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METHOD FOR SEPARATING LIQUIDS

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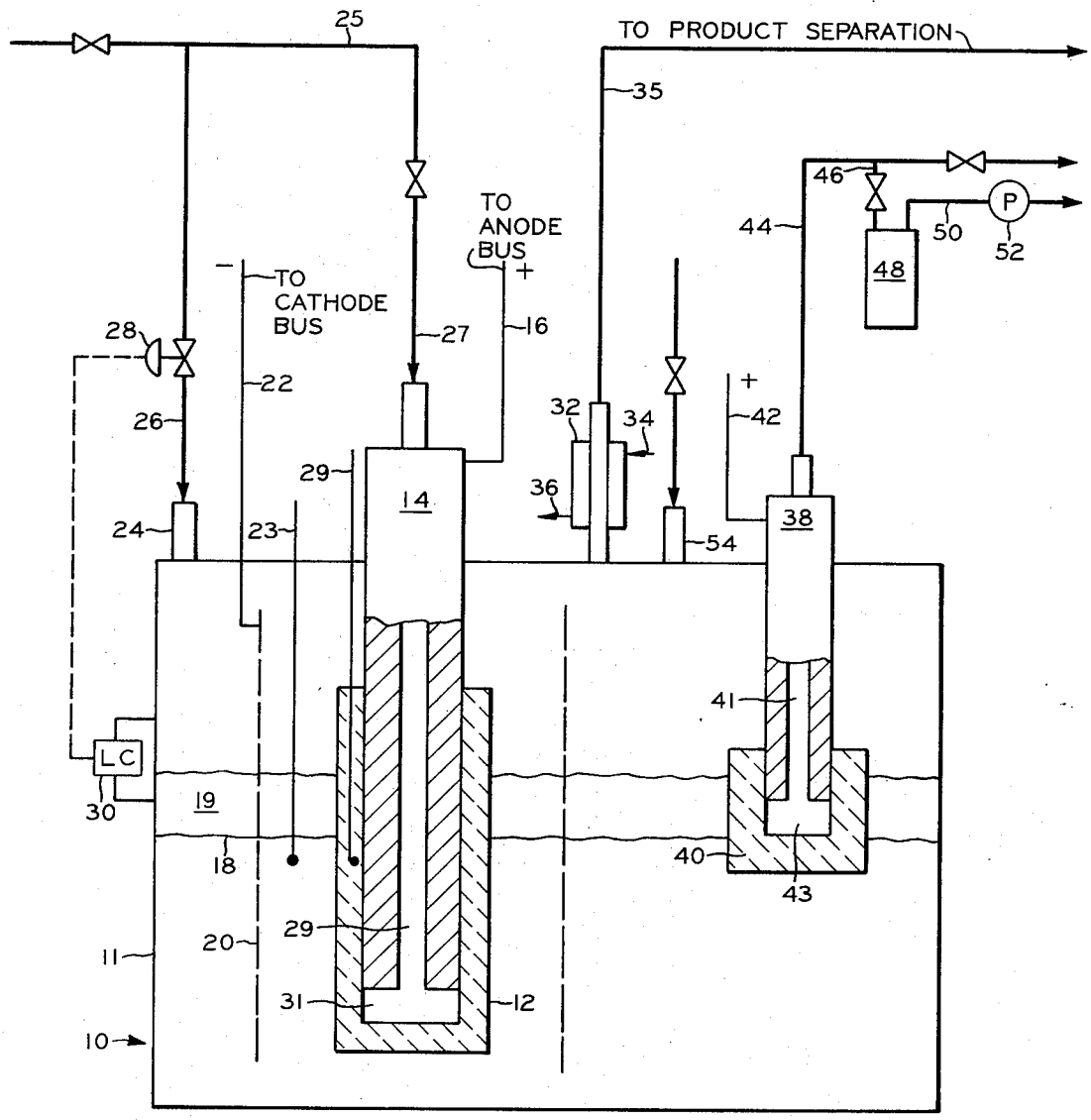

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METHOD FOR SEPARATING LIQUIDS

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U.S. Cl. 204—186 6 Claims

ABSTRACT OF THE DISCLOSURE

Method and apparatus for removing a layer of a first liquid from a body of a second liquid. Said first liquid is caused to selectively flow through the pores of and into a porous collection cup immersed therein. Application of an electric current to said cup increases the selectivity thereof for said first liquid.

This application is a division of my copending application Ser. No. 858,734, filed Sept. 17, 1969, now U.S. Pat. No. 3,617,453, issued Nov. 2, 1971.

This invention relates to an electrochemical conversion process.

Electrochemical conversion processes for converting a wide variety of feedstocks to desirable products are well known in the art. These processes include processes described an anode processes, e.g., processes wherein the desired reaction is carried out at or in the region of the anode, and also processes described as cathode processes, e.g., processes wherein the desired reaction is carried out at or in the region of the cathode. In many electrochemical conversion processes it is often desirable to maintain the electrolyte temperature at a desired value or at least within a narrow range of temperature. This sometimes becomes quite difficult due to I^2R losses within the electrolyte, coupled with the unavoidable heat of reaction. It is known to cool electrolytic cells by circulating various coolants in coils or tubes disposed within the cell. However, the most convenient coolant, water, frequently reacts with the electrolyte when leakage of the coolant occurs. In many cells there is also the danger of contaminating the products of the process with the coolant or with products of the reaction between the coolant and the electrolyte. Leakage of cooling water into the electrolyte is not an uncommon occurrence in view of the thin-walled cooling tubes employed and the corrosiveness of some cooling waters and some electrolytes.

The invention now being claimed in said copending application provides an electrochemical conversion process comprising a novel method of feeding a porous electrode and wherein a solution is provided for the problem of maintaining the cell temperature within desired limits. Broadly speaking, in the practice of said invention a liquid layer comprising the feedstock to the cell is maintained on the surface of the electrolyte in said cell. A portion of said liquid layer passes into the pores of a porous electrode in the cell and within said pores is at least partially converted. A vaporous cell effluent stream comprising converted products and unconverted feedstock is withdrawn through a reflux condenser. Condensate from said condenser is returned to the cell to cool the electrolyte therein. Conversion products are recovered from the noncondensed portion of said cell effluent stream. In one presently preferred embodiment, a portion of the feedstock is also introduced into the bottom portion of said porous electrode.

According to the invention being claimed in this application, there is provided a method of removing a layer of a second liquid from a body of a first liquid, said liquids being substantially insoluble in each other, which method comprises: causing said second liquid to selectively flow through the pores of and into a porous collection cup immersed therein; and then flowing said second liquid from said cup through a conduit connected thereto.

Further according to the invention being claimed in this application, there is provided apparatus comprising, in combination: a vessel for containing a body of a first liquid having a body of a second liquid, essentially insoluble in said first liquid, disposed as a layer on the surface of said first liquid; a phase splitter means disposed in said container, extending through said layer of second liquid and into said first liquid, for selectively removing said second liquid from the surface of said first liquid; and means for causing said second liquid to selectively flow into said phase splitter means and be removed from said cell.

The invention is particularly applicable to electrochemical conversion processes in which porous electrodes can be employed. Some examples of such processes are electrochemical halogenation, electrochemical cyanation, and cathodic conversions such as the reduction of alcohols to hydrocarbons, the reduction of organic ozonolysis products, or the reduction of organic acids to alcohols. One electrochemical conversion process in which the invention is particularly valuable is the electrochemical fluorination of fluorinatable materials in the presence of an essentially anhydrous liquid hydrogen fluoride-containing electrolyte. Thus, for purposes of convenience, and not by way of limitation, the invention will be further described in terms of being employed in the electrochemical fluorination of fluorinatable materials when using said hydrogen fluoride-containing electrolyte.

Various processes for carrying out electrochemical fluorination reactions are known. In one presently preferred process a current-conducting, essentially anhydrous, liquid hydrogen fluoride electrolyte is electrolyzed in an electrolysis cell provided with a cathode and a porous anode (preferably porous carbon), a fluorinatable feedstock is introduced into the pores of said anode and at least a portion of said feedstock is at least partially fluorinated within the pores of said anode, and fluorinated products are recovered from the cell.

Very few organic compounds are resistant to fluorination. Consequently, a wide variety of feed materials, both normally liquid and normally gaseous compounds, can be used as feedstocks in said process. Generally speaking, desirable organic starting materials which can be used are those containing from 2 to 12, preferably 2 to 10, carbon atoms per molecule. Some general types of organic starting materials which can be used include, among others, the following: alkanes, alkenes, alkynes, amines, ethers, esters, mercaptans, nitriles, alcohols, aromatic compounds, and partially halogenated compounds of both the aliphatic and aromatic series. It will be understood that the above-named types of compounds can be either straight chain, branched chain, or cyclic compounds.

The hydrogen fluoride electrolyte can contain small amounts of water, such as up to about 5 weight percent. However, it is preferred that said electrolyte be essentially anhydrous, e.g., contain not more than about 0.1 weight percent water. Commercial anhydrous liquid hydrogen fluoride containing up to about 1 percent by weight of water can be used. Thus, as used herein and in the claims, unless otherwise specified, the term "essentially anhydrous liquid hydrogen fluoride" includes liquid hydrogen fluoride which can contain water not exceeding up to about 1 percent by weight. As the electrolysis reaction proceeds, any water contained in the hydrogen fluoride electrolyte is slowly decomposed and said electrolyte concomitantly approaches the anhydrous state. Pure anhydrous liquid hydrogen fluoride is nonconductive. To provide adequate conductivity in the electrolyte, and to reduce the hydrogen fluoride vapor pressure at cell operating conditions, an in-

organic additive can be incorporated in the electrolyte. Presently preferred additives for this purpose are the alkali metal fluorides and ammonium fluoride. Said additives can be utilized in any suitable molar ratio of additive to hydrogen fluoride within the range of from 1:4.5 to 1:1, preferably 1:4 to 1:2.

Generally speaking, the fluorination process can be carried out at temperatures within the range of from —80 to 500° C. at which the vapor pressure of the electrolyte is not excessive, e.g., less than 250 mm. Hg. It is preferred to operate at temperatures such that the vapor pressure of the electrolyte is less than about 50 mm. Hg. A presently preferred range of temperature is from about 60 to about 120° C.

Pressures substantially above or below atmospheric can be employed if desired, depending upon the vapor pressure of the electrolyte and the vapor pressure of the feedstock as discussed above. Generally speaking, the process is conveniently carried out at substantially atmospheric pressure.

Current densities within the range of 30 to 1000, or more, preferably 50 to 500, milliamps per square centimeter of anode geometric surface can be used. The voltage which is normally employed will vary depending upon the particular cell configuration employed and the current density desired. Under normal operating conditions, however, the cell voltage or potential will be less than that required to evolve or generate free or elemental fluorine. Voltages in the range of 4 to 12 volts are typical. Generally speaking, the maximum normal voltage will not exceed 20 volts per unit cell. The term "anode geometric surface" refers to the outer geometric surface area of the porous element of the anode which is exposed to the electrolyte and does not include the pore surfaces of said porous element.

Feed rates which can be employed will preferably be within the range of from 0.5 to 10 ml. per minute per square centimeter of anode geometric surface area. For convenience, the volumetric feed rates have been expressed in terms of gaseous volume calculated at standard conditions, even though the feedstock may be introduced into the porous anode in liquid state.

Further details regarding fluorinatable feedstocks, feed rates, and other information concerning said preferred electrochemical fluorination process can be found in said copending application Ser. No. 858,734, filed Sept. 17, 1969, now U.S. Pat. 3,617,453, issued Nov. 2, 1971.

Referring now to the drawing, the invention will be more fully explained. In the drawing there is illustrated an electrolytic cell, denoted generally by the reference numeral **10**, comprising a cell body **11** having an anode **12** disposed therein. As here illustrated, said anode comprises a cylinder of porous carbon. Preferably, said anode is vertically disposed as illustrated. A current collector **14**, formed of copper or other suitable conducting material, is provided in intimate contact with the interior of said porous carbon cylinder. The intimate contact between said current collector and said cylinder of porous carbon can be provided by threads, a tight wedge fit, or other suitable means. As illustrated, said current collector comprises a tubular conduit having a passageway **29** therein and extending into said cylinder of porous carbon to a point near the bottom thereof. Said current collector is connected by means of lead **16** to the anode bus of the current supply. It will be noted that the upper end portion of said anode **12** extends above the electrolyte level **18**. A circular cathode **20**, which can be a screen formed of a suitable metal such as a stainless steel, surrounds said anode **12** and is connected to the cathode bus of the current supply by a suitable lead wire **22**. Any suitable source of current and connections thereto can be employed in the practice of the invention. Thermocouple means **23** is provided for determining the temperature of the electrolyte. A feedstock inlet **24** is provided in the upper portion, preferably the top, of said cell. A feedstock conduit **26** is connected to said feedstock inlet. A valve **28** is disposed in said feedstock conduit. Said valve **28** can be any suitable type of valve. As here illustrated, said valve comprises a motor valve. A liquid level control means **30** is mounted on the wall of said cell body **11** and is operatively connected in conventional manner to said valve **28** for controlling the introduction of feedstock into the cell responsive to said liquid level controller **30**. Any suitable type of liquid level controller can be employed. One suitable type is a Dynatrol detector type CL–10–RH manufactured by the Automation Products, Inc., Houston, Tex. A reflux condenser means **32** is operatively connected to the upper portion of said cell body **11**, preferably the top, and is in communication with the vapor space within said cell. Conduits **34** and **36** are provided for the supply of a suitable coolant to said reflux condenser **32**.

A phase splitter means comprising a tubular conduit **38** having a passageway **41** therein, formed of a suitable metal or other conducting material, and a porous cup **40** mounted on and closing the lower end of said tubular conduit, is disposed in said cell body **11**. Preferably, said cup **40** is mounted on said tubular conduit **38** in such a manner as to leave an enclosed space at the lower end of said tubular conduit. Preferably, said tubular conduit **38** of the phase splitter extends through the top or lid of the cell body **11**. However, if desired, it is within the scope of the invention for said tubular conduit **38** to be curved and extend through a side wall of cell body **11**. Said tubular conduit **38** is connected by means of a suitable lead wire **42** to the anode bus of the current supply. A withdrawal conduit **44** is connected to the passageway **41** formed within said tubular conduit **38**. Conduit **46**, connected to said withdrawal conduit **44**, extends into trap **48** as illustrated. Conduit **50**, having vacuum pump means **52** disposed therein, is connected to the top of said trap **48**. Returning to said anode, a conduit **27** is connected to the passageway **29** formed within the tubular current collector **14**. Said conduit **27** is also connected at its other end to feedstock header conduit **25**. An inlet **54** is connected to the top of cell body **11** for introducing gas pressure into the vapor space within said cell body.

In the operation of the apparatus illustrated in the drawing, for example, for the electrochemical fluorination of ethylene dichloride (1,2-dichloroethane) having a boiling point of about 83.5° C. and when using a KF·2HF electrolyte, the temperature of said electrolyte can be maintained at about 80° C. and the temperature of the anode can be maintained at about 100° C. The temperature of the electrolyte can be controlled by the amount of reflux returned to the cell from reflux condenser **32**. In some instances, it is desirable to maintain the temperature of the electrolyte slightly below, e.g., within the range of about 2 to about 60, preferably about 3 to about 20°, below the boiling point of the liquid layer maintained on top of the electrolyte. However, in other instances, it will be desirable to maintain the temperature of the electrolyte essentially at the boiling point of said liquid layer. The temperature of the anode can be controlled by controlling the amount of reaction taking place within the pores of said anode. This can be accomplished by balancing or correlating the feed flow rate and the current density applied to the anode. For a given feed flow rate to the anode, an increase in current density will result in a higher temperature within the pores of the anode, and vice versa. Generally speaking, it is desirable to maintain the temperature within the pores of the anode within the range of about 5 to about 20, preferably about 7 to about 15° C., above the electrolyte temperature. The temperature within the pores of anode **12** can be determined by means of thermocouple(s) **29** embedded therein.

In one embodiment, the fresh feedstock is introduced to the cell exclusively through feed inlet **24** and a layer of feedstock is established on the surface of the electrolyte. The depth of said layer will depend upon the particular

feedstock, the type of reaction being carried out, the size of the cell, the size and number of anodes in the cell, etc. Generally speaking, it will be desirable to maintain the depth of said layer within the range of about 0.1 to 2 inches, preferably about 0.5 to 1 inch. After the layer of feedstock has been established on the surface of the electrolyte, the current is turned on. The feedstock enters into the pores of the anode wherein it diffuses through the pores of the anode, is vaporized, contacts the fluorinating species, and at least a portion of said feedstock is at least partially fluorinated. Fluorinated product and any unfluorinated feedstock are passed from the pores of the anode above the level of the electrolyte and the supernatant layer thereon and into the vapor space in the upper portion of the cell. A vaporous cell effluent stream is withdrawn through reflux condenser **32**. Said condenser is operated at a temperature and a pressure such that hydrogen fluoride and at least a portion of the unfluorinated feedstock will be condensed. The non-condensed portion of said vaporous cell effluent stream is passed through conduit **35** to a product separation zone wherein separation of the fluorinated products is effected in conventional manner.

In another preferred embodiment, the feeding of the anode from the supernatant layer of feedstock is supplemented by introducing fresh feedstock into the lower portion of the anode. In this embodiment, at least a portion of the fresh feedstock is introduced via conduit **27** and passed through passageway **29** into space **31** in the lower portion of the anode. In this embodiment, it is sometimes preferred to introduce all the fresh feedstock via space **31**. From said space **31** the vaporized feedstock enters the pores of the anode, travels upward through the pores of the anode, and exits from the anode above the level of the electrolyte and supernatant liquid layer thereon, and into the vapor space in the upper portion of the cell. During passage of said feedstock through said pores at least a portion of the feedstock is at least partially fluorinated. A vaporous cell effluent stream is withdrawn through reflux condenser **32** and treated in the manner described above. When operating with this dual feeding system, the ratio of the feed introduced through space **31** to the feed introduced into the pores of the anode from layer **19** will usually be within the range of 0.5 to 0.95, preferably within the range of from 0.5 to 0.75. An important advantage of said dual feeding system is that if the feed to the lower portion of the anode is inadvertently interrupted, the supernatant layer on the surface of the electrolyte comprises a reservoir of feedstock. This will prevent, or at least reduce, production of elemental fluorine such as would occur if feedstock flow were suddenly stopped.

In practice, there will sometimes be a buildup of concentration of higher boiling fluorinated products in layer **19** which is maintained on the surface of the electrolyte. When the concentration of said higher boiling fluorinated products in layer **19** reaches a desired or limiting value, e.g., about 50 percent, it is desirable to remove a portion of said layer. I have discovered that this can be accomplished efficiently by utilizing the difference in contact angle of the electrolyte and the contact angle of the liquid in layer **19**.

For example, the electrolyte KF·2HF does not wet porous carbon, i.e., the contact angle of said electrolyte with the porous carbon is greater than 90 degrees. Thus, the electrolyte KF·2HF resists flow into the pores of the porous carbon. The contact angle of 1,2-dichloroethane and its fluorinated products is less than the contact angle for said electrolyte. These materials will thus preferentially or selectively flow into and through the pores of the porous carbon cup **40**.

Referring to the drawing, this preferential or selective flow of layer **19** into and through the pores of porous cup **40** into collection zone **43** can be caused to take place by the application of gas pressure through inlet **54**. Any suitable inert gas, such as nitrogen, can be employed for applying gas pressure. The application of said gas pressure will cause the layer **19** to flow through the pores of porous cup **40** and pass upwardly through passageway **41** and into conduit **44** for disposal as desired. When all of the liquid in layer **19** has been forced out, the gas pressure will purge the system and leave the electrolyte behind essentially undisturbed. Said layer **19** can also be caused to flow through the pores of porous cup **40** by the application of vacuum. Said vacuum can be applied to trap **48** by means of pump **52** disposed in conduit **50** connected to the top of trap **48**. Thus, by opening the valve in conduit **46** and closing the valve in conduit **44**, layer **19** can be caused to flow through the pores of cup **40**, up through passageway **41**, and into tray **48**.

I have also discovered that the efficiency of the above method of separating layer **19** from the underlying layer of electrolyte can be increased by applying a positive voltage to the phase splitter device. Said voltage can be applied by connecting lead wire **42** to the anode bus of the system. Current flow will be established because cup **40** extends into the electrolyte which is in contact with cathode **20**. It will generally be desirable to apply from 3 to 8 volts of direct current to the phase splitter at a current density level within the range of from about 1 to about 300 milliamps per square centimeter of geometric surface area.

The above-described method of separating two phases can be applied to any system in which the contact angle of one phase (either phase) is greater than 90 degrees, and the contact angle of the other phase is sufficiently different from, preferably less than, the contact angle of the first-mentioned phase. Generally speaking, it is desirable that the difference in said contact angles be at least 10 degrees. However, by the application of electric current as described above, the difference in contact angle can be increased and the initial difference in contact angle of the two phases is not unduly restrictive. While said phase splitter and its operation have been described as employing porous carbon for the porous cup **40**, the invention is not limited to the use of porous carbon. Other suitable porous materials, such as porous Teflon, can be employed in the practice of the invention.

While certain embodiments of the invention have been described for illustrative purposes, the invention is not limited thereto. Various other modifications of the invention will be apparent to those skilled in the art in view of this disclosure. Such modifications are within the spirit and scope of the disclosure.

I claim:

1. A method of separating a layer of a second liquid from a layer of a first liquid, said liquids being substantially insoluble in each other, which method comprises:

causing one of said liquids to selectively flow through the pores of and into an electrically conductive porous collection cup which is in contact with both of said liquids; and

applying a positive electric voltage to said cup so as to increase the selectivity of said cup for the flow of said one liquid through the pores of said cup.

2. A method according to claim **1** wherein: said second liquid comprises a fluorinatable organic material; said first liquid comprises a current-conducting, essentially anhydrous, hydrogen fluoride electrolyte; and said collection cup is formed of porous carbon.

3. A method according to claim **2** wherein: said voltage is within the range of from about 3 to about 8 volts and is applied to said collection cup at a current density within the range of from about 1 to about 300 milliamps per square centimeter of geometric surface area of said cup.

4. A method according to claim **1** wherein:

said liquids are disposed in a container;

said porous cup and a conduit connected thereto define an enclosed space within said container which is not in communication with said liquids except through the pores of said cup; and

said one liquid is caused to selectively flow into said cup by (a) the application of gas pressure to the surface of one of said liquids, or (b) the application of vacuum to a conduit connected to said cup.

5. A method according to claim **4** wherein:

said second liquid comprises a fluorinatable organic material; and

said first liquid comprises a current-conducting, essentially anhydrous, hydrogen fluoride electrolyte.

6. A method according to claim **5** wherein: said voltage is within the range of from about 3 to about 8 volts and is applied to said collection cup at a current density

within the range of from about 1 to about 300 milliamps per square centimeter of geometric surface area of said cup.

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