

[54] **ELECTROCHEMICAL ADIPONITRILE
PROCESS**
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[73] Assignee: **Standard Oil Company**, Chicago, Ill.
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[51] **Int. Cl. C07b 29/06, C07c 121/02, C07c 121/26**
[58] **Field of Search**..... **204/73 A**

[56] **References Cited**
UNITED STATES PATENTS
3,250,690 5/1966 Baizer..... 204/73 A
3,427,234 2/1969 Guthke et al..... 204/73 A

3,689,382 5/1972 Fox et al..... 204/73 A
FOREIGN PATENTS OR APPLICATIONS
61,262 4/1968 Germany 204/73 A

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[57] **ABSTRACT**
Electrochemical hydrodimerization of acrylonitrile to adiponitrile in an electrochemical, preferably undivided, cell containing acrylonitrile dissolved in an aqueous electrolyte, wherein ammonia is added to the cell and oxidized at or near the anode.

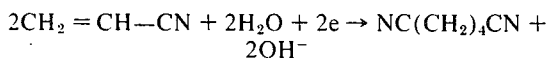
10 Claims, No Drawings

ELECTROCHEMICAL ADIPONITRILE PROCESS

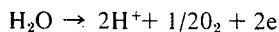
This invention relates to the electrochemical hydrodimerization of acrylonitrile to adiponitrile, wherein ammonia is oxidized at or near the anode. More particularly, this invention relates to the electrochemical hydrodimerization of acrylonitrile to adiponitrile in an undivided cell, wherein ammonia is oxidized at or near the anode.

Adiponitrile is a very important intermediate in the production of nylon 6,6. Accordingly, there has been considerable research on new methods of producing this monomer. During the last 10 years, interest has focused on various electrochemical methods of producing adiponitrile from acrylonitrile. (See, for example, Monsanto U.S. Pat. Nos. 3,193,476 to 483 and Asahi British No. 1,169,525.) The Apr. 17, 1970 European Chemical News reports at page 47 that Monsanto has a 45 million pound per year plant using a divided-cell hydrodimerization process for producing adiponitrile.

In these processes, the principal reaction at or near the cathode is



and the principal reaction at or near the anode is



As in all electrochemical reactions, the solutions must be conductive (contain an electrolyte) and the anode reaction must either be compatible with the cathode reaction or isolated from it. However, it is difficult to design electrochemical systems where the cathode and anode reactions are compatible since electrolytes stable at one electrode are usually unstable at the other and products of one electrode reaction are usually reactive at the opposite electrode. The preferred electrolytes (tetraalkyl ammonium sulfonates) used in the Monsanto patents have the additional functions of promoting the solubility of acrylonitrile and preventing electroreduction of water at the cathode. These patents prefer the use of a divided cell (e.g., a cation exchange membrane), thereby preventing destruction of electrolyte, acrylonitrile and adiponitrile at the anode.

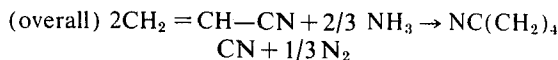
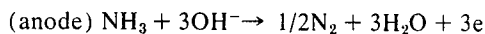
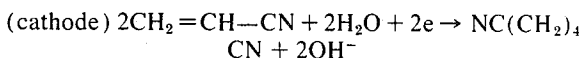
The use of a divided cell has several disadvantages. For example, U.S. Pat. No. 3,193,481, points out at column 5, line 66, through column 6, line 27, that alkalinity increases in the catholyte. The alkalinity must be controlled in order to avoid side reactions. In addition to its much higher cost, the divided cell has a relatively large electric-power loss and heat evolution. The total voltage drop of the divided cell is at least double the undivided and the resistivity drop is triple. Further, on a commercial basis, product buildup is limited to about 15% by weight in a divided cell due to higher electrical requirements as the solution viscosity increases. For example, as the adiponitrile concentration increases from about 15% to 30% by weight in an undivided cell, voltage rises about 1.5 volts. Other things being equal, voltage rises about 5 volts in the divided cell. Accordingly, the electric-power cost is substantially greater in the divided cell. Moreover, separator life is reduced by heat buildup and chemical attack in the warm solution.

The general object of this invention is to provide a new electrochemical process for producing adiponitrile from acrylonitrile. The principal object of this invention is to provide a new electrochemical undivided cell

process for producing adiponitrile from acrylonitrile. other objects appear hereinafter.

The objects of this invention can be attained by the electrochemical hydrodimerization of acrylonitrile to adiponitrile in an electrochemical cell containing acrylonitrile dissolved in an aqueous electrolyte, wherein ammonia is added to the solution in an amount at least equal to that stoichiometrically required for service as a proton replenisher. The present invention, like U.S. Pat. No. 3,699,020, which is incorporated by reference, makes use of the fact that ammonia can be oxidized electrochemically at a lower voltage than water. Since ammonia can be oxidized electrochemically without danger of oxidizing electrolyte, acrylonitrile or adiponitrile at the anode, it is possible to carry out the process in an undivided cell. Accordingly, when an undivided cell is employed in the process of this invention, there is no substantial buildup of hydroxyl ions in the cathode chamber eliminating the alkalinity-control problems of the divided cell; there is less heat buildup, lower power costs, lower equipment investment and the possibility of recovering more concentrated adiponitrile compositions.

In somewhat greater detail, the electrochemical reaction in the present process can be represented as:



As indicated above (see the equations above), the present electrochemical process requires the presence of water, which is continuously regenerated, and also an electrolyte salt which must be soluble in the combination of water and aprotic solvent. In general, the higher the concentration of water, the higher the current density. Accordingly, water should comprise at least 15% by weight of the electrolysis composition. Various aprotic solvents, such as acetonitrile, can be added to the system to increase the solubility of acrylonitrile in the aqueous-electrolyte.

Suitable electrolyte salts include tetraalkyl ammonium salts such as tetraethylammonium bromide, tetramethyl ammonium chloride, tetrapropylammonium bromide, tetrabutylammonium bromide, tetraethylammonium paratoluene sulfonate, etc. Of these, best results have been obtained with the bromides, particularly tetraethylammonium bromide.

Since acrylonitrile is consumed in this process, acrylonitrile can be added to the electrolysis cell through a separate dip tube. If the solution is continuously removed from the cell for recovery of adiponitrile and/or for cycling through a cooling system, acrylonitrile can be injected into the recycled solvent-electrolyte.

Ammonia is consumed in my process and accordingly should always be present in some excess concentration over that stoichiometrically required for the electro-reduction. However, a high concentration of ammonia lowers selectivity. Accordingly, it has been found convenient to maintain the solvent-electrolyte system about 0.1 to 0.5 molar in ammonia, preferably 0.2 to 0.3 molar. This can be maintained approximately by continuously bubbling ammonia into the solution contained in the electrolysis cell during reduction. If the solution is continuously removed from the cell for

cycling through a cooling system, ammonia can be conveniently injected into the line, preferably downstream of the pumping means.

In the practice of my invention, carbon anodes, preferably graphite anodes, have been satisfactory. The carbon may be impregnated with a metal; e.g., platinum, although metals tend to oxidize and then plate out on the cathode. The cathode must be a material exhibiting a high hydrogen over-voltage such as lead, mercury, aluminum, tin, zinc and cadmium. Lead and mercury are especially suitable.

In the preferred system, ammonia is the most easily oxidized entity so that oxidation of halide ion is essentially eliminated. In general, an impressed current density in the range from about 30 to about 1000 amps/Ft², and preferably from 300 to 500 amps/Ft², may be employed. Cell voltage will accordingly vary within the range from 2 to 10, and desirably 3 to 6, volts. Failure to supply ammonia to the system results in oxidation of the halide, formation of copious precipitates, decreased selectivity and low current efficiency.

Electrolysis temperature is not a critical variable and hydrodimerization may readily be conducted within the range from 70° to 140°F. The solvent-electrolyte solution must be fluid at the selected temperature and the solubility of ammonia must be adequate to satisfy mass transfer (stoichiometric) requirements. Operation at or near room temperature (80° to 120° F.) is preferred. During electrolysis part of the solution may be continuously removed from the cell, passed through a cooling coil and returned to the cell.

As the hydrodimerization progresses, the impressed voltage is increased to maintain the desired current density whenever there is a slow corrosion of the graphite anode (for example, a loss amounting to about 0.0005 inch per 24 hours). Salt consumption is low, although it tends to increase at low water concentrations while hydrogen evolution occurs at high water concentrations. No separator is required in this system. Indeed, presence of a separator to afford compartments and minimize mixing between reagents could lead to an inoperable system by effecting precipitation of, for example, ammonium bromide on the separator frit, and thus gradually shut off the electrochemical reaction.

When the reduction operation is complete, the cell contents can be transferred to a still and heated under mild vacuum to remove aprotic solvent, water, ammonia, acrylonitrile and adiponitrile. Tetraalkyl ammonium salt is recovered from the residue.

In continuous operation, my process comprises the use of banks of electrolytic cells, each bank including a plurality of cells arranged in a line and having abutting walls to conserve space. Each cell is relatively narrow and deep and fitted with thin, flat facing electrodes disposed vertically. One such cell-bank has a number of bielectrodes (anode-cathode pairs sealed back to back) of carbon and lead (or some other high hydrogen-overvoltage metal) punched in the center, faced at either end with a separate anode and cathode, and spaced by plastic inserts. Solution is introduced at the center of the separate cathode (or anode) and then flows, in parallel, between the bielectrics and out to a reservoir. An exit line transports solution from the reservoir and, after addition of ammonia and acrylonitrile, back to the cell-bank.

Within a cell-bank, only the two end electrodes have electrical connections, i.e., the electrodes are arranged

in series. Between cell-banks electrical connections may be either in series or in parallel arrangement. The solution flow pattern may be arranged in parallel within a cell-bank and in series between a plurality of banks as required. Provision can be made for cooling the solution outside the cells as needed. Solution may also be recycled, in whole or in part, as required.

The following examples are merely illustrative.

EXAMPLE I

An electrolytic cell was fitted with disc electrodes 4.5 inches in diameter and ¼ inch thick. A graphite anode was disposed horizontally near the bottom of the cell. A lead cathode was punched out at its center to receive a hollow cylindrical support rod and was maintained parallel to and above the anode by insulating spacers placed therebetween. The separation between the electrodes was 0.03 inch. A suction tube was extended from the cell to a circulating pump. The effluent line from the pump passed through a cooling bath and adapted to returning to the cell through the hollow support rod. The effluent line contained Ts for continuously adding ammonia and acrylonitrile downstream from the cooling coil. Sheathed wires connected the electrodes to a D.C. power source. A voltmeter and an ammeter were provided in the circuit. The cell was filled with a solution containing 40 grams acrylonitrile, 90 grams water, 120 grams tetraethylammonium bromide and 150 grams acetonitrile. Five thousand c.c. ammonia (3.8 grams) was then added to provide a 0.3 molar solution of ammonia. The composition was electrolyzed at 35A (350 ma/cm²), 4.1 volts (average) and 29°C. for 2 hours while adding ammonia at 160 cc/min and acrylonitrile at 1.0 g/min. After two hours, by analysis, the electrolysis solution contained 21% by weight adiponitrile, selectivity was 92%, current efficiency was 83% and conversion was 77%.

EXAMPLE II

Example I was repeated, except that the solution was electrolyzed at 40A (400 ma/cm²), 4.8 volts (average) and 26°C. for 2 hours while adding ammonia at 180 cc/min. and acrylonitrile at 1.3 g/min. After two hours, by analysis, the electrolysis solution contained 24% by weight adiponitrile, selectivity was 91%, current efficiency was 83% and conversion was 77%.

I claim:

1. The process for the electrochemical hydrodimerization of acrylonitrile to adiponitrile in an electrochemical cell containing acrylonitrile dissolved in an aqueous-electrolyte, wherein ammonia is added to the cell and oxidized at or near the anode.

2. The process of claim 1, wherein the aqueous-electrolyte composition comprises acetonitrile as a component.

3. The process of claim 1, wherein the electrolyte comprises a tetraalkyl ammonium salt.

4. The process for the electrochemical hydrodimerization of acrylonitrile to adiponitrile in an undivided electrochemical cell containing acrylonitrile dissolved in an aqueous-electrolyte, wherein ammonia is added to the cell and oxidized at or near the anode.

5. The process of claim 4, wherein ammonia is added to the cell in an amount at least equal to that stoichiometrically required for service as a proton replenisher in the hydrodimerization reaction.

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6. The process of claim 4, wherein acrylonitrile is continuously supplied to the cell.

7. The process of claim 4, wherein said cell comprises an aprotic solvent.

8. The process of claim 4, wherein said aprotic solvent comprises acetonitrile.

9. The process of claim 4, wherein said electrolyte comprises tetraethyl ammonium bromide.

10. The process of claim 4, wherein said cell contains at least 15% by weight water.

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