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ELECTROLYTIC CONVERSIONS WITH PERMSELECTIVE MEMBRANES

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Fig. 1

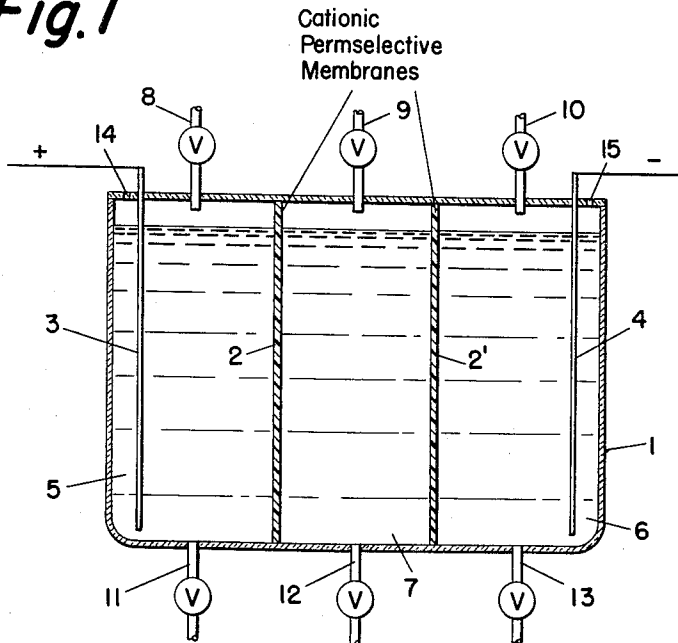
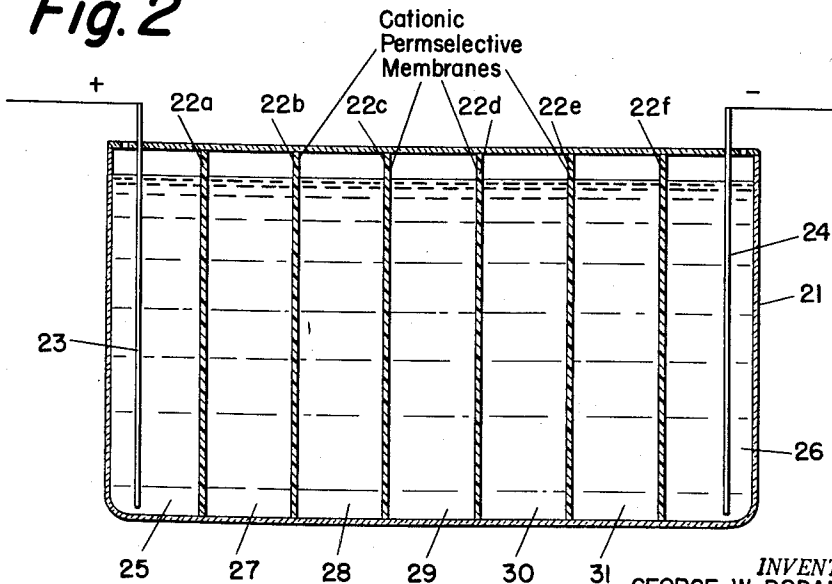


Fig. 2



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ELECTROLYTIC CONVERSIONS WITH PERMSELECTIVE MEMBRANES

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8 Claims. (Cl. 204—72)

This invention relates to the production of weak organic and weak inorganic acids. It has for an object the electrolytic conversion of water-soluble salts of weak acids to the weak acids per se. It also relates to, and has for an object, the construction of electrolysis cells in which the process is carried out. It relates particularly to the production of weak organic acids.

The process of this invention comprises converting a water-soluble salt of a weak acid into the corresponding weak acid per se by passing a direct electric current through an aqueous solution of said salt while the salt solution is contained between two cationic permselective membranes on the opposite sides of which membranes are aqueous solutions, one a solution of a strong mineral acid and the other a solution of an electrolyte. The direct current is passed through the three solutions in a direction so that hydrogen ions migrate from the acid solution through one membrane into the salt solution and there combine with the anions of the salt to form a weak acid while the metal ions of the salt migrate through the second membrane into the solution of electrolyte. Because the weak acid is only slightly ionized, having a dissociation constant of less than 0.1, only relatively few hydrogen ions are present to migrate together with the metal ions through the second membrane into the electrolyte solution. Consequently, the salt is gradually converted into the corresponding weak acid.

The process is eminently suited for the preparation of weak acids which are subject to electrolytic oxidation or decomposition. It represents an improvement over previous electrolytic processes for producing acids, including the process described in my application for Letters Patent, Serial No. 279,904, filed April 1, 1952, now abandoned, because during the instant process the weak acids are never in contact with an electrode and consequently they are never exposed to conditions which induce electrolytic oxidation or decomposition. Thus the instant process is employed to advantage in the production, for example, of the following weak organic acids which are known to decompose to hydrocarbons, carbon dioxide and other products when they are exposed, during conventional electrolysis processes, to the oxidative conditions which surround an anode: acetic, propionic, butyric, itaconic, maleic, fumaric, acrylic, tartaric, citric, sebacic and ascorbic acids. The process is likewise employed to advantage for the preparation of weak inorganic acids such as sulfurous, arsenous and silicic acids.

The practical and efficient conversion of salts to acids is accomplished according to the process of this invention by electrolyzing an aqueous solution of a water-soluble salt, preferably an alkali metal salt, of a weak acid in a special kind of electrolysis cell which can best be understood by a reference to the attached drawings wherein Figure 1 is a representation of a simple but typical electrolysis cell which is divided into three compartments by means of a pair of cationic permselective membranes or films, and Figure 2 is a representation of a similar electrolysis cell containing seven compartments

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separated by partitions of cationic permselective membranes.

In said Figure 1, the numeral 1 identifies a container which is divided into three compartments 5, 6 and 7 by two cationic permselective membranes 2 and 2', which serve as partitions between compartments 5 and 7 and between compartments 6 and 7. The membranes are described below in greater detail. Compartment 5 is an anode compartment by virtue of the presence therein of the anode 3, while compartment 6 is the cathode compartment containing the cathode 4. The intermediate compartment 7 is that one in which the acid is formed. When the cell is in operation the electrodes 3 and 4 are connected to a source of electric power not shown.

In Figure 2, the numeral 21 identifies a container which is divided into seven compartments, 25 to 31 inclusive, by six cationic permselective membranes 22a to 22f inclusive which serve as partitions between the compartments. Compartment 25 is an anode compartment since it contains the anode 23 while compartment 26 is the cathode compartment containing the cathode 24. The other compartments, 27 to 31 inclusive, are intermediate compartments between anode compartment 25 and cathode compartment 26. When the cell is in operation the electrodes 23 and 24 are connected to a source of electric power not shown.

In the simplest embodiment of this invention an electrolysis cell is employed which is like that shown in Figure 1. An aqueous solution of a salt of a weak acid is placed in compartment 7, while an aqueous solution of a mineral acid, preferably sulfuric acid, is placed in the anode compartment 5 and an aqueous solution of an electrolyte, preferably of an hydroxide of an alkali metal, is placed in the cathode compartment 6. A direct current of electricity is passed through the cell and the ions in the three compartments tend to migrate toward the electrodes of opposite charge. Hydrogen ions resulting from the ionization of the acid in compartment 5 migrate through the cationic permselective membrane 2 into compartment 7 while at the same time the cations of the water-soluble salt of the organic acid pass through the cationic permselective barrier 2' into cathode compartment 6 where, according to the well established principles of electrolysis, hydrogen is liberated and the hydroxide of the metal is formed. At the same time oxygen is liberated at the anode when sulfuric acid is employed or chlorine is liberated if hydrochloric acid is used. The anions of the salt in compartment 7 tend to migrate toward the anode but are constrained by the permselective barrier 2 which, because it is cationically permselective, repels the anions and confines them to the compartment 7. Hydroxyl ions formed in the cathode compartment likewise migrate toward the electrode but are repelled by the permselective barrier 2' and remain in compartment 6. Relatively few hydrogen ions pass from compartment 7 into the cathode compartment 6 because the acids, in contrast to the salts of the organic acids, are either insoluble in the aqueous solution of compartment 7 or are weakly ionized.

The net result is that oxygen or chlorine is liberated from compartment 5 through outlet 14 and hydrogen, as ions, leaves the same compartment; a weak acid is formed in compartment 7; hydrogen gas is liberated and escapes through outlet 15 while the hydroxide of the metal is formed in compartment 6.

It will be noted that no acid, aside from the small amount in compartment 5, is required when sulfuric acid is employed. Hydrogen and oxygen are obtained; and the hydroxide of the metal is produced which can, of course, be utilized.

The process can be operated batchwise or continuously. When operated continuously water or dilute acid is

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admitted to compartment 5 through inlet 8 at a rate sufficient to replace that which is lost by electrolysis; a solution of the salt of the weak acid is admitted to compartment 7 through inlet 9 and a solution or slurry of the weak acid is removed from compartment 7 through outlet 12; and the relatively concentrated solution of metallic hydroxide is removed from compartment 6 through outlet 13 and is replaced by a dilute solution of an electrolyte through inlet 10.

In the operation of the electrolysis cell shown in Figure 2, an aqueous solution of a salt of a weak acid is placed in the alternate compartments 27, 29 and 31. An aqueous solution of a mineral acid, preferably sulfuric acid, is placed in the anode compartment 25 and also in alternate compartments 28 and 30 while an aqueous solution of an electrolyte, preferably an hydroxide of an alkali metal, is placed in the cathode compartment 26. A direct current of electricity is passed through the cell and the ions in all of the compartments tend to migrate towards the electrodes of opposite charge. Hydrogen ions resulting from the ionization of the acid in compartment 25 migrate through the cationic permselective membrane 22a into compartment 27 while at the same time the cations of the water-soluble salt of the weak acid in compartment 27 pass through the cationic permselective membrane 22b into the next compartment 28. In a similar way, the cations in compartments 28, 29, 30 and 31 migrate toward the cathode 24, pass through the cationic permselective films 22c, 22d, 22e and 22f. In the cathode compartment 26, the hydroxide of the metal is formed together with water and hydrogen. While cations pass through the permselective films during their migration to the cathode, the anions in compartments 26 to 31 inclusive tend to migrate towards the anode but are constrained by the permselective barriers 22a to 22f inclusive which, because they are cationically permselective, repel the anions and confine them to their original compartments. In the anode compartment 25 a gas is liberated, oxygen when sulfuric acid is employed or chlorine if hydrochloric acid is used. The hydrogen ions which enter compartments 27, 29 and 31 tend to migrate through the cationic membranes 22b, 22d and 22f toward the cathode but their number is relatively low because the acids are weak or insoluble and consequently the concentration of the weak acid in compartments 27, 29 and 31 increases while the concentration of the metallic ions diminishes in the same amount. As indicated above, hydrogen ions and metallic cations pass in and out of compartments 28 and 30 in the direction of the cathode. In these compartments, however, the inorganic acid is substantially completely ionized and substantially all of the hydrogen can migrate as ions together with the metallic ions. But since the mobility of hydrogen ions is several times that of metallic cations, more hydrogen ions than metallic cations pass from compartments 28 and 30 into compartments 29 and 31 respectively. That is to say, the concentration of metallic cations increases in compartments 28 and 30.

The net result of this modification is that oxygen or chlorine is liberated in the anode compartment 25; hydrogen is liberated in the cathode compartment 26; the hydroxide of the metal of the original salt of the organic acid is generated in the cathode compartment 26; the salt of the weak acid is converted to the acid per se in compartments 27, 29 and 31; and the strong mineral acid is converted to an inorganic salt in compartments 28 and 30. It should be pointed out that the conversion of the salt to the acid is more complete in the compartment adjacent to the anode compartment 25 than it is in the alternating compartments 29 and 31 because only hydrogen ions enter compartment 27 whereas both metallic ions and hydrogen ions enter compartments 29 and 31. A particularly efficient method is to remove the liquid containing the weak acid from compartment 27 continuously and to replace it with the solution of acid and salt

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from compartments 29 and 31. It is preferred that this process be run continuously by withdrawing the solutions from the compartments and replacing the solutions by fresh solutions through inlets and outlets at the tops and bottoms of the compartments corresponding to elements 8 to 13 inclusive of Figure 1 but which elements have been omitted from Figure 2 for the sake of simplicity. Furthermore, the number of chambers between the anode compartment and the cathode compartment can be many more than the five which are shown in Figure 2, but in all cases there are an uneven number of such intermediate compartments.

The cells which are employed in this invention can be varied as to size, shape, closures, construction materials, controls, size of the individual compartments, reinforcement of the membranes, stirring devices, location of inlets and outlets, embellishments et cetera. What is essential, however, is that the cell—and by "cell" is meant the complete apparatus for carrying out the invention—have an anode compartment, a cathode compartment, and an uneven number (1, 3, 7, 25, 49 et cetera) of intermediate compartments, and that the barriers which actually divide the space in the container into compartments and thereby serve as the walls or partitions for the compartments be cationic permselective diaphragms.

The cationic permselective membranes which divide the electrolytic cells into three compartments are all important to the success of this process. They are diaphragms which function by allowing only one kind of ions, namely cations, to pass through them while at the same time preventing—or at least restraining—the passage of anions through them from one compartment of the cell to another.

The composition of the cationic permselective diaphragms can vary within reasonable limits but it is essential to this invention that the diaphragms contain a cation-exchange resin and that the amount of cation-exchange resin be such that the diaphragms have suitably high conductance when employed in an electrolysis cell.

The permselective films which have proven to be most suitable for use in this process are those made by incorporating particles of a cation-exchange resin in a film-forming matrix such as polyethylene, polyvinyl chloride, natural rubber or synthetic rubber. Such films are the subject of my application, Serial No. 202,577, filed December 23, 1950, now Patent No. 2,681,320, to which reference is made, and they contain from 25% to 75% of a cation-exchange resin of either the sulfonic type or the carboxylic type. The particular films described in my above-noted application are very permselective in that they allow the passage through them of cations while excluding anions. In addition they are physically strong and flexible so that they can be mounted easily in the cell. Furthermore, they are resistant to the action of chemicals and are not destroyed by the solution of sodium hydroxide or potassium hydroxide with which they are in contact during the electrolysis. Other cationic permselective films are known such as those based on cellophane or collodion; but these do not contain cation-exchange resins and are not recommended for use in the instant invention because of their destruction by alkaline solutions.

What is required here is a film or layer containing a cation-exchange resin. Cation-exchange resins are well known and are widely used in the removal of ions from fluids, as, for example, in the softening of water. Suitable cation-exchange resins are described in U.S. Patents Nos. 2,184,943; 2,195,196; 2,204,539; 2,228,159; 2,228,160; 2,230,641; 2,259,455; 2,285,750; 2,319,359; 2,366,007; 2,340,110; and 2,340,111. Some of the resins can be cast or otherwise produced in the form of free sheets or membranes. Or the cation-exchange resins can be made on a porous support such as a piece of cloth or plastic screening. As indicated above, the much preferred cationic permselective membranes are those con-

taining a cation-exchange resin, preferably a sulfonated phenol-formaldehyde resin or a sulfonated copolymer of a monovinyl hydrocarbon such as styrene and a polyvinyl hydrocarbon such as divinylbenzene, dispersed as particles in a layer of an alkali-resistant matrix. Since the electric current must be carried through the permselective film by cations in association with the cation-exchange resin it is ordinarily advisable that the amount of resin constitute a substantial part of the permselective membrane.

The words "membrane," "film," "sheet," "layer," "pellicle," and "diaphragm" are used synonymously herein to describe the barriers or partitions between the compartments in the electrolysis cell. The barriers are usually thin—of the order of thickness of 20 to 100 mils—although thicker membranes have been used successfully.

The electric current is direct; and a current density of about 10 to 200—and preferably from 60 to 180—amperes per square foot is maintained. The current density can, of course, be varied and just what current density is maintained depends upon the construction of the cell and other prevailing conditions of operation.

The salt of the weak acid which is electrolytically converted to the acid must be water-soluble, and usually it is a salt of sodium or potassium or mixtures of the two. The acid itself, however, need not be water-soluble. In fact, the process is most efficient when applied to water-soluble salts of water-insoluble acids because in those cases there is no difficulty whatever with the passage of hydrogen ions from the compartment containing the insoluble acid. Thus, the process is particularly suitable for the conversion of salts, e.g., sodium sebacate, sodium oleate, potassium stearate, and the salts obtained by the alkali-refining of vegetable oils, into the corresponding weak acids.

The particular concentration of the electrolyte in the cathode compartment at the start of the operation is not critical since cations enter the compartment as the electrolysis progresses. However, it is recommended that the concentration be at least one-tenth normal, and preferably normal, at the outset. Any convenient electrolyte, such as sodium chloride, can be used in the cathode compartment if desired; but it is apparent that such a material will contaminate the metal hydroxide which is formed during electrolysis. For this reason it is much preferred to start with a solution of the hydroxide of the same metal as is combined in the salt of the organic acid being treated.

Likewise the concentration of the acid in the anode compartment and in any intermediate compartments is not critical but enough should be present to insure good conductivity.

As a means of further illustrating this invention, the following example is given:

Example

An electrolysis cell of the type shown in Figure 1 was employed. It was divided into an anode compartment containing a platinum electrode, a cathode compartment, containing a platinum electrode, and an intermediate compartment between the anode compartment and the cathode compartment and separated therefrom by a pair of cationic permselective films or diaphragms. The permselective films were made according to my application for Letters Patent, Serial No. 202,577, filed December 23, 1950, now Patent No. 2,681,320, by dispersing on a rubber mill a commercially available cation-exchange resin in a film of polyethylene. The cation-exchange resin, which constituted 70% by weight of the permselective film, was a sulfonated copolymer of styrene and divinylbenzene (Amberlite IR 120), and was itself made by the process of U.S. Patent No. 2,366,007.

In the anode compartment was placed 75 parts of a 0.1 N aqueous solution of sulfuric acid. In the cathode compartment was placed 75 parts of a 0.1 N aqueous solution of sodium hydroxide. The intermediate com-

partment was charged with 50 parts of a 10% aqueous solution of sodium acetate.

A direct current was passed through the cell for 3½ hours under an impressed potential of 11–12 volts, at a current density of approximately 60 amperes per square foot, which current density, however, fell to about 6 amperes per square foot towards the end of the operation. During the electrolysis, oxygen was liberated at the anode and hydrogen at the cathode. The contents of the three cells were analyzed and it was found that the anode compartment had gained 1.3 milliequivalents of acid as a result of a slight leakage through the permselective film. The amount of sodium hydroxide in the cathode compartment was increased by 63.5 milliequivalents, and 64 milliequivalents of acetic acid was found in the center compartment indicating virtually complete conversion of sodium acetate to acetic acid.

The advantage of the process of this invention over an electrolytic process of electrolyzing sodium acetate in a two-compartment cell, in which the two compartments were separated by a single permselective film, is evidenced by the fact that 75.8% of the acetic acid was lost by electrolytic oxidation in the anode compartment of the cell. In the instant process such decomposition is avoided because the organic acid is prevented from coming in contact with the anode.

I claim:

1. An electrolytic process for converting a water-soluble salt of an aliphatic acid into said acid which comprises passing a direct electric current through an aqueous solution of said salt while it is positioned between a first cationic permselective membrane adjacent the anode and a second cationic permselective membrane, which membranes contain a cation-exchange resin, on the opposite sides of which membranes are conductive aqueous solutions, one of which is an anolyte capable of producing hydrogen ions at said anode immersed therein, said electric current being passed through all said solutions and said first and second membranes in a direction to cause hydrogen ions to migrate from said anolyte through said first membrane into said solution of said salt and to cause metal ions to migrate from said salt solution through said second membrane into the other conductive aqueous solution.

2. An electrolytic process for converting a water-soluble salt of a weak acid into said acid which comprises passing a direct electric current through an aqueous solution of said salt while it is positioned between a first cationic permselective membrane adjacent the anode and a second cationic permselective membrane, which membranes contain a cation-exchange resin, on the opposite sides of which membranes are conductive aqueous solutions, one of which is an anolyte capable of producing hydrogen ions at said anode immersed therein, said electric current being passed through all said solutions and said first and second membranes in a direction to cause hydrogen ions to migrate from said anolyte through said first membrane into said solution of said salt and to cause metal ions to migrate from said salt solution through said second membrane into the other conductive aqueous solution.

3. An electrolytic process for converting a water-soluble salt of a weak acid into said acid which comprises passing a direct electric current through an aqueous solution of said salt while it is positioned between a first cationic permselective membrane adjacent the anode and a second cationic permselective membrane, which membranes contain a cation-exchange resin, on the opposite sides of which membranes are conductive aqueous solutions, one of which is an anolyte capable of producing hydrogen ions at said anode immersed therein, said electric current being passed through all said solutions and said first and second membranes in a direction to cause hydrogen ions to migrate from said anolyte through said first membrane into said solution.

of said salt and to cause metal ions to migrate from said salt solution through said second membrane into the other conductive aqueous solution, in which said anolyte is a strong mineral acid.

4. An electrolytic process for converting a water-soluble salt of a weak acid into said acid which comprises passing a direct electric current through an aqueous solution of said salt while it is positioned between a first cationic permselective membrane adjacent the anode and a second cationic permselective membrane, which membranes contain a cation-exchange resin, on the opposite sides of which membranes are conductive aqueous solutions, one of which is an anolyte capable of producing hydrogen ions at said anode immersed therein, said electric current being passed through all said solutions and said first and second membranes in a direction to cause hydrogen ions to migrate from said anolyte through said first membrane into said solution of said salt and to cause metal ions to migrate from said salt solution through said second membrane into the other conductive aqueous solution, in which said anolyte is sulfuric acid and said water-soluble salt is sodium acetate.

5. An electrolytic process for converting a water-soluble salt of a weak acid into said weak acid which comprises passing direct electric current through an electrolysis cell, which has an anode compartment containing a conductive aqueous solution which is an anolyte capable of producing hydrogen ions at the anode immersed therein, a cathode compartment containing a conductive aqueous solution in which the cathode is immersed therein and an intermediate compartment containing a conductive aqueous solution of said water-soluble salt of said weak acid, all of said compartments being separated by cation permselective membranes, which membranes contain a cation-exchange resin, one of said membranes being adjacent the anode, said electric current being passed through all said solutions and said membranes in a direction to cause hydrogen ions to migrate from said anolyte through the membrane adjacent the anode into said solution of said salt and to cause metal ions to migrate from said salt solution through the other membrane into the other conductive aqueous solution.

6. An electrolytic process for converting a water-soluble salt of an aliphatic acid into said aliphatic acid which comprises passing a direct electric current through an electrolysis cell, which has an anode compartment containing a conductive aqueous solution which is an anolyte capable of producing hydrogen ions at the anode immersed therein, a cathode compartment containing a conductive aqueous solution in which the cathode is immersed therein and an intermediate compartment containing a conductive aqueous solution of said water-soluble salt of said aliphatic acid, all of said compartments being separated by cation permselective membranes, which membranes contain a cation-exchange resin, one of said membranes being adjacent the anode, said electric current being passed through all said solutions and said membranes in a direction to cause hydrogen ions to migrate from said anolyte through the membrane adjacent the anode into said solution of said salt and to cause metal ions to migrate from said salt solution through the other membrane into the other conductive aqueous solution.

7. An electrolytic process for converting a water-soluble salt of a weak acid into said weak acid which comprises

passing direct electric current through an electrolysis cell, which has an anode compartment containing a conductive aqueous solution which is an anolyte capable of producing hydrogen ions at the anode immersed therein, a cathode compartment containing a conductive aqueous solution in which the cathode is immersed therein and an uneven number of intermediate compartments between said anode and said cathode compartments alternately containing a conductive aqueous solution of said water-soluble salt and a conductive aqueous solution which is an anolyte capable of producing hydrogen ions, the compartment adjacent to said anode compartment containing a conductive aqueous solution of said water-soluble salt, all of said compartments being separated by cationic permselective membranes, which membranes contain a cation-exchange resin, one of said membranes being adjacent the anode, said electric current being passed through all said conductive solutions and said membranes in a direction to cause hydrogen ions to migrate from said anolytes through the proximate said membranes into said conductive solutions of said salt and to cause metal ions to migrate from said salt solutions through other said membranes into the other conductive aqueous solutions.

8. An electrolytic process for converting a water-soluble salt of an aliphatic acid into said aliphatic acid which comprises passing direct electric current through an electrolysis cell, which has an anode compartment containing a conductive aqueous solution which is an anolyte capable of producing hydrogen ions at the anode immersed therein, a cathode compartment containing a conductive aqueous solution in which the cathode is immersed therein and an uneven number of intermediate compartments between said anode and said cathode compartments alternately containing a conductive aqueous solution of said water-soluble salt and a conductive aqueous solution which is an anolyte capable of producing hydrogen ions, the compartment adjacent to said anode compartment containing a conductive aqueous solution of said water-soluble salt, all of said compartments being separated by cationic permselective membranes, which membranes contain a cation-exchange resin, one of said membranes being adjacent the anode, said electric current being passed through all said conductive solutions and said membranes in a direction to cause hydrogen ions to migrate from said anolytes through the proximate said membranes into said conductive solutions of said salt and to cause metal ions to migrate from said salt solutions through other said membranes into the other conductive aqueous solutions.

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