

- [54] **PROCESS FOR ELECTROLYSING BRINE**
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Related U.S. Application Data

- [63] Continuation-in-part of Ser. No. 284,022, Aug. 28, 1972, , which is a continuation-in-part of Ser. No. 179,151, Sept. 9, 1971.
 [52] U.S. Cl. **204/98, 204/128, 204/296**
 [51] Int. Cl. **C01d 1/06, C01b 7/06**
 [58] Field of Search..... **204/128, 98, 296**

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[57] ABSTRACT

Novel diaphragms for use in chlor-alkali cells are disclosed. The diaphragms are electrolyte-permeable, asbestos diaphragms having an organic, ion exchange resin contained therein. Also disclosed is the electrolysis of brines in an electrolytic cell having such a diaphragm and a method of preparing and installing such diaphragms. Additionally, there is also disclosed a particularly adherent fluorocarbon coating on asbestos.

10 Claims, No Drawings

PROCESS FOR ELECTROLYSING BRINE

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of our commonly assigned, copending application Ser. No. 284,022, filed Aug. 28, 1972, for "Diaphragms for Electrolytic Cells" which is a continuation-in-part of our commonly assigned, copending Application Ser. No. 179,151, filed Sept. 9, 1971, for "Diaphragms for Electrolytic Cells."

BACKGROUND

According to one process for the production of chlorine, alkali metal chlorides are electrolyzed to produce chlorine and alkali metal hydroxide in a diaphragm cell. Such electrolytic cells have a structure substantially as shown in U.S. Pat. No. 3,337,443 to C. W. Ratzsch et al. for "Electrolytic Cell" and in U.S. Pat. No. 3,022,244 to Carrol P. Le Blanc et al. for "Electrolytic Alkali-Chlorine Diaphragm Cell."

The diaphragm serves to separate the anolyte compartment from the catholyte compartment. An aqueous solution of an alkali metal chloride, i.e., brine, is fed into the anolyte compartment. In the anolyte compartment the chloride ion of the disassociated alkali metal chloride forms chlorine at the anode. The anolyte liquor, including alkali metal ion, hydroxyl ion, and chloride ion, travel through the diaphragm to the catholyte compartment. In the catholyte compartment alkali metal hydroxide and gaseous hydrogen are liberated at the cathode, and catholyte liquor containing alkali metal chloride and alkali metal hydroxide is recovered from the catholyte compartment.

The diaphragm also serves to maintain a difference in pH between the two compartments. Typically, the electrolyte in the anolyte compartment will have a pH of from about 3.5 to about 5.5, while the electrolyte in the catholyte compartment will have a pH of 12.0 or greater. The diaphragm, in a typical electrolytic cell of the type hereinabove described, serves to maintain this difference in pH, while permitting the flow of electrolyte therethrough.

Typically, such diaphragms have been prepared from asbestos. In the electrolytic cells of the prior art, the asbestos has been of the type referred to in the literature as chrysotile asbestos. Chrysotile asbestos has a structure characterized as tubular fibers, and an empirical formula of $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.

Asbestos diaphragms generally have a weight of from about 0.30 to about 0.40 pounds per square foot of diaphragm surface area, a thickness of about $\frac{1}{8}$ inch when installed and "swell" by about 100 percent to a thickness of about $\frac{1}{4}$ inch when in service.

Such asbestos diaphragms of the prior art have a service life of about 4 months to about 7 months in electrolytic cell service where the anodes of the electrolytic cell are graphite. In the electrolytic cells wherein the anodes are dimensionally stable anodes (i.e., where the anodes are a metal substrate having an electrocatalytic metal or metal compound surface thereon), the service life of the diaphragm is typically from about 3 months to about 7 months. This contrasts with a service life typically in excess of 18 months for the dimensionally stable anodes themselves, thereby requiring several renewals of the asbestos diaphragm between each renewal of the anodes.

SUMMARY

It has now been found that diaphragms suitable for use in alkali metal chloride electrolytic cells of the diaphragm type, particularly when such cells have dimensionally-stable anodes, may be provided by an asbestos diaphragm that has been treated with small amounts of an electrolyte-resistant, ion exchange resin.

Diaphragms of this invention are long lived in the electrolytic chlorine cell environment, being characterized by their increased life over conventional electrolytic cell diaphragms containing asbestos alone. Diaphragms of this invention are further characterized by being gas and electrolyte-permeable, functioning as a diaphragm rather than as a permionic membrane. Diaphragms of this invention are also characterized in that they may be prepared at lower cost than diaphragms or permionic membranes having as their principal constituent a synthetic, ion exchange resin.

Diaphragms of this invention are characterized in that they have a resistance voltage drop across the diaphragm of as much as 0.2 to 0.3 volt less than an untreated asbestos diaphragm of the same thickness, and as much as 10 to 20 volts less than a permionic membrane of the same thickness.

DESCRIPTION OF THE INVENTION

Diaphragms are used in alkali metal hydroxide-chlorine cells to separate the anolyte, having a pH of about 3.5 to about 5.5, from the catholyte having a pH of 12 or greater. Such cells typically have an anolyte compartment or chamber containing an anode, a catholyte compartment or chamber containing a cathode, a diaphragm to separate the anolyte from the catholyte, and external power supply means for imposing an electromotive force between the anode and the cathode. The cathode is a catholyte resistant metal structure, e.g. iron, open to the flow of electrolyte. The cathode may be iron mesh, iron screen, or a perforate plate. The anode may be graphite, or it may be a valve metal, e.g. titanium, with an electrocatalytic surface, e.g. a platinum group metal.

In the operation of commercial chlorine-caustic soda diaphragm cells, brine containing from about 280 to about 315 grams per liter of sodium chloride is fed into the anolyte chamber of the cell. An electromotive force is established between the anode and the cathode. In the anolyte chamber chlorine is evolved at the anode. Additionally, anolyte liquor, containing sodium chloride passes through the diaphragm to the catholyte chamber. In the catholyte chamber hydrogen is evolved at the cathode, and catholyte liquor containing from about 7 to about 15 weight percent of sodium chloride and from about 10 to about 15 weight percent of sodium hydroxide is recovered.

Diaphragms of this invention, having a thickness of from about 0.001 inch to about 0.250 inch, and a voltage drop of less than about 0.6 volt at a current density of 190 Amperes per square foot, can operate at an inter-electrode gap (i.e., a spacing between a cathode and the next adjacent anode in the cell) of less than about 0.50 inch and in some cases even less than 0.25 inch.

Moreover, inasmuch as the diaphragms of this invention are less subject to swelling than the diaphragms of

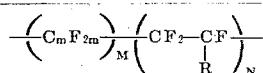
the prior art, the anodes may be closer to the cathode than was previously the case.

Diaphragms of this invention are electrolyte-permeable asbestos members, such as fibrous asbestos sheets and mats, or asbestos paper, that have been treated with small amounts of electrolyte resistant, ion exchange resins. Typically, the ion exchange resins are hydrophilic, cation-selective resins substantially inert to the electrolyte. By "hydrophilic" it is meant that the ion exchange resins are readily wetted by the electrolyte. By "cation selective" it is meant that the ion exchange resins useful in preparing diaphragms of this invention preferentially allow the migration of cations such as Na⁺ and H⁺ through the diaphragm to a greater extent than the migration of anions such as chloride ions (Cl⁻) through the diaphragm. By "inert" it is meant that the ion exchange resins useful in preparing the diaphragm of this invention are substantially immune to attack by the electrolyte e.g. chloride ions, hypochlorite ions, hydroxyl ions, hydronium ions, sodium ions, and the like, and by the electrolysis products, e.g. chlorine.

The inert polymer chains of the ion exchange resins serve to impart physical strength and durability to the porous asbestos diaphragm structure. The cation-selective ion exchange groups on the ion exchange resins render the diaphragm hydrophilic, allowing the diaphragm to exhibit permeability to the electrolyte with a minimum hydrostatic head of anolyte.

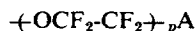
According to this invention, ion exchange resins having the properties of cation selectivity, wettability, and inertness are preferentially provided by fluorocarbons having acid groups, fluorocarbon interpolymers having fluorocarbon and fluorocarbon acid moieties, and interpolymers having aryl and arylacid moieties where the main chain is a fluorocarbon, e.g. fluoro styrenes.

One class of fluorocarbons useful in providing the ion exchange resins of this invention are those having the empirical formula:

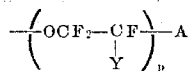


where m is from 2 to 10, the ratio of M to N is sufficient to provide an equivalent weight of from 600 to 2,000 as will be more fully elucidated hereinafter, and R is chosen from the group consisting of:

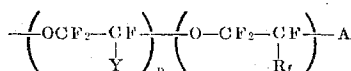
A,



where p is from 1 to 3,



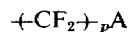
where p is from 1 to 3 and Y is $-\text{F}$ or a perfluoroalkyl having from 1 to 10 carbon atoms,



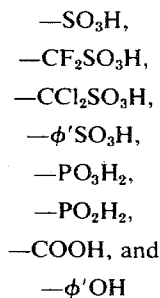
where p is from 1 to 3, Y is $-\text{F}$ or a perfluoroalkyl having from 1 to 10 carbon atoms, and R_f is $-\text{F}$ or a perfluoroalkyl having from 1 to 10 carbon atoms,



where ϕ is an aryl group, and



where p is from 1 to 3; and where A is an acid group chosen from the group consisting of:

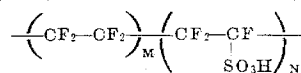


where ϕ' is an aryl group.

When the fluorocarbon is one having short side chains, such as poly(perfluoroethylene-trifluorovinyl sulfonic acid) or $-(\text{CF}_2 - \text{CF}_2)_M - (\text{CF}_2 - \text{CF}(\text{O} - \text{CF}_2 - \text{CF}_2 - \text{SO}_3\text{H}))_N$, the ratio of M to N , that is, the ratio of the moles of fluorocarbon to the moles of the fluorocarbon acid, is typically about 8, thereby providing an equivalent weight of about 1,000 grams per mole of acid. In the case of such polymers having short side chains, the ratio of M to N is from about 5 to about 20, and preferably from about 6 to about 14. When the ratio of the moles of fluorocarbon to moles of fluorocarbon acid is below about 5, the ion exchange agent shows a decrease in physical strength and becomes subject to the abrasive effects of the evolved gas and the flowing electrolyte. When the ratio of the moles of halocarbon to the moles of halocarbon acid is in excess of about 20, the hydrophobic properties of the fluorocarbon member of the interpolymers begin to predominate, causing the diaphragm to behave as a permionic membrane.

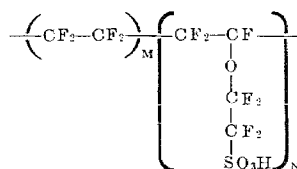
The ion exchange resin is preferably fully fluorinated. By "fully fluorinated" is meant that both nuclear magnetic resonance examination and infrared spectroscopic examination of the interpolymers show less than one percent C-H bonds in the polymer. However, the polymer need not be completely fluorinated inasmuch as the asbestos is the structural member of the diaphragm and some minimal degradation of the ion-exchange resin can be tolerated.

In a preferred exemplification of this invention the ion exchange resin has the empirical formula:



where M and N are as described above.

In another preferred exemplification the ion exchange resin has the empirical formula:

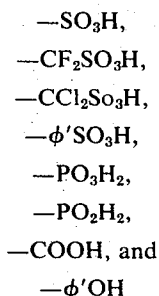


where M and N are as described above.

While the ion exchange resin is spoken of as being a polymer, poly functional perfluoroalkyl acids may also be used in preparing diaphragms according to this invention. Such poly functional perfluoroalkyl acids include those having the empirical formula:



where A and A' are acid groups chosen from the group consisting of:

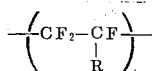


where ϕ' is an aryl group, and q is greater than 8. A and A' may be the same acid groups or they may be different acid groups. Most frequently A is $-\text{SO}_3\text{H}$ and A' is either a second $-\text{SO}_3\text{H}$ group, a $-\text{COOH}$ group, a $\phi'\text{SO}_3\text{H}$ group or a $\phi'\text{OH}$ group. While other combinations of acid groups are useful in providing diaphragms, they are not as readily available and no significant additional benefit is gained by their use. The length of the perfluoroalkyl unit, q , is greater than 8, generally between 8 and 20, and most frequently between 10 and 16. While longer non-polymeric perfluoroalkyls may be used, they are not generally commercially available. Additionally, ether bonds may be present within the acid, e.g., the formula may be $A-(CF_2)_q-O-(CF_2)_{q'}-A'$ where $q'+q''=q$.

When, however, the ion exchange resin is polymeric, the fluorocarbon moiety is a fluorinated olefin such as tetrafluoroethylene, hexafluoropropylene, octafluorobutylene, or further homologues thereof. Tetrafluoroethylene is preferred.

There may, also, be fluorocarbon moieties, present in the interpolymer, having as their precursors fluorinated acetylenes such as difluoroacetylene or fluorinated diolefins such as hexafluorobutadiene. Such fluoroacetylenes and fluorodiolefins may serve as cross-linking agents cross-linking the fluoroolefin polymers and in that way impart additional strength to the diaphragms of this invention.

The acid moiety



may be a fluoroolefin acid such as the trifluoroethylene acids, the pentafluoropropylene acids, the heptafluorobutylene acids, and further homologues thereof. The pendant group may also be a poly(perfluoroether) or poly(perfluoroalkyl) side chain with a terminal acid group. The pendant acid group A is a cation-selective, ion exchange acid group such as a sulfonic ($-\text{SO}_3\text{H}$), a fluoromethylene sulfonic ($-\text{CF}_2\text{SO}_3\text{H}$), a chloromethylene sulfonic ($-\text{CCl}_2\text{SO}_3\text{H}$), a benzene sulfonic ($-\phi'\text{SO}_3\text{H}$), a carboxylic ($-\text{COOH}$), a phosphonic (PO_3H_2), a phosphonous (PO_2H_2), or a phenolic

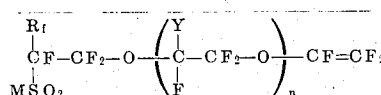
($-\phi'\text{OH}$) acid group. When ϕ' is used herein, it refers to the aryl group $-\text{C}_6\text{H}_4-$.

While the preferred acids are the trifluorovinyl acids, both with and without perfluorinated side chains, it is to be understood that other halocarbon acids may be used with entirely satisfactory results.

The preferred acid groups are the sulfonic acid groups including the benzene sulfonic acid group ($-\phi'\text{SO}_3\text{H}$), the fluoromethylene sulfonic acid group ($-\text{CF}_2\text{SO}_3\text{H}$), the chloromethylene sulfonic acid group ($-\text{CCl}_2\text{SO}_3\text{H}$), the sulfonic acid group ($-\text{SO}_3\text{H}$), and perfluoro side chains have terminal sulfonic acid groups, in that they have the greatest cation selectivity.

Particularly satisfactory ion exchange resins are the copolymers of fluoro-olefins and trifluorovinyl sulfonic acid. A particularly satisfactory ion exchange resin useful in preparing diaphragms of this invention is a tetrafluoroethylene and trifluorovinyl sulfonic acid interpolymer, as disclosed, for example, in U.S. Pat. No. 3,624,053 to Gibbs and Griffin for TRIFLUOROVINYL SULFONIC ACID POLYMERS.

While the fluorocarbon ion exchange resin described above is illustrated as a polyolefin, it should be noted that other polymeric fluorocarbons may be used with equally satisfactory results. One particularly satisfactory group of ion exchange resins are the fluorocarbon-fluorocarbon acid vinyl ether polymers, such as those disclosed in U.S. Pat. No. 3,282,875 to Connolly and Gresham for FLUOROCARBON VINYL ETHER POLYMERS; British Patent 1,034,197; and German Offenlegungsschrift 1,806,097 of D. P. Carlson, based on U.S. Application Ser. No. 697,162, filed Oct. 30, 1967. Disclosed by Connolly and Gresham are fluorocarbon-fluorocarbon acid vinyl ether polymers prepared from monomers having the empirical formula:



where R_f is a radical selected from the group consisting of fluorine and perfluoroalkyl radicals having from 1 to 10 carbon atoms, Y is a radical selected from the group consisting of fluorine and perfluorinated alkyls having from 1 to 10 carbon atoms, n is an integer from 1 to 3, and M is a radical selected from the group consisting of fluorine, the hydroxyl radical, the amino radical, and radicals having the formula $-\text{OMe}$ where Me is a radical selected from the group of alkali metals and the quaternary ammonium radicals.

According to this invention, a thin adherent coating is provided, for example, by contacting properly the asbestos diaphragm with the ion exchange resin. Quite small amounts of the resin provide effective treatment. The ion exchange resin is typically from about 0.01 weight percent to about 22 weight percent of the total diaphragm (basis a typical chlorine-caustic cell diaphragm), and preferably from about 0.3 to about 7.0 weight percent of the total diaphragm. Concentrations of ion exchange resin of less than about 0.01 weight percent, although beneficial, do not impart sufficient additional physical strength to the diaphragm to justify normally using such small amounts. Concentrations of ion exchange resin of greater than about 22 weight per-

cent, while useful, are not usually recommended for diaphragms more than $\frac{1}{8}$ inch thick since they tend to decrease porosity and necessitate higher hydrostatic beads of anolyte for proper cell operation. Higher concentrations of ion exchange resin, e.g., amounts greater than about 22 weight percent in a diaphragm more than $\frac{1}{8}$ inch thick, cause the diaphragm to behave as a permionic membrane, yielding a catholyte liquor containing less than about 1.5 weight percent of sodium chloride.

The ion exchange resin may be dispersed through the asbestos mat or sheet, coating individual fibers within the asbestos mat or sheet. Alternatively, the ion exchange resin may only coat the fibers on the exterior surfaces of the asbestos mat or sheet, or the ion exchange resin may only coat bundles of asbestos fibers. In a preferred exemplification of this invention, the ion exchange agent will be both dispersed through the asbestos member, i.e., mat or sheet, coating the individual asbestos fibers and fiber bundles within the asbestos member as well as on the external surface of the asbestos member, between the asbestos body and the anolyte.

Moreover, it has been found that for any given porosity, pore size distribution, and thickness of diaphragm, best results are obtained if the ion exchange resin extends at least as far into the diaphragm from the anolyte surface as the "gel layer" in an untreated diaphragm of like porosity, pore size distribution, and thickness. This "gel layer" is described by Kircher, "Electrolysis of Brines in Diaphragm Cells," in Sconce, ed., Chlorine, A.C.S. Monograph Series, No. 154, Rienhold Publishing Co., New York (1962), at Page 105, as a layer "formed within the asbestos mat which is sensitive to pH and which tends to dissolve, precipitate and reform depending upon flow rate and salt content and pH of the flowing liquor."

Typically, the "gel layer" extends approximately 0.08 to about 0.12 inch into the diaphragm. Therefore, an optimal depth of penetration of the ion exchange resin is at least 0.08 inch, and preferably about 0.15 inch, or even to the full thickness of the diaphragm, especially when the diaphragm is less than about 0.15 inch thick.

While in terms of location and concentration the ion exchange resin is spoken of as being dispersed through the asbestos member, coating various individual asbestos fibers, and fiber bundles, the precise chemical relationship between the resin and the asbestos is believed to be more complicated.

Thus, one of the particularly effective types of diaphragms of this invention is obtained by forming a strongly adherent, protective film or coating of these polymers on the anolyte-facing surface of the asbestos diaphragm member. Particularly good adherence is accomplished by effecting what appears to be a chemical reaction between acidic moieties of the polymer and the asbestos, notably magnesium of the asbestos. That is, when the polymer and asbestos are appropriately contacted it is possible for form a thin (possibly even a substantially monomolecular) tenacious, polymer coating on the surface of the asbestos fiber. In one embodiment, only a portion of these acidic moieties are involved in the reaction with the magnesium, leaving free acid moieties in the coating.

One way of assuring formation of such a coating is to apply a solution of the resin to the asbestos (whether

in dispersed fiber form or as a diaphragm member) under conditions which do not interfere with the reaction or interaction between the polymer and the asbestos. For example, when the asbestos is drawn from cell liquor, the diaphragms are dired to precipitate sodium chloride and other sodium salt crystals and then washed to remove the sodium chloride and other sodium salt crystals before coating with the ion exchange resin.

Thus, while not wishing to be bound by this theory, the mechanism by which tenacious adhesion of the polymer to asbestos occurs is believed to be the result of causing some of the polymer to react with the magnesium of the asbestos. Most likely the acid group of the polymer reacts with the $-\text{OH}$ groups bonded to the magnesium of the asbestos. The reaction product, a complex polymer having organic moieties, i.e., the perfluoroethylene containing polymer, and inorganic moieties, i.e., the complex polymeric asbestos silicate structure, appears to be particularly resistant to electrolytic cell conditions. One form of the reaction product of chrysotile asbestos and 22 weight percent of a perfluorinated ion exchange resin having sulfonic acid ion exchange groups has the X-ray diffraction pattern tabulated in Table I when subjected to X-rays at a wavelength of 1.5405 angstroms. While the peaks normally associated with chrysotile asbestos are present, the peaks normally associated with the sulfonic acid groups of the resin e.g., 17.50° two theta and a broad band centered at 39° two theta, are not observed. Particularly to be noted are the peaks in the treated asbestos at 12 and 24.35° two theta, having intensities, above background, of 69 and 65 respectively. These peaks are significantly attenuated from their values in original untreated chrysotile asbestos.

The reaction product of chrysotile asbestos and a perfluorinated ion exchange resin having sulfonic acid ion exchange groups has exotherms at 410° and 470°C. when analyzed by differential scanning calorimetry. The reaction product between the resin and the asbestos is further characterized by its insolubility in liquids such as cell liquor, aqueous sodium hydroxide, aqueous sodium chloride, ethanol, ethylene glycol, acetone, and the like.

Table I

X-Ray Diffraction Pattern of the Reaction Product of Chrysotile Asbestos and 22 Weight Percent of a Perfluorinated, Sulfonated Ion Exchange Resin Having an Equivalent Weight of about 1300

Degrees two theta	(Intensity/Full Scale) $\times 100$
10.92	4
12.00	69
18.50	14
20.00	16
22.08	2
24.35	65
30.30	2
34.40	2
35.40	3
36.90	3
49.84	1
60.30	8
63.60	2

Thus, according to one exemplification of this invention, the resin may be present on the asbestos fibers as a chemical compound formed by the reaction of the ion exchange group, e.g. the sulfonic acid group, and the

mangesium of the asbestos. The resin may also be present as an insoluble salt of the resin with a heavy metal ion such as the magnesium ion from the asbestos, or as an insoluble salt of sodium.

Diaphragms of this invention, having an asbestos member with ion exchange agent therein, contain from about 0.01 gram of the ion exchange agent per square foot of exposed diaphragm area to about 10 grams of ion exchange agent per square foot of diaphragm area.

In providing diaphragms according to this invention, chrysotile asbestos may be used. Such asbestos has an empirical formula of $3\text{MgO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$. Alternatively, other forms of asbestos such as anthophyllite asbestos may be used with entirely satisfactory results. Additionally crocidolite may be present in the diaphragm, with the chrysotile or anthophyllite asbestos. Additionally or alternatively amosite, tremolite or actinolite asbestos may be used in providing the diaphragm of this invention.

The chrysotile asbestos useful in providing the diaphragm of this invention typically has a fiber length of from about 1/32 inch to about 1 1/2 inches and a fiber diameter of from about 0.01 micron to about 20 microns.

Particularly satisfactory diaphragms may be prepared containing chrysotile asbestos and having a second fibrous material dispersed therethrough. Such diaphragms maintain a high porosity, on the order of from about 0.1 gallon per square foot per hour to about 3.0 gallons per square foot per hour, after treatment with ion exchange resin. Furthermore, when diaphragms are prepared having a second fibrous material they appear to have greater reproducibility and less variance in porosity.

The second fibrous material should have a fiber diameter at least two times greater than the fiber diameter of the chrysotile asbestos. Preferably, the second fibrous material has a fiber diameter of from about 2 to about 1000 times greater than the fiber diameter of the chrysotile asbestos, with particularly good results being obtained when the second fibrous material has a diameter of from 200 to 400 times the diameter of the chrysotile asbestos.

Chrysotile has a fiber diameter of from about 0.015 to about 0.030 micron. Materials suitable for use as the second fibrous material include crocidolite or anthophyllite asbestos, having a fiber diameter of from about 0.061 to about 0.090 micron, fiberglass, having a fiber diameter of from about 8 to 12 microns, and cellulose, having a fiber diameter of from about 6 to about 15 microns.

Other materials, having some chemical resistance to the liquid used in preparing the asbestos slurry, and having fiber diameters of from about 0.060 micron to about 15 microns, may be used as the second fibrous material. Such materials include polyperfluoroethylene, polyvinylchloride, polyvinylidene chloride, polyvinylfluoride, polyvinylidene fluoride, and the like. By "chemical resistance" is meant that the material is not significantly attacked by the liquid during the time the slurry is being "aged."

The second fibrous material, when present, should be from about 5 to about 20 weight percent of the total weight of the diaphragm. Amounts less than about 5 weight percent do not impart any additional porosity over a diaphragm not containing the second fibrous

material, while amounts greater than about 20 weight percent yield a diaphragm that is too porous.

Thus, according to the exemplification a diaphragm is prepared having a weight of 0.40 pound per square foot, containing 85 weight percent chrysotile asbestos, about 15 weight percent cellulose, and about 0.5 gram per square foot of an ion exchange resin.

While diaphragms have been described herein as deposited asbestos diaphragms, it is of course to be understood that asbestos paper may be substituted for the deposited asbestos. The asbestos paper may be impregnated with the ion exchange resin either before or after installation of the asbestos on the cathode.

Asbestos diaphragms may be also treated with the ion exchange resin while in service. Thus, for example, a solution of ion exchange resin may be added to the brine feed of an electrolytic cell that shows signs of diaphragms deterioration to improve the operation of the cell. Alternatively, asbestos that has been pretreated with the ion exchange resin may be added to the brine feed of an electrolytic cell that shows signs of diaphragm deterioration, thereby improving the operating characteristics of the cell.

The amount of ion exchange resin added should be sufficient to provide from about 0.01 to about 10.0 grams of the resin per square foot of diaphragm area. However, inasmuch as the brine feed to the cell may be remote from the diaphragm, and hydraulic flows within the cell itself may be complex, the amount of ion exchange resin necessary to actually obtain a concentration of 0.1 gram per square foot at all points on the diaphragm may be greater than used otherwise. A four or five fold excess of resin, for example, might be necessary to assure a minimum diaphragm coating throughout the cell.

Alternatively, the ion exchange resin may be added to an electrolytic cell in the form of ion exchange resin treated asbestos. When ion exchange resin treated asbestos is added to the cell, only a small amount need be added to obtain satisfactory results, e.g., from about 0.005 to about 1.0 pound of asbestos per square foot of cathode area per day, need be added to the electrolyte during electrolysis.

Preferably, the asbestos so added to the brine during electrolysis is chrysotile asbestos that has been pretreated with the ion exchange resin. Typically, the chrysotile asbestos has a fiber length of from about 1/64 inch to about 1/2 inch. One suitable chrysotile asbestos useful for addition to the anolyte is Asbestos Corporation of America "7MO5" (Trademark) asbestos.

In an expedient of an exemplification of this invention wherein ion exchange resin treated asbestos is fed to the cell to maintain the diaphragm, the asbestos is added to the cell in the form of a slurry of asbestos in either brine, cell liquor, or water, and it may be fed with the feed brine. Typically, the slurry contains from about one gram per liter to about 100 grams per liter of resin treated asbestos. Best results are obtained when the content of asbestos in the slurry is from about two grams per liter to about 20 grams per liter. Alternatively, the asbestos may be added directly through openings in the cell body.

This method of treatment may be used with conventional asbestos diaphragms as well as with diaphragms containing ion exchange resin treated asbestos. This method of treatment is especially useful in renewing a

diaphragm that has failed prematurely in one cell of a bipolar electrolyzer, thereby obviating the necessity of tearing down a complete electrolyzer in advance of its regularly scheduled maintenance.

Diaphragms of this invention may be prepared according to a number of methods.

In one method, the asbestos is drawn from a cell liquor slurry onto an electrolyte-permeable cathode by any of the conventional methods known in the art, the sodium ion present in the deposited asbestos as a result of the deposition process is removed, and the ion exchange resin is deposited on the asbestos.

In such a method, the asbestos is slurried in cell liquor. Typically, a slurry containing from about 2 to about 9 percent chrysotile asbestos by weight is prepared in a solution containing from about 10 to about 15 weight percent caustic soda and from about 10 to about 15 weight percent sodium chloride, thereby providing a solution of about 25 to about 30 weight percent total caustic soda and sodium chloride.

The asbestos is drawn onto the cathode screen by inserting the cathode into the slurry of cell liquor and asbestos and drawing a vacuum within the cathode. The cathode-asbestos diaphragm combination is then removed from the slurry and may be washed to reduce the concentration of sodium ion. If the diaphragm is washed, it may be washed by drawing water through the diaphragm or by hosing the diaphragm with water. Thereafter, whether or not the diaphragm is washed, it is dried and then the asbestos is coated with the ion exchange resin.

The ion exchange resin is typically applied to the diaphragm by applying a dilute solution or colloidal dispersion of the resin in water or an organic solvent to the asbestos. The application of ion exchange resin may be by spraying, brushing, dipping, or rolling the solution onto the asbestos. Additionally, a slight vacuum may be applied to the diaphragm to draw the ion exchange resin into the diaphragm. After the application of the ion exchange resin to the asbestos, the diaphragm may be dried to remove the solvent. Thereafter, electrolysis may be carried out.

According to another method, diaphragms may be prepared having less of a tendency to "tighten" after treatment with the ion exchange resin. In this method, the diaphragm is drawn from a slurry containing both chrysotile asbestos and a second fibrous material. The second fibrous material present with the chrysotile asbestos is characterized in that the individual fibers have mean fiber diameters greater than the mean fiber diameter of chrysotile asbestos.

The mean fiber diameter of the second fibrous material should be at least two times as great as the mean fiber diameters of the chrysotile asbestos, and preferably at least two orders of magnitude (i.e., 100 times) greater than the mean fiber diameter of the chrysotile asbestos and may be as much as 1,000 times greater than the fiber diameter of the chrysotile asbestos. Particularly good results have been obtained when mean fiber diameter of the second fibrous material is from about 200 to about 400 times greater than the mean fiber diameter of the chrysotile asbestos. Satisfactory results are even obtained when the second fibrous material has a diameter 1,000 times greater than the fiber diameter of the chrysotile asbestos.

Chrysotile asbestos has a mean fiber diameter of from about 0.015 micron to about 0.030 micron.

Therefore, according to this method, the second fibrous material may be crocidolite or anthophyllite asbestos, having a mean fiber diameter from about 0.060 micron to about 0.090 micron, fiberglass, having a mean fiber diameter of from about 8 to about 12 microns, or cellulose, having a mean fiber diameter of from about 6 to about 15 microns.

The slurry used in preparing diaphragms according to this method may contain from about 0.3 weight percent to about 3.0 weight percent chrysotile asbestos, and from about 0.015 weight percent to about 1.5 weight percent of the second fibrous material. In this way, from about 1 to about 50 weight percent of the total solids in the slurry is the second fibrous material. The liquid used in preparing diaphragms according to this method may be cell liquor, aqueous sodium chloride, aqueous sodium hydroxide, water, water containing a surfactant, or an organic solvent.

The asbestos diaphragm is drawn onto the cathode in the conventional way, allowed to dry. Thereafter the asbestos diaphragm may be washed or rinsed with water or an organic solvent to remove the solid sodium chloride precipitated in and on the diaphragm. The diaphragm is then treated with the ion exchange resin as described above. Thereafter the cathode, having an ion exchange resin treated asbestos diaphragm, is installed in an electrolytic cell, and electrolysis carried out.

Suitable slurries that provide a diaphragm containing from about 5 to about 50 weight percent cellulose may be prepared by adding cellulose and asbestos to cell liquor. Particularly satisfactory slurries contain from about 0.6 to about 2 weight percent asbestos, and from about 0.03 to about 0.6 weight percent cellulose. By "cell liquor" is meant a solution containing from about 10 to about 15 weight percent of NaOH and from about 7 to about 15 weight percent of NaCl.

The slurry of asbestos and cellulose in cell liquor may be aged for from about 1 to about 7 days. Additionally air or nitrogen may be bubbled through the slurry.

The asbestos-cellulose diaphragm may be drawn onto the cathode structure by vacuum deposition, as is well known in the art.

According to a still further method, a particularly thin, rugged diaphragm may be prepared by drawing the asbestos onto the electrolyte-permeable cathode from a liquid composition of a suitable organic solvent and the ion exchange resin.

According to this method, the asbestos is slurried in a liquid composition containing an organic solvent and the ion exchange resin. Typically, the slurry contains from about 0.5 percent to about 2.0 percent asbestos by weight. The liquid composition, that is, the solvent and the ion exchange resin, typically contains from about 0.0005 percent to about 0.05 percent by weight of the ion exchange resin, with the balance being the organic solvent.

Suitable organic solvents are those organic materials having hydroxyl groups. The preferred solvents are polyfunctional alcohols, e.g. glycols. Included therein are ethylene glycol, propylene glycol, and glycerol. Alcohols may be used in lieu of glycols, although with less satisfactory results. For example, ethanol, propanol, and butanol, may be used. The asbestos is drawn onto the cathode screen by inserting the cathode into the liquid composition and drawing a vacuum within the cathode, until a sufficient deposit of asbestos is provided on the cathode. The cathode-asbestos diaphragm combi-

nation is then removed from the liquid composition. Thereafter, electrolysis may be carried out.

Diaphragms may also be prepared according to this invention by coating the individual fibers of the asbestos prior to drawing the fibers onto the cathode structure. Thus, a liquid composition is provided which contains asbestos fibers previously coated with ion exchange resin and a liquid. The liquid may be water, cell liquor, or an organic solvent. The asbestos fibers, having been coated or treated with the ion exchange resin, are drawn onto the cathode structure.

Various methods may be used to treat the asbestos fibers with the ion exchange resin prior to placing the fibers into the liquid composition. According to one method, the asbestos fibers may be placed into a rotating drum, or they may be subjected to a flow of gas, i.e., air, causing the fibers to appear fluidized. While the fibers are being fluidized, a liquid composition containing the ion exchange resin and a solvent is sprayed onto the fibers. During this treatment, the temperature of the agitated fibers is maintained above the boiling temperature of the solvent, causing the solvent to vaporize and deposit the ion exchange resin on the individual fibers. Thus, agitated asbestos fibers, maintained at a temperature of about 100°C. to about 120°C. may be sprayed with a liquid composition containing from about 1 percent by weight to about 10 percent by weight of the ion exchange resin, e.g. poly(tetrafluoroethylene-trifluorovinyl sulfonic acid) in ethyl alcohol. The ethyl alcohol evaporates upon contact with the heated asbestos, depositing a film of the ion exchange resin onto the asbestos.

Alternatively, the asbestos fibers may be precoated with the ion exchange resin by another method which assures a high degree of contact between the surface of the asbestos fibers and the ion exchange resin. For example, the solution containing the ion exchange resin may be sprayed onto the asbestos while the asbestos is agitated in a vibratory bin or in a mixer.

Alternatively, the ion exchange resin may be present in the liquid composition with the dispersed asbestos fibers. Thus, a liquid composition may be prepared containing from about 0.5 to about 10 percent by weight asbestos fibers and from about 0.001 percent to about 0.1 percent by weight of an ion exchange resin, e.g. poly(tetrafluoroethylene-trifluorovinyl sulfonic acid) in a suitable solvent. When this is done, the sulfonic acid groups of the ion exchange resin may react with the clumps of asbestos or with ions in the solvent thereby either having a lower rate of adsorption with the asbestos or forming an insoluble precipitate. Accordingly, best results are obtained if the sulfonic acid groups are "blocked." Suitable blocking agents include esters, acetals, ketals, anhydrides, and ethers. Thereafter, the asbestos, treated with the ion-exchange resin, may be drawn onto the cathode structure and the ion-exchange resin converted to the insoluble sodium form after installation in the cell.

EXAMPLE I

A cathode-diaphragm assembly was prepared having an ion exchange resin treated porous asbestos diaphragm and utilized in a diaphragm electrolytic cell.

A solution of 132 grams per liter of sodium chloride and 121 grams per liter of sodium hydroxide was prepared. To 1,626 milliliters of this solution were added 22.1 grams of Johns-Manville "4T" asbestos and 9.9

grams of Johns-Manville "3T" asbestos. Johns-Manville "4T" asbestos is a short-fiber chrysotile asbestos having a Quebec Asbestos Producers Association Quebec Screen Test of 0, 2, 10, 4, a range of fiber lengths of from about 1/16 to 1/2 inch, and a range of fiber diameters from about 0.5 to about 39 microns. Johns-Manville "3T" asbestos is a long-fiber chrysotile having a Quebec Asbestos Producers Association Quebec Screen Test of 2, 8, 4, 2, a range of fiber lengths of from about 1/4 to 1 inch, and a range of fiber diameters of from about 0.5 to about 30 microns.

The slurry was aged for 3 days. After the aging the asbestos was deposited onto an iron mesh cathode screen. Deposition was accomplished by drawing the slurry through the cathode screen three times. Thereafter the cathode and diaphragm were dried in air, at room temperature, for 15 days.

An ethanol solution containing 2 weight percent DuPont "XR" (Trademark) Resin, a polymeric fluorocarbon sulfonic acid ion exchange resin having an equivalent weight of about 670 grams per acid unit, and having less than 1 percent C-H bonds as determined by nuclear magnetic resonance and infrared spectroscopy was brushed onto the asbestos diaphragm surface. The cathode-diaphragm assembly prepared in this way was heated in air to 200°C. for 6 hours, then allowed to cool in air. The cathode-diaphragm assembly was then installed in a laboratory diaphragm cell.

The laboratory electrolytic diaphragm cell used in this example had a 1,000 cubic centimeter capacity catholyte compartment fabricated of 10 gauge steel sheet, and an anolyte compartment having a 1,000 cubic centimeter capacity fabricated of 1/2 inch thick Grade-1 titanium. The anode, measuring 5 inches by 7 inches, was 1/16 inch Grade-1 titanium mesh coated with platinum and iridium. The cathode was 6 by 6 mesh to the inch, 3/16 inch, number 13 steel screen. The gap between the anode and the diaphragm was 1/4 inch.

Electrolysis was conducted with a brine feed containing 257 grams per liter of sodium chloride and having a pH of about 10.3 to 11.0. Electrolysis was commenced at a current density of 120 amperes per square foot. After 13 days the current density was increased to 190 amperes per square foot.

Initial current efficiency was 73 percent but increased to 84 percent after 5 days and to 89 percent after 14 days. Thereafter until the fifty-second day cell efficiency remained between 85 and 90 percent and caustic concentration in the cathode product remained between 125 and 130 grams per liter.

EXAMPLE II

Two diaphragms were prepared for use in identical laboratory diaphragm cells. One diaphragm was asbestos with an ion exchange resin coating. The other diaphragm was drawn from the same asbestos slurry but was not given an ion exchange resin coating. Both diaphragms were prepared from a slurry prepared as in Example I hereinabove. The slurry was aged for 18 days, deposited on the iron mesh cathodes, the diaphragms washed by drawing water through the diaphragms, and dried in air at 50°C. for 3 hours.

After drying, one diaphragm was coated with 12.5 grams of a solution of 1 weight percent DuPont "XR" (Trademark) fluorocarbon sulfonic acid ion exchange resin described in Example I above, but having an

equivalent weight of about 1,300 grams, in ethanol, and dried in air, thereby providing a cathode-diaphragm assembly containing an asbestos member with 0.53 gram of ion exchange resin per square foot of diaphragm area. The second diaphragm was drawn from the same slurry in the same way, but did not receive any resin coating.

The cathode-diaphragm assemblies were utilized in laboratory diaphragm cells as described in Example I hereinabove. Electrolysis of a brine containing 257 grams per liter of sodium chloride, at a pH of 10.3 to 11.0 was conducted at a current density of 500 amperes per square foot and an inter-electrode gap of $\frac{1}{8}$ inch.

The resin-treated diaphragm had a cell voltage of 4.06 volts compared with 4.40 volts for the untreated diaphragm. After 28 days of electrolysis the resin-treated diaphragm appeared to be uneroded while the non-treated diaphragm appeared to be substantially eroded.

EXAMPLE III

A cathode-diaphragm assembly was prepared having an ion exchange resin treated porous asbestos diaphragm.

A cell liquor was prepared containing 135 grams per liter of sodium hydroxide and 175 grams per liter of sodium chloride. To this cell liquor solution was added sufficient Johns-Manville 3T-4T asbestos to provide a slurry containing 1.5 weight percent asbestos. The slurry was aged for 3 days. Thereafter, sufficient Solka-Floc cellulose was added to the slurry to provide a cellulose concentration of 15 weight percent cellulose based on the total weight of the solids, i.e., asbestos and cellulose. The asbestos and cellulose were deposited onto an iron mesh cathode by drawing the slurry onto the cathode screen at a vacuum of 7 inches of mercury. The deposited diaphragm was then washed with water, and then maintained at a vacuum of 16 inches of mercury and dried at 100°C. for 22 hours.

A solution was prepared containing 10 weight percent DuPont "XR" (Trademark) resin, described in Example II above, in ethanol. The cathode-diaphragm structure was dipped into the resin-ethanol solution and the solution was allowed to permeate the diaphragm. Thereafter, the diaphragm-cathode assembly was heated at 100°C. for 4½ hours.

At a brine head of 9 inches, the diaphragm had a porosity of 1.10 gallons of brine per hour per square foot. The voltage across the diaphragm was then tested at a minimum anode to diaphragm gap, i.e., with the anode touching the diaphragm, at current densities of from 20 to 81 amperes per square foot. The resulting voltages were extrapolated to 190 amperes per square foot indicating a predicted cell voltage of 2.9 volts.

Thereafter, the cathode-diaphragm assembly was installed in a laboratory electrolytic cell. After 7 days of electrolysis, the cell current efficiency was 96.5 percent, the cell liquor had between 0.01 and 0.02 weight percent NaClO_3 , the cell gas contained between 0.01 and 0.10 volume percent hydrogen, the cell voltage was 3.09 volts, and the cell liquor and diaphragm IR drop was 0.69 volts.

EXAMPLE IV

A cathode-diaphragm assembly was prepared having an ion-exchange resin treated asbestos diaphragm.

An asbestos-cellulose slurry was prepared as described in Example III hereinabove. The asbestos and cellulose were drawn onto an iron mesh cathode as described in Example III hereinabove. The resulting diaphragm was not washed but was dried under a vacuum of 20 inches of mercury applied to the cathode side at 85°C. for 72 hours.

A liquid composition containing 1.0 weight percent DuPont "XR" (Trademark) resin, described in Example II above, in ethanol, was poured onto the surface of the diaphragm and a vacuum of 17 inches of mercury was drawn within the cathode. The resulting resin impregnated diaphragm, containing 2.0 grams of resin per square foot of diaphragm surface was heated at 100°C. for 1 hour.

The porosity of the diaphragm was tested as described in Example III hereinabove and a porosity of 0.71 gallons per square foot per hour of brine was measured. Thereafter, the diaphragm IR drop at a minimum anode to diaphragm gap was measured as described in Example III and extrapolated to 190 amperes per square foot yielding a predicted cell voltage of 3.02 volts.

The cathode-diaphragm assembly was installed in a laboratory diaphragm cell. Electrolysis was commenced and chlorine was seen to be evolved. After 7 days of electrolysis, the cell liquor contained 0.01 weight percent of NaClO_3 , the cell gas contained 0.01 volume percent hydrogen, the cell voltage was 3.40 volts, and the cell liquor and diaphragm IR drop was 1.01 volts.

EXAMPLE V

A cathode-diaphragm assembly was prepared having an ion exchange resin treated asbestos diaphragm.

A slurry of cellulose and asbestos in cell liquor was prepared and drawn onto an iron mesh cathode as described in Example III hereinabove. The diaphragm was not washed after pulling but was dried under a vacuum of 23 inches of mercury on the cathode side at a temperature of 85°C. for 72 hours.

A 10 weight percent solution of DuPont "XR" (Trademark) resin described in Example II above, was poured onto the surface of the asbestos diaphragm and a vacuum of 17 inches of mercury was established in the cathode-diaphragm structure. The resulting diaphragm having approximately 3.0 grams of XR-resin per square foot was heated at a temperature of 100°C. for 77 hours.

The resulting cathode-diaphragm assembly had a porosity of 0.61 gallon of brine per square foot per hour determined as described in Example III hereinabove. The minimum anode to diaphragm gap voltage drop, measured and calculated as described in Example III hereinabove, yielded a predicted cell voltage of 3.0 volts at 190 amperes per square foot.

The cathode-diaphragm assembly was installed in a laboratory diaphragm cell. Electrolysis was commenced and chlorine was seen to be evolved. After 7 days of electrolysis, the cell liquor contained 0.02 weight percent NaClO_3 , the cell gas contained 2.4 volume percent hydrogen, the cell voltage was 3.24 volts, and the diaphragm-cell IR liquor voltage drop was 0.78 volt.

EXAMPLE VI

A cathode-diaphragm assembly was prepared having

an ion exchange resin treated porous asbestos diaphragm.

A slurry of asbestos and cellulose in cell liquor was prepared as described in Example III hereinabove. The slurry was aged for 3 days. The asbestos and cellulose were drawn onto a mesh cathode as described in Example III hereinabove. The cathode-diaphragm assembly was not washed but was dried with a vacuum on the cathode side of 23 inches of mercury at 85°C. for 72 hours.

A solution containing 10 weight percent DuPont "XR" (Trademark), described in Example II above, resin in ethanol was poured onto the surface of the asbestos diaphragm and a vacuum of 17 inches of mercury was established inside the cathode. The resulting diaphragm, which contained about 1.0 gram of the ion exchange resin per square foot of asbestos, was dried at 100°C. for 72 hours.

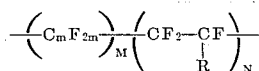
The porosity of the diaphragm, determined as described in Example III hereinabove, was 0.74 gallon per square foot per hour. The minimum anode to diaphragm gap cell voltage was measured and calculated as described in Example III hereinabove and yielded a predicted cell voltage of 3.13 volts at 190 amperes per square foot.

The resulting cathode-diaphragm assembly was installed in a laboratory diaphragm cell. Electrolysis was commenced; chlorine was seen to be evolved. After 7 days of electrolysis, the cell liquor contained 0.01 weight percent NaClO_3 , the cell gas contained from about 0.3 to about 2.4 volume percent hydrogen, cell voltage was 3.39 volts, and the cell liquor and diaphragm IR drop was found to be 0.69 volt.

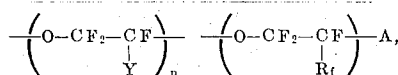
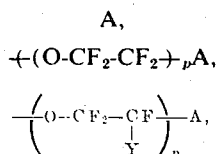
Although the invention has been described with reference to particular specific details and contains preferred exemplifications, it is not intended to thereby limit the scope of this invention except insofar as the details are recited in the appended claims.

We claim:

1. In a process for electrolyzing alkali metal chloride brines in an electrolytic cell having an anolyte compartment and a catholyte compartment separated therefrom by an alkali metal chloride brine permeable, fluorocarbon resin containing, asbestos diaphragm, wherein alkali metal chloride brine is fed to said cell and catholyte liquor containing alkali metal chloride and alkali metal hydroxide is recovered from said cell, the improvement wherein said diaphragm contains from about 0.01 to about 22 weight percent of fluorocarbon resin, the fluorocarbon resin being dispersed into the diaphragm to a depth of at least 0.08 inch from one surface thereof, said fluorocarbon resin providing a coating on individual asbestos fiber bundles, and said fluorocarbon resin having the empirical formula:



where m is from 2 to 10, the ratio of M to N is sufficient to provide an equivalent weight of from 600 to 2,000, R is chosen from:



$-\phi\text{A}$, and

$+\text{CF}_2)_p\text{A}$;

where p is from 1 to 3, Y is chosen from the group consisting of $-\text{F}$ and perfluoroalkyls having from 1 to 10 carbon atoms, R_f is chosen from the group consisting of $-\text{F}$ and perfluoroalkyls having from 1 to 10 carbon atoms, and ϕ is an aryl group; and where A is an acid group chosen from the group consisting of

$-\text{SO}_3\text{H}$,
 $-\text{CF}_2\text{SO}_3\text{H}$,
 $-\text{CCl}_2\text{SO}_3\text{H}$,
 $-\phi'\text{SO}_3\text{H}$,
 $-\text{PO}_3\text{H}_2$,
 $-\text{PO}_2\text{H}_2$,
 $-\text{COOH}$, and

$\phi'\text{OH}$ where ϕ' is an aryl group.

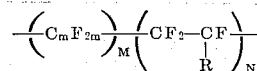
2. The process of claim 1 wherein said diaphragm contains from about 0.3 to about 7.0 weight percent of fluorocarbon resin.

3. The of claim of claim 1 wherein said fluorocarbon resin is dispersed into said diaphragm to a depth of at least 0.15 inch from one surface thereof.

4. The process of claim 1 wherein said diaphragm contains from about 0.01 gram to about 10 grams of fluorocarbon resin per square foot of diaphragm area.

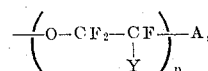
5. The process of claim 1 wherein brine containing from about 280 to about 315 grams per liter of sodium chloride is fed to said cell and a catholyte liquor containing from about 7 to about 15 weight percent sodium chloride and about 10 to about 15 weight percent sodium hydroxide is recovered from said cell.

6. A method of reducing the voltage drop across a sodium chloride brine permeable, fluorocarbon containing, asbestos diaphragm of a chlor-alkali cell while maintaining its physical strength during its use over extended periods of electrolysis, said method comprising providing as the fluorocarbon from about 0.01 to 22 weight percent basis total diaphragm, a hydrophilic fluorocarbon having the empirical formula:



where m is from 2 to 10, the ratio of M to N is sufficient to provide an equivalent weight of from 600 to 2,000, R is chosen from:

A ,
 $+\text{O}-\text{CF}_2-\text{CF}_2)_p\text{A}$,



19

 $-\phi A$, and $-(CF_2)_p A$;

where p is from 1 to 3, Y is chosen from the group consisting of $-F$ and perfluoroalkyls having from 1 to 10 carbon atoms, R_f is chosen from the group consisting of $-F$ and perfluoroalkyls having from 1 to 10 carbon atoms, and ϕ is an aryl group; and where A is an acid group chosen from the group consisting of

 $-\text{SO}_3\text{H}$, $-\text{CF}_2\text{SO}_3\text{H}$, $-\text{CCl}_2\text{SO}_3\text{H}$, $-\phi'\text{SO}_3\text{H}$, $-\text{PO}_3\text{H}_2$, $-\text{PO}_2\text{H}_2$, $-\text{COOH}$, and $\phi'\text{OH}$ where ϕ' is an aryl group.

7. The method of claim 6 wherein said diaphragm

20

contains from about 0.3 to about 7.0 weight percent of hydrophilic fluorocarbon.

8. The method of claim 6 wherein said diaphragm contains from about 0.01 gram to about 10.0 grams of hydrophilic fluorocarbon per square foot of diaphragm area.

9. The method of claim 6 wherein said hydrophilic fluorocarbon is dispersed into said diaphragm to a depth of at least 0.08 inch from one surface thereof.

10. The method of claim 9 wherein said hydrophilic fluorocarbon is dispersed into said diaphragm to a depth of at least 0.15 inch from one surface thereof.

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