

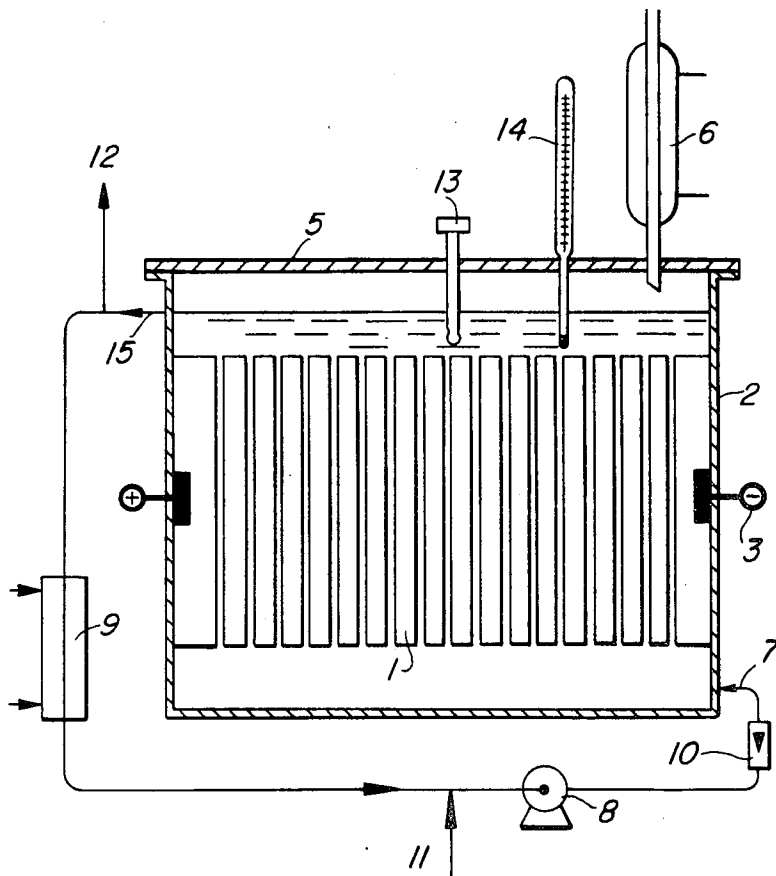
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 [32] Priority **Oct. 24, 1968**
 [33] **Germany**
 [31] **P 18 04 809.4**

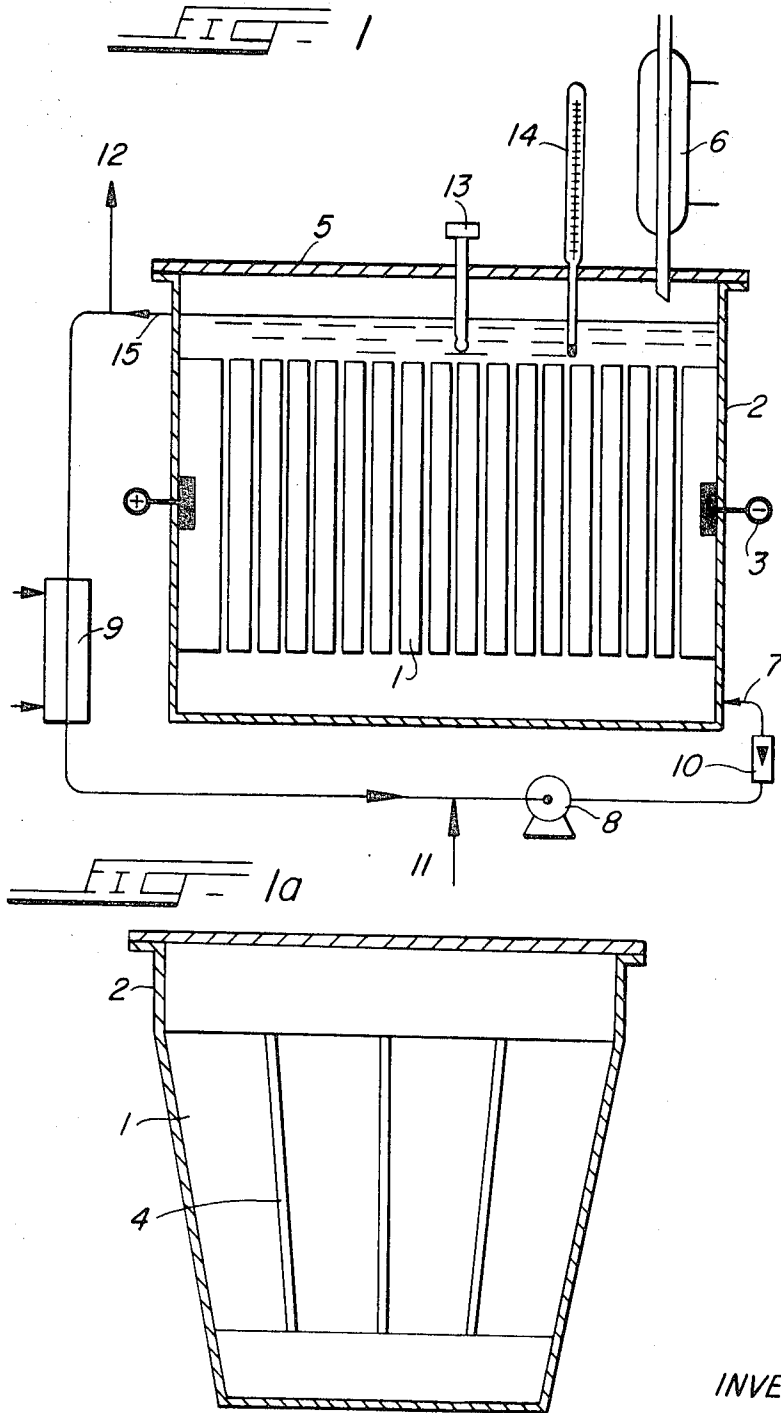
[56] **References Cited**
UNITED STATES PATENTS
 3,193,480 7/1965 Baizer et al. 204/73 A
 3,427,234 2/1969 Guthke et al. 204/73 A
 3,511,765 5/1970 Beck et al. 204/73 X
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[54] **PRODUCTION OF ADIPONITRILE**
4 Claims, 4 Drawing Figs.

[52] U.S. Cl. **204/73 A,**
204/269
 [51] Int. Cl. **C07b 29/06,**
B01k 3/00
 [50] Field of Search **204/73, 73**
A

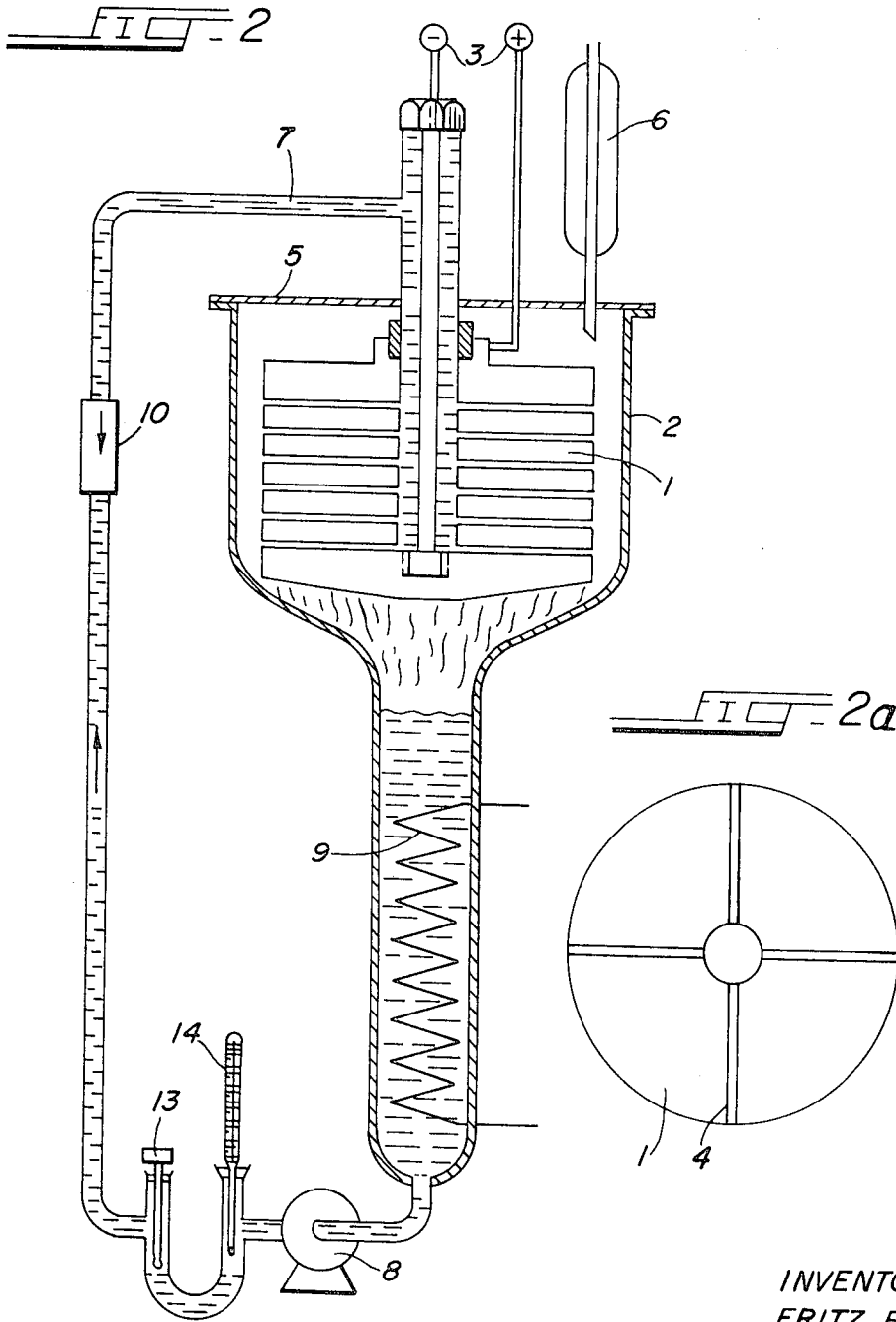
ABSTRACT: Production of adiponitrile by direct electrochemical hydrodimerization of acrylonitrile in a medium which contains acrylonitrile, and electrolyte salt, water and, if desired, a solvent at a temperature of from 10° to 60° C. and a pH value of from 1 to 10 using liquid-impermeable electrodes. The medium is passed through the pairs of electrodes which are 0.05 to 2 mm. apart. Adiponitrile is an important intermediate for synthetic fiber manufacture.





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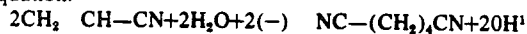
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PRODUCTION OF ADIPONITRILE

The present invention relates to a process for the production of adiponitrile by electrochemical hydrodimerization of acrylonitrile.

The production of adiponitrile by electrochemical hydrodimerization of acrylonitrile according to the empirical equation:



is of great practical interest because the desired substance is obtained direct from an easily accessible starting material. In recent years quite a number of methods for carrying out this reaction have become known, for example direct electrolysis is a cell divided by diaphragms or in undivided cells or by indirect electrolysis by reaction of acrylonitrile with alkali metal amalgam and electrolytic production of the alkali metal amalgam. Undivided cells have the advantage over cells divided by diaphragms or being easier to operate industrially and of simplicity in design. The amalgam method has the disadvantage that it is carried out in two stages and that large amounts of inorganic salts are formed.

A number of methods for electrochemical hydrodimerization of acrylonitrile in undivided cells are known. In the method described in *J. Electrochem. Soc.*, 111, 215 (1964), (1964), however, considerable anodic degradation is observed of the organic salts which are used in high concentration.

It is known from Belgian Pat. Specification No. 683,934 that one or more pairs of liquid-permeable electrodes whose electrodes are only a short distance apart and which can be set in vibration can be used for electrochemical hydrodimerization. This method enables the electrolysis to be carried out at industrially adequate current densities with only low concentrations of quaternary ammonium salts so that anodic degradation of the electrolytes is very slight. The method is however relatively expensive in terms of equipment.

In Belgian Pat. Specification No. 684,436 it is disclosed that electrolysis can be carried out in a conventional undivided cell using graphite cathodes in the presence of high concentrations of alkali metal phosphates and small additions of quaternary ammonium salts. In this method the reaction mixture which is present as an emulsion has to be circulated very rapidly. Moreover the current/potential values are very unfavorable.

It is known from Dutch Pat. Application No. 67 04 123 that for the electrochemical hydrodimerization of acrylonitrile in undivided cells, reaction mixtures can be used which contain high concentrations of salts such as sodium perchlorate or potassium thiocyanate and high concentrations of aprotic solvents such as dimethylformamide or dimethylsulfoxide. Our own experiments have shown that these solvents are however appreciably degraded anodically at the high concentrations used.

It is an object of the present invention to provide a process for the electrochemical hydrodimerization of acrylonitrile which gives adiponitrile in very high yields and excellent purity. Another object of the invention is to provide a process offering high space-time yields even at low current densities.

In accordance with this invention these and other objects and advantages of the invention are achieved in a process for the production of adiponitrile by direct electrochemical hydrodimerization of acrylonitrile in a medium which contains acrylonitrile, an electrolyte salt, water and, if desired, a solvent at a temperature of from 10° to 60° C. and a pH value of from 1 to 10 using liquid-impermeable electrodes which comprises moving the medium through one or more pairs of electrodes which are 0.05 to 2 mm. apart and may be separated by liquid-permeable insulators.

The low current densities which may be used in the new process result in very favorably cell potentials even at low concentrations of electrolyte salt, for example at concentrations of about 1 percent by weight.

Starting materials, auxiliaries and reaction conditions do not differ from those of prior methods.

An electrolysis mixture is generally used which contains from 10 to 90 percent by weight, advantageously from 15 to

65 percent by weight, of acrylonitrile. A mixture having a content of from 20 to 35 percent by weight of acrylonitrile may be used with particular advantage.

Water is used as a proton donor, usually in a concentration of from 3 to 40 percent by weight; higher or lower water contents may however be used, for example down to 1 percent or up to 94 percent by weight. It is advantageous to use mixtures which from a homogeneous liquid phase. Both acrylonitrile solutions in water and solutions of water in acrylonitrile may be used. Although the reaction may be carried out without a solvent or diluent, it may be advantageous to use polar solvents in order to set up specific concentrations of acrylonitrile and water in the mixture. Such solvents may either be inert or to some extent undergo change during the reaction and they may also themselves act as proton donors. The following are particularly suitable as solvents: lower aliphatic alcohols such as methanol, ethanol, butanol and preferably isopropanol; acetonitrile; ethers which are wholly or partly miscible with water such as tetrahydrofuran, dioxane and glycol monomethyl ether; or open or cyclic amides or lower carboxylic acids which may be substituted by alkyl or dialkyl on the nitrogen atom, for example formamide, monomethylformamide, dimethylformamide, dimethylacetamide, diethylacetamide, N-methylpyrrolidone, or also the end product adiponitrile. When solvents or diluents are used they are generally used in concentration of from 5 to 40 percent by weight.

It is advantageous to add to the electrolysis mixture a small amount of a substance which is more easily oxidized anodically than the electrolyte salt, acrylonitrile or adiponitrile. Anodic oxidation of the starting material or reaction product which occurs as a secondary reaction and results in loss of yield is suppressed by such an addition. Examples of suitable substances are lower alcohols, particularly methanol, and lower aldehydes. The substance which is more easily oxidized is advantageously added to the reaction mixture in an amount of from 5 to 30 percent by weight. If the whole of the oxygen normally formed in the reaction was to be used up for oxidation of methanol, about 100 g. of methanol per kg. of adiponitrile would be required.

It is preferred to use quaternary ammonium salts of certain acids, preferably in concentrations of less than 5 percent by weight, as electrolyte salts. The salt may however be used in higher concentrations, for example up to 20 percent by weight. The cations of the salts have a very negative discharge potential. Those anions are particularly suitable which are only difficultly oxidizable or not at all, for example monoalkyl sulfates, sulfates, fluorides, tetrafluoroborates, fluorosulfonates, toluene sulfonates and benzene sulfonates. It is preferred to use tetramethylammonium and tetraethylammonium salts, particularly of ethyl sulfate and p-toluene sulfonate. Other salts which have proved to be suitable are for example triethylmethylammonium methyl sulfate, bis-tetraethylammonium sulfate, bis-tetrabutylammonium sulfate, tetramethylammonium methyl sulfate and tetramethylammonium fluorosulfate. Mixtures of salts may also be used, sometimes with advantage.

Materials which do not pass into solution anodically under electrolysis conditions, for example platinum in the form of platinumized titanium or in the form of platinum foil which has been struck by means of a conducting adhesive to graphite are suitable as anodes. Coatings of lead dioxide which may be applied to conducting materials such as graphite, nickel or titanium, for example in a thickness of from 20 to 200 microns, are particularly advantageous owing to their favorable price and high resistance in electrolytes containing acrylonitrile. A completely smooth and level anode surface can be prepared on lead dioxide by polishing with carborundum powder. Other suitable anodes consist of magnetite, graphite or gold.

The cathode surface generally consists of lead, amalgamated lead, copper, electrolytically amalgamated copper, silver, amalgamated silver and preferably of graphite or plastics-bonded graphite.

The process according to the invention may be carried out advantageously when the anodes consist of lead dioxide and the cathodes of graphite. When using these electrodes the electrode arrangement to be used according to the invention is surprisingly insensitive to short circuits, in that the potential does not collapse upon slight contact of the electrodes.

It is an essential feature of the process according to the invention that in each electrode pair to be used the electrodes are 0.05 to 2 mm. apart, preferably from 0.1 to 0.5 mm. Such a small gap may be provided most simply by using plate electrodes having the smoothest possible surface. Electrodes having other shapes may however be used, for example pairs of concentric cylindrical electrodes. It is not expedient to use gaps smaller than 0.05 mm. because the risk of contact is appreciable with smaller gaps and the residence time of the electrolytes in the capillary gap is too long.

The reaction mixture is advantageously moved through in the form of a capillary flow between the anode and cathode. It is also possible however to pass the reaction mixture at such a rate between the electrodes that conveyance takes place in the form of a turbulent flow.

The yield of adiponitrile is generally more or less independent of the pH at values between 1 and 10. The addition of acids or bases during electrolysis for controlling the pH is therefore usually unnecessary. When carbon dioxide or boron trifluoride is added during electrolysis to the reaction mixture, a certain increase in yield is however obtained. These gaseous substances are advantageously added in an amount of from 0.5 to 10 ml. per minute per ampere.

Temperatures generally of from 10° to 60°, preferably from 20° to 50° C., particularly from 25° to 40° C., are used for the electrolysis.

It is advantageous to carry out the process according to the invention at current densities of from 1 to 30 amperes per square decimeter, preferably from 3 to 10 a./dm². Cell potentials of from 3.8 to 6 volts are generally necessary to set up these current densities.

Conversion of the acrylonitrile used is from 10 to 80 percent. Electrolysis can be carried out batchwise or continuously. The continuous method may be carried out by allowing the reaction mixture to circulate and after attainment of the desired conversion keeping this constant by metering in fresh reaction mixture with simultaneous withdrawal of reacted mixture from the cell.

An apparatus for carrying out the process according to the invention is shown diagrammatically in FIGS. 1 and 1a of the drawings. A plurality of flat plate bipolar electrodes 1 are connected in series. The plates having a thickness of for example from 5 to 20 mm. may be consist for example of graphite, and the anode side can be coated with lead dioxide. The cathode side may be coated with lead or with copper in pure or amalgamated form. The electrodes have a slightly trapezoidal shape so that they have liquidtight contact with the sidewalls of the tank 2. The current leads 3 are connected to the end plates. To maintain a uniform spacing between the plates, small strips 4 of insulating material, for example plastic film, such as polyester film, may be arranged between the plates parallel to the flow. The thickness of the strips depends on the desired gap and may be from 0.05 to 2 mm. An offgas pipe 6 passes through cover 5 of the cell. The reaction mixture supplied through feed line 7 is moved through the pairs of electrodes, leaves the cell through a discharge 15 and is circulated by means of a centrifugal pump 8, passing through a heat exchanger 9 and a flowmeter 10. For continuous operation the cell is also fitted with an inlet 11 for fresh reaction solution and an outlet 12 for partly reacted mixture. The pH is measured at 13 and the temperature at 14. The process makes possible the use of low concentrations of salt. Particularly at low concentrations of salt the discharge is very easy to process. It may be carried out for example by removing the components of low boiling point, namely unreacted acrylonitrile, any solvent present, propionitrile and water in a film evaporator. High-boiling components (adiponitrile and

cynoethylation products of water and of the alcohol, if any are separated for example by fractional distillation. Oligomeric acrylonitrile and salt remain as residue.

The following examples will further illustrate the invention. In the examples: PN=propionitrile; AN=adiponitrile; CEE=biscyanodiethyl ether; HPN= β -hydroxypropionitrile; SN=succinonitrile; BP=other byproducts; R=residue; TEAES=tetraethylammonium ethyl sulfate.

Yields are all given in percent with reference to acrylonitrile reacted.

EXAMPLE 1

Electrolysis is carried out in an apparatus as shown diagrammatically in FIGS. 2 and 2a.

The cell is built up from circular graphite discs 1 having a diameter of 117 mm. and a thickness of 10 mm. which have a central bore having a diameter of 30 mm. The area of the electrode is exactly 1 square decimeter. The arrangement is located in a glass cell 2. The terminals are connected by leads 3 with a source of direct current. Between each pair of electrodes there are provided four small strips 4 of polyester film having a thickness of 0.2 mm. An offgas pipe 6 passes through the cover 5. The reaction solution is pumped through a feed line 7 by means of a circulating pump 8 into the cavity of the electrode system, flows through the capillary gaps and returns over a cooler 9 and a flow meter 10. The pH and temperature of the circulated mixture are measured with a glass electrode 13 and a thermometer 14. The anode side of each graphite disc is covered with a layer of lead dioxide having a thickness of 190 microns which has been applied by electrolytic deposition from nitric acid lead nitrate solution at 65° C. and a current density of 2 a./dm². Both sides of each graphite disc are ground completely flat with fine carborundum powder.

At the beginning of electrolysis 1,000 g. of a mixture of 55 percent by weight of acrylonitrile, 28 percent by weight of isopropanol, 16 percent by weight of water and 1 percent by weight of TEAES is introduced into the cell. Electrolysis of the recirculating reaction mixture is carried out at 10 amperes, i.e. 10 a./dm². The temperature is kept at 30° C. by water cooling. A potential of 23.4 volts is set up at the six pairs of bipolar electrodes, equivalent to an average individual potential of 3.9 volts. After 1 hour and 23 minutes, i.e. 83.4 ampere hours, and a theoretical conversion of acrylonitrile of 30 percent the electrolysis is discontinued. The reaction mixture is clear and colored quite pale yellow. The pH value is 3.5 during electrolysis.

The product worked up by distillation of the low-boiling components in a film evaporator followed by distillation of the high-boiling components at subatmospheric pressure. Analysis for sulfur and nitrogen are carried out in the residue and the content of oligomeric acrylonitrile is calculated therefrom; the PN is determined by gas chromatography in the low-boiling fraction and the AN, CEE, HPN, SN and BP in the high-boiling fraction.

The yields, together with three other experiments with lower salt concentrations are given in table 1. CS=concentration of salt in percent.

TABLE 1

CS	Yield (percent)						Current efficiency (percent)		V ₀ (volts)
	AN	PN	CEE+HPN	SN	BP	R	AN	PN	
1.0	81.0	1.4	1.2	0.3	1.7	14.4	80	3	3.9
0.75	82.2	0.6	0.7	0.3	1.0	14.2	80	1	4.3
0.50	84.0	1.0	1.0	0.2	1.8	12.0	81	2	4.5
0.25	86.0	0.6	0.8	0.4	0.8	11.2	80	1	5.0

When electrolysis is carried out for comparison under the same reaction conditions as in experiment 1 using the vibrating cell (electrode gap also 0.2 mm.) described in Belgian Pat. Specification No. 683,934 a cell potential of 4.5 volts (as com-

pared with 3.9 volts in the present example) is necessary to set up the current density.

EXAMPLE 2

The reaction is carried out in the cell described in example 1 under the conditions specified therein but with the difference that the pH is kept at a value between 1 and 8 during the electrolysis by adding 1.6 M of tetramethylammonium hydroxide solution or concentrated sulfuric acid. The concentration of salt is 0.75 percent by weight. The results are collected in table 2.

TABLE 2

pH	Yield (percent)						Current efficiency (percent)			V _c (volts)
	AN	PN	CEE+HPN	SN	BP	R	AN	PN		
8	80.6	1.4	0.5	1.0	1.2	15.3	75	2	4.5	
7	82.2	0.8	0.5	1.3	0.8	14.4	78	2	4.3	
6	82.7	0.7	0.5	0.5	1.9	13.7	80	2	4.5	
5	82.2	0.6	0.7	0.3	1.9	14.2	80	1	4.3	
4	84.1	0.3	0.6	0.3	1.7	12.0	82	1	4.5	
3	81.3	0.5	0.4	0.0	1.8	16.0	80	1	4.5	
2 ¹	81.7	0.6	0.4	0.0	1.9	15.4	80	1	4.5	
1 ¹	84.7	0.3	0.3	0.3	0.6	13.8	80	1	4.7	

¹ With only 0.5% of salt.

EXAMPLE 3

The reaction is carried out in a cell as described in example 1 under the conditions therein specified but at different current densities. The concentration of salt is 0.75 percent by weight. The results obtained are collected in table 3 where *j* is measured in amperes per square decimeter.

TABLE 3

<i>j</i>	Yield (percent)						Current efficiency (percent)			V _c (volts)
	AN	PN	CEE+HPN	SN	BP	R	AN	PN		
5	85.7	0.3	0.3	0.3	2.0	11.4	80	1	3.8	
7	85.3	1.2	1.5	0.7	1.8	9.5	81	2	4.0	
10	82.2	0.6	0.7	0.3	1.9	14.2	80	1	4.3	
13	83.6	0.9	1.9	0.4	3.4	9.8	81	2	4.8	
20	80.4	0.3	2.3	0.0	2.7	14.3	80	1	5.5	

EXAMPLE 4

The reaction is carried out in the cell described in example 1 under the conditions described therein but with higher conversions. The concentration of salt is 0.75 percent by weight. The results are collected in table 4
TCC=theoretical current conversion in percent.

TABLE 4

TCC	Yield (percent)						Current efficiency (percent)			V _c (volts)
	AN	PN	CEE+HPN	SN	BP	R	AN	PN		
30	82.2	0.6	0.7	0.3	1.9	14.2	80	1	4.3	
40	80.6	1.2	1.5	0.3	1.9	14.5	83	2	4.5	
50	82.5	1.8	0.6	0.2	2.0	12.9	80	3	4.3	
60	82.0	2.4	0.6	0.2	2.4	12.6	78	4	4.5	
70	80.1	4.3	0.6	0.3	2.8	11.9	70	7	4.2	

EXAMPLE 5

The reaction is carried out in the cell described in example 1 under the conditions specified therein but using other cathodes. The metals used are applied direct to the graphite by electrolytic deposition in a layer thickness of 100 microns. Amalgamation takes place in the case of lead by treatment with a nitric acid solution of mercury(II) nitrate and in the

case of copper by electrolytic deposition from a sulfuric acid solution of mercury(II) sulfate. The concentration of salt is 0.75 percent by weight and the current density is 7 amperes per square decimeter. The results are collected in table 5. In the table:

Ca=cathode

A=scraped lead

B=amalgamated lead

C=amalgamated copper

10 D=A graphite-filled phenol-formaldehyde resin known under the registered trademark Bascodur.

TABLE 5

Ca	Yield (percent)						Current efficiency (percent)			V _c (volts)
	AN	PN	CEE+HPN	SN	BP	R	AN	PN		
15 A	83.8	2.0	0.3	2.3	11.6	80	4	4.2		
20 B	81.0	2.4	0.6	0.3	4.1	11.6	82	5	4.1	
C	80.1	9.8	0.4	3.9	5.8	64	16	4.0		
D	83.6	1.3	0.3	2.3	12.5	76	2	4.2		

EXAMPLE 6

The reaction is carried out in the cell described in example 1 under the conditions specified therein, but during electrolysis carbon dioxide is passed at a rate of 20 ml. per minute or boron trifluoride at a rate of 5 ml. per minute is passed into the reaction mixture at the lower end of the cooler in FIG. 2. The concentration of salt is 0.75 percent by weight. The yield of AN can thus be raised to 86.8 percent and 87.5 percent, respectively, at current efficiencies of 80 percent and 82 percent.

EXAMPLE 7

In a cell as described in example 1 at the beginning of the electrolysis 1,000 g. of a mixture of 25 percent by weight of acrylonitrile, 30 percent by weight of acetonitrile, 28.5 percent by weight of isopropanol, 16 percent by weight of water, 0.35 percent by weight of TEAES and 0.15 percent by weight of tramethylammonium methyl sulfate is fed in. Electrolysis is carried out at 7 amperes (=7 a./dm²), 30° C. and a pH of about 3. During the electrolysis, nothing is added to control the pH. The cell potential per pair of electrodes is 4.3 volts. After 1 hour 48.5 minutes, (i.e. 75.9 ampere hours and a theoretical current conversion of acrylonitrile of 60 percent) the electrolysis is discontinued. The discharge from the electrolysis is quite clear and pale yellow in color. After conventional distillation the following yields are determined:

Yields with reference to acrylonitrile reacted:

55 AN	92.0%
PN	4.5%
CEE	
HPN	
SN	
BP	1.7%
R	1.8%

Current efficiencies: PS

AN	82.0%
PN	8.0%

65 Energy yield:

2.61 kwh. per kg. of AN

We claim:

1. In a process for the production of adiponitrile in an electrolytic cell undivided by diaphragms by direct electrochemical hydrodimerization of acrylonitrile in a medium which contains acrylonitrile, an electrolyte salt, water and, if desired, a solvent at a temperature of from 10° to 60° C. and a pH value of from 1 to 10 using at least one pair of liquid-impermeable electrodes, the improvement which comprises: passing the

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medium in the form of a capillary flow through a uniform area separating the anode and cathode of said paired electrodes, said electrodes being for 0.05 to 2 apart.

2. A process as in claim 1 wherein the electrodes of each pair are separated by a liquid-permeable insulator.

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3. A process as in claim 1 wherein a plurality of pairs of electrodes is used.

4. A process as in claim 1 wherein in each electrode pair the anode consists of lead dioxide and the cathode consists of graphite.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,616,320 Dated October 26, 1971

Inventor(s) Fritz Beck and Hans Leitner

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

First page, left-hand column, seventh line, "Amlin-" should read -- Anilin- --.

Column 1, line 8, " $2\text{CH}_2\text{CH-CN}+2\text{H}_2\text{O}+2(-)\text{NC}-(\text{CH}_2)_4\text{CN}+2\text{OH}^2$ " should read -- $2\text{CH}_2=\text{CH-CN}+2\text{H}_2\text{O}+2(-)\rightarrow\text{NC}-(\text{CH}_2)_4\text{CN}+2\text{OH}^-$ --; line 24, delete "(1964)"; line 69, "favorably" should read -- favorable --.

Column 2, line 8, "from" should read -- form --; line 13, "inert" should read -- inert or --; line 63, "struck" should read -- stuck --.

Column 4, line 23, "offgas pipe" should read -- offgas gap pipe --.

Column 6, line 39, "28.5" should read -- 28.5 percent --.

Column 7, line 3, Claim 1, "2 apart" should read -- 2 mm. apart --.

Signed and sealed this 9th day of May 1972.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents