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3,694,281

PROCESS FOR FORMING A DIAPHRAGM FOR USE IN AN ELECTROLYTIC CELL

Joseph-Adrien Leduc, Short Hills, N.J., assignor to Pullman Incorporated, Chicago, Ill.

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2 Claims

ABSTRACT OF THE DISCLOSURE

An improvement in the operation of an electrolytic cell having a diaphragm positioned between an anode and a cathode of the cell is provided by employing a diaphragm comprising an asbestos matrix impregnated with at least one of a group of polymers including synthetic rubbers and thermoplastic and thermosetting polymers and copolymers. A controlled amount of the polymeric impregnant is deposited in the spaces between the asbestos fibers to provide controlled and reproducible permeability and density in a diaphragm having greatly improved wet strength. Because of the superior strength of the impregnated diaphragm, they can be employed in the electrolytic cell without support and can be subjected to the conditions of lamination so as to be combined on an inseparable sheet or layer of wire mesh of a plastic woven fabric or a sintered porous plastic and employed in laminated form as the diaphragm in an electrolytic cell.

This application is a continuation-in-part of copending application Ser. No. 814,821, filed Apr. 9, 1969, now abandoned.

This invention relates to an improved method for carrying out electrochemical reactions in a system comprising an electrolytic cell and more particularly relates to the use of a particular composition as the diaphragm separating the anode chamber containing anolyte from the cathode chamber containing catholyte in the electrolytic cell.

In effecting electrochemical reactions, a separator is usually provided within the electrochemical cell to divide the cell into an anode chamber and a cathode chamber, the liquid medium contained therein commonly being referred to as the anolyte and catholyte, respectively. The separator may be formed such that the liquid medium is substantially prevented from passing between the chambers allowing only for the passage of current or ionic transfer through the diaphragm separator. Such separators are referred to as liquid impermeable barriers or diaphragms. These separators also may be such that the electrolyte actually flows therethrough from one chamber to the other, such separators thus being liquid permeable. Irrespective of whether the separator is liquid impermeable or liquid permeable, it should be resistant to chemical deterioration caused by its contact with both the anolyte and the catholyte, the chemical properties of which are often significantly different. For example, in the manufacture of molecular chlorine by the well known electrolysis of aqueous metal chloride solutions, the anolyte is acidic and the catholyte is alkaline. Although certain diaphragms composed entirely of "white asbestos" or chrysotile are substantially resistant to aqueous alkaline solutions, they undergo rapid disintegration in an aqueous acidic medium. The deterioration of white asbestos is aggravated in cells in which an initially formed electrolyte soluble product is converted within the cell to another product which under operating conditions is produced in a gaseous state. Such a process is illustrated by the manufacture of propylene oxide by contacting propylene

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with anolyte in which halogen has been generated to form propylene halohydrin and the halohydrin is dehydrohalogenated upon contact with the alkaline catholyte to form gaseous propylene oxide.

Generally, the asbestos diaphragms used in commercial electrochemical processes show some decline in mechanical strength when employed over extended periods of continuous operation. It has been proposed to strengthen the asbestos matrix. While these binders have provided improved results in increasing the mechanical strength of the diaphragm, the selection of binder has been limited to those types which have a natural affinity for the asbestos fiber or which can be made compatible with the fibers by the addition of surfactants so that they will adhere to the asbestos fibers when the binder particles are mixed as a dispersion or emulsion with the asbestos in the form of a slurry. Most of these additives, however, do not contribute to the strength or chemical resistance of the diaphragm and in some cases may even reduce, to some extent, the chemical resistance of certain asbestos materials such as chrysotile.

Certain electrochemical reactions provide for the separation of intermediate products produced in the course of the reaction. In these cases, it is desirable to employ a liquid impermeable diaphragm which permits only the passage of current therethrough. Although previous diaphragms have been rendered substantially liquid impermeable, the required thickness (about 300 mils) of such a separator causes it to be inconveniently employed in electrolytic cells of commercial design.

It is, therefore, an object of this invention to provide an improvement in the manufacture of chemicals in systems comprising an electrolytic cell in which the anode and cathode compartments are separated by a diaphragm, including power consuming as well as power producing cells.

Another object is to provide a particular diaphragm composition for use in such systems which has improved chemical and physical resistance under conditions of operation.

Another object is to provide a diaphragm having a composition selected from a wide variety of components which enhance the properties of the diaphragm without the incorporation of non-beneficial secondary additives.

Another object is to provide a liquid impermeable diaphragm of greatly reduced thickness.

Still another object of this invention is to provide a diaphragm composition which is suitably laminated on a porous plastic or metal substrate.

Another object of this invention is to provide an asbestos diaphragm composition of superior wet tensile strength.

A further object of this invention is to provide an asbestos diaphragm having a uniform composition and a controlled permeability.

A further object is to provide an improvement in the electrolytic manufacture of halogen in a diaphragm-compartmented electrolytic cell.

A still further object is to provide an improvement in the manufacture of oxygenated derivatives of C₂ to C₄ olefinic compounds in an electrochemical system comprising a diaphragm-compartmented electrolytic cell.

Various other objects and advantages of this invention will become apparent to those skilled in the art from the accompanying description and disclosure.

According to this invention, an improvement is provided in an electrolytic cell in which it is desired to separate portions of the electrolyte while allowing at least the flow of electrical current between the opposing electrodes, which improvement comprises operating the cell with an impregnated asbestos diaphragm positioned where such separation is desired.

The asbestos comprising the matrix of the present diaphragm can be of the serpentine type such as, for example, chrysotile, which is a magnesia silicate having a magnesia content of from about 39 to about 44 percent, or the matrix can be composed of asbestos of the amphibole type, such as crocidolite, amosite, anthophyllite, tremolite and actinolite or blends of these types of asbestos materials. Such matrices can be prepared on a Hand-sheet paper-making machine and provide a paper matrix of substantially pure asbestos fibers. The asbestos matrix can also be composed of any of the above asbestos types or blends of these types wherein other additives, such as binders or binder compositions, are incorporated. Suitable binders and binder compositions are those which are disclosed in copending Application Ser. No. 814,821, filed April 9, 1969, and which are herein incorporated by reference. Of these binders, high polymers and copolymers of butadiene, vinyl chloride, ethylene, propylene and tetrafluoroethylene are preferred. The matrices composed of asbestos and binder are referred to as asbestos matrix compositions and are generally prepared by mixing and paper manufacture in a Fourdrinier paper-making machine. The preferred asbestos matrices are those of the amphibole type having a magnesia content of from 0 to about 20 weight percent, most preferably a magnesia content of from 0 to about 8 percent by weight of magnesia such as the types known as crocidolite and amosite. Because of the high magnesia content above about 20 percent of certain other asbestos, it is desirable that they are employed as a blend with low magnesia amphibole types.

The accepted formula for crocidolite, which is a sodium iron silicate, is $\text{Na}_2\text{O} \cdot 3\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot 8\text{SiO}_2 \cdot \text{H}_2\text{O}$, although some grades may additionally contain small amounts of magnesia, for example, up to about 3 weight percent. Actinolite is a calcium magnesia iron silicate having an empirical formula $\text{Ca}_2(\text{MgFe})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$, which has a magnesia content, for example, up to about 18 percent. Amosite is a low-magnesia iron silicate (for example, from about 1 to above 7 weight percent magnesia) the formula for which is expressed as $\text{Fe}_3\text{Mg}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$. Crocidolite asbestos is commonly referred to as "blue asbestos," although it is to be understood that often other amphiboles having magnesia content less than 8 percent are also referred to as "blue asbestos." Any of the above asbestos types, blends of asbestos types, which may or may not contain binders and other additives such as plasticizers, surfactants, etc., are suitably employed as the dried paper or matrix composition which is subjected to the impregnation of the present invention. It is to be understood, however, that the matrix composition employed in the present process may be dried only to the extent that they provide a formed sheet and not subjected to temperatures which would render them anhydrous. Thus, the matrices employed in the impregnation operation actually can be in a wet or dry form.

Suitable impregnants employed as solutions for incorporation into the matrices of the present invention are any of those materials disclosed as binders in my copending application Ser. No. 814, 821, filed April 9, 1969, as well as other polymeric compounds, such as cotton, nylon, orlon fibers, which do not possess affinity for the asbestos fibers and which are substantially insoluble in aqueous media. Since the purpose of the impregnant is to fill the pores or spaces between the asbestos fiber of the matrix, it need not adhere or be compatible with the asbestos fibers. Thus, the selection of desired compositions for the diaphragm can be extended to compounds which have not previously been employed with asbestos but which provide beneficial properties in the diaphragm compositions of the present invention.

The impregnation of the matrix also provides for more uniform distribution of polymeric particles in the matrix and allows for controlling the permeability of the diaphragm to low levels, if desired, by directly controlling the

concentration of the impregnant in the liquid medium applied to the asbestos matrix. Thus, a diaphragm of much higher density per diaphragm thickness can be produced than any previously obtainable. For example, a liquid impermeable diaphragm can be produced which has a thickness not greater than 150 mils. In general, the diaphragms of the present invention can be made to provide a controlled and reproducible permeability best suited for the requirements of a particular electrochemical reaction.

Another improvement in the diaphragms of the present invention is evidenced by the greatly improved wet tensile strength of the diaphragm structure which allows operation of the electrochemical process in a continuous manner for periods of more than one year without interruption.

Specifically, the impregnants of the present invention comprise high polymers of the rubber type, such as polychloroprene (neoprene), polyisobutylene, polybutadiene, polydimethylbutadiene, polymethylbutadiene (isoprene), polyvinyl chloride and butadiene polymers and copolymers with styrene and acrylonitrile and organic polysulfide types such as the ethylene chloride-sodium tetrasulfide and dichloroethyl ether-sodium tetrasulfide copolymers, and thermoplastic and thermosetting polymers and copolymers, such as polyethylene, polypropylene, polybutylene, polystyrene, polystyrol, polytetrafluoroethylene, polychlorotrifluoroethylene, polyvinylidene chloride, polyacrylonitrile, polyester, chlorinated polyvinyl chloride, polyurethane, polyvinylpropionate, polyvinylacetate and acrylic, cellulose acetate and methacrylate polymers and copolymers such as butadiene-styrol, and any of the known copolymers which combine monomers of the above mentioned polymers.

The compositions used as impregnants can be employed in mixture and may contain resinous thickening agents such as methyl cellulose known as Methocel and a hydrophilic colloid such as Carbopol which provide thixotropic properties and increased resistance to separation of impregnant from the matrix.

Preferred impregnants of the above group of polymeric materials are the polymers and copolymers of butadiene, vinyl chloride, chloroprene, isoprene, polyethylene, polybutylene, polypropylene, polychlorotrifluoroethylene, and polytetrafluoroethylene.

Polytetrafluoroethylene, known as Teflon, is commercially supplied in a hydrophobic colloidal dispersion of negatively charged particles (0.05 to 0.5 micron) suspended in water. These colloidal dispersions are ideally adapted for incorporating impregnant into an asbestos sheet in the manufacture of the diaphragm. The aqueous dispersions are provided in various concentrations containing from about 30 percent to about 65 percent Teflon solids.

Polyethylene aqueous dispersions are also supplied commercially under the trade name Microthene dispersions. The size of the polymer particles in the dispersion range from 8 to 30 microns and dispersions of from 10 percent to 70 percent solids are available. Aqueous organic dispersions of up to 55 percent solids are marked for polyethylene.

Because impregnation is employed in incorporating polymeric materials into a preformed asbestos matrix, the additive is not limited to aqueous mixtures which in other techniques of incorporation must be mixed with an aqueous slurry of asbestos fibers. In the present invention where the asbestos sheet is already formed, the impregnants are incorporated by the use of solutions, emulsions or dispersions of impregnant either in organic liquids or in water, depending upon the impregnant selected.

Non-aqueous or aqueous solutions of the following liquids can be employed as carriers for the impregnant which is contained in the liquid in a concentration of between about 50 and about 98 weight percent. Suitable

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liquids include hydronaphthalenes, such as Decalin and Tetralin, toluene, ethyl acetate, mineral spirits, ethanol, methylisobutyl ketone, tetrachloroethylene, trichloroethylene, amyl acetate, xylene, dichloroethane, methyl ethyl ketone, methylene chloride, dichloropropane, ethylene- and propylene-chlorohydrins, ether and esters. Observance of the solubility of impregnants in certain organic liquids should be keyed to the type of electrochemical process in which the diaphragm is to be employed. Thus, an impregnant which is soluble in chlorohydrin, dichloropropane, dichloroethane, dichloroether, or alcohols, should obviously not be employed in organic processes such as the propylene oxide process where chlorohydrin or a product similar to the solvent is produced as an intermediate or final product of the reaction. However, impregnants which are soluble in these solvents are suitably employed in the electrolytic process for the preparation of halogen which employ cells containing a solid anode and cathode as well as cells containing a mercury amalgam cathode. Of the above list of suitable solvents or dispersants, water, Tetralin, Decalin, dichloroethane and methyl isobutyl ketone are preferred.

The general impregnation procedure comprises impregnating an asbestos matrix with a degradation resistant material to strengthen the asbestos matrix in the resulting diaphragm material. Impregnation with the above-mentioned impregnants affords control of diaphragm characteristics such as permeability, strength, thickness and voltage drop through the resulting diaphragm.

The procedure of incorporation applies to an asbestos matrix which may be in the form of a sheet or mat made from pure or admixed fibers which may or may not contain a binder, a surfactant, a precipitating agent or other solid additive. Between about 0.1 and about 50 weight percent preferably between about 2 and about 20 weight percent of impregnant is incorporated into the asbestos matrix. The procedure comprises treating a formed asbestos matrix in a dry or damp state by spraying with an impregnant containing solution or by immersion in a tank containing a dispersion, emulsion or solution of the impregnant. In the latter procedure, the preformed asbestos matrix is passed through the tank of liquid containing impregnant while permitting a residence time in the tank of from about 0.1 to about 60 minutes for impregnation to be effected. The immersion liquid is maintained at a temperature of from about 20° C. to about 250° C. and agitation of either the matrix and/or the immersion liquid may be provided, if desired. After immersion for a suitable period, the impregnated matrix is withdrawn from the tank and allowed to drain so as to remove a major portion of the mother liquor. Pressing the impregnated matrix to assist in the removal of mother liquor can be accomplished by passing the impregnated sheet between a pair of pressure (1 to 50 p.s.i.g.) rollers or pressing plates which are preferably adapted to return the liquid to the immersion tank. Alternatively, the impregnated sheet can be treated for removal of liquid by suction or can be pitched at an angle to remove liquid. The entire procedure of immersion and drainage can be repeated or the asbestos mat can be subjected to a succession of immersions in the tank prior to pressure drainage when it is desired to incorporate additional amounts of impregnant in the asbestos matrix.

The drained impregnated matrix or sprayed matrix is subsequently subjected to drying, preferably by the use of heated rollers, heated plates, or a heated chamber maintained at a temperature between about 25° C. and about 120° C. depending upon the flash point of the solvent employed. After drying in the drying zone, the impregnated diaphragm may be heat treated at a higher temperature to the sintering temperature of the impregnant, for example, from about 40° C. to about 400° C. so as to cause adhesion of impregnant particles in the pores and/or on the surface of the asbestos matrix of the

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diaphragm. The heat setting operation can be controlled to sinter either impregnant particles dispersed throughout the matrices or to affect sintering of particles on only one or both surfaces of the matrix.

It is to be understood that additional steps or stages can be interposed or added to the sequence of steps recited above. For example, calender rollers can replace the drain rollers in the above procedure and a pressure from 50 to 1500 p.s.i.g. preferably between about 50 to 1000 p.s.i.g., can be applied to the wet impregnated asbestos sheet. Usually, the higher pressures are applied when a high density diaphragm is desired and when it is desirable to reimmerge the impregnated sheet in the same or a different impregnating liquid.

A lamination of the impregnated diaphragm can be combined with the above impregnation technique. For example, the dried asbestos paper sheet or mat can be passed into a hot solution of impregnant such as, for example, polyethylene in a hot Decalin solution and impregnated to a desired level before removing and draining the impregnated mat. The impregnated mat can then be pressed to a desired uniform thickness, for example, from 10 to 50 mils, and partially dried before passing the mat to a second immersion tank or it can be directly introduced therein. The second immersion tank contains a solvent for the impregnant distributed in matrix during the first immersion and this solvent is maintained at a temperature sufficient to cause softening of the impregnant particles either on the surface of the mat or throughout the mat structure. The solvent treated mat is subsequently passed through a second pair of calender rollers adapted to drain solvent back into the second immersion tank and finally transferred to a drying and compression zone wherein it is applied to a substrate, for example, a porous plastic material or wire screen, and pressured under a pressure of from about 10 p.s.i.g. to about 1000 p.s.i.g., at a temperature from about 40° C. to about 250° C. The substrate which is a foraminous material, may be composed of glass, metal or a woven or knitted material.

A convenient method of applying the impregnated asbestos to the substrate comprises simultaneously feeding a sheet of impregnated diaphragm material and the substrate over at least one pair of calender rollers, thereby heating under sintering conditions while compressing to form a strong adhesive layer. It is to be understood in the above embodiment that the second immersion tank containing only solvent can be omitted when the temperature of the first immersion tank and the concentration of impregnant solution in the first immersion tank is controlled to maintain softening of at least the impregnant particles distributed on the surface of the asbestos matrix.

Another embodiment for forming a laminate comprises coating the surface of the substrate with particles of the impregnant at sintering temperature or applying sufficiently hot solvent for the impregnant to the surface of the substrate so as to soften the surface and pressing the impregnated asbestos mat to the surface of the substrate under sintering conditions. In this way threads, fibers or particles may be imbedded in the interface between the impregnated asbestos and the substrate. The amount of plastic incorporated into the asbestos matrix may vary from complete impregnation or saturation to the minimum required to bond the reinforcing material. Generally, high impregnation results in increased density of the diaphragm.

Other methods of lamination will become apparent to those skilled in the art from the accompanying description and disclosure. For example, it will be apparent that the substrate can be applied to one or both surfaces of the impregnated asbestos matrix or the impregnated asbestos diaphragm can be applied to one or both surfaces of the substrate.

Also, other methods of forming the diaphragm may be employed, such as placing the asbestos mat directly on a

stainless steel wire mesh cathode and spraying or dipping the cathode assembly so that the asbestos matrix becomes impregnated and finally drying the impregnated diaphragm disposed on the cathode which is then employed in the operation of the electrolytic cell.

The density of the diaphragm of the present invention varies over a wide range depending upon the degree of permeability desired. Thus, the density can be varied from about 0.3 gram to about 1 gram per cc., preferably from about 0.4 to about 0.7 gram per cc. If the diaphragm is to be liquid permeable, it is preferred that the density or thickness of the diaphragm be such as to permit an electrolyte flow rate through the diaphragm of from about 10 to about 2000 cc. per minute per square foot of diaphragm. When chlorine is the intended end product of the electrochemical cell, the flow rate of electrolyte through the diaphragm is from about 20 to about 300 cc. per minute per square foot of diaphragm, preferably from about 10 to about 50 cc. per minute per square foot of diaphragm. However, when an olefin oxide is the intended end product, the flow rate is from about 100 to about 2000 cc. per minute per square foot of diaphragm, preferably from about 200 to about 1000 cc. per minute per square foot of diaphragm. Substantially liquid impermeable diaphragms have a permeability as low as 0.05 cc. per minute per square foot of diaphragm.

The impregnated asbestos matrices of the present invention display greatly improved mechanical strength when employed under conditions of continuous operation in an electrolyte cell containing an aqueous electrolyte solution. The mechanical strength of the diaphragms of the present invention are measured by the wet tensile strength (dead weight) method. Generally at least 50% improvement over non-impregnated diaphragms is realized.

The wet tensile strength of the diaphragm measured in the examples is expressed as the number of grams weight necessary to cause rupture of the diaphragm material at the isthmus. Each sample tested has a width of 6 cm. at its widest point and a length of 14 cm. Midway between the ends, the sample has a narrow isthmus 1 cm. wide which extends $\frac{1}{3}$ of the length of the sample. The samples are cut to a uniform size by means of a stencil and are soaked in water at room temperature for 3 hours before testing. The test comprises clamping the sample at one end to a support and clamping the other end to a scale to which weights are added until the sample ruptures at the isthmus.

The preferred electrolyte which is charged to the electrolytic cell is an aqueous solution of a metal halide, chlorides and bromides being most preferred. Usually employed are the halides of sodium, potassium, lithium, barium, calcium, strontium, magnesium or mixtures thereof.

A mixed electrolyte system can be employed for improving the conductivity inasmuch as the metal hydroxide which forms at the cathode is utilized within the system and since economics of the process does not depend upon recovery of hydroxide as a product of the process, mixed electrolytes are useful and, from the standpoint of improvement of conductivity, are advantageously employed. Salts which can be added to increase the electrical conductivity of the electrolyte include soluble alkali metal, and alkaline earth metal sulfates, sulfides, chromates, phosphates and carbonates, such as sodium sulfate, potassium sulfate, lithium sulfate, calcium sulfate, sodium sulfide, potassium sulfide, lithium sulfide, sodium nitrate, calcium nitrate, potassium nitrate, lithium nitrate, sodium chromate, potassium chromate, potassium dichromate, calcium chromate, sodium orthophosphate, sodium pyrophosphate, potassium carbonate, sodium carbonate, lithium carbonate, etc. The promoters of conductivity can be used in amounts from about 1 to about 25 weight percent or more of the electrolyte solution. In the preferred aqueous electrolyte solutions, the metal halide content can vary

from dilute to saturated solutions which are usually charged to and withdrawn from the cell at a rate of from about 10 to about 1000 cubic centimeters per minute per square foot of apparent electrode surface where the area of electrode is equal to the area of the diaphragm. Most preferably the electrolyte is present in aqueous solution in a concentration of between about 2 and about 35 weight percent. In some cases the electrolyte solution contains solid particles which adhere to the diaphragm as it is passed therethrough. When such solid particles become troublesome, the flow of electrolyte in the cell and through the diaphragm can be reversed in order to dislodge the solid impurities which may be deposited on one side thereof.

The diaphragm of the present invention may be disposed in a horizontal or vertical position within the cell between the anode and the cathode thereby dividing the cell into an anode chamber and a cathode chamber. The diaphragm can be mounted against the cathode or against a barrier disposed in the cell in spaced relationship between the anode and the cathode or it can be unsupported, or substantially unsupported except for a frame which is positioned in the cell by retaining means. In the latter case mechanical support can be supplied by transverse the frame holding the diaphragm with one or a plurality of threads, e.g., plastic filaments on one or both sides of the diaphragm surface. This type of mechanical support is beneficial in reinforcing diaphragms which are retained in frames or clamping means within the cell but which are not supported on one of their surfaces by a barrier or cathode screen.

The permeability of the diaphragms of the present invention can vary over a wide range so that between about 0.1 and about 2000 cc. of liquid can be passed per minute per square foot of diaphragm surface. The thickness of the diaphragm generally varies from about 10 to about 150 mils, preferably from about 20 to about 50 mils. In certain processes in which it is desirable to separate and recover an intermediate product of a reaction, a liquid impermeable diaphragm may be desired, such as the diaphragm of 250 mils thickness.

In a preferred aspect of this invention, a method is provided which comprises subjecting an aqueous medium contained in a diaphragm-compartmented electrolytic cell and having a halide electrolyte dissolved therein to the action of a direct electric current to generate halogen at the anode and hydroxyl ion at the cathode in the cathode compartment, introducing an olefinic compound into the anolyte and reacting this olefinic compound with halogen produced in the aqueous anolyte thereby forming the halohydrin derivative of the olefin, passing halohydrin containing electrolyte through the diaphragm, dehydrohalogenating the halohydrin to olefin oxide in an alkaline catholyte produced at the cathode of the cell, separating olefin oxide from the aqueous medium, and recycling aqueous electrolyte to the anode compartment of the electrolytic cell.

The halohydrin forming reaction may be effected by contacting the olefin with anolyte within the cell or in a contacting tower external of the cell proper or partially in both. The halohydrin containing aqueous medium is then subjected to dehydrohalogenation in order to convert the halohydrin to olefin oxide by treatment with the catholyte which is alkaline due to the cathodic reaction which results in the formation of hydroxyl ion. The dehydrohalogenation may be effected in the alkaline catholyte contained within the cell or in a step external of the cell or partially in both. These various methods are described in further detail in U.S. Pat. No. 3,288,692 and Belgian Pats. No. 705,083 and No. 705,084, the details of which are incorporated by reference herein.

The present process can be applied to any electrochemical process wherein an unsaturated organic compound is oxidized. Illustrative of processes in this category other than the preferred process described above, are

the electrochemical processes for producing a glycol from an olefin or an olefin from acetylene in addition to olefin oxide from olefin as described and referred to in U.S. Pat. No. 1,253,617.

The anode of the cell comprises a solid or a porous material or a substrate having distributed thereon electrolyte-porous and electrolyte-impervious surfaces and can also contain a hollow core or an internal chamber for the introduction of the organic reactant into the electrolyte solution. The anode may be composed of graphite, platinum, platinized titanium, platinized tantalum, titanium coated with a mixture of platinum and at least one other noble metal such as iridium or rhodium, platinized iridium, magnetite, titanium, lead, or an inert substrate such as polyethylene, polypropylene, polyurethane, Teflon, or a perfluorochloro plastic, etc. metallized with copper or silver and having platinum deposited thereon as the metal which is exposed to the electrolyte medium. Electrodes of the latter type are prepared in accordance with the techniques described in U.S. Pat. No. 3,235,473. The preferred anodes of the present invention, however, comprise a metal substrate, most preferably titanium, coated with a noble metal or alloy of a noble metal in the form of elemental metal or metal oxide as described and referred to in U.S. Pat. No. 3,379,627.

The cathode may be composed of any conductive material which is chemically inert to caustic and is usually composed of steel, stainless steel or an amalgam such as the amalgam cells described or referred to in U.S. Pats. No. 3,394,059 and No. 3,288,692. The cathode is more often in the form of a ferrous metal screen or expanded sheet and may be used in contact with or separated from the diaphragm.

The organic reactant of the present invention is an olefinic compound, that is, a compound having at least one ethylenically unsaturated carbon-to-carbon double bond which is the reactive site at which the oxygen linkage is formed during the process. Included within the scope of the invention is the use of the unsubstituted and aryl and/or halogen substituted acyclic and alicyclic monoolefins and polyolefins including straight and branched chain olefins, as well as those in which the ethylenic double bond is in the terminal or non-terminal position or within a cycloaliphatic ring. The olefin may be normally gaseous or liquid. Olefins may be diluted with any suitable inert solvent such as a paraffinic or aromatic hydrocarbon or mixtures thereof including petroleum fractions such as kerosene, etc. Other liquid diluents include cyclohexane, toluene, benzene, xylene, hexane, heptane, iso-octane and those mentioned in U.S. Pat. No. 3,394,059.

Typical examples of suitable olefins for use in the preferred process of this invention are the alkenes of the homologous series C_nH_{2n} wherein n is an integer from 2 to 12, such as ethylene, propylene, butene, pentene, hexene, heptene, . . . dodecene, etc., including olefins in which the double bond is in a non-terminal position, such as 2-butene, 2-pentene, etc., and branched olefins such as isobutene, isopentene, 4-ethyl-2-hexene, as well as branched compounds in which the double bond is in the side chain, such as 2-methylene pentane and alkenyl compounds, such as 4-propene-4'-yl-octane and cyclic olefins, such as cyclopentene, cyclohexene, cyclooctene, cyclononene, etc. Polyolefins may also be reacted in the electrochemical reaction of the present invention. Suitable polyolefins include those containing isolated, cumulative or conjugated double bonds, such as diallyl, allene, butadiene, isoprene, 2,3-dimethylbutadiene, etc. As pointed out above, olefins substituted with aryl and halogen groups, such as, for example, styrene, stilbene, allyl chloride, chloropropene, vinyl chloride, vinyl bromide, etc. may also be used as the olefin reactant in the present process.

The olefin need not be pure and may contain paraffinic or other impurities or diluents normally found in commercially available olefins. For example, commercial

grades of ethylene and propylene are suitable and normally contain low molecular weight paraffins, such as ethane, propane, etc. When a low molecular weight olefin is reacted, a gaseous diluent, such as nitrogen, methane, ethane, propane, etc. may be admixed with the olefin and may be used in amounts between 5 and about 95 volume percent of the total feed.

The throughput of olefin through the anode compartment or a reaction space outside of the electrochemical system may be selected in such way, for example, that approximately 5 to 95 percent is converted per single pass. It has been shown to be an especially favorable technique to introduce into the anode compartment or conversion chamber a gaseous mixture of the olefin to be converted and an inert gas, the concentration of olefin in the mixture amounting, for example, to 25 to 65 volume percent, preferably 35 to 55 volume percent and to convert per single pass of the gaseous mixture through the anode compartment or conversion chamber, 75 to 95 percent, preferably 30 to 90 percent of the introduced olefin. As inert gas, the gaseous paraffins corresponding to the olefin used are especially suitable.

In the diaphragm-compartmented electrolytic cell wherein olefin is reacted to form halohydrin and the halohydrin is dehydrohalogenated to form olefin, a gaseous effluent is withdrawn from the anode section of the cell which contains unreacted olefin and dihaloparaffinic derivative as a by-product of the process and a gaseous effluent containing a portion of the olefin oxide product and hydrogen is recovered from the cathode section of the cell. After the olefin oxide is formed in the catholyte, the resulting electrolyte solution is passed into a separation or stripping zone wherein dissolved oxide product is separated from the electrolyte by distillation and/or by means of a stripping gas, such as nitrogen, steam, methane, ethane, etc. or any other gas which is inert to the oxidation product. The olefin oxide can then be subjected to further purification, if required, and recovered as a product of the process.

The resulting electrolyte solution separated from the oxide product, usually contain contaminants which form a tarry or tacky coating on the anode of the electrolytic cell. Therefore the separated electrolyte is generally subjected to decontamination, e.g., by treatment with an oxidant treatment followed by filtration prior to recycle as described in copending applications Ser. No. 809,961 Ser. No. 809,962 both filed on Mar. 24, 1969. The pH of the recycle electrolyte is adjusted with acid, e.g., a hydrogen halide to maintain a desired pH range in the electrolytic cell, usually, between about pH 6 and about pH of 12.

The electrolytic reaction zone may be operated over a wide range of current density such as between 20 and about 1500 amperes per square foot of apparent electrode surface. The operating voltage of the cell is at least the voltage required to obtain electrolysis of the metal halide. The minimum voltage, therefore, depends upon the particular electrolytic system. For example, when sodium chloride is used as the source of halogen for the halohydrin intermediate, a voltage of at least 2.2 volts is required, assuming unit activities and standard conditions. Usually the voltage applied is within the range of between about 3 and about 7 volts. In operation, however, the voltage demand is increased above the minimum or decomposition voltage due to a combination of a variety of factors such as, for example activity and overvoltage. It has been found that the olefin reactant introduced to the vicinity of the anode reduces the electrode overvoltage depending upon the particular anode material. In this connection, porous, hollow anodes instead of solid electrodes can be used to introduce the olefin to the anode in a way such that the olefin reactant diffuses through the pores were contact between the olefin, electrolyte and electrode occurs thereby producing product, reducing overvoltage and polarization. Theoretically, during operation, the cur-

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rent density can be varied within a desired range or the current may be reversed to minimize polarization.

The electrolytic cell can be operated over a relatively wide range of temperatures and pressures, i.e. from about -5°C . to the boiling point of the aqueous electrolyte which, at atmospheric pressure, is usually about 105°C . A pressure within the range of subatmospheric, for example about 0 p.s.i.g., to 300 p.s.i.g. or more can be employed. The temperature and pressure are interrelated to the extent that they are controlled to maintain the aqueous electrolyte system in the liquid phase. Thus, when the cell is operated at a temperature above the atmospheric boiling point of the aqueous electrolyte system, the cell is operated at a pressure sufficiently high to maintain the liquid phase.

Having discussed many aspects, reference is now had to the accompanying examples which further illustrate the invention. It is to be understood, however, that these examples are presented for a better understanding and are not to be construed as unnecessarily limiting to the scope of this invention as set forth and described in the foregoing disclosure and the claims.

EXAMPLE 1

A blue asbestos sheet composed of crocidolite fibers is made from an aqueous slurry containing 80 grams of the fibers in a Hand-sheet machine. The sheet is compressed under 100 p.s.i.g. between two stainless steel plates to a thickness of 68 mils and dried. The dried asbestos sheet has a wet tensile strength of 150 grams. A solution of 75 grams per liter of polyethylene dissolved in decahydronaphthalene is made by stirring low density (density of 0.90 to 0.92) polyethylene into a Decalin solution (decahydronaphthalene) heated to a temperature of between 100°C . and 113°C . The solution is then introduced into an immersion tank and is heated therein to a temperature of 115°C .

The blue asbestos sheet of 68 mils thickness is placed between two 10 x 10 mesh stainless steel screens. This assembly of the asbestos sheet between screens is preheated by holding it over the hot liquid in the immersion bath for 1 minute. After preheating, the assembly is immersed in the impregnation solution in the immersion tank and agitated every 20 seconds for a period of about 2 minutes. The resulting impregnated asbestos paper is then withdrawn from the impregnating solution and tilted on the stainless steel screen (at an angle of about 45°) for about 15 seconds to allow for drainage of mother liquor into the immersion tank. The drained impregnated asbestos is then air dried for 2 minutes between the screens after which the upper screen is removed and the impregnated asbestos sheet is turned over onto a polished stainless steel plate located in a separate drying zone whereon it is vacuum dried at 75°C . for 24 hours.

The impregnated diaphragm is removed from the drying zone and measured for wet tensile strength. The impregnated blue asbestos shows a wet tensile strength of 4196 grams.

EXAMPLES 2 THROUGH 11

An aqueous solution of Teflon is made from an emulsion of a negatively charged hydrophobic colloid containing Teflon resin particles of from 0.05 to 0.5 micron. The Teflon emulsion contains 59% by weight solids and is stabilized with 6% of a nonionic wetting agent such as an alkyl aryl polyether alcohol, sulfonate or sulfate (in this case, Triton X-100). The solution is diluted with water to a concentration of from 6 to 12 weight percent Teflon and introduced into an immersion tank.

A blue asbestos paper having a thickness of 0.040 inch containing 4% copolymer of butadiene and styrene (buna-S) as a binder is placed between 2 screens and is immersed in the impregnating solution for 1 minute. After thorough wetting of the paper with the solution, the paper and the screen assembly are removed from the tank, pitched at

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an angle (45°) to allow drain-off of the solution into the tank for 2 minutes and transferred to a stainless steel plate mounted in an oven where the impregnated blue asbestos-binder paper is dried at a temperature of 110°C . for a period of 24 hours.

The permeability of non-impregnated samples and samples impregnated by the above method are measured and the results reported in Table I.

TABLE I

Example	Impregnant solution (wt. percent Teflon)	Wt. percent increase of sample	Permeability ¹ of sample
2.....			6.20
3.....			5.98
4.....			6.03
5.....			5.31
6.....	6.0	5.54	7.90
7.....	7.5	7.67	9.00
8.....	6.0	10.4	² 12.00
9.....	12.0	11.7	13.7
10.....	7.5	13.3	² 25.4
11.....	12.0	14.2	47.7

¹ Expressed as head of water pressure in inches at a fixed flow rate of 300 cc./minute/square foot of diaphragm.

² Double immersion of sample at 1 minute per immersion.

Three samples corresponding to the sample of Example 9 are prepared and their wet strength measured. The wet tensile strength of the three samples were 1980 grams, 2016 grams and 2365 grams.

The blue asbestos paper of 0.040 inch thickness and containing 4% buna-S as a binder material (i.e., the asbestos paper from which the impregnated samples are made) is cut into three samples of the size and shape required by the wet tensile strength test and soaked in water at room temperature for 3 hours before testing. The wet tensile strength of these non-impregnated samples is measured and found to be 1270 grams, 1420 grams and 1458 grams.

The above tests illustrate the improvement of mechanical strength effected by impregnation, in most cases, more than 50% improvement is noted.

EXAMPLES 12 THROUGH 16

A solution of high melting polyethylene powder (density of 0.90 to 0.92) comprising spherical shaped particles of 30 micron minimum size in decahydronaphthalene is prepared. After 30 minutes at 110°C . the dissolution is complete and solution is transferred to an immersion tank. A dry crocidolite paper containing 4 weight percent buna-S rubber binder and having a thickness of 0.020 inch is placed between two stainless steel screens and the assembly is immersed for about 1 to 3 minutes in the impregnating solution in the immersion tank maintained at 120°C .

After immersion the impregnated paper-screen assembly is withdrawn from the liquid and tilted at a 45° angle over the tank to allow for drainage of mother liquor from the impregnated matrix over a period of about 2 minutes. The drained matrix is then transferred from the screen assembly to a vacuum oven where the impregnated matrix is dried at 80°C . for 12 hours on a polished stainless steel plate.

This procedure of impregnating the blue asbestos paper described above is repeated 4 times except that different concentrations of the impregnant in the impregnation liquid are employed. The permeability of a non-impregnated blue asbestos paper of the type used in this example is compared with the samples impregnated at various concentrations of impregnant by the above method and the results of this comparison are reported in Table II.

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TABLE II

Example	Period of immersion (min.)	Impregnant solution (g./liter)	Wt. percent increase of sample	Permeability ¹ of diaphragm
12	2	15	1.6	5.8
13	2	15	2.9	7.6
14	2	25	5.7	7.8
15	2	40	6.7	8.1
16	2	40	6.7	8.7

¹ Expressed as head of water pressure in inches at a fixed flow rate of 300 cc./minute/square foot of diaphragm.

EXAMPLES 17 TO 22

The same impregnation treatment described above for Examples 13 through 16 is repeated except that a pure crocidolite paper without binder or other additive is employed as the asbestos matrix. The matrix is prepared from a 1% slurry of 35 grams per liter of crocidolite asbestos fibers in a 5% potassium chloride brine solution at 125° F. and a mixing time of 30 minutes. The slurry is transferred to a Hand-sheet paper making machine where the diaphragm matrix is formed. The water leg of the machine is previously filled to the mold level with a brine solution (50 grams of potassium chloride per liter) and the release valve is opened so as to empty the hopper over a period of 2 minutes.

About 120 seconds drain time is allowed for the asbestos matrix on the mold after which the asbestos sheet is removed from the mold, placed between two polyethylene sheets and pressed in a 40 ton hydraulic laboratory press at 1000 pounds per square foot. The asbestos sheet is then dried in an air oven at 110° C. for 20 hours and 5 samples of this preformed asbestos sheet are subjected to the impregnation treatment described in Examples 13 through 16. The permeability of the samples is reported in Table III. Example 17 is reported for a sample of this paper which is not impregnated.

TABLE III

Example	Impregnant solution (grams/liter)	Wt. percent increase of sample	Permeability ¹
17			0.91
18	10	1.0	1.2
19	25	4.3	2.8
20	20	6.7	10.8
21	25	8.0	30.0
22	25	11.0	300.0

¹ Expressed as head of water pressure in inches at a fixed flow rate of 300 cc./minute/square foot of diaphragm.

EXAMPLES 23 THROUGH 26

The same impregnation treatment described for Examples 13 through 16 is repeated except that the asbestos matrix contains 3 weight to butyl rubber (copolymer of butylene and butadiene) as a binder instead of 4 weight percent buna-S rubber binder. The permeability of 4 samples of this matrix (one unimpregnated and 3 impregnated) is reported in Table IV.

TABLE IV

Example	Impregnant solution (grams/liter)	Wt. percent increase of sample	Permeability ¹
23			5.5
24	10	1.3	6.7
25	20	2.1	22.3
26	40	6.0	23.7

¹ Expressed as head of water pressure in inches at a fixed flow rate of 300 cc./minute/square foot of diaphragm.

EXAMPLES 27 THROUGH 29

The same impregnation treatment described above for Examples 13 through 16 is repeated except that the asbestos matrix is 0.040 inch thick and the impregnant is high density polyethylene (density of from 0.94 to 0.96) dissolved in Tetralin. The permeability of 3 samples of this matrix (one unimpregnated) is reported in Table V.

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TABLE V

Example	Impregnant solution (grams/liter)	Wt. percent increase of sample	Permeability ¹
27			5.7
28	20	2.9	17.6
29	50	6.3	32.5

¹ Expressed as head of water pressure in inches at a fixed flow rate of 300 cc./minute/square foot of diaphragm.

EXAMPLE 30

The following crocidolite paper diaphragms were measured for wet tensile strength and results reported in Table VI.

TABLE VI

Paper of Example No.—	Thickness of sample (inch)	Permeability ¹	Binder, percent rubber	Impregnant C ₂ H ₄ polymer (g./liter)	Wet tensile strength (g.)
17	0.02	0.91			250
3	0.02	5.98	4 buna-S		1,270
23	0.02	5.50	3 butyl		965
27	0.04	5.70	4 buna-S		765
16	0.02	8.70	do.	40	2,054
25	0.02	22.3	3 butyl	20	1,773
28	0.04	17.6	4 buna-S	20	2,534

¹ Expressed as head of water in inches at a flow rate of 300 cc. per minute per square foot of diaphragm.

EXAMPLE 31

Eight parts of polyurethane resin (density 1.07, viscosity 200 poise) is dissolved in 100 parts of methyl ethyl ketone (80% aqueous solution). About 3 liters of the solution is introduced into an immersion tank wherein it is maintained at 90° C. A dry sheet of amosite containing 6% buna-S rubber binder having a thickness of 0.030 inch is immersed in the impregnation solution for 2 minutes and then removed and allowed to drain for 1.5 minutes. The impregnated sample is dried at 60° C. for 20 hours in a vacuum oven (15 inch vacuum) after which it is subjected to heat setting at 135° C. and pressed between calender rollers to a thickness of 25 mils. The amount of polyurethane impregnant added to the asbestos matrix is 2.5% and the permeability measured is 7.0 (head of water at 300 cc./minute/square foot of diaphragm).

EXAMPLE 32

Five parts of polysulfide rubber (molecular weight of 4,000) is dissolved in 95 parts of ethyl acetate. About 5 liters of the resulting solution is introduced into an immersion tank where it is maintained at 85° C. A dry sheet of crocidolite paper containing 6% buna-S rubber as a binder and having a thickness of 0.025 inch is immersed in the impregnation solution for 1.8 minutes while agitating. After this period of impregnation, the sample is removed from the liquid, drained by passing it at a 45° angle between rollers and dried in a vacuum oven (16 inch vacuum) for 20 hours at 65° C. The amount of copolymer impregnant added to the asbestos matrix is 3.1 weight percent, and the permeability measured is 8.3 (head of water in inches at a flow rate of 300 cc. per minute per square foot of diaphragm).

A second solution of 20 parts of polypropylene dissolved in 80 parts of Tetralin is sprayed on the surfaces of the impregnated sample is air dried for 10 hours at a temperature of 110° C. The amount of polypropylene impregnant added is 1.5 weight percent and the permeability of the sample is 15.6 (head of water in inches at 300 cc. per minute per square foot of diaphragm).

EXAMPLE 33

Twenty parts of polyvinyl chloride resin having an average particle size of from about 1 to about 3 microns is added to 80 parts of isobutanol and dispersed therein. To this dispersion is added 0.2 weight percent of Methocel as a thickening agent and 0.4 weight percent of ammonium stearate as a surfactant. The mixture is emul-

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sified in a three-roll paint mill for 15 hours. The resulting emulsion is added to an equal portion of 5% sodium chloride solution in an immersion tank and the mixture is stirred for one hour at 55° C. Crocidolite paper containing 3% polypropylene and having a wet tensile strength of 835 grams is immersed in the tank for 2 minutes, then drained for 1 minute and dried at 120° C. for 12 hours. The resulting diaphragm contains 2.5 weight percent impregnant and other solids, the permeability is 9.5 (head of water in inches at a flow rate of 300 cc. per minute per square foot of diaphragm) and the wet tensile strength is 1735 grams.

EXAMPLE 34

Five parts of chloroprene and 5 parts of polyurethane are dissolved in 90 parts of methylene chloride at 70° C. The resulting solution is sprayed for 15 minutes under a pressure of 25 p.s.i.g. onto both surfaces of a crocidolite asbestos mat having a wet tensile strength of 350 grams. The impregnated mat is dried at 125° C. for 12 hours and the resulting diaphragm contains 6 weight percent chloroprene and polyurethane impregnant, the permeability of the sample is 17.0 (head of water in inches at 30 cc./minute/square foot of diaphragm) and the wet tensile strength is 2140 grams.

EXAMPLE 35

A liquid permeable diaphragm for use in an electrochemical system for the oxidation of propylene to propylene oxide is prepared by employing the impregnated blue asbestos paper of Example 1. The polyethylene impregnated paper is soaked in hot Decalin (115° C.) for 20 seconds, then placed between two polyethylene screens (4 x 4 mesh) and held in a hydraulic press for 10 minutes at 180° F. under 10 p.s.i.g. The resulting lamination contains a center layer of impregnated asbestos paper, both sides of which are bonded to a polyethylene screen for reinforcement.

It is to be understood that any of the rubber, thermoplastic, or thermosetting impregnants or mixtures of the impregnants individually defined above, particularly the synthetic rubbers and the polymeric compositions of C₂ to C₈ hydrocarbon monomers which are unsubstituted or substituted with a halogen, cyano (e.g. CN), amino (e.g. NH₂) acryl (e.g. C₆H₅O) or carbonyloxy (e.g. CO.O) group can be substituted in any of the above examples which are drawn to impregnation to provide an asbestos diaphragm of greatly improved mechanical strength for use in a continuous electrochemical process.

It is further to be understood that any of the asbestos matrices, or matrices containing blends of asbestos or asbestos compositions, such as those disclosed in copending patent application Ser. No. 814,821, filed Apr. 9, 1969, can also be substituted in any of the above examples which are drawn to impregnation to provide diaphragms of greatly improved mechanical strength for use in electrochemical processes. These diaphragms can be subsequently laminated to a porous metal or plastic substrate, if desired.

Having thus described my invention, I claim:

1. A process for producing a diaphragm for an electrolytic cell which comprises:

treating a preformed asbestos diaphragm matrix with a preformed polymeric impregnant in a liquid me-

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dium, said polymeric impregnant being selected from the group consisting essentially of polybutadiene, polyvinyl chloride, polychloroprene, polyisoprene, polyethylene, polybutylene, polypropylene, polyurethane, polychlorotrifluoroethylene, and polytetrafluoroethylene;

heating the resulting wet impregnated matrix in a heating zone to a temperature between about 25° C. and about 400° C., said heating zone comprising a drying zone wherein the impregnated matrix is dried at a temperature between about 25° C. and about 120° C. and a sintering zone following said drying zone operated at a temperature between about 40° C. and about 400° C. so that at least the impregnated asbestos diaphragm are softened; and

laminating said impregnated asbestos diaphragm to a porous metal or plastic substrate at the sintering temperature of the impregnant particles and under a pressure of from about 10 to about 1500 p.s.i.g.

2. A process for producing a diaphragm for an electrolytic cell which comprises:

treating a preformed asbestos diaphragm matrix with a preformed polymeric impregnant in a liquid medium, said polymeric impregnant being selected from the group consisting essentially of polybutadiene, polyvinyl chloride, polychloroprene, polyisoprene, polyethylene, polybutylene, polypropylene, polyurethane, polychlorotrifluoroethylene, and polytetrafluoroethylene;

heating the resulting wet impregnated matrix in a heating zone to a temperature between about 85° C. and about 400° C.;

treating said impregnated matrix with a second liquid medium which is a solvent for the impregnant at a temperature sufficient to soften at least the impregnant particles on the surface of the impregnated matrix; and

laminating said solvent treated impregnated matrix to a porous metal or plastic substrate by applying a pressure of from about 10 to about 1500 p.s.i.g. under a sintering temperature of from about 40° C. to about 400° C.

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JOHN H. MACK, Primary Examiner

R. L. ANDREWS, Assistant Examiner

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