Nov. 7, 1967 C. A. LEVINE ETAL 3,351,487

PROCESS FOR PLATING PERMEABLE MEMBRANE

Filed Nov. 6, 1963 2 Sheets-Sheet 1

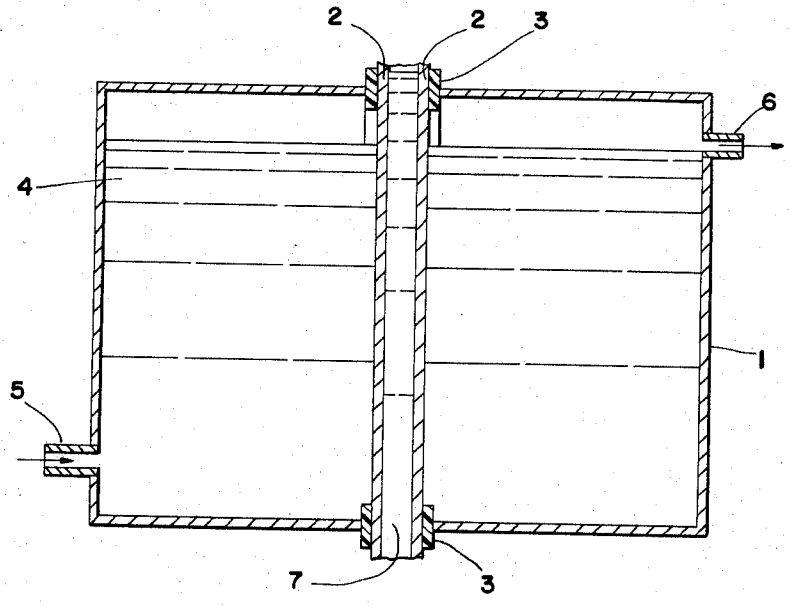


Fig. 1

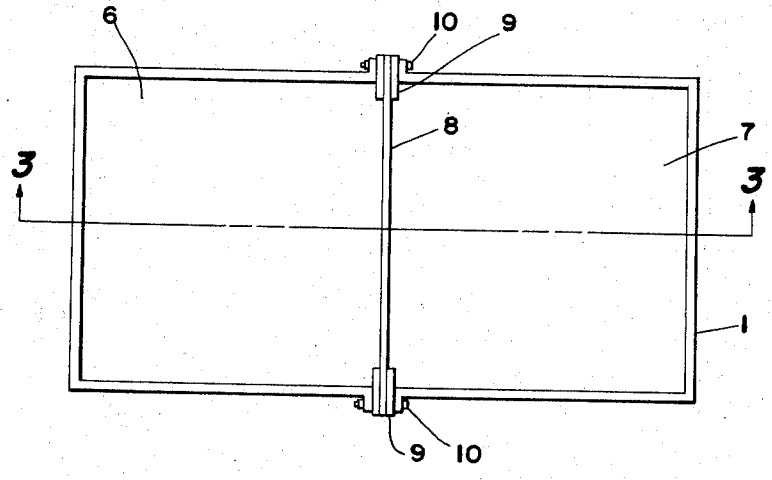


Fig. 2

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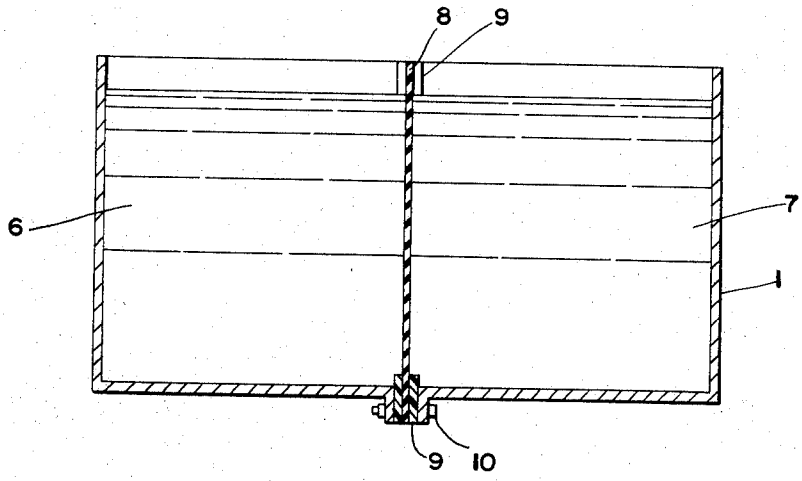


Fig. 3

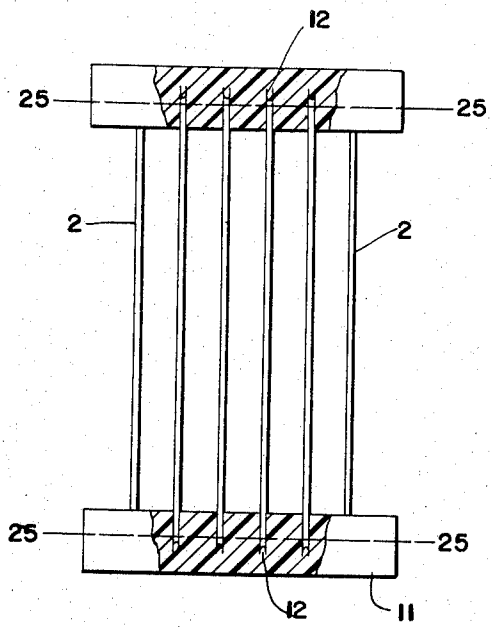


Fig. 4

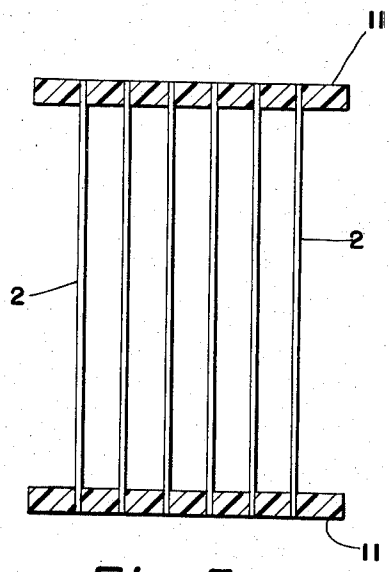


Fig. 5

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3,351,487 PROCESS FOR PLATING PERMEABLE MEMBRANE

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33 Claims. (Cl. 117—227)

This invention relates to an improved method of coating a permeable membrane with an electrically conductive metallic film. More specifically, it rates to a method suitable for coating the inner surface of a hollow fiber membrane with an electrically conductive metallic film.

The plating of metallic film on the surface of electrically non-conducting materials such as plastic film has been desirable for a number of purposes. One of the most important of these is for use in the manufacture of fuel cells in which electrical current is generated by the energy given off during the course of a controlled chemical reaction. For such purpose it has been found desirable to have a permeable plastic membrane as the non-conducting material and to have one or both surfaces of the membrane coated with a film of an electrically conductive metal in such a manner that the pores of the permeable membrane are not blocked by the metal coating.

Chemical plating of metal film on the surface of electrically non-conducting materials has been performed by several methods as disclosed in Patents 3,011,970 and 3,012,906. The methods of the prior art involve dipping of the surface to be plated in bulk mixtures of the desired metal cation and a reducing agent, or co-impingement of the reagent solutions as separate sprays on the surface to be plated. Generally, in such methods the surface to be plated requires pretreatment before an adherent deposit can be made. Moreover, careful temperature control and control of agitation and flow rates are necessary for uniform plating.

However, such methods as are known in the prior art are not readily applicable to plating of interior surfaces of small objects, particularly with regard to fine, hollow fibers. For such purposes, the methods of application known in the prior art are inappropriate, especially since the deposited metal tends to plug the interior passageway of the hollow fibers and also the pores of the permeable membrane. Even when sheets of permeable membrane are plated by prior art methods the pores become plugged by the metal deposition.

When reagent solutions are flowed through the interior of a hollow fiber, the deposit at the entrance end of the fiber builds up much more rapidly and to greater thickness than at points further advanced along the length of the fiber. This results in plugging one end of the fiber or depositing a thicker coat at that end. Attempts to reduce this tendency by alternately flowing the reagent solution into one end and then the opposite end merely causes thicker deposits at both ends and thinner deposits toward the middle.

In accordance with the present invention, it has now been found possible to take advantage of the ability of a permeable ion exchange membrane to exclude or pass certain ionic or molecular species selectively through the pores in the membrane. Consequently, it has now been found possible to metal-plate the interior surface of hollow fibers made of a permeable membrane by passing one of the reagent solutions through the interior of the hollow fiber and allowing the other reagent to permeate through the pores in the membrane by having the second reagent solution in contact with the outside surface of the hollow fibers.

For example, in plating the inner surface of a hollow fiber made of a permeable membrane, the solution of an

appropriate reducing agent can be flowed through the interior of the fiber and the solution of metal ion placed in contact with the exterior surface of the fiber under appropriate conditions for permeation through the membrane. As the metal ion passes through the pores of the membrane, it comes in contact with the reducing agent and the metal is deposited on the interior of the fiber.

Since the pores in the permeable membrane are distributed uniformly through the length of the fiber, the resulting interior plating is deposited in a uniform coating on the interior of the fiber. Surprisingly, however, this metal plating does not block the pores and is instead deposited on the area of the membrane between pores. Because of this uniformity of deposition caused by the uniformity of flow through out the length of the fiber, there is no need for the careful control of conditions generally required in the prior art methods even where the plating is being performed on sheets of permeable membrane.

Likewise, the metal cation solution can be flowed through the interior of the hollow fibers and the reducing agent allowed to flow from the outside of the fibers through the pores of the membrane and, upon contact with the metal cation solution, to cause deposition of the metal on the interior surface of the fibers. This is especially the case with anion exchange membranes. It may be desirable to complex the metal cation to make it bulky enough to prevent flow of the cation solution through the pores of the membrane. It is also possible to adjust the respective pressures of the solutions inside and outside of the hollow fiber to control the flow in the direction desired. In general, reducing anions are too bulky to pass through the membrane pores. However neutral molecular species, such as hydrazine, etc. are effective reducing agents also capable of permeation, if desired, through any permeable membrane.

In addition to effecting uniform deposition as pointed out above, the process of this invention has the additional advantage that the initial contact of the two reagent solutions is in close proximiy to the surface on which deposition is desired. In contrast, when solutions of reducing agents and metal ions are mixed in bulk to provide dipping or spraying mixtures, the reduction or reaction which results in free metal takes place not only near the surface to be plated but also throughout the mixture as a whole. This means that some of the metal can remain suspended in the product solution or form a more porous or bulky plating which gives poor adherence and greater loss of metal where flow conditions can mechanically erode such plated surface. Consequently in addition to the greater plating uniformity, the process of this invention gives more efficient use of the plating reagents by reducing the waste, and also provides a more dense plating with improved adherence. The reduction of waste is particularly important in the conservation of expensive metal ions such as those of the noble metals which are very often used for these purposes.

Since one of the reagents enters the interior of the hollow fiber at a plurality of points uniformly distributed throughout the membrane, this minimizes any localized catalytic effect of prior deposits or condition of the membrane. Moreover, since the flow rate of the solution going through the hollow fiber does not have to be as rapid as in utilizing any prior art method where it would be necessary to have a substantial rate of flow in order to minimize greater deposition near the entrance to the fiber interior, the flow rate of solution through the interior of the fiber can be very slow and need be only fast enough to provide sufficient concentration of desired reagent and to remove reaction byproducts therefrom. This decrease in flow rate has the additional advantage

that there is not any eroding action on the metal plating as it is being deposited.

While the process of this invention is particularly designed for use with hollow fibers and has a particular utility therefor, this process can also be used for plating of a sheet of permeable membrane by having the two reagent solutions as described above on opposite sides of the membrane and allowing one of the reagents to permeate through the membrane and come in contact with the other solution immediately upon passing through the pores of the membrane, thereby causing deposition of the metal on the adjacent surface of the membrane. With membrane in sheet form, it is found that the resulant plating has similar advantages as recited above, many of which cannot be attained by the prior art methods even though there is not the additional handicap of applying such methods in small spaces, such as the inside of hollow fibers, as described above. For example, even with sheet membrane the plating is much more uniform, more dense, of improved adherence, and less waste of reagents.

FIG. 1 illustrates an arrangement of equipment for plating the interior of a single hollow fiber.

FIG. 2 is a top view of equipment suitable for plating a sheet of permeable membrane, and FIG. 3 is an elevational cross-sectional view of the same equipment.

FIG. 4 illustrates a bundle of hollow fibers which have had both ends set in a casting resin with partial cross-section of the two ends of the bundle showing how the ends of the fibers are plugged with a casting resin.

FIG. 5 shows the same bundle of FIG. 4 in which the cast resin has been cut or machined to a point where the plugged ends of the fibers have been cut away so as to provide free passageway through the interior of the fibers.

Fuel cells using gaseous reagents have been known in the art for many years. Such cells have certain inherent advantages over other forms of converting chemical energy into electrical energy. Among these advantages is the high efficiency of energy conversion which in most instances is much greater than is achieved with standard fuel conversions.

The use of a solid ion exchange membrane as the electrolyte in gaseous fuel cells has been suggested. Such membranes may be formed of cation exchange resins or anion exchange resins of various suitable materials. The use of these solid ion exchange membranes as the electrolyte in gaseous fuel cells is particularly advantageous. Since no other electrolyte is required, there is no problem regarding storage of electrolytic solution. Moreover, there is no dilution of the electrolyte since these membrane materials are solid and insoluble in water and in various other materials with which they may come in contact.

In a particularly useful fuel cell design, the ion exchange membrane is used in the form of hollow fibers having a catalytic electrode material coated on the exterior surface of the hollow fiber and also a catalytic electrode material coated on the interior surface of the fiber, with the exterior and interior coatings being electrically discontinuous with each other. The cells are advantageously made of a plurality of such coated fibers with preferably at least a thousand of such coated fibers being employed per cell and in fact millions of such fibers per cell may be employed.

Such fuel cells comprise an important utility for the metal-coated permeable hollow fibers produced by the process of this invention. The interior wall is coated according to the process of this invention and while other methods might be capable of producing the exterior coating of the hollow fibers, the exterior coating produced by the process of this invention has many improvements as noted above. By reversing the position of the respective solutions and/or the direction of solution permeation flow, it is possible to produce such an exterior coating.

Various methods or means can be provided for assembling such bundles and for sealing the space between the ends of the fibers so as to provide separate contact of the individual reagent solutions with the interior or exterior respectively of the fibers without intermingling of the solutions. A typical method or means for such purposes is described hereinafter.

Various methods of sealing can be used. For example a suitable casting and adhesive composition can be applied to the fiber ends to fill the space between fibers but allowed to penetrate into the hollow fibers a distance less than the distance which they project beyond the resulting casting. Then the projecting ends can be cut off to expose open terminal portions of the fiber.

Various means and techniques can be used for connecting the individual interior and exterior metallic coatings in parallel electrical conductive relationship. Obviously, where there are thousands or millions of individual fibers, it would be impractical to attempt to connect individually the various conductors to each of the myriad of individual hollow fiber fuel cell elements.

In one method of making such electrical connections, the inner metallic plating of each hollow fiber extends substantially throughout the active length of the fiber and through that portion of the fiber which extends through the cast end wall or sealing means. At the opposite end of this fiber bundle, the interior coating of the hollow fibers is terminated before the end of the fiber and the exterior coating is extended all the way to the end of the hollow fiber.

In the operation of such a gaseous fuel cell, a fuel such as hydrogen is fed through the fibers passing through the interior of the hollow fibers and out the opposite end of the cell. An oxidizing gas such as oxygen is fed into the space between the various fibers and into contact with the exterior of said fibers. Upon permeation of one of the reactant ion species through the pores of the hollow permeable fibers, the reactants come into contact with each other and react to generate electricity as a result of the chemical reaction. The reaction product, which in the case of hydrogen and oxygen is water, is passed out of the system by the flow of reactant gas passing through the region in which said condensate or reaction product is formed. Means can be provided for separation and recovery of the product, and for regeneration of the starting reagents where desired.

Gaseous fuel cells in which the metal coated products of the present invention can be utilized are those which operate in any suitable process utilizing known fuel gases and oxidants. Suitable fuel gases can be generally characterized as gaseous compounds which oxidize to give a negative free energy change (ΔF). Fuel gases suitable for use in such fuel cells include hydrogen, ethylene, propylene, butene, methane, carbon monoxide, etc. While the preferred oxidant is oxygen, other suitable oxidizing gases such as air, etc. can be utilized.

In a typical reaction wherein the membrane hollow fiber is a cation permeable membrane, having H ions as the resultant mobile ion, using hydrogen as a fuel gas and oxygen as the oxidizing gas, the overall cell reaction is the oxidation of hydrogen to water. The respective resultant reactions at the anode and cathode are as follows:

$$H_2 \rightarrow 2H^+ + 2e$$
$$\tfrac{1}{2}O_2 + 2H^+ + 2e \rightarrow H_2O$$

If the fuel cell of the present invention has the hydrogen fed into the interior of the hollow fibers and the oxygen fed around the exteriors thereof, then the interior surface electrode will be the anode and the exterior surface electrode will be the cathode.

While the above equations may be used to summarize the respective reaction at the anode and cathode, it is believed that the H^+ is actually passed through the mem-

brane in the form of H_3^+O to react with the oxygen at the anode, forming water. It will be seen that the formation of H_2^+O from H^+ is by the equation

$$H^+ + H_2O \rightarrow H_3^+O$$

This reaction tends to deplete the anode side of the membrane of water.

The various ion exchange resins which are utilizable in gaseous ion exchange fuel cells all have a common characteristic of having retained therein water in percentages generally varying between 15 and 50%, so that the resinous material is hydrated. This water cannot be removed from the resin by mechanical force, since it is retained therein by secondary Van Der Waals forces. In order for the exchange ions to be transported across the membrane from one electrode to another, it is essential that this water be present throughout the membrane structure. By reference to the above equation it can be seen that the oxidation process of the cell can cause a depletion of water from the anode side of the membrane. If water molecules are removed from the anode side of the membrane faster than they can diffuse back, then this anode side will be partially dried out, resulting in a considerably lessened current density available from the cell. The various prior art devices, relying upon thick membranes, have been subject to this process of anode membrane drying, since their thickness is so great that the removed water molecules cannot be adequately replaced by rediffusion of the newly formed water molecules back to the anode side of the membrane. In the coated fiber structure of the present invention, the membrane walls are sufficiently thin so that this back diffusion of water is not impaired and proceeds at a rate sufficiently great to prevent anode dehydration.

Assuming the fuel cell set up for gas feed as outlined above, and assuming an anion permeable membrane with hydrogen and oxygen as the fuel and oxidant gases, the overall reaction of the cell is again the oxidation of hydrogen to water with the electrode reactions at the respective anode and cathode being as follows:

$$H_2 + 2OH^- \rightarrow 2HO + 2$$
$$\tfrac{1}{2}O_2 + H_2O + 2e \rightarrow 2OH^-$$

It will be understood that similar reactions occur with various other fuel gases dependent upon which ion is transported by the ion exchange membrane.

Ion exchange resin membranes suitable for formation into hollow fibers utilizable in the gaseous fuel cells of the present invention generally fall within three classes. The first of these classes is a hollow fiber consisting entirely of ion exchange resin. The second of these classes consists of a hollow fiber formed from a base resin having incorporated therein an ion exchange resin. The third class consists of a hollow fiber formed from a grafted base resin reacted with ion exchange forming materials. Any of the ion exchange resins known to the art may be utilized in the fuel cells of the present invention. Inorganic ion exchange materials are also suitable, either as such when they can be made in permeable membranes or when embedded in a permeable membrane material, such as zeolite in polyethylene.

As is well known, such resins contain a mobile ionic substituent. In the case of cation exchange resins, these ions are generally attached to acidic groups such as a sulfonic acid group, a carboxyl group, and the like. These acidic groups are attached to a polymeric material such as phenol-aldehyde resins, polystyrene-divinyl benzene, polystyrene, polyethylene-grafted with styrene, sulfonated polyolefin, or other organic substrate. This cation component is a mobile and replaceable ion electrostatically associated with the fused component of the resin molecule. It is the ability of the cation to be replaced under appropriate conditions by other cations which imparts the ion exchange characteristics to these materials. For suitable cationic exchange materials, reference is made to Juda et al. Reissue 24,865, Johnson 2,658,042, Ferris 2,678,306, and Bodamer 2,681,320. As preferred cationic exchange resins may be mentioned: (1) sulphonated polystyrene formed by sulfonating polystyrene or by forming an admixture of sulfonated polystyrene and other polymers, and (2) polyethylene having styrene grafted thereto by chemical or radiation means followed by reaction with chlorosulfonic acid.

Anion exchange resin hollow fibers may be formed of any of the suitable materials known to the art and are similar in their action to the cation exchange resins except that in the anion exchange resins it is the ability of the anion to be replaced which causes the ion exchange activity. Generally speaking, such anion resins are formed by incorporating an amine group in the resin. Particularly suitable are quaternary amines. Preferred anion membranes suitable for use in the present invention are the following:

(1) polystyrene chloromethylated and reacted with a tertiary amine;

(2) polyethylene having incorporated therein quaternary amine ion exchange beads, such as Dowex 1;

(3) polyethylene tubing having styrene grafted thereto by chemical or radiation means and reacted with chloromethyl ether, this reaction product being further reacted with triethyl amine.

For other suitable anion exchange resins reference is made to the above-mentioned Juda patent, Kropa 2,663,-702 and Bodamer 2,681,319.

The various resinous materials discussed above may be formed into hollow fibers suitable for use in the present invention by any suitable process and apparatus known to the art, such as that shown in British Patent 514,638. Depending upon the fiber-forming material employed, there may be used melt, dry and wet spinning procedures using spinerettes of any design apt for the purpose or by any other techniques, such as will occur to those who were skilled in the art. Such a process may include the incorporation of a soluble core material in the fiber, which if used, is dissolved out of the fiber to produce the hollow uniform interior bore. Fibers so formed will have a continuous uniform bore as well as uniform outer and inner diameters. It is usually expedient to take up the hollow fibers on a reel or other suitable means for collection prior to assembling them in cells or bundles for plating by the process of the invention; i.e., the fibers are formed as continuous filaments which are stored and otherwise treated prior to their formation into the desired length fibers utilized in the gaseous fuel cells.

The contemplated fibers, in order to best take advantage of their large surface area, are formed in as small dimensions as is permissible, which dimensions will still support an inner electrode coating and at the same time provide an unobstructed uniform bore for the passage of gas interiorly of the fibers. Generally speaking, such fibers should not have an outside diameter in excess of 1000 microns. The preferred range of outside diameter of these fibers is between 10 and 200 microns. The inner diameter should be so selected in the preferred fibers as to hold within the limits of between about 1/3 and 1/8 of the outside diameter the thickness of the uniform walls of the fibers. This would correspond to a wall thickness range of between about 3 to about 66 microns. It will be understood that the thickness of the electrode coatings on the interior and exterior walls of the fibers will generally be less than the thickness of the walls of the fibers, although this is not necessarily the case. In a preferred embodiment, these coatings are held as a maximum to the thickness necessary to carry all the current without undue ohmic resistance. This is ordinarily no more than a few microns, for example no more than 2 or 3 microns.

Generally speaking, any suitable catalytic material may be used for the catalytic electrode coatings. As suitable materials may be mentioned the following: metallic silver deposited by reduction in place of silver nitrate, platinum

black deposited from chloroplatinic acid, metallic nickel, rhodium, palladium, iridium, copper, etc.

Reference is made again to the extremely small dimensions of the fuel cells utilizing the present invention. Such construction provides a fuel cell surface area many multiples or times greater than has hitherto been achieved per unit volume. The extreme thinness of the membranes also reduces the electrical resistivity of the individual cells and insures adequate rediffusion of the water within the membrane.

In the drawings, FIG. 1 represents an arrangement of equipment which can be used to plate the inside of a single fiber. Container **1** has a single fiber **2** sealed into position by sealing Composition **3** so that the metal ion solution **4** can be passed through inlet **5** into the container and out through outlet **6** without intermingling with the reductant solution **7** which is passed through the inside of the fiber. As explained herein when the metal ions permeate the fiber wall and come in contact with the reductant solution inside the fiber, the metal is plated on the inside of the fiber.

FIG. 2 shows a plan or top view and FIG. 3 an elevational cross-sectional view of a container **1** in which a membrane sheet **8** is positioned with metal ion solution **6** on one side and reductant solution **7** on the opposite side. The membrane is fastened into position with gasket **9** providing a seal between the membrane and the joined sections of the container which is held firmly in position by bolt **10**. As one of the solutions permeates the membrane and comes in contact with the solution on the opposite side the metal is plated onto the membrane.

FIG. 4 shows an arrangement of a plurality of hollow fibers **2** cast in a casting resin **11**. The ends **12** of the various fibers are plugged with casting resin although not to a very great distance from the end of the fibers. This is demonstrated by the partial sectional views at the top and bottom of the figure.

FIG. 5 shows the same fiber bundle of FIG. 4 after the cast resin **11** has been machined or cut along the lines **25** shown in FIG. 4. Cutting along these lines has removed the plugged ends **12** and leaves the fibers open to the entire portion extending through the casting resin **11** and free for the flow of fluid therethrough.

Coatings of catalytic material applied by the process of this invention are more uniform in thickness, density and of improved adherence as compared to coatings applied by various other methods. Also in such cases, porosity of the fiber and of the metallic coating is retained to a degree sufficient to allow passage of ions from the interior to the exterior of the coated fiber, or vice versa, depending on the application and the manner in which the coated fiber is to be used.

In a preferred embodiment of the invention, a strong solution of a metallic cation, in a solvent which will wet the membrane, is placed on the outside of a permeable hollow fiber. A reducing solution is made to flow through the fiber. As metallic ions pass through the pores in the permeable membrane, they are reduced by the solution flowing through the interior of the fiber and are deposited in situ to form a porous but continuous coating of the metal on the interior surface of the hollow fiber.

The invention is best illustrated by the following examples. These examples are intended merely for purposes of illustration and are not intended to limit in any way the scope of the invention nor the manner in which it may be practiced. Unless specifically provided otherwise, reference to parts and percentages in the examples and throughout the specification are to parts and percentages by weight.

EXAMPLE I

Hollow permeable polyethylene fiber having an outside diameter of 190 microns and inside diameter of about 120 microns, produced by melt spinning through an annular orifice, is chlorosulfonated with 10 percent chlorosulfonic acid. The treated fiber is hydrolyzed and washed with water several times. The fiber or tubing has a capacity of 3.5 meq./gm. A bundle of such fiber is cast into a bundle by having its ends sealed in accordance with the technique shown in FIGS. 3 and 4 by using an epoxy resin composition consisting of 14.7 parts of the diglycidyl ether of bisphenol, 6.8 parts of soya-1,3-propylene diamine, and 1.1 parts of dimethylaminopropylamine. This bundle is placed in a device such as shown in FIG. 5. On the outside of the fibers is placed a solution consisting of 3.5 parts $AgNO_3$ in 3.0 parts of water plus enough NH_4OH to dissolve the precipitate which initially forms. Through the interior of the fibers a continuous flow is maintained of a solution made as follows: A solution of 0.2 part $AgNO_3$ and 100 parts of water is boiled. Then 0.166 part of Rochelle salt is added and the boiling continued for at least another five minutes. The resultant solution is filtered to remove any gray precipitate. The solutions are used at room temperature in the plating operation and the plating operation continued for one hour. The inside of the fibers acquires a good adherent coating of silver.

EXAMPLE II

The procedure of Example I is repeated using four bundles of hollow fibers made of a sulfonated ion exchange membrane (made by National Aluminate Co. and sold as "Nalfilm I" cation exchange membrane). Two solutions are prepared and applied to each bundle respectively in the same manner as in Example I. After 9 minutes, one of the bundles is removed and the fibers cut open for inspection; no noticeable deposit has been formed. After 22 minutes, another bundle is similarly inspected and dark patches are formed on the inside surface. After 39 minutes, the third bundle is inspected and a dull, shiny deposit is found on the inside of the fibers and very little deposited on the outside. Upon measuring the resistance of the respective coatings of the fibers of the third bundle, it is found that the resistance of the inside coating is approximately 3000 ohm/cm., and that on the outside surface has a resistance of greater than 50,000 ohms/cm. After 59 minutes the fourth bundle is inspected and the hollow fibers have a shiny surface on the inside and a dark surface on the outside of the hollow fibers. Upon measuring the resistance of the respective coatings as above, the resistance of the inside coating is found to be about 5 ohms/cm., and that of the outside coating is greater than 40,000 ohms/cm. The adherent silver film on the inside is measured by a film micrometer and is found to be 5–6 microns thick.

EXAMPLE III

The procedure of Example I is repeated using a chlorosulfonated polyethylene hollow fiber having an ion exchange capacity of 1.5 meq./gm. The same solution is used externally to the fiber as in Example I but the solution passed internally through the fibers is made of one part phenylhydrazine, 11 parts ethanol and 10 parts water. After 1.5 hours, the interior surface has an adherent conducting silver film with a resistance of about 15 ohms/cm. and the exterior surface has no coating. The exterior surface has a resistance greater than 5000 ohms/cm.

EXAMPLE IV

The procedure of Example III is repeated using as the external solution a nickel ion solution consisting of 400 grams nickel sulfate and 200 grams of citric acid per liter of solution. The solution used on the inside of the hollow fibers consists of 8.1 grams sodium hydroxide, 70.5 grams sodium hydrosulfide, and 10.1 grams sodium hypophosphite. The solutions are maintained at 58° C. during the plating. At the end of 5.5 hours, the interior surface of the fibers has an adherent, smooth coat of metallic nickel with a thickness less than 0.0002 inch and a resistance of approximately 15 ohms per cm. The exterior surface of the fibers has no metallic or conductive coating.

EXAMPLE V

The procedure of Example IV is repeated using hollow fibers of the type used in Example II. After a plating period of 4 hours and 55 minutes, the plating results are identical to those of Example IV.

EXAMPLE VI

The procedure of Example V is repeated using as the external solution one made of 10 volumes of concentrated NH_4OH plus 4 volumes of a 30% solution of nickelous sulfate. The interior solution is a 5% solution of sodium hydrosulfite. The plating is conducted at 45–50° C. for 8 hours. At the end of this period, a thin, adherent nickel metal plating is deposited on the interior surface. This plating has a resistivity of approximately 300 ohms/cm.

EXAMPLE VII

The procedure of Example III is repeated using as the external solution a concentrated copper ion solution made by saturating a concentrated NH_4OH solution with freshly precipitated copper oxide. The internal solution is an equal volume mixture of a 10% potassium hydroxide aqueous solution and a solution made by adding 4.5 grams of hydrazine sulfate and 4.3 ml. of hydrazine hydrate to 100 ml. of water. The plating is conducted at 60° C. for 7.5 hours, at the end of which time there is a metallic copper film on the interior surface of the hollow fibers but none on the exterior surface. The copper film has a resistivity of 70 ohms/cm.

EXAMPLE VIII

The procedure of Example VII is repeated except that the plating is conducted at 55° C. for 4 hours. The resultant interior copper film has a resistivity of 30 ohms/cm.

EXAMPLE IX

The procedures of Examples I–VIII are repeated using in place of the hollow fibers, a sheet of the same membrane having the same thickness as the wall thickness of the corresponding hollow fiber. The membrane sheet is assembled in the equipment as shown in FIG. 2. In each case the solution previously flowed through the interior of the hollow fibers is placed in chamber B and the external solution is placed in chamber A. In each case similar results are obtained as with the hollow fibers in the respective examples.

EXAMPLE X

The procedure of Example IX is repeated using as the permeable membrane sheet a permeable membrane made of a commercial anion exchange resin having quaternary ammonium groups attached thereto (made by National Aluminate Co. and sold as "Nalfilm II"). In chamber B is placed a 0.1 molar solution of silver nitrate to which sufficient NH_4OH has been added to redissolve the precipitate which originally forms. In chamber A a 5% aqueous solution of hydrazine hydrate is placed. After plating at 14° C. for 1.25 hours, a heavy adherent metallic deposit of silver is formed on the surface in contact with the silver solution. The electrical resistance of the silver plating is less than 0.5 ohms-cm. There is no deposit on the opposite side. The above procedure is repeated with similar results with a permeable membrane made of polystyrene chloromethylated and then reacted with trimethylamine.

EXAMPLE XI

A flat permeable ion exchange membrane is made by sulfonating a polyethylene sheet with chlorosulfonic acid and hydrolyzing the product. On one side of this membrane is placed a platinum solution consisting of a mixture of 8 milliliters of 2.67% chloroplatinic acid and 0.96 milliliters of 0.94 molar sodium hydroxide. On the other side is placed a 4% aqueous solution of hydrazine hydrate. After standing at room temperature for 1½ hours, a thin coating of platinum is deposited on the side of the membrane in contact with the hydrazine solution.

EXAMPLE XII

Hollow fibers made of sulfonated polyethylene are used as described in Example I. On the outside of the fibers is placed an aqueous palladium solution consisting of .03M palladium chloride and 2M ammonium hydroxide. Inside the fibers is placed a 5% aqueous solution of hydrazine hydrate. After standing at room temperature for one hour, the insides of the fibers are plated with palladium metal.

EXAMPLE XIII

A sulfonated nylon permeable membrane (available commercially from Gelman Instrument Company, of Chelsea, Mich. and sold under the trademark Accropore No. 5A 6404 Resin) is used in sheet form. On one side is placed an aqueous solution containing 1% $HAuCl_4$ made slightly alkaline with KOH. On the other side is placed a 1% hydrazine hydride solution in water. At the end of two hours, a gold plating has formed on the side of the membrane in contact with the solution of gold.

Optimum conditions for the practice of this invention vary according to the particular metal being used and the metal ion concentration. Generally, however, highly concentrated metal ion solutions are preferred. The reducing solution, however, must be weak enough so that the reducing reagent contained therein will not penetrate the membrane too fast and thereby reduce the metal ion so fast as to adversely affect the adherence of the metal coating. However, the reducing solution must be of sufficient strength to reduce the metal ion at a practical rate. Appropriate concentrations differ for different reducing agents, pH conditions, etc.

Where cation transmigration through either a cation exchange or anion exchange membrane is desired, the cation concentration should be sufficient to overcome the ion exclusion action of the membrane. With an anion exchange membrane, the minimum concentration of cation suitable will be higher than with a cation exchange membrane.

In the practice of this invention where the reducing reagent is designed to transmigrate through the membrane, the cation concentration is desirably maintained at a level which will minimize the rate of cation transmigration through the membrane. However, it is desired to have sufficient concentration to give an adequate rate of deposition. This particular embodiment is more practical with an ion exchange membrane since this type of membrane will have a much stronger exclusion action and therefore permit a higher cation concentration thereby giving a better deposition rate. As an alternative, the cation concentration can be increased by using it in the form of a bulky complex in which case the ion exclusion action of the membrane is increased and can tolerate higher concentrations of the cation without permitting transmigration.

Where an ionic reductant is used as the migrating species, similar but converse considerations apply. If a neutral reductive is to be used, it should be of a molecular species such that effective exclusion or transmigration is favored according to the application desired.

However, concentrations found particularly suitable in the practice of this invention are 0.2% to 50% for the metallic component and 0.12% to 10% for the reducing component.

Although aqueous solutions have generally been indicated herein, the solvent can be any other solvent in which the reactants are soluble and which solvent does not dissolve the membrane or otherwise adversely affect it. For example, alcohol solutions of the metal and the reductant can be used where desired.

Advantageously, the plating temperature is in the range of 0°–100° C., preferably 10° to 80° C.

In addition to the Ag, Cu, Ni, Au, Pd and Pt shown in the examples, various other metal ions which are capable of being reduced chemically can also be used, such as Cr, etc. Moreover, other reducing agents such as sodium phosphite, etc. can also be used.

Although the ionic type of permeable membranes have been illustrated in the examples above, it is also possible to deposit a metal plating on hollow fibers or sheet membranes made of non-ionic permeable membranes. Typical of such materials are various organic polymeric materials such as the acetate, triacetate, formate, propionate, nitrate, etc. Esters of cellulose, including the mono-, di-, and triesters in mixtures of such esters; cellulose ethers, such as methyl, ethyl, hydroxyalkyl, carboxyalkyl, etc., including mixed cellulose ethers; regenerated cellulose; polyvinyl alcohols; polysaccharides; casein and its derivatives; synthetic linear polyamides, polycarbonates, polyvinyl chloride and its copolymers, polyvinylidene chloride and its copolymers, acrylic ester polymers, organic silicon polymers, polyurethanes, polyvinyl formals and butyrals, and mixtures thereof, methacrylate polymers, styrene polymers, polyolefins such as polyethylene, polypropylene, etc., and other polyesters, and mixtures of the foregoing.

Methods of making continuous hollow fibers suitable for the practice of this invention are known in the art, for example see British Patent 514,638. In general, such fibers are spun by melt, dry or wet spinning techniques depending upon the particular fiber-forming materials being used. The spinnerette is selected according to the type of spinning procedure used and the particular dimensions desired in the hollow fiber. For the production of the hollow fiber, the spinnerette has a small annular opening in the orifice through which the spinning composition is extruded.

As a typical example, cellulose triacetate is spun into continuous hollow fibers by a wet spinning process in which the cellulose triacetate, together with whatever plasticizer or modifier is considered desirable to impart ultimately the permeable character, is dissolved in a suitable solvent to form a viscous spinning solution. This solution is extruded through the spinnerette into a coagulant bath. As the extruded solution comes in contact with the bath the cellulose triacetate coagulates or gells in the desired form of a continuously hollow fiber of uniform wall thickness. If the coagulant bath is appropriate for imparting permeability to the fiber material, this characteristic is imparted to the fiber directly. If the coagulant bath is not so constituted, the fiber is led into a second bath to perform this function. The hollow fiber is then washed free of solvent or reagents and then either is used directly in accordance with the practice of this invention or is stored on a reel or bobbin or other suitable device for subsequent use.

According to this technique, extremely fine hollow fibers can be produced. The wall thickness is desirably sufficient to withstand pressures that may be exerted in the subsequent utilization of these fibers. It is found that the small diameters of these fine hollow fibers permit the self-supporting membrane walls of the fiber to withstand considerable pressures.

It is generally advantageous that the outside diameter of the hollow fibers does not exceed 300 microns. Preferably the outside diameters are in the range of about 10 to about 200 microns. Advantageously, the wall thickness of the fibers is in the range of about 1 micron to about 80 microns, preferably from about 2 to about 15 microns. Wall thicknesses below this range may result in an inability to withstand the desired pressures, whereas thicknesses above this range increase the resistance to permeation through the fiber wall. Obviously, these characteristics will vary somewhat with the particular material being used and also the particular type of separation involved. Corresponding methods of preparing the permeable membrane and sheet form are well known in the art.

EXAMPLE XIV

The procedure of Example I is repeated using hollow permeable fibers of the type used in Example X. In each case an aqueous hydrosulfite solution is passed on the outside of the fibers and an aqueous nickel solution is passed through the inside of the fibers. The aqueous hydrosulfite solution consists of 0.74 percent NaOH and 6.5 percent $Na_2S_2O_4$. The nickel solution consists of 26 percent nickelous acetate and 13.7 percent citric acid. The plating is conducted at 20–30° C. After 4 hours a nickel plating is satisfactorily effected and the thickness of the plating increases as the plating is continued for 24 hours.

EXAMPLE XV

The procedures of Examples I and II are each repeated twice in one case passing 0.5 percent aqueous hydrazine hydrate solution through the inside of the fibers and a 0.03 molar aqueous solution of $PdCl_2$ in contact with the outside of the fibers, and in the other case passing a solution of 4 percent hydrazine hydrate aqueous solution inside the fibers and a 0.05 molar $PdCl_2$ solution outside the fibers. After one-half hour of plating a layer of palladium is coated on the inside of the fibers. This plating is increased in thickness as the plating is continued through a period of 4 hours.

The reducing agent used in any particular plating operation is selected as one having a reducing potential greater than the reducing potential of the metal compound from which the metal is to be plated. Preferred reducing agents are hydrazine, hydrazine hydrate, acid salts of hydrazine such as the sulfate, chloride, phosphate, etc., the alkali metal borohydrides such as the sodium and potassium borohydrides, Rochelle salts, alkali metal hydrosulfites and alkali metal phosphites. With such preferred compounds, a selection is made according to which of these reducing agents has a greater reducing potential than the particular metal compound from which the metal is to be plated.

The permeable membranes used in the practice of this invention can be of a heterogeneous type in addition to the various homogeneous types indicated above. For example, palladium ions have been passed through a membrane made by hot pressing a mixture of powdered zeolite and powdered polyethylene as illustrated below in Example XVI. Moreover permeable membranes can be derived by partially impregnating a pressed mat of glass wool or other fibers such as asbestos.

EXAMPLE XVI

A permeable membrane is made by mixing 30 percent by weight powdered polyethylene and 70 percent by weight of zeolite (Linde 4 A Molecular Sieve). This mixture is pressed at 140° C. for 2 minutes to give a membrane thickness of 4 mils. This membrane is plated on one side with palladium metal by the use of equipment shown in FIG. 2, using a solution of 0.07 moles $PdCl_2$ and 4 moles NH_4OH on one side of the membrane and a solution of 4 percent $N_2H_4 \cdot H_2O$ on the other side. After allowing this to stand at room temperature for 45 minutes, palladium metal is deposited on the side of the membrane in contact with the hydrazine solution. No visible palladium is seen in the still clear hydrazine solution and the $PdCl_2$ solution is also still clear.

In addition to the uses indicated above, the internally plated, permeable hollow fibers produced by this invention can be used for conducting in solution various reactions catalysed by a metal, particularly where it is necessary to minimize secondary reactions between the desired product and one of the reagents. By use of the permeable hollow fibers of this invention, one of the reactants can be introduced to the reaction zone and into contact with the metal surface by permeation, or a reactive product can be removed from the reaction zone by permeation. A reactor made of such hollow fibers

provides a very large surface of catalyst per unit volume of reaction mixture.

Such fibers are also suitable for high pressure reactions. Furthermore these plated fibers are also suited to electrochemical reactions where the plate acts as an electrode. Furthermore, even if secondary reactions are not involved, the permeable membrane of this invention is useful as a means for driving or promoting by removal of product a reaction which would otherwise slow down or stop because of equilibrium conditions attained.

While certain features of this invention have been described in detail with respect to various embodiments thereof, it will, of course, be apparent that other modifications can be made within the sphere and scope of this invention and it is not intended to limit the invention to the exact details shown above except insofar as they are defined in the following claims:

The invention claimed is:

1. The process of plating a permeable membrane with a thin metallic coating comprising the steps of:

(a) contacting one side of said membrane with a solution of a compound of the metal to be plated,

(b) contacting the opposite side of the said membrane wih a solution of a reagent capable of reducing said metal in said metal compound solution to a metallic state,

(c) effecting permeation of said membrane by the one of said solutions which is on the opposite of said membrane from that on which said metal is to be plated, and

(d) maintaining said contacting and said permeation of said membrane at a temperature of 0° to 100° C. until a sufficient thickness of metal plating has been effected.

2. The process of claim **1** in which said solution of said reducing reagent is in contact with that side of said permeable membrane which is to be plated, and said solution of said metal compound is in contact with the opposite side of said membrane and is permeated through said membrane.

3. The process of claim **1** in which said solution of said metal compound is in contact with said side of said permeable membrane which is to be plated, and said solution of said reducing agent is in contact with the opposite side of said membrane and is permeated through said membrane.

4. The process of claim **1** in which said permeable membrane is a cationic membrane.

5. The process of claim **1** in which said permeable membrane is an ionic membrane.

6. The process of claim **1** in which said permeable membrane is shaped in the form of a hollow fiber.

7. The process of claim **6** in which said permeable membrane is a non-ionic permeable membrane.

8. The process of claim **6** in which said permeable membrane is a cationic permeable membrane.

9. The process of claim **8** in which said hollow fiber has an outer diameter of 10–300 microns and a wall thickness of 1–80 microns.

10. The process of claim **9** in which said reducing solution is passed through the interior of said fiber and said metal compound solution is contacted with the exterior surface of said permeable hollow fiber and permeated into the interior region of said hollow fiber thereby to deposit a plating of metal on the interior surface of said hollow fiber.

11. The process of claim **10** in which said cation permeable membrane consists essentially of a sulfonated polyolefin material.

12. The process of claim **10** in which said cation permeable membrane consists essentially of an inorganic ion-exchange material.

13. The process of claim **10** in which said cationic membrane consists essentially of an organic substrate having acidic groups.

14. The process of claim **9** in which said metal compound solution is passed through the interior of said hollow fiber and said reducing solution is contacted with the exterior of said hollow fiber and permeated into the interior of said hollow fiber, thereby to deposit a metal plating on the interior surface of said hollow fiber.

15. The process of claim **14** in which said reducing agent has a reducing potential greater than the reducing potential of the metal compound from which the metal is to be plated and is selected from the class consisting of hydrazine, hydrazine hydrate, acid salts of hydrazine, alkali metal borohydrides, Rochelle salts, alkali metal hydrosulfites and alkali metal phosphites.

16. The process of claim **15** in which said metal compound solution has a concentration in the range of 0.1–50 percent by weight.

17. The process of claim **16** in which said reducing reagent soltuion has a concentration of 0.1–20 percent by weight.

18. The process of claim **6** in which said hollow fiber is made of an anion permeable membrane.

19. The process of claim **18** in which said hollow fiber has an outer diameter of 10 to 300 microns and a wall thickness of 1 to 80 microns.

20. The process of claim **19** in which said reducing solution is passed through the interior of said fiber and the exterior of said fiber is in contact with said metal solution which is allowed to permeate therethrough.

21. The process of claim **20** in which said metal compound is a compound of a metal selected from the class consisting of Ag, Au, Pt, Ni, Cu, Rh, Pd and Cr.

22. The process of claim **21** in which said reducing reagent has a reducing potential greater than the reducing potential of the metal compound from which the metal is to be plated and is selected from the class consisting of hydrazine, hydrazine hydrate, acid salts of hydrazine, alkali metal borohydrides, Rochelle salts, alkali metal hydrosulfites and alkali metal phosphites.

23. The process of claim **22** in which said metal compound solution has a concentration in the range of 0.1 to 50 percent by weight.

24. The process of claim **23** in which said reducing reagent has a concentration in the range of 0.1 to 20 percent by weight.

25. The process of claim **20** in which said anion permeable membrane is a heterogeneous membrane consisting essentially of fine particles of an anion exchange resin uniformly dispersed in a support sheet.

26. The process of claim **20** in which said anion permeable membrane is a homogeneous membrane consisting essentially of any organic substrate having chemically bonded thereto anion releasing groups.

27. The process of claim **26** in which an aqueous hydrosulfite solution is in contact with the outside surface of hollow fibers made of said anion permeable membrane and an aqueous nickel solution is passed through the interior of said hollow fibers, said aqueous hydrosulfite solution having a composition of approximately 0.74 percent by weight of NaOH and 6.5 percent by weight of $Na_2S_2O_4$, and said aqueous nickel solution having a concentration of approximately 26 percent by weight of nickelous acetate and 13.7 percent by weight of citric acid.

28. The process of claim **27** in which said anion permeable membrane is a membrane having quaternary ammonium groups attached thereto.

29. The process of claim **27** in which said anion exchange membrane is a polystyrene resin having a methylene group attached to each of a plurality of aromatic nuclei in said polystyrene, and said methylene group having also attached thereto a trimethyl-ammonium chloride radical.

30. The process of claim **20** in which said anion permeable membrane is a hydrocarbon polymer having alkyl ammonium halide radicals attached thereto.

31. The process of claim 30 in which alkyl ammonium halide radicals are trimethyl ammonium chloride radicals attached to a methyl group attached to aromatic nuclei in polystyrene.

32. The process of claim 1 in which said permeable membrane is a sulfonated polyethylene and is in the form of hollow fibers.

33. The process of claim 32 in which an aqueous solution having not less than 0.5 percent by weight and not more than 4 percent by weight of hydrazine hydrate therein is passed through the interior of said fibers, and an aqueous solution having not less than 0.03 molar percent and not more than 0.05 molar percent of $PdCl_2$ is passed in contact with the outside of said fibers for a period of not less than one-half hour.

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