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ELECTROLYTIC CELL DIAPHRAGM

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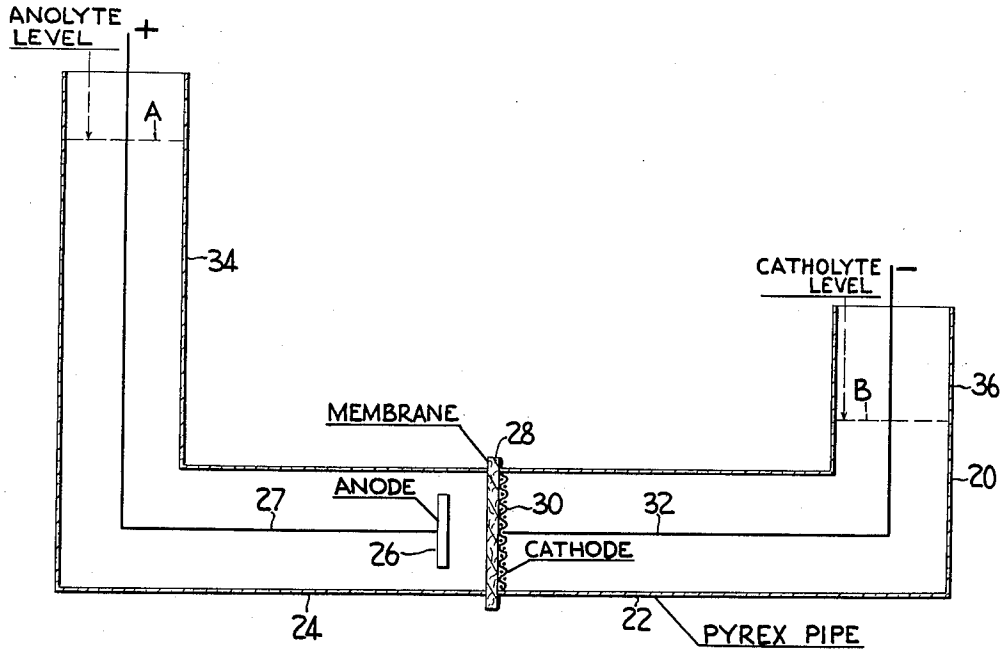


FIG. 1

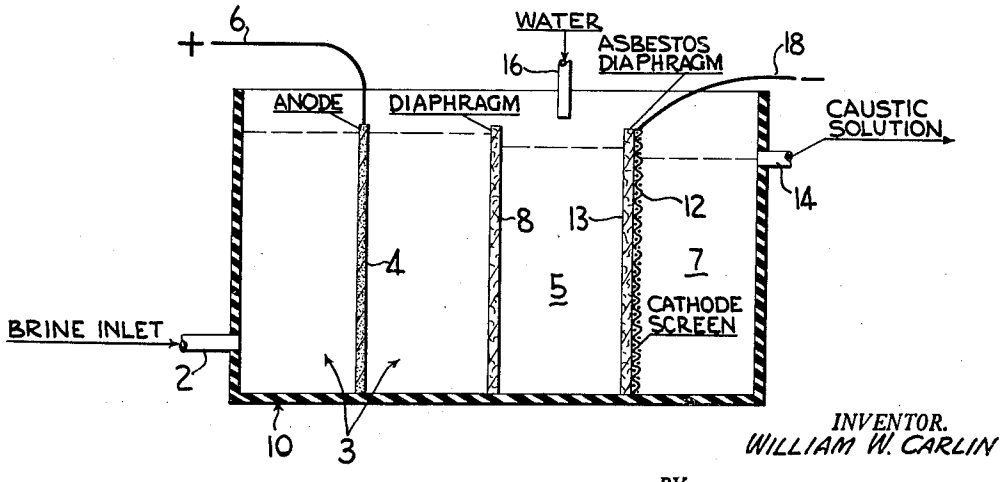


FIG. 2

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ELECTROLYTIC CELL DIAPHRAGM

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This invention relates to a novel type of electrolytic cell suitable for use in the production of alkali metal hydroxide and chlorine.

It is well known that alkali metal chloride solutions may be electrolyzed in so-called diaphragm cells to produce chlorine and alkali metal hydroxide, such as sodium hydroxide. Thus, in diaphragm cells there is normally one of a plurality of anodes disposed opposite one or a plurality of cathodes with a brine solution therebetween. The cathodes normally are perforate in structure and usually are in the form of heavy wire screens. The anodes are separated from the cathodes by a diaphragm, usually of asbestos, in the form of asbestos paper or asbestos felt, which engages and is in contact with the cathode screen on the anode side thereof. The diaphragm thus serves to separate the electrolytic cell into an anode compartment and a cathode compartment.

In the course of operation of a cell of this character, aqueous alkali metal chloride, such as sodium chloride brine, is fed into the anode compartment and a differential hydrostatic pressure is established between the anode compartment and the cathode compartment while an electric potential sufficient to cause electrolysis of the brine and to produce sodium hydroxide and chlorine is established between the anode and the cathode. As a consequence, chlorine is evolved at the anode and is withdrawn from the anode compartment of the cell and the brine flows through the diaphragm and through the cathode screen with consequent evolution of sodium hydroxide and hydrogen at the cathode. The resulting brine-sodium hydroxide solution is then withdrawn from the cathode compartment, and hydrogen is collected at the upper portion of this compartment.

In the usual operation of a cell of this character, it is necessary to avoid establishment of an unduly high concentration of alkali metal hydroxide in the brine solution leaving the cell. Usually, this brine solution contains from 120 to 135 grams per liter of alkali metal hydroxide. Furthermore, it is substantially saturated with the alkali metal chloride and is almost invariably contaminated with a substantial amount of chlorate which must be ultimately removed for many purposes, such as to permit use of the caustic soda or other alkali metal hydroxide in the rayon industry.

According to the present invention, a new cell has been provided which produces sodium hydroxide solution or like alkali metal hydroxide solution having an alkal metal chloride content which is substantially below saturation usually below 0.3 percent and generally in the range of between 0.08 percent and 0.2 percent. In many cases the alkali metal hydroxide thus produced contains little or no chlorate.

The electrolytic cell herein contemplated and which has been provided in accordance with this invention is provided with an asbestos diaphragm which is impregnated with a halogenated drying oil or halogenated solidified drying oil particularly a chlorinated or fluorinated oil or solidified oil. The term "drying oil," as used herein, is intended to include the various oils having drying properties which are normally used in the production of paint films and the like usually having an iodine number above about 130. This term thus includes both drying oils and semi-drying oils. Typical oils contemplated are linseed oil, tung oil, soybean oil, dehydrated castor oil, sunflower seed oil and the like.

The halogenated oil used may be prepared by any convenient method of halogenating the above oils. In the usual practice, the solidified oil is exposed to the action of chlorine or like halogen while the chlorine is held in liquid phase, either as liquid chlorine itself or as an organic solution thereof. Normally the oil is solidified by oxidation and/or polymerization by normal drying methods and then chlorinated or otherwise halogenated. Halogenation normally is continued until the oil or solidified oil contains at least 20 percent, usually 35 to 70 percent by weight of chlorine or a molecular equivalent amount of other halogen; best results being obtained when the chlorine content ranges from about 30 to 45 percent.

Two convenient methods have been used. According to one method, the oil is prehalogenated before contact with the asbestos. According to another method, the asbestos is impregnated with the oil and thereafter the oil is reacted with the liquid chlorine in situ before or after allowing the oil to dry and/or to solidify. In any case, care must be exercised because liquid chlorine tends to react with certain drying oils, such as linseed oil, with explosive violence.

In general, it is desirable to maintain a diluent, such as a halogenated hydrocarbon, present in order to reduce the intensity of the reaction. Typical halogenated hydrocarbons which can be used are methylene chloride, chloroform, carbon tetrachloride, perchloroethylene, trichloroethylene, and like halogenated hydrocarbons which boil at temperatures below about 125° C.

Following impregnation of the asbestos with the halogenated oil, removal of the solvent is conveniently effected by drying the asbestos at a temperature of 110° C. to 150° C. until the solvent has been evaporated. The halogenated oil content of the asbestos usually is 5 percent to 75 percent by weight of the impregnated asbestos.

The resulting asbestos which is impregnated with the chlorinated drying oil is then capable of use as a diaphragm for an electrolytic cell of the type described above. This asbestos usually is in sheet form and appears, upon visual inspection without magnification to be impermeable, and usually is a tough, well-bonded, impregnated fabric having the flexibility of waterproofed cloth. The asbestos fabric thus obtained may be applied readily to the anode side of a cathode screen commonly used in alkali metal chlorine cells substantially in the same way as other diaphragms which are normally used in these cells are applied.

The diaphragms prepared in the above-described manner when operated on the anode side of the cathode screen of alkali metal chlorine cells operate as permionic membranes in such a cell and permit the easy passage of sodium ions across the diaphragm while substantially preventing chloride ion migration from the anode compartment to the cathode compartment. Thus, by substantially wetting the asbestos diaphragm with a chlorinated oil to fill substantially all of the pores of the asbestos utilized with halogenated oil permiselectivity is imparted to the asbestos and the caustic soda produced when such a membrane is utilized in an alkali chlorine cell is substantially free of chlorides. The diaphragms in cells of this character are essentially impervious to the flow of brine and the ions contained therein with the exception of the sodium ion which can migrate across the diaphragm and find its way into the catholyte of the cell thereby producing sodium hydroxide.

The accompanying drawing diagrammatically illustrates certain typical alternative embodiments in which the diaphragms herein contemplated may be used. In this drawing:

FIG. 1 illustrates a laboratory electrolytic cell use-

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ful for testing diaphragms of this character; and

FIG. 2 illustrates a diagrammatic vertical sectional view of another type of cell which may be used for production of chlorine and caustic soda.

As shown in FIG. 1, an electrolytic cell **20** is composed of two abutting L-shaped sections of pipe **22** and **24**, respectively. This pipe conveniently may be of any corrosion-resistant material but, for laboratory purposes, may be made of Pyrex or like transparent material. A cathode **30** of wire screen, having disposed thereon a diaphragm or membrane **28** of the type described above, engages the respective ends of the pipes **24** and **22**, and the entire assembly is clamped tightly to produce a seal. The cathode **30** is held in contact with the membrane **28**.

In pipe **24** there is disposed a suitable anode of any corrosion-resistant material, such as carbon or platinum, which is connected through line **27** to the positive pole of a direct current power source. The cathode is connected through line **32**, which runs through pipe **22**, to the negative pole of such power source.

The leg **34** of the cell section **24** is longer in length than the leg **36** of the cell section **22**. This provides a simple means whereby the level of the anolyte in cell section **24** may be held at a level (designated "A") substantially above the level of the liquor in the cathode compartment **22** (designated "B"). As a consequence, it is possible to establish a substantial hydrostatic head of the order of 1 to 20 inches of brine between the anode compartment and the cathode compartment.

In the operation of the cell illustrated in FIG. 1, a diaphragm prepared substantially as described above and impregnated with a chlorinated drying oil is mounted in the place designated in the drawing, the anolyte compartment is filled with a saturated brine, such as saturated sodium chloride or potassium chloride solution in water, and the cathode compartment is filled with water. During the operation, the anolyte is maintained near saturation with the alkali metal chloride. Chlorine and hydrogen evolved in the course of the operation are separately withdrawn as formed from the anolyte or anode containing compartment and the catholyte or cathode containing compartment respectively.

The following is a typical example of a suitable manner of performing this invention using the cell illustrated in FIG. 1:

Example I

Enough liquid chlorine was placed in a 2-liter Pyrex jar which was immersed in a Dry-Ice-methylene chloride bath at minus 40° C. to provide a pool of the liquid chlorine about one-half inch deep. Additional liquid chlorine was introduced into the jar at the rate of about 2 milliliters per minute and drying oil was fed in a continuous stream into the chlorine pool at the rate of 1.5 milliliters per minute, until about 350 milliliters of drying oil had been added. During this addition, the oil and chlorine were mixed together vigorously.

Following this, the drying oil thus chlorinated and which contains about 20 percent to 70 percent by weight of combined chlorine, was dissolved in methylene chloride in a ratio of one part by volume of the chlorinated oil to 3 volumes of the methylene chloride. Asbestos paper was immersed in the oil methylene chloride mixture and completely wetted. The paper was removed and the solvent allowed to evaporate. The paper thus produced was dried in an oven in an air atmosphere at a temperature of 110° C. for one hour.

In a test using a cell of the type illustrated in FIG. 1, the cathode was a perforated metal disc having an effective area of one square inch. The level of the liquor in the anode compartment was held six inches above that in the cathode compartment. During operation of the cell, suitable means (not shown) were provided to withdraw the anolyte and circulate it through a bed of sodium chloride in order to saturate the brine. Evolved chlorine was removed from the anolyte compartment by a two-inch water vacuum.

Using a membrane in which soybean oil was the drying oil used and the oil obtained contained about 42 percent by weight of combined chlorine, electrolysis was continued for a period of 40 hours with a cathode current density of one ampere per square inch, the cell voltage between the anode and the cathode being 3.75 volts. The cell liquid obtained from the cathode compartment at the end of the 40-hour period contained 325.5 grams per liter of sodium hydroxide and only 0.08 percent by weight of sodium chloride measured on the anhydrous sodium hydroxide basis.

Similar results were obtained using linseed oil, boiled linseed oil, and tung oil.

Example II

A membrane prepared, as in Example I, except that boiled linseed oil was used, was placed in a cell of the type illustrated in FIG. 1 and the process described in Example I was repeated. The chlorinated linseed oil contained 40 percent by weight of chlorine. Electrolysis was continued over a period of 12 days at a cathode current density of 0.8 ampere per square inch and a cell voltage of 3.45 volts. The liquor in the catholyte contained 187 grams per liter of sodium hydroxide and the NaCl content was 0.23 percent by weight measured on the basis of the anhydrous sodium hydroxide.

According to another method of preparing a diaphragm, the asbestos sheet may be saturated with a solution of the unhalogenated drying oil and the solvent drawn off. Thereafter, the oil impregnated asbestos sheet may be immersed in liquid chlorine for a short time, for example, one or two minutes and thus chlorinated. The product thus heated is dried at an elevated temperature, for example, 100–150° C.

It is also possible to impregnate the asbestos sheet with drying oil (linseed tung or the like) and to dry the oil by allowing the impregnated sheet to stand in air, by heating, irradiating with infra red or the like. The thus cured sheet may then be chlorinated as described above.

In general, the chlorination is conducted by contacting the oil with chlorine in liquid phase, that is liquefied chlorine or elemental chlorine dissolved in a solvent such as a liquid hydrocarbon chloride (carbon tetrachloride, chloroform, trichloroethylene, methylene chloride, tetrachloroethane, ethylene dichloride or the like). This treatment produces products which are most durable. Somewhat less durable products may be obtained by treating asbestos impregnated with a drying oil or solidified drying oil with gaseous chlorine. Diaphragm impregnated with the corresponding fluorinated drying oils may be prepared by immersing in or otherwise placing in contact diaphragms impregnated with the chlorinated oil or solidified oil, hydrogen fluoride or a solution thereof, whereby to replace with fluorine partially or completely the chlorine atoms combined with the oil.

As stated above, FIG. 2 is a diagrammatic view of another type of cell which can be used in the testing of the diaphragms herein contemplated. As therein shown, there is provided an electrolytic cell **10** having brine inlet **2** and caustic soda outlet **14** on opposite sides of the cell. The cell is divided by a diaphragm **8** constructed as described above. This diaphragm divides the cell into an anolyte compartment which contains anode **4** and a catholyte compartment which contains cathode **12** typically in the form of wire screen. An asbestos diaphragm **13** of the usual unimpregnated type is disposed on and in contact with the wire screen. A water pipe **16** is disposed above the central compartment **5** of the cell between diaphragm **8** and asbestos diaphragm **13**. A brine outlet not shown is provided for compartment **3**. The cell also is provided with a suitable cover adapted to collect separately chlorine and hydrogen evolved in operation of the cell. This is a feature well understood in the art and need not be discussed here.

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In the operation of this cell, the anolyte compartment is filled with sodium chloride brine, usually saturated brine, and the central compartment and the catholyte compartment are filled with water. The respective hydrostatic heads between the compartments are adjusted so that the highest head is in compartment **3** and the lowest head is in compartment **7**. Brine is fed through inlet **2** into compartment **3** at a controlled rate, and removed therefrom on a continuous basis. Water is continuously fed into compartment **5** and caustic liquor is removed at **14** continuously, the rates of feed and removal being adjusted to provide a higher liquid level in compartment **5**. An electric potential is established between the anode and the cathode.

When this cell is operated, it has been found that a sodium hydroxide solution is formed both in compartment **5** and compartment **7**.

The following example illustrates the manner in which the cell illustrated in FIG. 2 is employed to produce chlorine and sodium hydroxide from sodium chloride brine.

Example III

The cell of FIG. **2** composed of three compartments **3**, **5** and **7** is employed to produce chlorine and caustic soda from a sodium chloride brine. The asbestos diaphragm **8** of the cell is prepared as in Example I by impregnation with chlorinated soybean oil as the drying oil containing about 42 percent by weight of combined chlorine. Steel, wire screen cathode **12**, having an unimpregnated diaphragm **13** disposed on and in contact with the screen is employed. Cell anode **4** is a graphite electrode constructed of AGR-Acheson graphite. Diaphragm **8**, cathode **12** and its associated diaphragm **13** divide the cell into three compartments **3**, **5** and **7**. Brine (a saturated aqueous solution of NaCl) is introduced through inlet **2** and compartment **3** is filled to a point about 1–2 inches below the top of diaphragm **8**. Water is introduced through inlet **16** into compartments **5** and **7**. The liquid level in the three compartments is controlled so that compartment **3** has the highest hydrostatic head, compartment **7** has the lowest hydrostatic head and the hydrostatic head in compartment **5** is intermediate the heads maintained in compartments **7** and **3**. Control of the respective hydrostatic heads is obtained by regulating the respective brine and water flow rates and the rate at which caustic soda is discharged from the cell.

The hydrostatic head in compartment **3** is controlled to 1 to 2 inches above the head in compartment **5** and the hydrostatic head in compartment **5** is controlled to 1 to 4 inches higher than the head in compartment **7**. Current is passed though the cell at a cathode current density of 0.8–1.0 amperes per square inch and a cell voltage of 3.8–4.2 volts. Brine and water feed rates to the cell and caustic liquor and brine flow rates from the cell are regulated to maintain the hydrostatic heads in the compartments at the indicated levels. The liquor taken from the caustic outlet contains 120–300 grams per liter of sodium hydroxide and the NaCl content is less than 0.25 percent by weight measured on the basis of the anhydrous sodium hydroxide.

The above electrolytic cells are simply typical of the type of cells which may be used in demonstrating the utility of the diaphragms herein contemplated. However, the diaphragms illustrated and described in the cells disclosed in United States Letters Patents Nos. 1,907,818, granted May 9, 1933, to Ralph M. Hunter; 2,078,517, granted April 27, 1937, to Lafayette D. Vorce; 2,149,004, granted February 28, 1939, to Herbert I. Allen; 2,368,861, granted February 6, 1945, to Dwight R. Means; 2,409,912, granted October 22, 1946, to Kenneth E. Stuart; 2,430,374, granted November 4, 1947, to Kenneth E. Stuart; and 2,681,887, granted June 22, 1954, to Clarence A. Butler, Jr., all may be impregnated with halogenated drying oil as herein contemplated and described.

If desired, the asbestos may be deposited upon the cathode before effecting the impregnation. Thus, one convenient method of depositing asbestos upon a cathode involves immersion of the cathode in an asbestos slurry and drawing the slurry through the cathode perforations in order to cause a deposition of the asbestos upon the cathode surface.

Following production of a diaphragm on the cathode in this manner, a solution of the halogenated oil may be sprayed or otherwise applied to the asbestos in order to impregnated the asbestos. Thereafter, the impregnated asbestos is dried.

According to a further embodiment of this invention, it is possible to produce improved diaphragms by impregnating the asbestos with polymers having ion exchange properties. This can be accomplished conveniently by forming a mixture of maleic anhydride and divinyl benzene or like polymerizable composition and impregnating the asbestos with this mixture. Thereafter, the mixture is polymerized by heat and/or ultraviolet light, so that a polymer containing the carboxylate groups —COO— is formed in the asbestos matrix due to the presence of maleic anhydride. Following this polymer formation the impregnated asbestos may be coated with the halogenated drying oil as described above to further improve the diaphragm.

Asbestos diaphragms may also be conveniently impregnated with other polymeric materials thereby giving rise to diaphragms having improved properties usually containing at least 6 percent by weight of resin based on the weight of the asbestos. Thus acid forming olefinic polymerizable monomers such as maleic anhydride, acrylic acid, crotonic acid, methacrylic acid, acrylic esters, (methylacrylate or the corresponding ethyl, propyl or like esters) methylmethacrylate or homologous methacrylic esters, anhydride and acid chlorides of acrylic acid, styrene parasulfonic acids or salts or esters thereof and other like monomers preferably having free carboxyl or sulfonic acid groups present therein in the acid, salt or anhydride form may be incorporated in the asbestos and copolymerized with polyvinyl aromatics such as divinyl benzene, divinyl toluenes, divinyl naphthalenes, divinyl phenyl vinyl ethers, divinyl diphenyls, substituted alkyl derivatives thereof, such as dimethyl divinyl benzenes and similar polymerizable aromatic compounds which are polyfunctional with respect to vinyl groups, or diallyl phthalate, (or like diallyl esters,), ethylene glycol dimethacrylate, or like materials which contain at least two polymerizable —C=C— groups and which polymerize to form a polymer which is insoluble in organic solvents such as acetone.

Copolymers of polyvinyl aromatic compounds, acid forming monomers and monovinyl aromatic compounds may also be utilized to impregnate the asbestos. Typical of monovinyl aromatic compounds utilized in copolymerization of this type are vinyl toluenes, vinyl naphthalenes, vinyl ethyl benzene, vinyl chlorobenzenes, vinyl xylenes, alpha substituted alkyl derivatives thereof such as alpha methyl vinyl benzene and other like polymerizable materials.

In addition other resins preferably containing free acid group may be utilized to impregnate asbestos and give rise to diaphragms having enhanced properties. Thus phenol-formaldehyde resin, aniline-formaldehyde resin, soybean oil epoxide and tolylene diisocyanate, silicone resin, copolymerized styrene and maleic anhydride, copolymerized styrene, maleic anhydride and linseed oil, copolymerized styrene with acrylic acid, copolymerized styrene and methacrylic acid, copolymerized maleic anhydride, divinyl benzene and styrene, para-dialkylamino styrene and acrylic acid, dialkyl paravinyl benzylamine and acrylic acid, copolymerized polyvinyl and monovinylaromatics including styrene such as styrene and divinyl toluenes, vinyl naphthalenes and dimethyl divinyl benzene, ethylene glycol dimethacrylate, vinyl ethyl benzene and

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divinyl naphthalenes and other like materials which contain two or more polymerizable —C=C— groups and which polymerize to form polymers which are insoluble in organic solvents such as acetone.

Polymers and copolymers of other ethylenically unsaturated compounds may also be utilized as the impregnating substance and may include butadiene-styrene copolymers, natural rubber, butadiene-acrylonitrile copolymers, isobutylene polymers, and copolymers of isobutylene and other polymerizable compounds such as vinyl acetate, vinyl chloride, styrene, methyl methacrylate and the like.

While polymers and copolymers which are substantially water insoluble and relatively inert in acid and alkali solutions in general impart to asbestos diaphragms enhanced properties, it is preferred that the polymeric impregnant present in the asbestos contain free acid groups. Thus, polymers and copolymers impregnated in an asbestos diaphragm which do not contain such groups are preferably treated by sulfonation or carboxylation to provide such groups in the finished polymeric impregnant. Thus, polymer impregnated asbestos not containing acid groups may be conveniently treated by contacting the polymer containing asbestos with chlorosulfonic acid, solutions of sulfur trioxide in an organic medium such as ethylene dichloride, carbon tetrachloride and the like.

The polymeric compounds utilized in impregnating the asbestos are conveniently present in a suitable solvent. Typical solvents suitable for this purpose are dioxane, and other ethers, chlorinated hydrocarbons such as ethylene chloride or ketones such as acetone. The solvent is satisfactory so long as it permits the formation of solutions containing the desired concentration of polymer and does not interfere with the polymerization.

Catalysts may also be incorporated in the solutions of polymeric compounds prior to polymerization and typical of catalysts which may be utilized are benzoyl peroxide, 2 azo-bis(isobutyronitrile), boron trifluoride and isopropyl peroxydicarbonates or like peroxy catalyst.

The polymer loading on the asbestos diaphragms prepared as set forth herein generally are in a range of 6 to 300 percent polymer by weight based on dry asbestos. Preferably the polymer is in a range of 82 to 122 percent by weight. Dry asbestos is asbestos dried at 100° C. to a constant weight. The polymer loading above set forth include polymers in which halogenated oils are also present.

The term "asbestos" used in the specification and claims refers to amphibole and serpentine mineral varieties and includes chrysotile, crocidolite, anthophyllite, amosite and like minerals. The preferred asbestos materials utilized to form the novel diaphragms herein described are the chrysotile and crocidolite varieties.

The following are typical examples of suitable methods of impregnating an asbestos diaphragm in accordance with this invention.

Example IV

A solution was prepared by mixing 54 grams of 20 to 25 percent divinyl benzene, 19.6 grams of maleic anhydride and 0.5 gram of benzoyl peroxide in 16 milliliters of dioxane. The solution was poured onto two 6-inch by 6-inch squares of North American, type 41, crocidolite asbestos. The wetted asbestos sheets were then placed between two glass plates and heated in an oven at between 70° to 90° C. for four hours. One of the membranes so prepared was placed in an electrolytic cell of the type shown in FIGURE 1 as the cathode diaphragm and the cell was operated under the same conditions as described in Example I. The cell liquor obtained from the cathode compartment at the end of a 40-hour period of electrolysis contained 150 grams per liter of sodium hydroxide and only 0.08 percent by weight of sodium chloride measured on the anhydrous sodium hydroxide basis.

Example V

A solution was prepared by mixing 54 grams of 20 to 25 percent divinyl benzene, 19.6 grams of maleic anhydride and 0.5 gram of benzoyl peroxide in 16 milliliters of dioxane. To this solution was added and mixed therewith 5 grams of chlorinated linseed oil. The solution was poured onto a 6-inch by 6-inch square sheet of North American, type 41, crocidolite asbestos. The wetted sheet was then placed between two glass plates and placed in an oven operated at 70° to 90° C. for a period of four hours.

The membrane so prepared was placed in an electrolytic cell of the type shown in FIGURE 1 as the cathodes diaphragm and the cell was operated under the same conditions described in Example I. The cell liquor obtained from the cathode compartment at the end of a 40-hour period of electrolysis contained 180 grams per liter of sodium hydroxide and less than 0.2 percent by weight of sodium chloride measured on the anhydrous sodium hydroxide basis.

Example VI

A solution is prepared by dissolving 12.7 grams of 26.4 percent divinyl benzene in 54.5 milliliters of toluene containing 0.123 grams of benzoyl peroxide. The solution is poured onto two 6-inch by 6-inch squares of North American, type 41, crocidolite asbestos 0.05 inches thick. The wetted asbestos sheets are then placed between two glass plates and heated in an oven at between 70° to 90° C. for four hours. The finished membranes are placed in electrolytic cells of the type shown in FIGURE 1 as the cathode diaphragm and the cells are operated under the same conditions as described in Example I. The cell liquor obtained from the cathode compartment at the end of a 40-hour period of electrolysis contains 60 grams per liter of sodium hydroxide and only 0.08 percent by weight of sodium chloride measured on the anhydrous sodium hydroxide basis.

Example VII

A solution of 28 grams of resorcinol in 100 milliliters of methanol is added to two 6-inch by 6-inch square sheets of chrysotile asbestos 0.05 inch thick. The wetted sheets are blotted with paper towels to remove excess solution and then are dried in an oven at 70° C. for four hours. To the dried asbestos sheets a solution containing 25 grams of diethylenetriamine and 78 grams of 36 percent formaldehyde is added to each of the membranes. Excess solution is blotted away with paper towels. One of the membranes is then placed in an electrolytic cell of the type shown in FIGURE 1 as the cathode diaphragm and the cell is operated under the same conditions as described in Example I. The cell liquor obtained from the cathode compartment at the end of a 40-hour period contains 78 grams per liter of sodium hydroxide and only 0.08 percent by weight of sodium chloride measured on the anhydrous sodium hydroxide basis.

Example VIII

A solution is prepared by mixing 22 grams of maleic anhydride, 5.8 grams of 50–60 percent divinyl benzene and 1.2 grams of styrene, and 1.8 grams of dichloro benzoyl peroxide in 14.5 grams of dioxane. 22 milliliters of this solution is added to a 6-inch by 6-inch sheet of crocidolite asbestos 0.047 inch thick. The moist sheet is then placed between two pieces of glass. The edges of the glass are sealed with cellophane tape and the glass is placed in an oven and heated at 55° C. for four hours. This treatment is repeated four additional times after the solvent and unreacted monomer have been evaporated. The sheet is removed and is placed in an electrolytic cell of the type shown in FIGURE 1 as the cathode diaphragm. The cell is operated under the same conditions as described in Example I. The cell liquor from the cathode compartment of the cell at the end of a 40-hour period contains 240 grams per liter of sodium hydroxide

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and less than 0.2 percent by weight of sodium chloride measured on the anhydrous sodium hydroxide basis.

The term "acid group" as used in the claims hereinafter appended means acidic groups including carboxylic, sulfonic and like groups as well as the anhydrides or salts thereof, notably the sodium, potassium or like alkali metal salts thereof.

Although the present invention has been described with reference to the specific details of certain embodiments, it is not intended that such embodiments shall be regarded as limitations upon the scope of the invention except insofar as included in the accompaying claims.

This application is a continuation-in-part of my copending application Seral No. 847,590, filed October 20, 1959, now abandoned.

I claim:

1. In an electrolytic cell for production of alkali metal hydroxide, having an anode and a cathode and a diaphragm therebetween, the improvement wherein the diaphragm is asbestos substantially completely impregnated with a halogenated drying oil said impregnated diaphraghm being essentially impervious to the flow of brine.

2. In an electrolytic cell for production of alkali metal hydroxide, having an anode and a cathode and a diaphragm therebetween, the improvement wherein the diaphragm is asbestos substantially completely impregnated with a chlorinated drying oil said impregnated diaphragm being essentially impervious to the flow of brine.

3. In an electrolytic cell for production of alkali metal hydroxide, having an anode and a cathode and a diaphragm therebetween, the improvement wherein the diaphragm is asbestos substantially completely impregnated with chlorinated linseed oil said impregnated diaphragm being essentially impervious to the flow of brine.

4. In an electrolytic cell for production of alkali metal hydroxide, having an anode and a cathode and a diaphragm therebetween, the improvement wherein the diaphragm is asbestos substantially completely impregnated with chlorinated tung oil said impregnated diaphragm being essentially impervious to the flow of brine.

5. In an electrolytic cell for production of alkali metal hydroxide, having an anode and a cathode and a diaphragm therebetween, the improvement wherein the diaphragm is asbestos substantially completely impregnated with chlorinated soybean oil said impregnated diaphragm being essentially impervious to the flow of brine.

6. In an electrolytic cell for production of alkali metal hydroxide, having an anode and a perforated cathode, the improvement wherein a diaphragm substantially completely impregnated with a halogenated drying oil is disposed between the anode and cathode and in contact with the cathode said impregnated diaphragm being essentially impervious to the flow of brine.

7. In an electrolytic cell for production of alkali metal hydroxide, having an anode and a perforated cathode, the improvement wherein a diaphragm substantially completely impregnated with a chlorinated drying oil is disposed between the anode and cathode and in contact with the cathode said impregnated diaphragm being essentially impervious to the flow of brine.

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