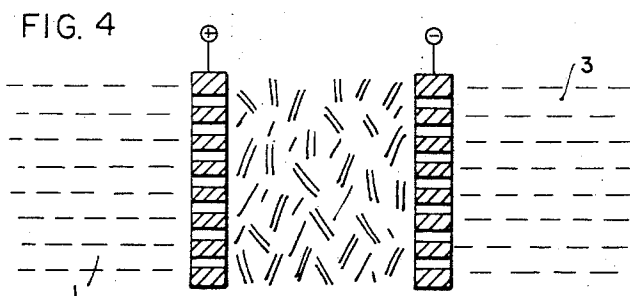
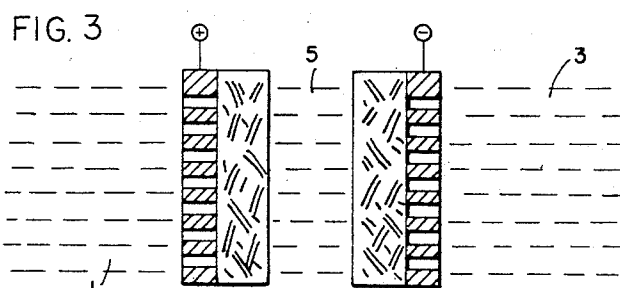
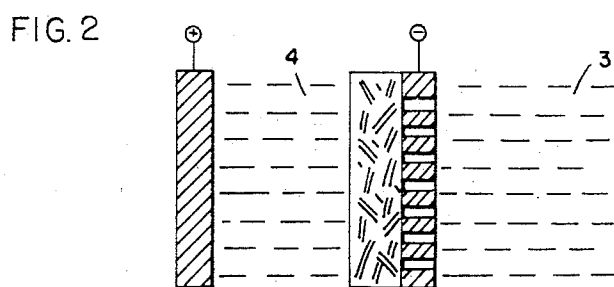
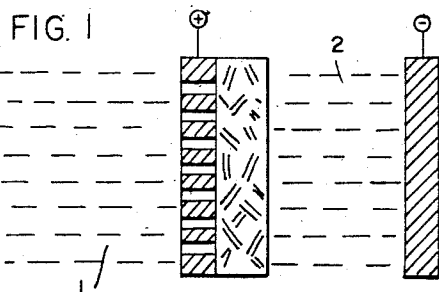


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ELECTROCHEMICAL HYDRODIMERIZATION OF
ALIPHATIC α,β -MONO-OLEFINICALLY
UNSATURATED NITRILES
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**ELECTROCHEMICAL HYDRODIMERIZATION
OF ALIPHATIC α,β -MONO-OLEFINICALLY
UNSATURATED NITRILES**

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9 Claims

This invention relates to a new process for electrochemical hydromerization of α,β -mono-olefinically unsaturated nitriles. It also relates to new apparatus for carrying out the said process.

In U.S. patent specification No. 3,193,480 it is stated that the reaction, known per se e.g. from British patent specification No. 967,956, of electrochemical hydromerization of acrylonitrile to adipodinitrile in which an electric current is passed through a catholyte consisting of a salt solution and containing acrylonitrile and through an anolyte consisting of a solution of a salt or acid and oxygen is disengaged at the anode may be carried out in an electrolytic cell in which the cathode space and the anode space are separated by an ion-exchange membrane. In this known arrangement, the ion-exchange membrane has no direct connection whatever with the electrodes.

We have found that electrochemical hydromerization of aliphatic α,β -mono-olefinically unsaturated nitriles by electrolysis of a system consisting of a catholyte containing a salt solution and acrylonitrile and an anolyte containing a solution of a salt or an acid, the catholyte and anolyte being separated by a solid polyelectrolyte, can be carried out more advantageously than by prior art methods by using an electrolytic cell in which at least one of the two electrodes is directly covered with a solid polyelectrolyte on the side facing the other electrode, the coated electrode having a certain permeability for the catholyte or anolyte and for the oxygen disengaged.

Referring to the accompanying diagrammatic drawings the anode is coated with a solid polyelectrolyte on the side facing the cathode (FIGURE 1), or the cathode is coated on the side facing the anode (FIGURE 2) or both anode and cathode are coated on the sides facing each other (FIGURE 3). In the case where both anode and cathode are covered with a solid polyelectrolyte, the latter may even extend from one electrode to the other, completely filling the space between them (FIGURE 4). The term "polyelectrolyte" comprises both inorganic and organic materials having ion-exchange properties.

The new process has further advantages in addition to those already mentioned. When the cathode is covered, the conducting salt and the solvent in the catholyte may be dispensed with; when the anode is covered, the salt and/or the acid in the anolyte may be dispensed with; and when using an electrolytic cell in which both cathode and anode are covered and connected by a solid polyelectrolyte, both the conducting salt and the acid may be dispensed with. The lower voltage drop in the electrolytic cell leads to better utilization of energy because heat loss is smaller.

The anode material should where possible be material having the lowest possible oxygen overvoltage, for examples less than 1 volt at 10 amps/sq. dm. When the anode is not covered with a solid polyelectrolyte, it may consist for example of platinum metals, graphite, lead, lead dioxide, nickel, nickel coated with nickel sulphide, nickel coated with nickel arsenide, or magnetite. Sintered graphite or sintered nickel material may also be used.

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Where the anode is covered on the side facing the cathode with a solid polyelectrolyte, the same anode material may be used as in the case of an uncovered anode, and then provision should be made by the design of the anode, for example in the form of netting or grids, or in the form of porous material, which may if desired be provided with grooves and/or channels, or in the form of a vibrating electrode, so that diffusion of the liquid anolyte can take place through the anode to the solid polyelectrolyte and the oxygen disengaged can escape. The anode itself may however partly consist of solid polyelectrolyte.

When using covered anodes, secondary reactions, for example oxidation reactions, are greatly decreased.

Similar considerations apply to the choice of the cathode material. It is advantageous to choose material having a high hydrogen overvoltage. When the cathode is not covered with a solid polyelectrolyte, it may consist for example of mercury, silver amalgam, lead, lead amalgam and lead alloys, particularly those with silver or mercury.

When the cathode is covered on the side facing the anode with a solid polyelectrolyte, the same cathode material (except the coherent layer of liquid mercury) may be used as in the case of the uncovered cathode. Again it is necessary to ensure, by the design, for example in the form of netting, grids, or heaped granulates, or by the use of sintered materials, that conveyance and convection of the liquid catholyte can take place through the cathode to the solid polyelectrolyte, while the electric current flows substantially direct from the cathode through the polyelectrolyte and not through the remaining cathode space containing the solution of catholyte containing the monomeric olefinically unsaturated nitrile. Cathodes consisting of silver amalgam or lead amalgam, but particularly those of superficially amalgamated silver, may be used with advantage.

The layers of polyelectrolyte used for the coating in general have thicknesses of 0.3 to 2 mm. and particularly of 0.5 to 1 mm. The cathode and anode are as a rule spaced apart by 0.5 to 5 mm., particularly 1 to 3 mm. In special cases, however, the spacing may amount to up to 20 mm. When using an arrangement in which the anode and cathode are merely connected together by a layer of solid polyelectrolyte, it is preferred to maintain a spacing of 0.5 to 2 mm., particularly 0.8 to 1 mm. The covered electrodes must be such that diffusion of the catholytes or anolytes towards the cover consisting of the solid polyelectrolyte and serving as diaphragm is possible to a certain extent and that the oxygen disengaged can diffuse back. The design of the electrolytic bath and the arrangement of the electrodes depends on the conditions of the electrolysis and may have different forms. For example, the arrangements which have been prepared as follows have proved to be suitable.

A layer about 0.5 to 2 mm. in thickness of an organic or inorganic ion exchanger, for example a diaphragm, is applied to a porous hollow cylinder of metal or graphite whose surface is provided with vertical grooves or concentric annular grooves which are connected with the interior of the cylinder by inclined or horizontal channels, and then a porous sintered article or a netting or a plurality of nettings are firmly pressed onto the layer of ion exchanger.

The porous metal sintered article or the netting is made the cathode and the porous hollow cylinder the anode. The anolyte is placed in the interior of the hollow cylinder and passes through the porous wall and the channels to the polyelectrolyte. The cathode is brought into contact with the catholyte by allowing the catholyte to flow in a thin film over the cathode or by causing it to flow past the cathode in laminar or turbulent flow. Tubular cells of this type may be arranged vertically, horizontally

or obliquely and may have the form of straight, angled or coiled tubes. Any cooling required may be effected by external flushing of the cathode space with the cooling medium or by cooling the anolyte or by installing cooling coils in the cell. Individual cells may be connected together in series or in parallel.

For the production of another arrangement which has proved to be suitable, netting electrodes or porous electrodes, which may contain polyelectrolyte, are firmly pressed onto both sides of an ion-exchange diaphragm and this arrangement is inserted in a frame which is installed in a trough where it separates the anode chamber from the cathode chamber.

According to another embodiment, an electrode is used which has such mechanical stability that it serves as support for the polyelectrolyte and counterelectrode. This arrangement is also installed in a trough and separates the anode chamber from the cathode chamber.

The electrodes may be arranged vertically, horizontally or obliquely in the cells. The catholyte and anolyte may as previously described flow over the electrodes in a thin film or may flow past them in laminar or turbulent flow, for example it may be pumped continuously over the electrodes or may remain stationary in contact therewith and be moved on periodically.

In yet another embodiment, a porous or netting anode is covered with a thin coherent layer of polyelectrolyte and this arrangement is used as a partition between the anode and cathode chambers in a trough. At a distance of 1 to 5 mm., an amalgamated lead electrode or another electrode having a high hydrogen overvoltage or a sheet of steel which is covered with mercury or over which mercury is flowing is arranged parallel to the polyelectrolyte layer. The catholyte is allowed to flow in a laminar or turbulent manner between the cathode and the polyelectrolyte layer, while the anolyte is stationary or moved in the anode chamber. Such a cell may be disposed vertically, horizontally or obliquely.

A porous or netting cathode may also be covered with polyelectrolyte and installed in a trough, as described above for the anode. The anode is then located on the polyelectrolyte side at a distance of about 0.5 to 5 mm. Porous, netting or compact anodes may be used.

Finally, one or both electrodes may consist of a finely grained or coarse bulk material of granulate or metal wool, the said material having if desired been enclosed in netting or pressed onto the polyelectrolyte. The thickness of such electrodes may be about 1 to 50 mm. An advantage of this arrangement is that worn electrode material may easily be replenished.

It is advantageous in all embodiments for the electrodes to be segmental, i.e. subdivided.

The electrolyte layers which cover at least one of the two electrodes, may be homogeneous, i.e. may consist of a uniform layer of polymer or copolymer containing charge-carrying groups, or may be heterogeneous, i.e. may consist of particles of ion exchanger distributed in a binder. Additional supporting material (skeleton), for example a netting, grid, fabric, or fibers, for example of glass, polyethylene, polystyrene, polyperhaloethenes, polytrifluoroethylene or polytetrafluoroethylene, for the layer of ion exchanger may in general be dispensed with because of the special design of the electrolytic cell. The ion exchanger, and also any binder used, may be organic or inorganic.

Both cation exchangers and anion exchangers are suitable as ion exchangers. Solid polyelectrolyte layers having amphoteric character may however also be used.

The polyelectrolyte layer should be mechanically stable and should be chemically resistant in the electrolyte used; it should also have good electrolytic conductivity. Thus the concentration of the ionic groups should be at least 1 milliequivalent per gram and these should as far as possible be completely dissociated in the electrolyte used.

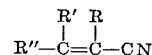
Examples of inorganic ion exchange materials are zirconium oxides, particularly hydrated zirconium oxides or those which have been obtained by precipitation of zirconium (IV) compounds, for example oxychlorides, with sodium triphosphate or sodium tungstate, but glauconite or zeolites, such as sodium permutite, apatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}^{(-)}$) or hydroxylapatite may also be used. These inorganic ion exchange materials may if desired be held together by an organic or inorganic binder, such as polystyrene, polybutadiene, polyisoprene or cement.

Condensed or polymerized high molecular weight organic compounds which contain ionic groups, basic or acid groups, are suitable as organic solid polyelectrolytes. They may contain for example acid groups, such as sulfonic acid groups, or also carboxylic acid groups, phosphonium groups, phosphine groups, arsenic acid groups or hydroxyl groups, ammonium groups or amino groups in a concentration of at least 2 milliequivalents per gram.

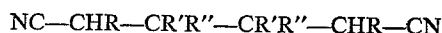
Examples of suitable compounds are particularly styrene polymers, such as polystyrene, copolymers of dimethylstyrene and divinylbenzene, styrene and divinylbenzene, or also phenyl-formaldehyde resins, or polymers or copolymers of vinyl chloride which contain phosphonium groups, sulfonic acid groups or carboxylic acid groups as cation exchangers, or those containing amino groups or quaternary ammonium groups as anion exchangers. For example polystyrene copolymers with 75 to 95% of styrene and 5 to 25% of divinylbenzene, which have been sulfonated to such an extent that they contain 5 to 5.2 milliequivalents of hydrogen ions per gram, or polystyrene copolymers with 70 to 96% of styrene, 0 to 15% of ethylstyrene, 4 to 16% of divinylbenzene containing 3 to 4 milliequivalents of amino groups per gram.

The layers containing ion exchangers may consist of particles of an ion exchanger which are held together by the ion exchanger itself or another ion exchanger, for example layers of 30 to 40% by weight of polystyrene or copolymers of styrene and divinylbenzene, which contain as charge carrying groups, quaternary ammonium groups or amino groups and 60 to 70% by weight of hydrated zirconium oxide, or of particles of an ion exchanger which is held together by a water-insoluble binder, for example of a mixture of 70 to 80% of fine-grained organic or inorganic ion exchangers, such as sulfonated polystyrene or hydrated zirconia and 20 to 30% by weight of a mixture of polyisoprene and polyisobutylene in the ratio 1:1 or polyvinyl chloride or polystyrene. The ion exchanger layers may be prepared by pressing or by consolidation from a dispersion or from a solution, and these layers may if desired be produced direct on the electrodes.

Starting materials, assistants and reaction conditions are equivalent to those in prior art methods, e.g. that described in French patent specification 1,328,327, for hydrodimerization of α,β -unsaturated nitriles. Those may be chosen which contain at least 3 but at most 8 carbon atoms, i.e. those having the formula



in which R, R' and R'' denote hydrogen or alkyl having from 1 to 5 carbon atoms. The process has particular importance for hydrodimerization of acrylonitrile. Dinitriles having the formula



are obtained.

Electrolysis is carried out as usual with cell voltages of 4.0 to 10 volts, particularly 4.5 to 7 volts, and with current densities of 2 to 20 amps/sq. dm. of electrode surface. Higher current densities, e.g. up to 80 amps/sq. dm. may also be used. Current densities of from 10 to 30 amps/sq. dm. have proved to be particularly suitable. The temperature in the catholyte is advantageously kept at 10 to 40° C., particularly 20° to 30° C., by cooling.

When the cathode is not covered, a multiphase system consisting of α,β -olefinically unsaturated nitrile, water and a conducting salt, if desired in the presence of an inert organic solvent, is used as the liquid phase in the cathode chamber.

It is preferred to use as the conducting salt one whose cations have a high discharge potential, e.g. above 1.8 volt (vs. a calomel electrode). Examples of suitable salts are those of tetraalkyl ammonium bases or tetraalkanol ammonium bases, and also those of alkylamines or alkanolamines. For example salts of tetramethyl ammonium, tetraethyl ammonium, trimethylethyl ammonium, butylamine, hexylamine, ethanolamine, diethanolamine or triethanolamine have proved to be particularly suitable. Particularly suitable anions for such salts are those which are derived from arylsulfonic acids or arylalkylsulfonic acids, for example from toluenesulfonic acids, benzenesulfonic acids, ethylbenzenesulfonic acids or salts of monoalkylsulfuric acids, for example ethylsulfuric acid. Examples of suitable salts are tetraethyl ammonium p-toluenesulfonate or tetraethyl ammonium ethylbenzenesulfonate or tetraethyl ammonium ethyl sulfate.

To improve electrolytic conductivity of the catholyte, it is also possible to add a liquid anion exchanger, for example amines having weakened basicity and having molecular weights of 250 to 500, such as trialkylmethylamines with alkyl groups having eighteen to twenty-four carbon atoms, N-dodecyl-N-(trialkylmethyl)-amines having eighteen to twenty-four carbon atoms in the alkyl groups or a liquid cation exchanger, for example monododecylphosphoric acid, monoheptadecylphosphoric acid or di-(2-ethylhexyl)-phosphoric acid. These additives may easily be separated when working up the catholyte. They dissolve in acrylonitrile or in the mixture of acrylonitrile and solvent. These solutions are themselves conducting.

Examples of organic solvents are polar solvents such as acetonitrile, dioxane, tetrahydrofuran, acetone, dialkylamides of lower carboxylic acids, such as dimethylformamide, and also N-alkyl lactams, for example N-methylpyrrolidone, glycols, such as ethylene glycol, or lower alcohols, such as methanol or ethanol.

The monomeric olefinic nitriles are usually employed in concentrations of 10 to 90%, particularly 40 to 65%, in the catholyte.

The conducting salt is usually used in amounts of 5 to 40% by weight on the multiphase system used as the catholyte. When organic solvents are added, up to about 40%, particularly 5 to 25%, by weight is added. The water content in the multiphase system containing the conducting salt and used as the catholyte is preferably kept at more than 15% by weight.

When the cathode is covered with a solid polyelectrolyte, either multiphase systems, such as are used in the case of an uncovered cathode, but in this case preferably with a higher concentration of monomeric olefinic nitrile, particularly more than 90%, are used as the liquid phase in the cathode chamber; it is however possible to dispense with the conducting salt and/or the organic solvent and, provided a cation exchanger is used in its $H^{(+)}$ -ion form as polyelectrolyte, even with the water, so that pure monomeric unsaturated nitrile may be used as the liquid phase in the cathode chamber. In this case conducting salt concentrations of from 0.5 to 3.0% by weight are preferred.

It is preferred to use a solution, if desired a saturated solution, of water in the monomeric olefinic nitrile as the liquid system in the cathode chamber.

When the anode is uncovered, the liquid phase in the anode chamber may be either aqueous conducting salt solutions as in the cathode chamber or aqueous solutions of salts, acids or bases, for example of phosphates, sulfates, phosphoric acid, sulfuric acid, benzenesulfonic acid or toluenesulfonic acid, or quaternary ammonium bases, and the conductivity-producing compounds should be correlated to the ion form of the ion exchanger. It is pre-

ferred to use electrolyte solution whose ions do not undergo any change during the electrolysis. The liquid phase in the anode chamber should preferably contain such an amount of electrolyte that it has a conductance of at least $10^{-2} S/cm.$ ($=\Omega^{-1}cm^{-1}$). Sulfuric acid, for example, is very suitable, but other mineral acids, particularly those having a high ionization constant, e.g. above 10^{-3} at $25^{\circ}C$.

When the anode is covered with solid polyelectrolyte there is used as liquid phase in the anode chamber a multiphase system as in the case of the uncovered anode, but it is also possible to dispense with the addition of electrolyte to the water.

It is preferable to maintain a pH value of 3 to 10, particularly 6 to 9, in the cathode chamber. Working in the acid range in the anode chamber is preferred when using a cation exchanger, and in the alkaline range when using an anion exchanger. Buffer substances may be added to set up a definite pH value. Thus a solution of a buffering system in monomers may be used. Weakly basic or weakly acidic substances whose cations are only discharged at high deposition potential are particularly suitable as buffering substances, examples being primary tetraalkyl ammonium phosphates, tetraalkyl ammonium acetates, acid alkyl ammonium sulfonates, acid alkyl ammonium sulfates, alkylaryl ammonium hydroxides, if desired in combination with weak acids. When using a covered anode and water in the anode chamber, it is advantageous to maintain therein, by a buffer substance, a definite pH value, for example when using a cation exchanger, by a mixture of a mineral acid and glyccoll or when using an anion exchanger, by a mixture of caustic alkali solution and glyccoll.

The essential advantage of the process according to the invention is that the conducting salt or the acid or base may be dispensed with in the catholyte when using a covered anode or in the anolyte when using a covered cathode. There are therefore the following possibilities which are explained with reference to the accompanying FIGURES 1 to 4.

If the anode is covered with a solid polyelectrolyte as shown diagrammatically in FIGURE 1, pure water or an electrolyte may be used on the side 1 remote from the cathode. A known multiphase system of α,β -unsaturated nitriles and conducting salts may be used on the side 2 facing the cathode but covered with polyelectrolyte. The solvent may however be dispensed with, especially when solubilizing conducting salts are used.

If, as shown diagrammatically in FIGURE 2, the cathode is covered with solid polyelectrolyte, either the usual multiphase system containing conducting salt may be used with the α,β -unsaturated nitrile on the side 3 remote from the anode, or the conducting salt and if desired the solvent may be dispensed with. All that is necessary then on the side 4 facing the anode is the presence of a suitable liquid electrolyte. It is preferred to use aqueous phosphoric acid, sulfuric acid or solutions of phosphates or sulfates. A particular advantage of using this arrangement results when the conducting salt is dispensed with because then the dimerization product produced in the cathode chamber, for example adipodinitrile, may be worked up in a particularly simple way. All that is needed is for the dimerization product obtained to be separated from the monomers by simple distillation.

If, as shown diagrammatically in FIGURE 3, both the anode and the cathode are covered with solid polyelectrolyte, the advantages of both arrangements, as described above, are obtained, i. e. it is possible to use pure water on the side 1 of the anode remote from the cathode and pure α,β -unsaturated nitrile on the side 3 of the cathode remote from the anode, while in the space 5 between the two electrodes only a liquid electrolyte is required. When using such an arrangement, a somewhat higher cell voltage, for example of 7 to 9 volts, is required as a rule than

when using the other arrangements according to the invention.

When using an arrangement as shown diagrammatically in FIGURE 4, there are the same advantages as when using an arrangement according to FIGURE 3, but there is the additional advantage that no liquid electrolyte is needed between the electrodes. Since it is possible in this arrangement to make the distance between the electrodes very small, the voltage drop is particularly low; a cell voltage of 4.5 to 6 volts is sufficient.

In all the arrangements it is advantageous to lead away both the heat of reaction and the heat of the current, for example by water cooling of the catholyte and anolyte. Moreover it is advantageous to provide a circulation of the monomers in the cathode chamber, e.g. in a flow-through cell by adequate flow velocity.

The invention is further illustrated in the following examples in which parts are by weight unless specified otherwise.

Example 1

The anode consists of a porous graphite tube surrounded by a dense layer of a copolymer of styrene and divinylbenzene into which sulfonate groups have been introduced. The counterelectrode is an amalgamated silver netting which is arranged as a tube around the anode. Pure water is filled into the graphite tube. The catholyte used is a mixture of 40% by weight of acrylonitrile, 34% by weight of water and 26% by weight of tetraethyl ammonium p-toluenesulfonate. The anode is completely separated from the cathode by the layer of ion exchanger.

At an effective current density of 6 amps/sq. dm. (with reference to the cathode surface) a conversion of 40% is obtained within six hours, and a yield of 85% by weight of adipodinitrile (on the reacted acrylonitrile) at a current yield of 61%. Hydroxypropionitrile cannot be detected in the reaction product and bis-cyanodiethyl ether is formed in an amount of 0.2% by weight on the acrylonitrile reacted.

At a maximum voltage of 6 volts, only 5 kwh. is required per kilogram of adipodinitrile formed.

No additional measures are necessary to maintain the pH value.

Example 2

The anode consists of a porous graphite tube. An amalgamated silver netting having 900 meshes per sq. cm. is arranged concentrically around this electrode. A layer 1 mm. in thickness of polystyrene into which sulfonic acid groups have been introduced is situated on the inside of this netting. A mixture of 40% by weight of acrylonitrile, 36% by weight of water and 34% by weight of tetraethyl ammonium p-toluenesulfonate is situated on the cathode side.

A 2.5% aqueous phosphoric acid is situated on the anode side.

At a conversion of 48%, a yield of adipodinitrile of 80.8% (on the reacted acrylonitrile) and a current yield of 65% are obtained at a current density of 3 amps/sq. dm. The pH value remains practically constant at 2 in the anode chamber and at 5 to 7 in the cathode chamber. The fact that the current yield is 65% means that adipodinitrile produced at an applied voltage of 4.5 v./kg. requires an energy of only 3.5 kwh.

Example 3

The electrolytic cell used has an anode of a porous graphite tube 45 mm. in height, 4 mm. in wall thickness and having a diameter of 38 mm. A layer of ion ex-

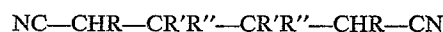
changer (consisting of highly crosslinked polystyrene into which quaternary ammonium groups have been introduced) is applied to the outer surface of the graphite tube. The ion exchanger is in the hydroxyl form. The thickness of the layer is 0.8 mm. An amalgamated silver netting is applied to this ion exchanger layer. The netting has 64 meshes per sq. cm. and the thickness of the wire is 0.5 mm.

Pure distilled water is filled into the hollow graphite cylinder (anode chamber), and the outer space is filled with pure acrylonitrile.

At an applied voltage of 4.5 to 5 volts and a maximum current density of 2 amps/sq. dm., a 75 to 80% yield of adipodinitrile (on reacted acrylonitrile) is obtained at a conversion of 25%. The current yield is at least 73% so that a maximum of 3.2 kwh. is required for 1 kg. of adipodinitrile.

We claim:

1. A process for hydrodimerizing mononitrile of the formula $R''R'C=CR-CN$ in which R, R' and R'' each represent hydrogen or alkyl having 1 to 5 carbon atoms to form a dinitrile of the formula



- in which R, R' and R'' have the same meaning as indicated above which comprises passing electric current through a catholyte containing at least 5% of the mononitrile and being separated by a solid polyelectrolyte from the anolyte, the solid polyelectrolyte covering at least one of the electrodes on the side facing the other electrode and the coated electrode having a certain permeability for the catholyte or the anolyte, respectively, and for the oxygen disengaged.

2. A process as claimed in claim 1 wherein the cathode is covered by the solid polyelectrolyte.

3. A process as claimed in claim 1 wherein the anode is covered with the solid polyelectrolyte.

4. A process as claimed in claim 1 wherein both cathode and anode are covered with solid polyelectrolyte on the sides which face each other.

5. A process as claimed in claim 4 wherein anode and cathode are joined together by solid polyelectrolyte.

6. A process as claimed in claim 2 carried out without an electrolyte salt in the catholyte.

7. A process as claimed in claim 3 wherein an anolyte is used which does not contain an electrolyte salt, an acid or an alkaline substance.

8. A process as claimed in claim 6 in which a mixture of a α,β -olefinic dinitrile and water is used as catholyte.

9. A process as claimed in claim 1 wherein a solid inorganic polyelectrolyte is used for covering the electrode or electrodes.

References Cited

UNITED STATES PATENTS

2,636,851	4/1953	Juda et al.	204—98
2,815,320	12/1957	Kollsman	204—180
3,124,520	3/1964	Juda	204—86
3,135,674	6/1964	Ruetschi	204—151
3,193,480	6/1965	Baizer et al.	204—73
3,245,889	4/1966	Baizer	204—73
3,244,612	4/1966	Murphy	204—290

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