower boiling component separator 16 at the bottom temperature of 180° C. under the still pressure of 40 mm. Hg. At this time the distillate 24 of the adiponitrile stripper 22 having the following composition was added to the solution charged to the lower boiling component separator 16 in an amount of about 1/20 of the amount of oil phase 13 charged.

Composition of the distillate of the adiponitrile stripper:		Percent
Ethylene cyanohydrin	-----	1.6
Adiponitrile	-----	40
Biscyanoethyl ether	-----	7
2-cyanoethyladiponitrile	-----	50

Then the bottom 18 having the following composition was obtained from the lower boiling component separator.

Composition of the bottom of the lower boiling component separator:		Percent
Ethylene cyanohydrin	-----	0.02
Water	-----	0.03
Acrylonitrile	-----	0.01
Adiponitrile	-----	93.3
Acrylonitrile oligomer	-----	6.0
Biscyanoethyl ether	-----	0.6
Supporting electrolyte	-----	0.03

The bottom was charged to the adiponitrile rectifying tower 19 and adiponitrile having the purity higher than 99.7% was obtained as the product.

At this time the bottom of the following composition was obtained at the bottom temperature of 200° C. under the still pressure of 15 mm. Hg.

	Percent
Adiponitrile	----- 26
Acrylonitrile oligomer	----- 73
Biscyanoethyl ether	----- 0.7

The bottom 21 was vaporized in the adiponitrile stripper 22 at the bottom temperature of 215° C. under the still pressure of 4 mm. Hg, and the bottom 23 having the following composition was obtained:

	Percent
Adiponitrile	----- 4.7
Acrylonitrile oligomer	----- 93.1
Biscyanoethyl ether	----- 1.5
Supporting electrolyte	----- 0.7

The distillate 25 of the acrylonitrile rectifying tower was rectified in the propionitrile separator 26 at the bottom temperature of 100° C. under the still pressure of an atmospheric pressure, and the bottom 27 having the following composition was obtained:

	Percent
Acrylonitrile	----- Trace
Propionitrile	----- 10.3
Ethylene cyanohydrin	----- 0.2
Adiponitrile	----- Trace
Water	----- 89.5

11 EXAMPLE 2

The plant setup of Example 1 was used. An emulsion consisting of an aqueous phase and the oil phase having the following composition was employed as the catholyte 2.

Composition of the aqueous phase in the catholyte:

	Percent
Acrylonitrile	1.0
Propionitrile	Trace
Ethylene cyanohydrin	Do.
Adiponitrile	3.0
Acrylonitrile oligomer	Trace
Biscyanoethyl ether	Do.
Water	86
Sodium sulfate	10
pH 4	

Composition of the oil phase in the catholyte:

Acrylonitrile	24
Propionitrile	12
Ethylene cyanohydrin	Trace
Adiponitrile	56
Acrylonitrile oligomer	3
Biscyanoethyl ether	0.1
Water	5.0
Sodium sulfate	0.005

The catholyte was composed of the said aqueous phase and oil phase in the mixing ratio of 60:40 by weight. A part of the catholyte was removed and separated by settling in the catholyte separator 3. 4 parts of the oil phase and 1 part of the aqueous phase was mixed and charged to the acrylonitrile rectification tower 7.

The acrylonitrile rectifying tower 7 was kept at the bottom temperature of 108° C. under an atmospheric pressure. The bottom obtained in the said tower was removed, cooled to 40° C. and separated by settling into the oil phase and the aqueous phase having the following compositions.

Composition of the oil phase:

	Percent
Acrylonitrile	0.2
Propionitrile	Trace
Ethylene cyanohydrin	Do.
Adiponitrile	89.0
Acrylonitrile oligomer	4.8
Biscyanoethyl ether	0.15
Water	5.7
Sodium sulfate	0.01

Composition of the aqueous phase:

Acrylonitrile	Trace
Propionitrile	Do.
Ethylene cyanohydrin	Do.
Acrylonitrile oligomer	Do.
Biscyanoethyl ether	Do.
Adiponitrile	0.16
Water	68
Sodium sulfate	32

The aqueous phase was returned to the catholyte tank. The oil phase was charged directly to the lower boiling component separator 16, without passing through the extractor 12 because it contained little supporting electrolyte.

After treating it in the adiponitrile rectifying tower 19 and the adiponitrile stripper 22 at the similar bottom temperature under the similar still pressure as used in Example 1, adiponitrile having purity higher than 99.7% was obtained.

The broad and preferred operating conditions which may be used in the process of the invention may be summarized as follows:

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	Broad	Preferred
Ratio of amounts of oil phase and aqueous phase distilled in the acrylonitrile rectifying tower 7 (by weight).....	0.05-0.8	0.15-0.5
5 Temperature distillation in acrylonitrile rectifying tower 7 (° C.).....	40-130	50-100
Pressure of distillation in acrylonitrile rectifying tower 7 (mm. Hg).....	0-1,500	30-760
Temperature of bottom separation in separator 9 (° C.).....	-10-80	10-50
Ratio of separated aqueous phase recycled from separator 3 to catholyte (by weight).....	0-0.8	0-0.5
10 Temperature for extractor 12 (° C.).....	0-80	10-50
Ratio of extracting agent to oil being extracted in extractor 12 (by weight).....	0.1-10	0.3-1
Temperature for adiponitrile rectifying tower 19 (° C.).....	150-250	180-200
Pressure for adiponitrile rectifying tower 19 (mm. Hg).....	0-400	10-100
15 Temperature for adiponitrile stripper 22 (° C.).....	180-300	200-250
Pressure for adiponitrile stripper 22 (mm. Hg).....	0-100	0-10
Temperature for propionitrile rectifying tower 26 (° C.).....	50-150	80-100
Temperature for cooling separator 30 (° C.).....	0-70	10-50

List of ingredients by weight percent with broad and preferred ranges for preferred catholyte emulsion to be treated.

	Broad	Preferred
Ratio of amounts of oil phase and aqueous phase of catholyte emulsion (by weight).....	0-0.05	0.15-0.30
Amounts of ingredients in oil phase (by weight percent):		
Acrylonitrile.....	5-100	10-50
Adiponitrile.....	0-90	50-80
Propionitrile.....	0-20	2-10
Oligomer.....	0-20	1-5
Amounts of ingredients in aqueous phase (by weight percent):		
Acrylonitrile.....	1-20	1-5
Adiponitrile.....	0-20	3-6
Propionitrile.....	0-5	0-3
Supporting electrolyte salt.....	5-50	10-30

While the invention has been described in detail with reference to certain specific embodiments, various changes and modifications which fall within the spirit of the invention and scope of the appended claims will become apparent to the skilled artisan. The invention is therefore only intended to be limited by the appended claims or their equivalents wherein we have endeavored to claim all inherent novelty.

We claim:

1. A process for recovering adiponitrile from a catholyte emulsion used in the electrolytic hydrodimerization of acrylonitrile which emulsion comprises an oil phase, a continuous aqueous phase, and a supporting electrolyte salt which process comprises directly distilling a mixture of said oil phase and said aqueous phase from said catholyte emulsion to thereby distill off acrylonitrile and water, separating the remaining distillation bottoms into an oil phase and aqueous phase and recovering adiponitrile from the separated oil phase.

2. Process according to claim 1 in which prior to said recovery of adiponitrile from the separated oil phase that phase is extracted with an aqueous extracting agent for the removal of supporting electrolyte salt.

3. Process according to claim 2 in which said aqueous extracting agent comprises an aqueous solution of acrylonitrile.

4. Process according to claim 1 in which said aqueous phase separated from the distillation bottom is recycled into admixture with the catholyte emulsion and in which said adiponitrile is recovered from the separated oil phase by distilling off lower boiling components including water, acrylonitrile and ethylene cyanohydrin therefrom and thereafter distilling off from the remaining bottom material containing adiponitrile, biscyanoethyl ether and acrylonitrile oligomer, pure adiponitrile in an adiponitrile rectifying tower and which includes passing the bottoms from the adiponitrile rectifying tower comprising adiponitrile, biscyanoethyl ether and acrylonitrile oligomer through an adiponitrile stripper and passing the vapor

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from the stripper to said distillation of the lower boiling components.

5. Process according to claim 4 in which prior to said recovery of adiponitrile from said separated oil phase the separated oil phase is extracted with an aqueous extracting agent for the removal of supporting electrolyte salt.

6. Process according to claim 4 in which the acrylonitrile phase distilled off in the initial distillation is recycled into admixture with the catholyte emulsion.

7. Process according to claim 4 in which the distillate from said initial distilling is subjected to a further distillation to distill off acrylonitrile and water and remove a bottom comprising propionitrile and water and in which at least a portion of the distilled off acrylonitrile and water is recycled to the catholyte.

8. Process according to claim 7 in which the acrylonitrile and water obtained from said further distillation is cooled to form an acrylonitrile phase and an acrylonitrile saturated aqueous phase and which includes recycling the acrylonitrile phase into admixture with the catholyte emulsion in which prior to said recovery of adiponitrile from said separated oil phase the separated oil phase is extracted with an extracting agent comprising said acrylonitrile saturated aqueous phase for the removal of supporting electrolyte salt.

9. Process according to claim 8 in which only a portion of the distillate from said initial distillation is subjected to said further distillation and in which the remaining distillate from said initial distillation is cooled with the distillate of said further distillation for said separation into said acrylonitrile phase and acrylonitrile saturated aqueous phase.

10. Process according to claim 1 in which said distillation is effected at a temperature between about 40 to 130° C.

11. Process according to claim 1 in which said catholyte emulsion contains a quaternary ammonium salt or an alkaline metal salt as said supporting electrolyte salt.

12. Process according to claim 1 in which said catholyte emulsion contains a sulfate or halide as said supporting electrolyte salt.

13. Process according to claim 1 in which the concentration of said supporting electrolyte salt in the aqueous phase of said catholyte emulsion is maintained at a value of less than about 30% by weight.

14. Process according to claim 1 in which said oil phase of the catholyte emulsion constitutes more than 15% thereof.

15. Process according to claim 1 in which the concentration of acrylonitrile in said aqueous phase of said catholyte emulsion is maintained at a value of less than 5% by weight.

16. Process according to claim 1 in which said catholyte emulsion contains an emulsifying agent.

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17. Process according to claim 16 in which said aqueous phase separated from the distillation bottom is recycled into admixture with the catholyte emulsion and in which said adiponitrile is recovered from the separated oil phase by distilling off lower boiling components including water, acrylonitrile and ethylene cyanohydrin therefrom and thereafter distilling off from the remaining bottom material containing adiponitrile, biscyanoethyl ether and acrylonitrile oligomer, pure adiponitrile in an adiponitrile rectifying tower and which includes passing the bottoms from the adiponitrile rectifying tower comprising adiponitrile, biscyanoethyl ether and acrylonitrile oligomer through an adiponitrile stripper and passing the vapor from the stripper to said distillation of the lower boiling components.

18. Process according to claim 17 in which prior to said recovery of adiponitrile from said separated oil phase the separated oil phase is extracted with an aqueous extracting agent for the removal of supporting electrolyte salt.

19. Process according to claim 18 in which the distillate from said initial distilling is subjected to a further distillation to distill off acrylonitrile and water and remove a bottom comprising propionitrile and water and in which at least a portion of the distilled off acrylonitrile and water is recycled into admixture with the catholyte emulsion.

20. Process according to claim 19 in which the acrylonitrile and water obtained from said further distillation is cooled to form an acrylonitrile phase and an acrylonitrile saturated aqueous phase and which includes recycling the acrylonitrile phase into admixture with the catholyte emulsion and in which prior to said recovery of adiponitrile from said separated oil phase the separated oil phase is extracted with an extracting agent comprising said acrylonitrile saturated aqueous phase for the removal of supporting electrolyte salt.

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WILBUR L. BASCOMB, JR., Primary Examiner

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