

[54] METHOD FOR PRODUCING ADIPONITRILE

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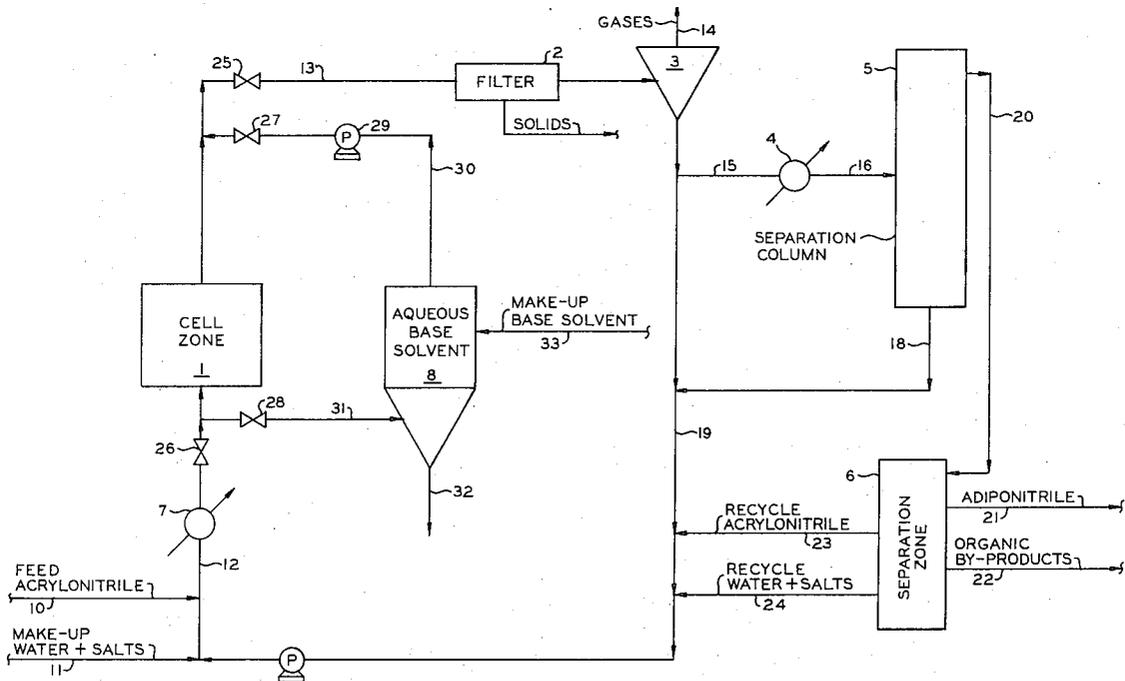
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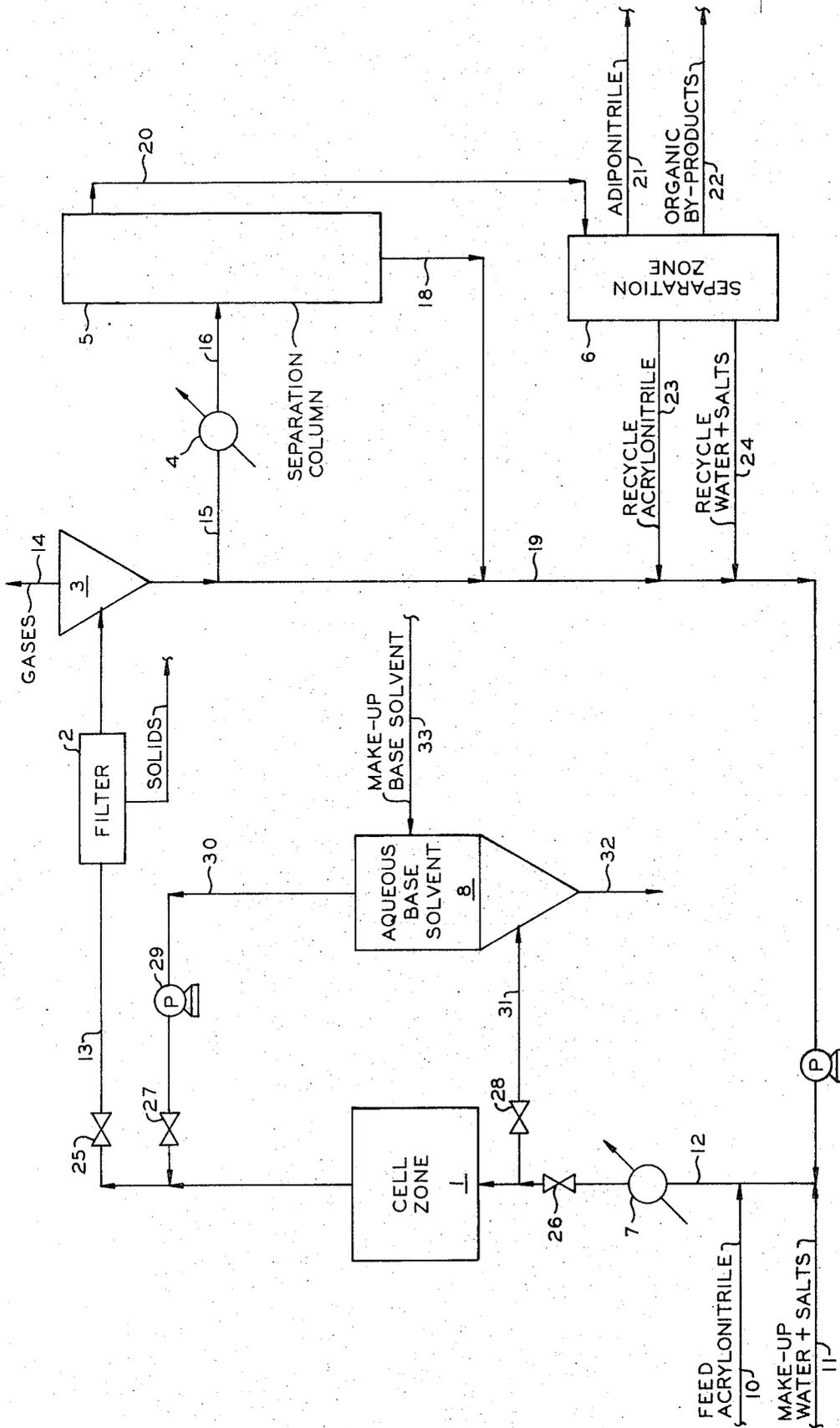
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[57] ABSTRACT

In a method for producing adiponitrile by electrolysis of an acrylonitrile composite stream passing through an undivided electrolytic cell having a cathode and an anode, flow of the acrylonitrile composite stream to the cell is periodically terminated, a wash stream is passed through the cell in contact with the cathode and anode, said wash stream being a basic aqueous solution having a concentration in the range of about 1–20 weight percent basic compound in the solution. The wash stream is passed through the cell in contact with the cathode and anode for a period of time in the range of about 1–60 minutes and thereafter the passage of the wash stream through the cell is terminated and the acrylonitrile composite stream is passed to the electrolytic cell for electrolysis.

14 Claims, 1 Drawing Figure





**METHOD FOR PRODUCING ADIPONITRILE**

This invention resides in an improved method for producing adiponitrile by electrolysis of an acrylonitrile stream passing through an undivided electrolytic cell having a cathode and an anode by periodically washing the cathode and anode of the cell with a basic aqueous wash stream having a concentration in the range of about 1–20 weight percent basic compound in the solution.

Electrohydrodimerization (EHD) of acrylonitrile to produce adiponitrile has been found to be economically attractive. Adiponitrile is a valuable precursor in the manufacture of nylon fibers.

In this process, an aqueous electrolyte, comprising a relatively large amount of a conducting inorganic salt such as a potassium phosphate, and a small amount of a directing (catalytic) organic salt such as tetrabutylammonium phosphate is continuously circulated between two suitable electrodes under electrolysis conditions. Acrylonitrile is continuously added to this circulating stream under conditions which provide an emulsion between the two electrodes. As the electrolysis proceeds, a small slipstream is removed from the circulating emulsion. It is allowed to settle, and an organic phase, which contains the desired adiponitrile product, is drawn off for isolation and recovery of the adiponitrile. The aqueous phase is returned to the circulating emulsion stream. A feature of the above-described process is that it operates with an undivided cell, that is, there is no membrane or other form of divider which divides the space between the electrodes into a cathode compartment and an anode compartment. Such undivided cell operation has the advantage of simple cell construction and relatively low internal resistance within the cell.

As is desirable as undivided cell portion is, long term smooth, continuous, and efficient operation is sometimes difficult to achieve because of the problem of anodic oxidation of organic feed and products. Moreover, anode corrosion is a frequent problem with undivided cells. For example, when a suitable reaction mixture is circulated between lead electrodes, the conditions under which high conversions and selectivities to desired products are obtained at the lead cathode are generally the same conditions which provide for significant corrosion of and deposits formation on the lead anode. Moreover, the corrosion of the anode is related to the oxidation losses in that it appears to cause even more oxidation of organic materials which are in the vicinity of the corroding anode. The products of the corrosion and/or oxidation sometimes tend to increase the internal resistance of the cell thereby requiring wasteful high levels of cell voltage.

It has now been found that, in a continuous process for the electro-hydrodimerization of acrylonitrile to adiponitrile wherein a suitable mixture of acrylonitrile, water, and conducting and directing salts are passed between suitable electrodes in an undivided electrolytic cell, and wherein an anode is subject to becoming coated with insulating deposits, smoother operation including lower voltage requirements and freedom from severe polarization are obtained by periodically circulating an aqueous solution of a strong base, such as aqueous potassium hydroxide through the cell to remove the deposits from the anode and restore its surface.

This invention, therefore, resides in an improved method for producing adiponitrile by electrolysis of acrylonitrile stream passing through an undivided electrolytic cell having a cathode and an anode by periodically washing the cathode and anode of the cell with a basic aqueous wash stream having a concentration in the range of about 1–20 weight percent basic compound in the solution.

Other aspects, objects, and advantages of the present invention will become apparent from a study of the disclosure, the appended claims, and the drawing.

The drawing is a diagrammatic view of the inventive process with apparatus for practicing the method of this invention.

Referring to FIG. 1, acrylonitrile feed and make-up water and salt pass into line 12 by means of lines 10 and 11, respectively. Line 12 carries a recirculating emulsion stream which passes into and through cell zone 1. The electrodes in the cell are generally positioned such that the gap between them is vertical. The emulsion can pass through this gap either from top to bottom or vice versa. Cell zone 1 comprises one or more cells operating under conditions suitable for the electrolytic conversion of acrylonitrile to adiponitrile. Line 12 carries an aqueous solution of conducting inorganic salts, such as alkali metal phosphate salts and a minor amount of a directing tetraalkylammonium (TAA) salt, such as tetrabutylammonium phosphate. Organic products and by-products are also present. The stream passing through line 12 will hereafter be referred to as an acrylonitrile composite stream. An emulsified mixture is removed from cell zone 1 through line 13, then passes through filter 2 and then passes into gas disengager unit 3. In this unit, gases, primarily oxygen, are removed from the system through line 14. The essentially gas-free liquid stream is then passed from gas disengager unit 3 into line 19, through heater 7, and then back into cell zone 1 by means of line 12. The positions of the filter, gas disengager, pump, heater, feed entries, etc., need not necessarily be located in the order shown in the circulation loop but can be arranged in other sequences.

Cell zone 1, for example, operates under conditions which include: a temperature of 90°–150°F; an atmospheric or near atmospheric pressure; an emulsion linear velocity of 0.05–6 ft/sec; an emulsion having an organic content of 2–12 weight percent based on the entire liquid stream; suitable electrodes having a composition such as lead, lead alloy, graphite, nickel, mercury, platinum, and the like; a current density of 50–400 amp/ft<sup>2</sup>; an emulsion pH of 6–12; a normality of 0.1–3 N with respect to inorganic conducting salts; a normality of 0.001–0.3 N with respect to TAA salts, an acrylonitrile per pass conversion of up to 10 percent; and an overall acrylonitrile conversion of up to 90 percent.

A minor part, corresponding to the desired acrylonitrile conversion, of the stream passing through line 19 is diverted and passed through line 15 into cooling zone 4 wherein that portion of the emulsion is cooled, using any conventional cooling means to a temperature suitable for the separation of the emulsion into separate liquid phases. The chilled emulsion leaves cooling zone 4 through line 16 and passes into separation column 5. Any suitable apparatus or combination of apparatus for settling an emulsified stream into an organic and an inorganic layer can be used in this separation column.

The lower aqueous phase leaves the separation zone 5 through line 18 and rejoins the recirculating emulsion stream in line 19. The organic phase is drawn off from separation column 5 through line 20 and proceeds to separation zone 6.

Separation zone 6 can and generally will comprise more than one separation unit such as a series of fractionation units for the separation, isolation, and recovery of products and organic by-products. In addition to distillation units, other units such as extraction units and absorption units can be used also.

Adiponitrile product leaves the separation zone through line 21 and other organic by-products such as propionitrile, and the like, leave separation zone 6 through line 22. Unconverted acrylonitrile is passed from separation zone 6 through line 23 to rejoin the recirculating emulsion stream in line 19. Similarly, recycled water and salts, both organic and inorganic, leave separation zone 6, pass through line 24 and also rejoin the recirculating emulsion in stream 19. The recombined materials in line 19 are blended with fresh acrylonitrile through line 10 and make-up water and salt through line 11 to form a mixture passing through line 12, through heater 7, wherein the mixture is adjusted to the desired cell temperature, and thence into cell zone 1.

At periodic time intervals, for example, when the cell voltage required to maintain a given current flow increases by about 0.5 volt from normal, the circulation of emulsion through cell zone 1 is halted, the cell can be drained, and valves 25 and 26 are closed. Valves 27 and 28 are then opened and a wash solution contained in zone 8 is recirculated through cell zone 1 by means of pump 29. The wash solution stream circulates from storage zone 8 through line 30 through cell zone 1 and returned through line 31 to storage zone 8. The recirculating washing solution accumulates solid particulate matter from cell zone 1. This solid particulate is removed from zone 8, either continuously or intermittently, through line 32. Make-up aqueous base solution is added to solution storage zone 8 through line 33.

Any suitable cell and electrode configuration which will accommodate a continuously circulating stream of liquid between the two electrodes can be used. The cell can be fabricated from any suitable material which is compatible with the electrolyte, and which is not attacked or corroded or only slowly corroded, under the operating conditions normally employed in the cell.

Preferred materials for the cathode are those having a fairly high hydrogen over-voltage, that is, a hydrogen over-voltage greater than that of copper. Examples of such materials include, among others, lead, graphite, nickel, silver, gold, lead alloys, and the like.

Examples of materials suitable for use as the anode include lead, lead alloys, platinum, gold, nickel, iron, and the like.

Lead-containing materials such as metallic lead, lead alloys, or lead dioxide are presently preferred as materials of construction for the anode. Similarly, lead or lead alloys are presently preferred for use in forming the cathode.

At periodic intervals, or when the cell voltage has been found to increase by about 0.5 volt or more over normal, the cell and electrodes are subjected to the washing with aqueous base according to the process of the present invention. Generally speaking, the EHD

process is interrupted at intervals of only 10 to 100 hours, ordinarily, 20-50 hours.

The washing or flushing operation is carried out very simply by temporarily halting the flow of emulsion through the cell and replacing it with a flow of aqueous base. The circulation of the aqueous base wash stream through the cell is carried out for a sufficient time to restore the surface of the anode to again provide efficient low voltage operation. Ordinarily, this can be accomplished by circulating the aqueous base for 1-60, preferably 5-30 minutes.

The temperature at which the electrodes are contacted with the aqueous base can vary widely, ranging from the freezing point to the boiling point of the solution. Room temperature operation is generally satisfactory. With lead dioxide anodes, however, temperatures in excess of 150°F are generally required. The circulation rate can also vary widely. A linear velocity through the cell in the range of 0.05-6 ft/second is desirable with operation toward the lower end of this range being preferred.

The base wash solution which is applicable for use in the inventive process is a strong base which has substantial solubility in water. Thus, preferred bases are alkali metal hydroxides although strong organic bases such as tetramethylammonium hydroxide can also be used if desired. To avoid unnecessarily contaminating the EHD process with foreign cations, the preferred base is one whose cation is already present in the process. For example, in a process employing a significant quantity of potassium phosphates as the circulating conducting salts, a solution of potassium hydroxide is the preferred aqueous base. The base can be present in the aqueous wash solution in any concentration which is effective for renewing the surface of the anode. Generally, the concentration will be 1-20, preferably 5-15, weight percent basic compound in the solution.

It is presently believed that the benefits of the present invention are obtained by the regular removal of the deposit that forms on the anode. For example, lead is a particularly active material in the EHD process. However, when using lead electrodes in systems containing salts such as phosphates as well as other organic reactants, a deposit is formed on the anode which contains combined lead, phosphorus, and organic material. When the anode is contacted with the aqueous base flushing solution, most, if not all, of the deposit appears to be removed while it is in a relatively manageable form. The present invention does not eliminate the corrosion of the electrodes such as lead anode corrosion, but it provides management of this type of corrosion so that it interferes little with the overall EHD process.

Because solid particles corrosion products are thus removed from the anode and passed into the circulating aqueous base solution, it is generally desired to provide means by which these particles can be conveniently removed from the process. This can be done easily by filtering out the solids which accumulate in the solution of aqueous base or by periodically discharging a settled slurry of solids from the aqueous base storage.

After the suitable solution of aqueous base has been circulated for a sufficient time to restore the surfaces of the electrode, the flushing operation is halted and the circulation of emulsion mixture through the cell and over the electrodes is resumed. If desired, the flushing operation can be carried out without interrupt-

ing the current flow. Thus, some hydrogen will be generated during the flushing operation but there would be no necessity for the cumbersome off-and-on switching of high flows of current.

### EXAMPLE

In a process using apparatus and a sequence of steps similar to that of FIG. 1, acrylonitrile was continuously converted to adiponitrile over a period of 202.7 hours at which time the run was terminated voluntarily. The aqueous portion of the recirculating emulsion was a solution of potassium phosphates, being 1.5 N in potassium ion and being neutralized to a pH of 7.5-7.7 with orthophosphoric acid. At steady state conditions, this aqueous stream is in the form of an emulsion with acrylonitrile and other organic products. The total organics amount to 4-5 weight percent based on the total emulsion. About 0.1 weight percent of tetrabutylammonium ion was also present in the emulsion.

The system was operated continuously in a manner similar to that of FIG. 1 except that neither acrylonitrile nor water nor salts were recycled back into the process from separation zone 6. At 24-36 hour intervals, the voltage across the cell was found to increase from the nominal 4.2 volts to a value of about 4.7 volts. At this time, the current and the circulation of emulsion through cell were halted and a 10 weight percent aqueous solution of potassium hydroxide was circulated through the cell at room temperature for 10-15 minutes. At the completion of this flushing period, the cell was drained of flushing solution and the current and circulation of reaction emulsion were resumed through the cell at the normal operating temperature of 120°-122°F.

A summary of other conditions as well as the results of the total run are shown in the following tabulation.

Table I

Length of Run	202.7 hr.
Electrodes	99.9% lead
Size	4 in. × 36 in. × 1/8 in.
Gap	1/8 in.
Volts across cell	
Prior to flushing	4.7 volts
Following flushing	4.2 volts
Current level	200 amp (200 amp/sq ft)
Emulsion temperature	120-122°F (cell)
Separation column temperature	50-55°F
Acrylonitrile feed rate	1.103 lb/hr
Emulsion flow rate	
To cell	39 lb/min
To separation column	55 lb/hr
Velocity through gap	3 ft/sec
Acrylonitrile conversion	
Per pass through cell	about 2%
Overall	77.9%
Material balance	98.3%
Adiponitrile yield	89.5 lb/100 lb acrylonitrile converted
Efficiency to adiponitrile	
Chemical	87.7% (based on acrylonitrile)
Current	86.5%
DC Power required (average)	1.15 KWH/lb adiponitrile
Lead Loss	0.0067 lb/lb adiponitrile
Product stream	
Adiponitrile	0.664 wt. fraction
Acrylonitrile	0.210 wt. fraction

Water	4.23
Acrylonitrile	19.88
Propionitrile	2.41
Succinonitrile	0.69
Tetrabutylammonium ion	0.59
Adiponitrile	67.78
Bis(2-cyanoethyl) ether	0.17
Hydrotrimer of acrylonitrile I	3.69
Hydrotrimer of acrylonitrile II	0.28
Methylglutaronitrile	0.24
Unknowns	0.04

The results of this relatively long run show that the cell and electrode flushing procedure of the present invention permits long periods of smooth operation, at a relatively constant and low voltage, free from polarization or other stoppages, and at high efficiency to desired products.

In closely identical comparison runs, which were carried out without the benefit of the invention flushing treatment, the voltage across the cell was found to slowly increase such that, after several days operation, the voltage required to maintain the desired current density exceeded the capacity of the power supply and the cell became polarized. This required periodic dismantling of the cell to remove and physically scrub the anode to restore the effective conducting surface. The present invention procedure has obviated the need for such relatively frequent dismantling of the cell.

In addition to EHD runs using lead anodes, equally successful runs were made under similar conditions using cells which contained a lead cathode and a lead dioxide anode. At intervals of 22-58 hours, the cell was flushed with 10 percent KOH solution (by weight) at 180°F. The periodic flushing prevented polarization and maintained a relatively low average voltage across the cell.

Other modifications and alterations of this invention will become apparent to those skilled in the art from

A typical organic phase effluent from the process was the composition of this product accumulated for the final 24-hour period and is shown below in weight percent.

the foregoing discussion and accompanying drawing, and it should be understood that this invention is not to be unduly limited thereto.

What is claimed is:

1. In a method for producing adiponitrile by electrolysis of an acrylonitrile composite stream passing through an undivided electrolytic cell having a cathode and an anode, the improvement comprising:

periodically terminating flow of the acrylonitrile composite stream to the cell;

passing a wash stream through the cell in contact with the cathode and the anode, said wash stream being a strong base aqueous solution having a concentration in the range of about 1-20 weight percent base compound in the solution;

continuing to pass the wash stream through the cell in contact with the electrodes for a period of time sufficient for removing deposits from the electrodes;

terminating the passage of the wash stream through the cell; and

initiating passage of the acrylonitrile composite stream through the cell and the production of adiponitrile.

2. A method, as set forth in claim 1, wherein the acrylonitrile stream is terminated and the wash stream is passed through the cell after the acrylonitrile stream has passed operably through the cell for a period of time in the range of about 10-100 hours.

3. A method, as set forth in claim 1, wherein the acrylonitrile stream is terminated and the wash stream is passed through the cell after the power requirements for the electrolysis process have increased to a value greater than about 0.5 volt.

4. A method, as set forth in claim 1, wherein the wash stream is passed through the cell at a linear velocity in the range of about 0.05 to about 6.0 feet per second.

5. A method, as set forth in claim 1, wherein at least one of the cathode or anode is formed of lead dioxide and including maintaining the wash stream at a temperature greater than about 150°F.

6. A method, as set forth in claim 1, wherein the wash stream is filtered after passing through the cell.

7. A method, as set forth in claim 1, wherein the wash stream comprises tetramethylammonium hydroxide.

8. A method, as set forth in claim 1, wherein cations of the wash stream are of the same type as cations of material discharging from the cell during electrolysis of the adiponitrile stream.

9. A method, as set forth in claim 1, wherein the flow

of the acrylonitrile composite stream to the cell is terminated in response to one of the power requirements of the electrolytic process having increased to a value greater than about 0.5 volt or the operation of the electrolytic cell for a period of time in the range of about 10-100 hours, the basic compound of the wash stream is at a concentration in the range of about 1-20 weight percent, and the time for passing said wash stream through the cell is a period of time in the range of about 1-60 minutes.

10. A method, as set forth in claim 9, wherein the wash stream is maintained at a temperature greater than about 150°F.

11. A method, as set forth in claim 10, wherein the wash stream comprises cations of the same type as cations of material discharging from the cell during electrolysis of the composite stream.

12. A method, as set forth in claim 9, wherein the wash stream comprises cations of the same type as cations of material discharging from the cell during electrolysis of the composite stream.

13. A method as set forth in claim 1, wherein the strong base is an alkali metal hydroxide.

14. In the method for producing adiponitrile by electrolysis of an acrylonitrile composite stream passing through an undivided electrolytic cell having a cathode and an anode, the improvement comprising:

terminating the flow of the acrylonitrile composite stream to the cell in response to the cell voltage increasing at least 0.5 volt during the operation of said cell;

passing a potassium hydroxide solution wash stream through the cell in contact with the electrodes for a period of time in the range of about 1-60 minutes, said wash stream having a potassium hydroxide concentration in the range of about 1 to about 20 weight percent, said wash stream also comprising cations of the same type as cations of material discharging from the cell during electrolysis of the composite stream, and said wash stream being maintained at a temperature greater than about 150° F.;

terminating the passage of the wash stream through the cell; and

initiating passage of acrylonitrile composite stream through the cell and the production of adiponitrile.

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