Jan. 27, 1970 G. T. MILLER 3,492,209

HYDRODIMERIZATION IN A WICKING TYPE CELL

Filed May 15, 1967 2 Sheets-Sheet 1

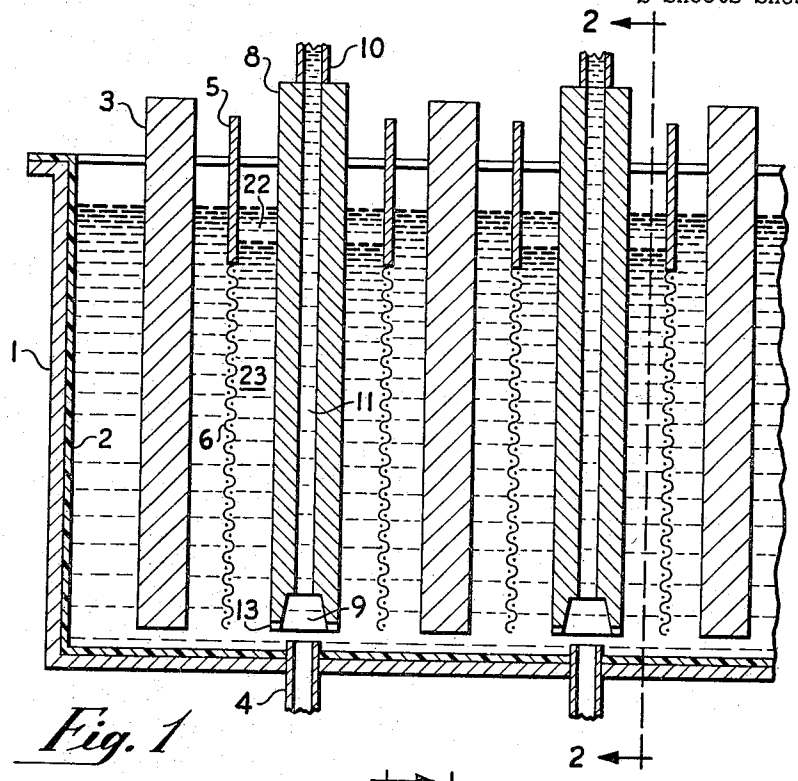

Fig. 1

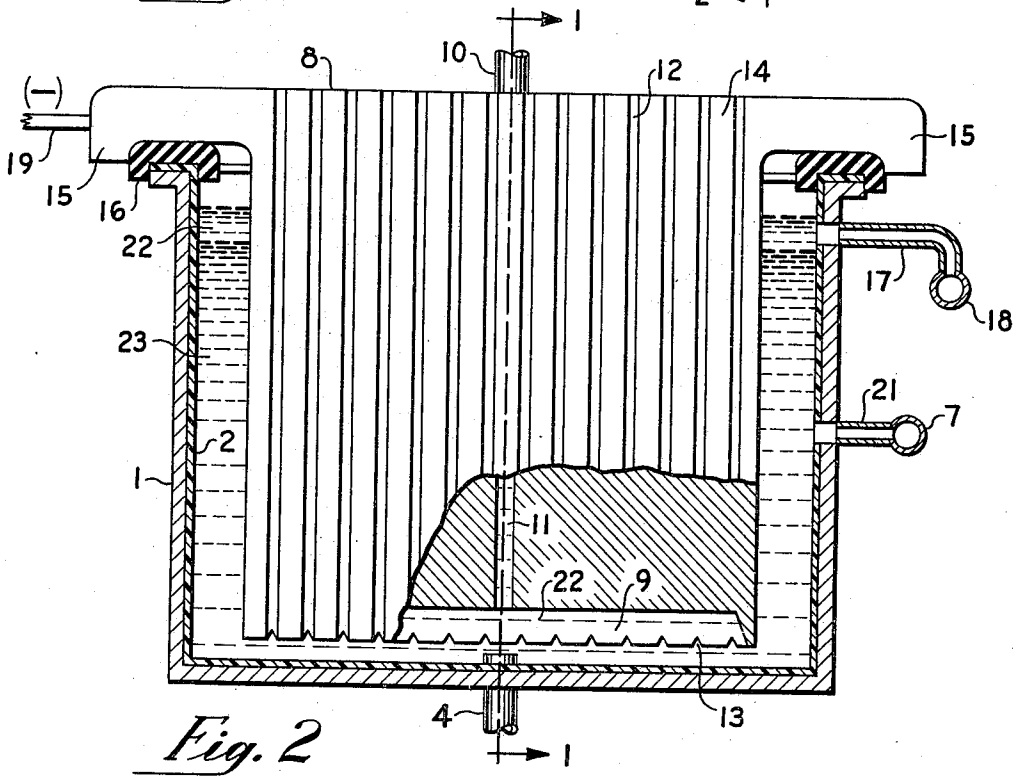

Fig. 2

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HYDRODIMERIZATION IN A WICKING TYPE CELL

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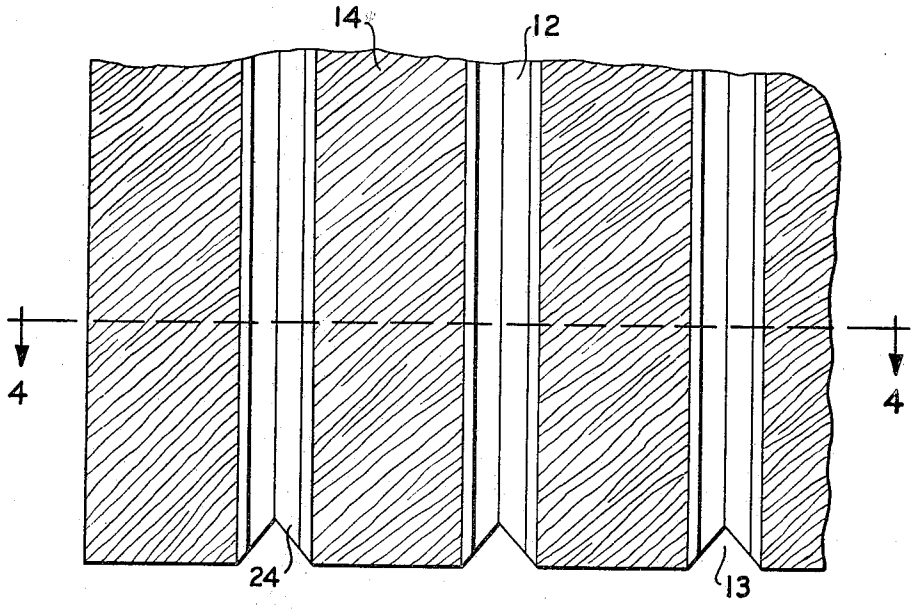

Fig. 3

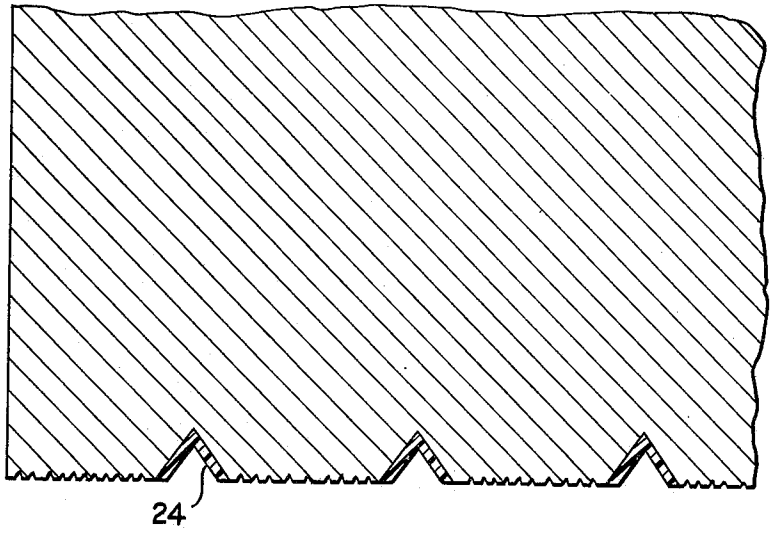

Fig. 4

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HYDRODIMERIZATION IN A WICKING TYPE CELL

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Continuation-in-part of applications Ser. No. 321,240, Nov. 4, 1963, and Ser. No. 550,245, May 16, 1966. This application May 15, 1967, Ser. No. 638,484

Int. Cl. B01k *1/00*

U.S. Cl. 204—73 6 Claims

ABSTRACT OF THE DISCLOSURE

The electrolytic coupling of olefinic compounds, e.g., the production of adiponitrile by hydrodimerization of acrylonitrile, is accomplished in an acid electrolyte by flowing a film of the olefinic compound onto the face of the cathode, which preferably is provided with vertical grooves. The product, together with any unreacted olefinic compound rises to the top of the electrolyte, from whence it may be continuously removed.

Cross reference

This is a continuation-in-part of my copending applications for U.S. Patents Ser. No. 321,240, filed Nov. 4, 1963, now Patent No. 3,361,653, and Ser. No. 550,245, filed May 16, 1966, now Patent No. 3,361,656.

Background of the invention

The electrolytic hydrodimerization of acrylonitrile to form adiponitrile is the subject of an article by Manual M. Baizer, Journal of the Electrochemical Society, vol. III, page 215, and in U.S. Patents 3,193,477 and 3,193,-477 and 3,193,480. This process utilizes a two-compartment cell wherein a permselective membrane diaphragm separates the anolyte from the catholyte, and a solution of acrylonitrile in the catholyte is maintained in the cathode compartment of the cell. Effluent from the cathode compartment is treated to recover adiponitrile product and unreacted acrylonitrile. In order to dissolve an adequate amount of the acrylonitrile in the catholyte, the catholyte solution is made from a quaternary ammonium salt or some similar salt which has the property of promoting solution of organic materials in aqueous liquids.

In this process, pH control of the catholyte is important, as an acidic catholyte causes the formation of acrylonitrile polymer while excessive alkalinity causes other undesirable side reactions. The process preferably is operated at a pH in the range of from about 7 to about 9.5 or 10. Generally, an acid will be used as anolyte and regulated amounts of the latter may be added to the catholyte to control the alkalinity, since the hydrodimerization reaction causes a gradual increase in the alkalinity if no acid is added to the catholyte. Generally, the best results are obtained when the catholyte is maintained just slightly alkaline.

Relatively expensive non-porous permselective cationic membranes are required to separate the anolyte from the catholyte. This complicates cell design; and difficulties are caused whenever the membrane becomes ruptured, as the consequent introduction of acid anolyte into the cathode compartment causes polymer formation and the cell must be disassembled and cleaned before it can, again, be placed in operation.

Description of the invention

I have now discovered a means for the electrolytic hydrodimerization of acrylonitrile to adiponitrile, whereby

an acidic electrolyte may be used in both the anode and cathode compartments of the cell with the formation of little or no polymer and very small amounts of other undesired by-products. My process obviates the necessity for permselective diaphragms between anolyte and catholyte, and it is only necessary to employ means for preventing oxygen or other gas evolved at the anode from coming in contact with the material reacting at the cathode.

The gist of my process is that a thin film of a liquid comprising acrylonitrile is maintained on the face of the cathode of an electrolyte cell employing an aqueous (preferably acidic) electrolyte, while direct current is applied to the cell. I have discovered that under these conditions, although acrylonitrile is somewhat soluble in aqueous liquids, the reaction to form adiponitrile proceeds substantially without polymer formation, despite the presence of the aqueous acid solution surrounding the cathode.

One method of practicing my invention is illustrated by the appended drawings. FIGURES 1 and 2 are cross-sectional views of an electrolytic cell, FIGURE 1 being a cross-section on plane **1**—**1** of FIGURE 2, and FIGURE 2 being a cross-section on plane **2**—**2** of FIGURE 1. FIGURE 3 is a greatly enlarged elevation of a portion of the cathode **8** of FIGURES 1 and 2; and FIGURE 4 is a cross-sectional view on plane **4**—**4** of FIGURE 3.

The cell is constructed with a steel tank **1** which is provided with a plastic lining **2**, lead alloy anodes **3** and lead cathodes **8**. As shown in FIG. 2, the cathodes **8** are supported by arms **15** resting on insulators **16** resting on the sides of tank **1**. The anodes are similarly supported by arms not shown. Partitions **5**, arranged between each anode and the cathodes, are supported on lugs not shown which rest on the side walls of tank **1**. Porous diaphragms **6** are suspended from the partitions **5**. The diaphragms may be made of any porous or foraminous sheet-like material which will permit passage of electrolyte while preventing contact of gaseous anodic products with the liquid organic materials in contact with the cathode. Each cathode **8** is provided with a channel **9** at the bottom and with pipe **10** which leads into a hole **11** which extends down to channel **9**. Both faces of cathode **8** are provided with a series of vertical grooves **12**. Horizontal grooves **13** are adapted to lead liquids from channel **9** into grooves **12**. Referring to FIGURES 3 and 4, the lands or spaces **14** between grooves **12** have been abraded to form a series of fine scratches extending at acute angles to the grooves on either side. The grooves **12** preferably are coated with an organic material **24** which is substantially inert to electrolyte and which is preferentially wetted by acrylonitrile. Teflon® polytetrafluoroethylene is suitable for this purpose. A product outlet pipe **17** opposite each cathode empties into a product manifold pipe **18**. An electric connection to the cathode is shown at **19**. The connections to the anodes are not shown. As suggested by FIGURE 1, which is cut away at one side, the cell may be made with an indefinite number of anodes and cathodes, e.g., cells with 10 to 20 cathodes are practical, although cells with from 1 to more than 100 could be used.

A series of pipes **21** connected to manifold pipe **7** serve for the introduction of water or electrolyte into the cell during cell operation, to maintain the electrolyte at a substantially constant level.

Aqueous acidic electrolyte, e.g., a solution of sulfuric or phosphoric acid, is introduced in the cell to a level above the bottoms of partitions **5**.

Acrylonitrile is fed into pipes **10**, which are connected to a common manifold not shown, so as to feed acrylonitrile down through the center of each cathode into channel **9** thereof, from whence it flows out through horizontal slots or grooves **13** into the vertical grooves **12**. Flow-

ng up in the vertical grooves **12**, acrylonitrile by capillary action spreads out over lands **14** between the grooves, over the face of the electrode, where it is converted to adiponitrile. The resulting adiponitrile, together with any unreacted acrylonitrile, flows upward and forms a liquid layer **22** floating on top of the electrolyte **23**, and continuously overflows out through pipes **17** and **18**. At the anode, oxygen gas is formed and flows up and out within the confines of diaphragms **6** and partitions **5**.

An alternate method of feeding in the acrylonitrile employs pipes **4** passing through the cell bottom to deliver the acrylonitrile into the channels **9**. With this method, pipes **10** and holes **11** may be eliminated.

In operating such a cell with sulfuric acid as electrolyte, I prefer to use from 1 to 5.5 molar acid solution (i.e., 98 to 539 grams per liter of sulfuric acid) and to operate the cell at a cathodic current density of from 5 to 200 amperes per square foot. Operating under these conditions, it is possible to obtain adiponitrile in good yields with little or no formation of polymer or other by-products.

The invention is further illustrated by the following example.

Example 1

A laboratory electrolytic cell was constructed of glass, with anode and cathode compartments separated by a fritted glass diaphragm. The cathode was a graphite cylinder having a series of vertical (longitudinal) grooves about 0.6 mm. wide by 1.0 mm. deep extending from one end to the other and an axial hole connected with a pipe leading to the exterior of the cell. The grooves on the cathode were coated with Teflon polytetrafluoroethylene. The cell was charged with 3.87 molar sulfuric acid solution and the graphite cathode was placed in a vertical position in the electrolyte. Acrylonitrile was fed into the cell so that it formed a separate layer floating on top of the aqueous acid electrolyte. A pump was arranged to take liquid from this acrylonitrile layer and force it down through the pipe and axial hole of the cathode, from which the acrylonitrile ascended in the grooves of the cathode and, when electric current was turned on, acrylonitrile spread over the face of the cathode and thence rose up into the supernatant layer of acrylonitrile.

A piece of platinum sheet was utilized as the cell anode. While acrylonitrile was pumped down through the electrode as above described, direct electric current was applied at a cathodic current density of about 9 amperes per square foot (one ampere per square decimeter). During electrolysis, acrylonitrile was added to the cell, to replace that lost by evaporation. After 20 hours of electrolysis, the resulting mixture of acrylonitrile and adiponitrile was removed, and the cell was washed out with fresh acrylonitrile. The acrylonitrile liquids were combined, evaporated down and the resulting liquid subjected to gas chromatography analysis, which gave the following results:

Adiponitrile	22.3 percent by weight.
Bis-cyanodiethyl ether	Trace.
Higher boilers	0.8 percent.
Solids	0.3 gram.

Any strongly acidic material soluble in water may be utilized as electrolyte, e.g., sulfuric, phosphoric, hydrochloric, hydrobromic acids, and even some organic acids such as formic acid, acetic acid, oxalic acid, and the like. I prefer, however, to use the mineral acids and to avoid the introduction of materials which would greatly increase the solubility of acrylonitrile in the electrolyte. Also, while small amounts of metallic compounds may be present, I prefer to use acidic solutions substantially free from metallic cations. Except when some particular gaseous anodic product is desired to be produced, I would prefer to utilize electrolytes such as sulfuric acid or phosphoric acid solutions, whereby the gaseous anodic product is simply oxygen, hydrogen ions liberated at the cathode being utilized for the hydrodimerization reaction. Essentially, then, with such acid as electrolyte, the electrolytic process constitutes an electrolysis of water, so that in continuous operation it is only necessary to continuously add a small amount of water to replace that which has become decomposed by electrolysis.

The concentration of acid in the aqueous electrolyte may be varied over a wide range from very dilute solutions to acids of considerable strength, e.g., having a concentration as high as 10 molar. Generally, I prefer to utilize mineral acid solutions of 1 to 5.5 molar strength.

While I prefer to use an acid as electrolyte, my invention is not restricted thereto, but I can also use water-soluble metal salts which do not greatly increase the solubility of acrylonitrile. Such salts include the alkali metal salts of inorganic acids, e.g., sodium sulfate, trisodium phosphate, potassium carbonate, potassium chloride, and the like. In any case, I prefer an electrolyte solution which will not dissolve more than about 10% by weight of acrylonitrile. Electrolytes dissolving larger amounts can be used, but the dissolved portion tends to undergo undesirable side reactions.

As cathode, I prefer to use one of the types disclosed in my aforesaid copending patent applications SN 321,240, filed Nov. 4, 1963, and SN 550,245, filed May 16, 1966. These electrodes, made of any suitable metal resistant to the electrolyte or of carbon, graphite or other conductive material, are provided with vertical grooves designed to uniformly flow films of liquid reactants over the electrode face. Liquid flowing up these grooves spreads out, by capillary action, over the flat areas or lands between the grooves, where apparently the reaction takes place. In a preferred modification, the lands between the grooves of the electrode are abraded or scratched so as to form tiny scratches at an angle to the grooves, as described in my aforesaid pending applications. This apparently facilitates the spreading of the acrylonitrile over the site of reaction and provides for the preferred simultaneous contact of electrode, electrolyte and reactant.

Also, it is sometimes preferable to coat the grooves with a plastic material, inert to the reactant and electrolyte, which is preferentially wet by the reactant, for example, Teflon polytetrafluoroethylene or the like. Other halogen-containing polymers that can be used for this purpose, include polytrifluoroethylene, polytrifluorochloroethylene, polyhexafluoropropylene, polyvinyl fluoride and polyvinylidene fluoride.

The rate of flow of the acrylonitrile across the cathode may be varied over a wide range if the flow rate is rapid, material arriving at the top of the cathode will be mostly acrylonitrile containing a small amount of the desired adiponitrile product; whereas if the flow rate is slow, the product will contain greater amounts of adiponitrile or may consist almost entirely of adiponitrile.

The temperature of the electrolyte is maintained below the boiling point of acrylonitrile, but otherwise may vary over a wide range, as low as 5 degrees centigrade, but I generally prefer to operate at a temperature of 50 to 70 degrees centigrade. If the temperature is excessively low, the acrylonitrile may not wet the electrode effectively. On the other hand, excessively high temperatures tend to increase the solubility of acrylonitrile in the electrolyte.

The cathodic current density may vary over a wide range, e.g., from about 5 to 200 amperes per square foot (0.5 to 20 amperes per square decimeter). Although adiponitrile can be produced at even higher current densities, the maximum preferred current density is that which molecular hydrogen just begins to appear on the cathode.

In place of pure acrylonitrile, I may feed to the electrolysis zone a mixture or solution of acrylonitrile with another liquid which is substantially insoluble and inert to the electrolyte and to the electrolytic reaction. Liquids

suitable for this purpose include hydrocarbons such as hexane, octane or other light petroleum fractions.

The small amount of acrylonitrile polymer which sometimes forms in the acidic electrolyte may be reduced or substantially eliminated by the addition of a polymerization inhibitor, e.g., hydroquinone, p-t-butyl catechol, quinone, p-nitrosodimethylaniline, di-t-butyl hydroquinone, 2,5-dihydroxy-1,4-benzoquinone, 1,4-naphthoquinone, chloranil, 9,10-phenanthraquinone, 4-amino-1-naphthol. The inhibitor preferably is mixed with the acrylonitrile before it is fed to the electrolytic cell, but it also may be added to the electrolyte, particularly if soluble therein. The optimum amount of inhibitor may vary from around 0.01 percent by weight or even less, to 5 percent by weight, or more. The types of material which inhibit polymerization of acrylic compounds, and their effective concentrations are well known.

In addition to the electrolytic hydrodimerization of acrylonitrile to adiponitrile, my invention is useful for accomplishing the electrolytic reductive coupling of a great many other olefinic compounds, particularly those having alpha, beta-unsaturation associated with a reactive group such as cyano, carboxylate or amido groups. Such compounds may be hydrodimerized, or other product of reductive coupling may be produced by subjecting mixtures of different olefinic compounds to electrolysis by my process. Examples of such compounds include methacrylonitrile, 1-chloroacrylonitrile, 1-fluoroacrylonitrile, crotononitrile, furmaronitrile, mucononitrile, 2-pentenenitrile, 2-methylenebutyronitrile, 1-propylacrylonitrile, acrylamide, 1-chloroacrylamide, 1-fluoroacrylamide, crotonamide, N,N'-dimethyl crotonamide and other crotonamides, methacrylamide, acrylic acid, methacrylic acid, 1-fluoroacrylic acid, crotonic acid, fumaric acid, cinnamic acid, methyl methacrylate, ethyl acrylate, butyl acrylate, ethyl cinnamate, monopropyl fumarate, ethyl crotonate, ethyl citraconate, 1-cyanobutadiene, 1-cyanocyclohexene, 1-cyano-3-ethyl-cyclohex-1-ene, 2-ethyloxyacrylamide, N,N'-diethylacrylamide and ethyl 2-ethoxyacrylate.

My invention further is useful for the reductive coupling of the above types of compounds with various olefinic ketones such as methyl vinyl ketone, mesityl oxide, etc., described in U.S. Patent 3,193,479, and for the coupling reactions with olefinic compounds having the pyridine ring, as disclosed in U.S. Patent 3,218,245. It also can be used for the reductive coupling of olefinic phosphonates, phosphinates, phosphine oxides and sulfones discolsed in U.S. Patent 3,249,521.

What is claimed is:

1. A process for the reductive coupling of an alpha, beta-olefinic compound which comprises passing a direct electric current through an aqueous electrolyte to a cathode, while maintaining a liquid film comprising said olefinic compound on the face of the cathode.

2. A process for the production of adiponitrile by electrolytic hydrodimerization of acrylonitrile which comprises passing a direct electric current through an acidic aqueous electrolyte to a cathode, while flowing a film of liquid comprising acrylonitrile across the face of the cathode.

3. A process according to claim **2** wherein the acrylonitrile flows upwardly in vertical grooves on the cathode face.

4. The process according to claim **3** wherein the electrolyte comprises a strong mineral acid.

5. A process according to claim **4** wherein a solution of 1 to 5.5 molar sulfuric acid is the electrolyte and the liquid rising in the electrode grooves is removed from the electrolyte and adiponitrile is recovered from said liquid.

6. A process according to claim **5** wherein the electrolyte is 1 to 6 normal phosphoric acid.

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