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3,723,264

ELECTROCHEMICAL OXIDATION OF OLEFINIC COMPOUNDS

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ABSTRACT OF THE DISCLOSURE

An improvement in the electrochemical oxidation of an olefinic compound comprising an electrochemical cell of the diaphragm type is provided by operating the cell with a diaphragm comprising asbestos as a diaphragm matrix combined with a high molecular weight polymer as a binder. The matrix is an asbestos of the serpentine or amphibole type while the binder comprises at least one of a group of certain polymeric compounds of the type including synthetic rubbers, and thermoplastic and thermosetting polymers and copolymers of hydrocarbon and substituted hydrocarbon compounds. The polymeric material incorporated into the asbestos matrix glues or binds the fibers of the asbestos in a linked or glued structure to strengthen the diaphragm and prevent rupture during continuous operation of the cell.

This invention relates to an improved method for carrying out olefin oxidation reactions in an electrolytic cell, and more particularly relates to the use of a particular composition as the diaphragm separating the anode chamber from the cathode chamber of the cell.

In carrying out many olefin oxidation reactions in an electrochemical process, a separator is provided within the electrolytic cell to divide the cell into an anode chamber and a cathode chamber. The liquid medium contained therein and passing either as a liquid or as ions through the diaphragm and between the electrodes of the cell, is referred to as the anolyte in the anode chamber of the cell and the catholyte in the cathode chamber of the cell. Irrespective of whether the diaphragm separator is liquid permeable or impermeable it should possess good mechanical strength and be resistant to chemical deterioration caused by its contact with both the anolyte and catholyte, the chemical properties of which are significantly different. For example, in the process for producing propylene oxide, the acid content of the anolyte is high due to the fact that acidic compounds (hydrochloric acid) are produced in the anolyte. On the other hand, the catholyte is alkaline due to the generation of hydroxyl ions at the cathode.

Although certain asbestos diaphragm materials are resistant to aqueous alkaline solutions, they undergo gradual disintegration in aqueous acidic media. All types of asbestos, whether or not they possess high chemical resistance to both acid and alkali, show some decline in mechanical strength when employed over extended periods of continuous operation. Since asbestos diaphragms are otherwise ideally suited to this type of reaction, it is important to find a method for strengthening

these materials without altering their desirable chemical properties.

It is therefore an object of this invention to provide an improvement in the oxidation of olefins in systems employing an electrochemical cell in which the anode and cathode compartments are separated by a diaphragm.

Another object is to provide a particular diaphragm composition for use in such systems which has improved mechanical strength.

Another object is to provide an electrochemical process for the oxidation of an olefin wherein the diaphragm has an extended life and can withstand substantial pressure over longer periods of continuous operation.

A further object is to provide a diaphragm material for the above reaction which can be operated under high current density and high electrolyte flow rate for extended periods of time.

Still another object is to provide an asbestos diaphragm of good mechanical strength without appreciable loss of desirable electrical and hydrodynamic properties.

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 improved diaphragm is provided in the electrochemical process for the oxidation of olefins wherein a diaphragm-compartmented electrolytic cell having an anode chamber containing anolyte and a cathode chamber containing catholyte is employed. The improved diaphragm of the present invention which separates the chambers comprises an asbestos matrix wherein asbestos fibers are bound by adhesion of a high molecular weight polymeric material.

The asbestos comprising the matrix 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 and which is known as "white asbestos" or the matrix can be composed of the amphibole type such as crocidolite, amosite, anthophyllite, tremolite and actinolite. The preferred asbestos matrices are those of the amphibole type having a magnesia content not more than about 20 weight percent; of these, crocidolite, actinolite and amosite commercially known as "blue asbestos" or blends of these amphibole types having a magnesia content of from 0 to 2 percent of 6 percent are most preferred because of their superior chemical resistance to acids and bases. An accepted formula for crocidolite, a sodium iron silicate, is



although some grades may contain small amounts of magnesia, for example, up to about 3 percent. Amosite is a low magnesia iron silicate having the empirical formula $\text{Fe}_3\text{Mg}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$ and usually containing from about 1 to about 7 percent magnesia.

The polymeric binder material employed in the diaphragm of the present invention is a polymeric or copolymeric compound of synthetic rubber, a thermoplastic polymer or a thermosetting resin. Suitable polymeric binders of the rubber type include polychloroprene (neoprene), polyisobutylene, polybutadiene, polydimethylbutadiene, polymethylbutadiene (isoprene), polyvinyl chloride and butadiene copolymers with styrene and acrylonitrile and organic polysulfide types such as the copolymers of ethylene chloride-sodium tetrasulfide and dichloroethyl ether-sodium tetrasulfide. The rubber

polymeric compositions may contain up to about 30 percent plasticizer. Suitable plasticizers include tricresyl phosphate, dioctyl isosebacate, Wareflex, Plastoleire, etc.

Other types of polymer suitable as binder in the present invention include polyethylene, polypropylene, polybutylene, polystyrene, polystyrol, polytetrafluoroethylene, polychlorotrifluoroethylene, polyvinylidene chloride, polyacrylonitrile, polyester, polyurethane, polyvinylpropionate, polyvinylacetate and acrylic and methacrylate polymers and copolymers such as butadiene-styrol, and any of the known copolymers which combine monomers of the above mentioned polymers.

Preferred binders of the above group of polymeric materials are the polymers and copolymers of butadiene, vinyl chloride, chloroprene, isoprene, polyethylene, polypropylene, 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 binder into an asbestos slurry 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 and may additionally contain from 5 percent to 7 percent wetting agent, such as Triton, Igepal and other known wetting agents.

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.

The dispersions of binder of the present invention may contain anti-foaming agents, such as for example methanol, isobutanol, and silicones and may also contain surfactants such as the non-ionic types of which Igepal, Poly Tergent, Dytol are representative; the anionic types of which Aerosol, ammonium stearate, and Maprosyl are examples; and the cationic types represented by Sarkosyl and Duomeen. The binder dispersions should have an affinity for the asbestos fibers so as to adhere to the fibers when dried.

In the process of the present invention, between about 1 and about 30 weight percent, preferably between about 3 and about 15 weight percent, binder is incorporated into the asbestos. For the purposes of mixing, the asbestos is desirably in the form of an aqueous slurry or pulp-like aqueous liquid. The binder is preferably added to the slurry in the form of a dispersion which may or may not contain a precipitating or coagulating agent, such as for example, aluminum sulfate, sodium aluminate, and other known types. It is to be understood, however, that binder may be incorporated into an asbestos slurry to form a mate. For example, fibers with binder in the form of pigments or dispersions can be deposited on the cathode screen positioned in the electrolytic cell before drying to form the diaphragm. However, for uniform distribution of fibers and simplification of treating steps, aqueous dispersions of binder in the form of a colloidal solution or emulsion is recommended. Types of apparatus for preparing the binder dispersions and asbestos slurry include planetary-action mixers, e.g., of the Hobart type, a sigma blade, a Cowles dissolver, a Waring blender, a colloid mill, and an Eppenbach homogenizer; although for asbestos slurries simple mechanical mixing is sufficient.

Irrespective of the method of mixing asbestos and binder, the binding operation is substantially the same. This treatment comprises subjecting the mixture to a temperature between about 90° F. and about 250° F. and a pressure of from about 15 p.s.i.g. to about 50 p.s.i.g. Under these conditions the asbestos fibers are linked with binder molecules or binder molecules are glued to the asbestos fibers in a substantially reinforced composition which, de-

pending on the amount and type of binder and the duration of the heat treatment, may be a tightly bound or loosely linked web-like structure.

In preparing the diaphragms of the present process, raw asbestos is usually subjected to a defibering treatment prior to admixing with binder. The defibering treatment comprises grinding and/or cutting the asbestos fibers in a suitable apparatus, e.g., a refiner having opposing rotating discs, etc., to a convenient fiber length, i.e. an average length of up to 10 mm., preferably up to 5 mm. The density of the aqueous asbestos slurry during the grinding operation is generally maintained below 10 percent based on anhydrous asbestos. It is particularly recommended that the mass density of the slurry be not more than 5 weight percent, preferably between about 0.5 and about 2.5 weight percent before adding the binder.

A specific and preferred embodiment of the process of preparing the diaphragm of the present invention comprises the following sequence of treating steps or stages; although it is to be understood that additional steps can be interposed or added in the sequence of steps discussed hereinafter.

In this embodiment a preformed aqueous slurry of blue asbestos is admixed with an aqueous preformed colloidal dispersion of binder in a mixing tank, e.g. a chest tank, until a substantially uniform mixture of asbestos and binder is obtained. After a mixing period of from about 5 minutes to about 2 hours, a pulpy liquid admixture is formed which can be diluted by addition of water if desired. The admixed slurry is transferred to a settling zone, e.g. a weir box containing a series of weirs over which the slurry is passed in succession while fibers exceeding the desired size are separated from the slurry by settling to the lower portion of the chambers between the weirs. A substantially uniform slurry is withdrawn from the settling zone and passed to a Fourdrinier paper making machine which comprises a sheet making screen with a suction box, a drying zone and a compression zone. The slurry from the settling zone is fed onto a continuously moving train comprising a wire screen. A vacuum, e.g., between about 15 inches Hg and about 20 inches Hg is applied below the screen to withdraw mother liquor from the slurry and to form an asbestos-binder mat on the upper surface of the screen. The compressed mat is then directed over or around one or a plurality of heating drums or dryers where it is dried at a temperature of from about 125° F. to about 250° F. over a period of about 5 to about 50 minutes. After drying the asbestos-binder paper is transferred to one or more pairs of calender rollers. Pressure is applied between the rollers to provide uniform thickness of the sheet. The higher temperatures within the above range are employed in the drying step when non-rubbery binders are used and the binder has low affinity for the asbestos fibers. In this case higher temperatures are employed to soften the polymer particles and cause adhesion between the asbestos fibers and the binder. The higher temperatures of drying, however, are usually unnecessary unless the surface finish of the diaphragm is a factor for consideration or when a more rigid diaphragm is desired.

Another embodiment in the preparation of a diaphragm for the present invention comprises predisposing a wet asbestos mat on a foraminous metal cathode or foraminous barrier positioned between the anode and the cathode of the electrolytic cell, by passing a weak slurry of the asbestos through the foraminous member in order to form a precoat, then passing electrolyte containing a slurry of asbestos and binder in the form of a dispersion through the precoat thereby depositing asbestos and binder substantially on one side of the cathode screen, and drying the mat retaining the deposited mixture to cause adhesion of the binder particles to the asbestos fibers in a fortified web-like structure. Still another method for forming the diaphragm involves depositing a

performed slurred mixture of asbestos and binder on the foraminous member and drying the mixture to effect binding as above. Various other methods of binding an asbestos diaphragm will become apparent to those skilled in the art from this description and disclosure.

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 meta 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. Most preferably the electrolyte is present in aqueous solution in a concentration of between about 2 and about 25 weight percent.

When the liquid permeable diaphragm of the present invention is employed, electrolyte is passed through the diaphragm at a flow rate of between about 100 to about 2000 cc. per minute per square foot of diaphragm, preferably at a rate of between about 200 to about 1000 cc. per minute per square foot of diaphragm. 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 transversing 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. It is to be understood, however, that when a liquid imper-

meable or substantially liquid impermeable diaphragm is desired, the thickness of the diaphragm is much higher, for example, about 300 mils thick for substantially liquid impermeable types. 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.

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. metalized 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 80 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 oxide, 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 or oxidant treatment followed by filtration prior to recycle. 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 where contact between the olefin, electrolyte and electrode occurs thereby producing product, reducing overvoltage and polarization. Theoretically, during operation, the current 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.

Reference is now had to the following examples which are provided for a better understanding of this invention and are not to be construed as unnecessarily limiting to the scope of the invention as set forth above.

EXAMPLE I

The diaphragm used in this example is manufactured as follows. Blue asbestos fibers of different lengths are ground for a short time on a hollander to a material density of 3 percent so that an average fiber length of approximately 4 mm. is obtained. Then, after reducing the material density to 0.7 percent, an aqueous anionic 35 percent polyethylene dispersion containing Maprosyl (3-10%) is added in an amount such that the weight proportion of binder to dry asbestos fiber is 1:11. Thereafter the polyethylene dispersion is precipitated with 5 percent (in relation to the fibers) aluminum sulfate (as a 10 percent aqueous solution) and on a Labor-sheet former paper is formed with a weight per unit area of 350

grams/m.². Finally the paper is treated in a vacuum, and heated for 15 minutes at 95° C.

An electrolytic cell is used with an anode of 1.75 dm.² made of solid titanium metal sheet which is plated with platinum/iridium at a ratio of 70:30 (20 grams per square meter). Opposite the anode is a stainless steel, wire mesh cathode of equal surface area spaced at a distance of 6 mm. The diaphragm described above having a thickness of about 25 mils and made of blue asbestos with a binder of polyethylene is supported by and attached to the cathode. The electrolysis cell is filled with an 8.5 percent aqueous potassium chloride solution. A direct current is applied across the electrodes, the anodic current density being 11.1 amperes/dm.². The temperature of the electrolyte in the cell is 55° C. The cell is operated at atmospheric pressure. About 44 liters of a C₃-hydrocarbon fraction containing 94 weight percent of propylene, the remainder being mainly propane, are introduced in finely dispersed form into the anode chamber through a sparge positioned below the anode. About 20 percent of the propylene is converted essentially to propylene chlorohydrin. The unconverted excess gas leaves the anode chamber after separation from the anolyte. About 4 liters per hour of the electrolyte flows from the anode chamber through the diaphragm into the cathode chamber. In the cathode chamber the propylene chlorohydrin content in the electrolyte is dehydrochlorinated to propylene oxide. An amount of catholyte corresponding to the addition of anolyte is removed from the cathode chamber of the cell and the propylene oxide contained therein is separated by distillation. The remaining electrolyte is returned to the anode chamber of the cell after treatment with halogen gas and filtration to remove contaminants.

After 100, 500 and 1000 hours of operation, the gases and fluid products permanently leaving the cell over a period of 4 hours are analyzed and used for calculating current yields.

The test results are listed on the following Table I:

TABLE I

Reaction product	Yield in current percent after—		
	100 hours	500 hours	1,000 hours
Propylene oxide.....	84.4	84.2	85.0
1,2-dichloropropane.....	11.6	11.9	11.4
Propanediol-1,2.....	1.7	1.5	1.3
Propylene chlorohydrin.....	0.6	0.6	0.7
Other organic products.....	1.0	1.1	0.9
Oxygen.....	0.5	0.5	0.5
Carbon dioxide.....	0.2	0.2	0.2
Pressure drop in diaphragm in cm. water column.	21	15	17

EXAMPLE II

The above example is repeated except that white asbestos fibers are substituted for blue asbestos so that a diaphragm of polyethylene binder incorporated into chrysotile is employed. After 40 hours the yield of reaction products in percent Faradays is substantially the same as reported in the preceding example after 100 hours of operation except that the yield of propylene oxide is about 13 percent lower and the yield of carbon dioxide is about 7.5 percent higher. However, after 60 hours the diaphragm was ruptured and the run discontinued.

EXAMPLE III

The process of Example II is repeated except that the white asbestos diaphragm does not contain a binder. The asbestos paper diaphragm beings to disintegrate within two hours. The pressure drop through the diaphragm is reduced and the formation of undesirable by-products increases due to the poor separation of the electrode chambers. The operation of the cell finally breaks down after four hours.

EXAMPLES IV THROUGH XI

The examples reported in Table II illustrate various binder dispersions incorporated with blue asbestos. Examples IV to V employ 40 percent crocidolite in an aqueous solution having a minimum fiber length of about 100 mesh; Examples VI to VIII employ 50 percent amosite in aqueous solution having a minimum fiber length of about 100 mesh; and Examples IX to XI employ 35 percent actinolite in aqueous solution having a minimum fiber length of about 100 mesh.

Binder dispersions in reported concentrations in aqueous solutions are mixed and slurried for 45 minutes with the slurries of blue asbestos in a mixing tank agitated with a paddle stirrer operating at 15 to 20 r.p.m. The uniform slurries of asbestos and binder are then fed into a sheet-making machine containing a screen-like mold whereon an asbestos-binder mat is formed. Mother liquor is drained from the mat over a drain time period of from about 7 to 12 minutes to form sheets of asbestos-binder compositions. The sheet is then removed from the mold and pressed between calendar rollers at the pressures reported to the desired uniform thickness and dried at the temperatures noted.

The diaphragms produced in Table H are then employed in an electrolytic cell by attaching each of the diaphragms to the surface of a stainless steel screen cathode facing the anode of the cell. The anode and the cathode of the cell each have a surface of 1.7 dm.² and the anode, composed of ruthenium oxide on titanium, is spaced 4 mm. from the cathode. The electrolyte solution introduced into the cell is a 5.0 weight percent aqueous solution of potassium chloride and the current density of the cell is 200 amperes per square foot of apparent electrode surface. Propylene is fed into the cell in the vicinity of the anode at a rate of 600 cc. per minute and a gaseous effluent comprising dichloropropane and unreacted propylene is removed from the anode chamber while a gaseous mixture of hydrogen and propylene oxide is withdrawn from the cathode chamber of the cell. The electrolyte solution is removed from the cathode chamber, stripped of propylene oxide and treated for recycle to the anode chamber of the cell for a continuous operation.

The diaphragms of Table II employed in the above propylene oxide cell continue to operate for more than 500 hours without showing any signs of deterioration. The pressure drop at the end of the 500 hour period shows substantially little change (about less than 5 cm.) and the yield of propylene oxide is maintained at a high percent Faraday (80 to 85%).

TABLE II

Example binder	Wt. percent	Additive	Weight ratio of binder: asbestos	Pressing, p.s.i.g.	Drying, ° F.	Thickness, mils	Permeability, cc./minute/ft. ² diameter
IV..... Chloroprene.....			1:50	3	165	26	210
V..... Polyvinyl chloride.....	0.5	Dioctyl sebacate.....	1:10	5	150	33	120
VI..... Polypropylene.....			1:100	7	210	48	640
VII..... Butadiene-styrene (60/40) copolymer.....			1:6	6	180	30	410
VIII..... Polystyrene.....	0.7	White oil.....	1:7	10	165	25	220
IX..... Polymethylbutadiene.....	0.3	White oil and benzene mix.....	1:16	8	160	30	380
X..... Polychlorobutadiene.....			1:20	8	155	28	450
XI..... Polystyrol.....			1:6	10	200	25	110

11 EXAMPLE XII

A slurry of crocidolite asbestos is prepared by mixing 40 percent of Blend I with 60 percent of Blend II. The fiber length of Blend I and Blend II (McNett test) is as reported in following Table III:

Mesh size	Percent	
	Blend I	Blend II
+4.....	87	74
+14.....	3	6
+35.....	2	5
+100.....	1	4
-100.....	7	11

About 40 grams of the mixed asbestos fibers are slurried in a 5 percent potassium chloride solution by moderate stirring at 15 to 20 r.p.m. for about 30 minutes. To this slurry is added an aqueous dispersion of polytetrafluoroethylene (Teflon, 3 grams in aqueous dispersion) and Igepal CO-430 (0.1% of the weight of fibers) and stirring is continued for 30 minutes. The resulting sheet is removed from the mold, pressed between two polished stainless steel plates under 8 p.s.i.g. and dried for 15 minutes at 240° F. and an asbestos diaphragm containing Teflon binder having a thickness of 30 mils is obtained.

The diaphragm thus produced is employed in the propylene oxide cell described above in Examples IV through XI except that the flow rate of electrolyte through the cell is varied to 37 cc. per minute and the cell is operated at 125° F. under atmospheric pressure. The product distribution in percent Faradays is as follows:

Reaction product:	Yield ¹
Propylene oxide	87.8
Dichloropropane	6.1
Propanediol-1,2	1.3
Propylene chlorohydrin	0.8
Other organic products	1.0
Oxygen	0.8
Carbon dioxide	1.6

¹ Percent Faradays after 3,000 hours operation with diaphragm.

EXAMPLE XIII

A blend of crocidolite and amosite (80:20 weight ratio) is prepared by dry mixing and refined by means of a disc refiner. About 44 percent of the fiber is passed through a -100 mesh screen. About 50 grams of these fibers are slurried in an 8.5% sodium chloride aqueous brine solution of 10 liters by slow stirring at 20 r.p.m. for 30 minutes at room temperature. A rubber emulsion of Buna rubber in a mixture of white oil and toluene containing 0.5 weight percent of a dispersing agent (Emulsifier-CO) is added to the slurry. The mixture is stirred for 2 hours and 0.1% by weight of a wetting agent (Titon X) is added to the mixture while stirring and diluting with water to 40 liters. The resulting mixture is then fed to a sheet-making machine and a drain time of the resulting mat of 30 seconds is allowed on the mold for removing mother liquid. The sheet is removed and pressed between two stainless steel plates at 10 p.s.i.g. and is then dried for 30 minutes at 210° F. The resulting diaphragm has a thickness of 45 mils and a liquid permeability of 560 cc. per minute per square foot of diaphragm at 1 inch water head.

This diaphragm when employed in the propylene oxide cell of the preceding example shows no sign of deterioration after 2,000 hours of continuous operation.

It is to be understood that any of the amphibole asbestos types can be substituted in Examples IV through XIII to provide substantially the same good results with the binders illustrated. Also, any of binders in aqueous

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dispersion which may or may not contain additives such as wetting agents and which are mentioned in the foregoing disclosure can be substituted in Examples IV through XIII to provide significantly strengthened asbestos binders which retain high resistance to acidic and basic solutions.

Of the binders included within the scope of this invention, the synthetic rubbers and polymeric compositions of C₃ 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 are particularly suitable.

Having thus described our invention, we claim:

1. A process for the electrochemical oxidation of an olefinic compound wherein a diaphragm-compartmented electrolytic cell having an anode chamber containing anolyte and a cathode chamber containing catholyte is employed and wherein the diaphragm comprises a serpentine or amphibole asbestos which has been subjected to binding with a high polymer binder of the rubber, thermoplastic or thermosetting type.

2. The process of claim 1 wherein the asbestos is an amphibole or blend of amphibole types having a magnesia content not greater than 20 percent.

3. The process of claim 2 wherein the asbestos is slurried with water to a density not greater than 10 percent solids having an average fiber length not greater than about 10 mm. and a dispersion of binder is added to the slurry and uniformly mixed therewith to provide a wet mixture containing between about 1 and about 30 weight percent binder, the mixture is dried to effect binding and subjected to the pressure of calender rollers to provide a uniform thickness within the range of from about 10 to about 150 mils in the finished diaphragm sheet.

4. The process of claim 3 wherein the binder dispersion is a substantially aqueous dispersion.

5. The process of claim 3 wherein the carrier of the binder in the dispersion is toluene, mineral spirits, ethanol, ethyl acetate, methylisobutyl ketone or perchloroethylene.

6. The process of claim 3 wherein the binder is a polymeric synthetic rubber and the dispersion contains between about 1 percent and about 30 percent plasticizer.

7. The process of claim 3 wherein the binder dispersion contains at least one additive such as a surfactant, and an anti-foaming agent, a precipitating agent and a wetting agent.

8. The process of claim 3 wherein an aqueous dispersion of tetrafluoroethylene containing between about 30 percent and about 65 percent solids is employed as a binder.

9. The process of claim 3 wherein an aqueous dispersion of polyethylene containing between about 10 percent and about 70 percent solids is employed as the binder.

10. The process of claim 2 wherein a mat of asbestos is deposited on a foraminous member situated between the anode and the cathode and transverses the electrolytic cell and wherein the binder is deposited on one side of the mat and the resulting mixture is dried to cause adhesion between the asbestos fibers and the polymeric binder.

11. The process of claim 10 wherein the foraminous member is a metal cathode screen.

12. The process of claim 2 wherein the diaphragm has a permeability to pass between about 100 and about 1000 cc. of liquid per minute per square foot of the diaphragm therethrough and has a thickness from about 10 to about 150 mils.

13. The process of claim 2 wherein the diaphragm has a thickness of between about 150 to about 300 mils and is substantially liquid impermeable.

14. The process of claim 2 wherein the olefinic compound is propylene and propylene oxide is produced as a product of the process.

15. The process of claim 2 wherein ethylene is the olefinic compound and ethylene oxide is produced as a product of the process.

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16. The process of claim 2 wherein the binder is a polymeric material containing monomers of butadiene.

17. The process of claim 2 wherein the binder is a polymeric material containing monomers of vinyl chloride.

18. The process of claim 2 wherein the binder is a polymeric material containing monomers of ethylene.

19. The process of claim 2 wherein the binder is a polymeric material containing monomers of tetrafluoromethylene.

20. The process of claim 2 wherein the binder is a polymeric material containing monomers of chloroprene.

21. The process of claim 2 wherein the amphibole is crocidolite.

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22. The process of claim 2 wherein the amphibole is amosite.

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