

[54] **PROCESS FOR PRODUCING AN ANODIC ALUMINUM OXIDE MEMBRANE**

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[52] **U.S. Cl.**..... **204/11, 204/24, 204/35 N**

[51] **Int. Cl.**..... **C23b 7/00, C23b 5/48, C23b 5/50**

[58] **Field of Search** ..... **204/11, 12, 24, 35 N, 37 R**

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Primary Examiner—T. M. Tufariello

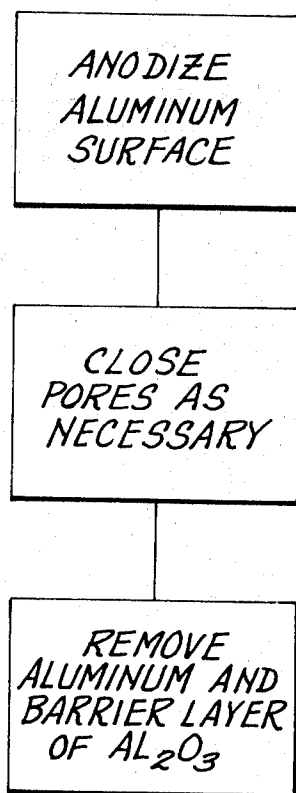
Attorney, Agent, or Firm—Donald A. Streck

[57]

**ABSTRACT**

The present invention discloses a novel method for manufacturing porous membranes for hyperfiltration and ultrafiltration by the process of anodizing aluminum to form a layer of porous aluminum oxide, closing the pores thus formed as necessary to achieve the desired pore diameter, and removing the aluminum and barrier layer of aluminum oxide by etching to leave only the desired membrane remaining.

**5 Claims, 11 Drawing Figures**

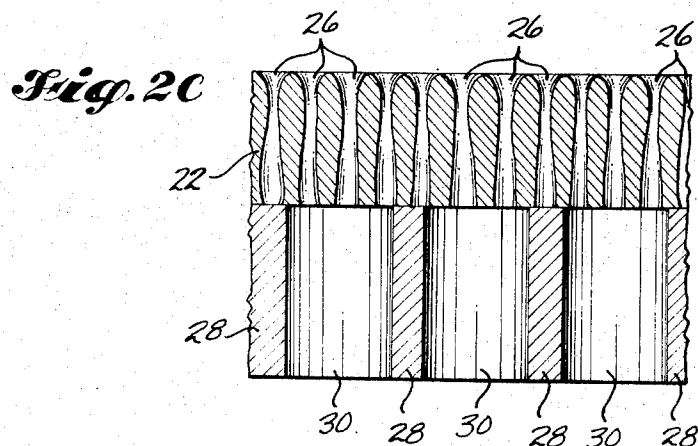
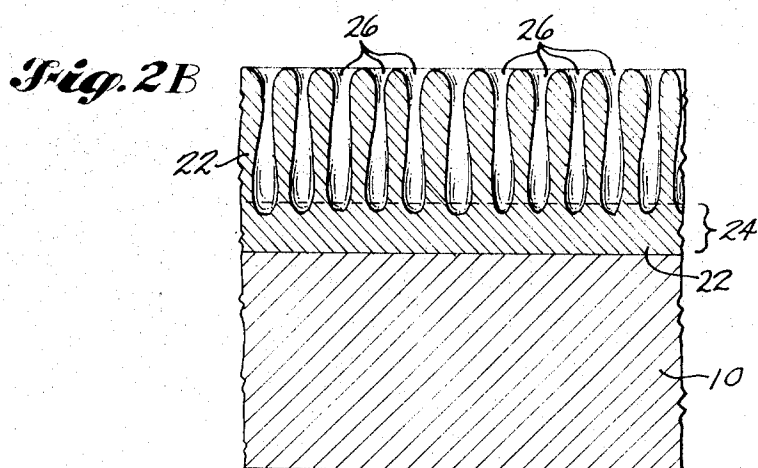
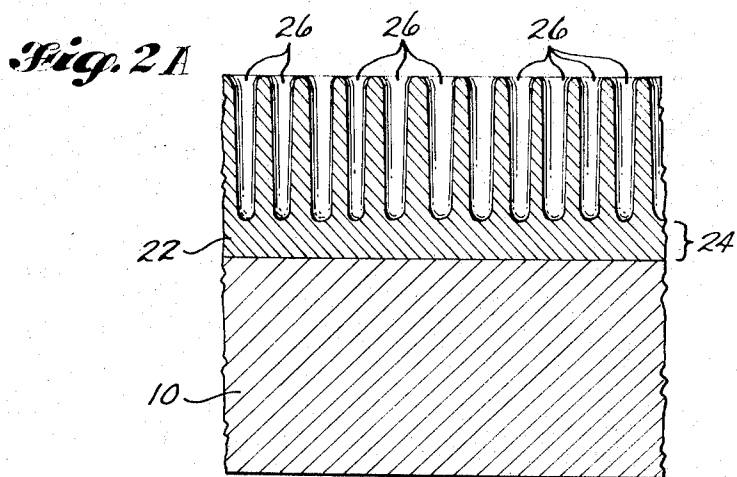


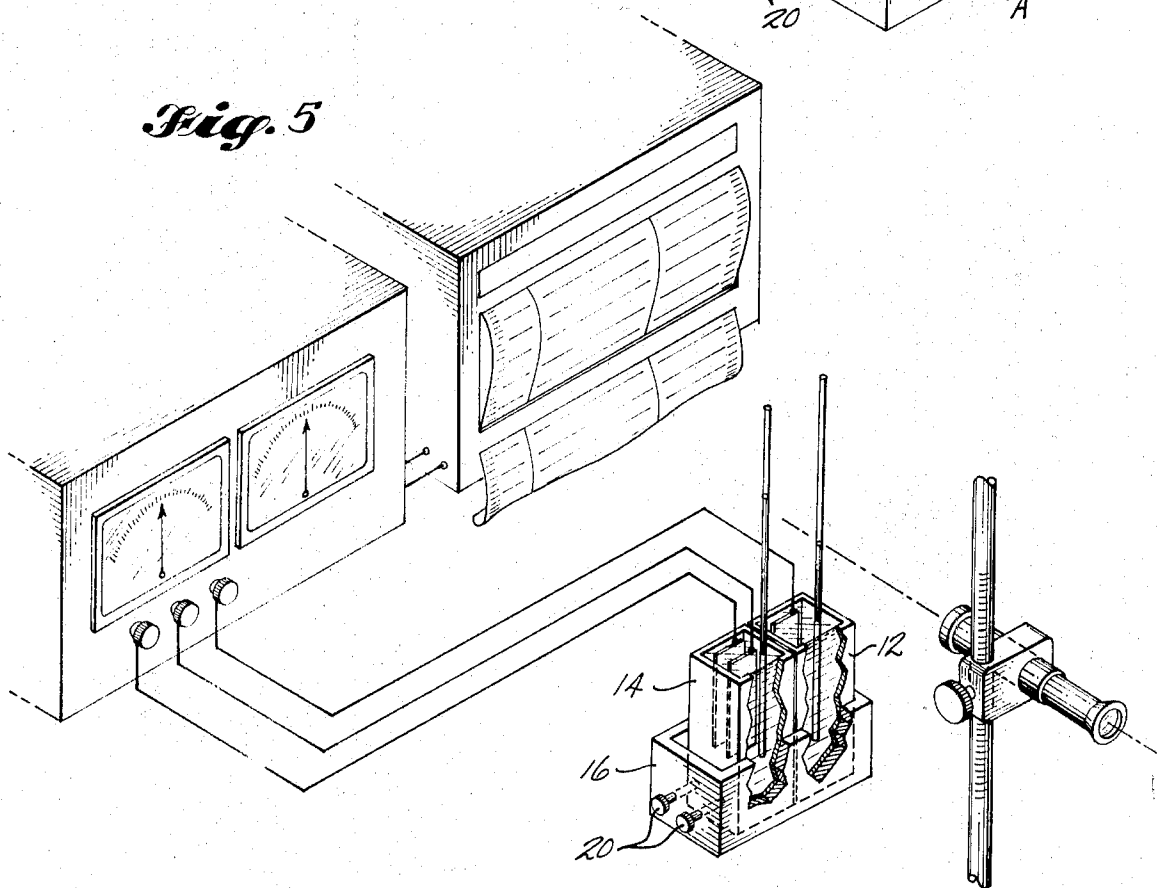
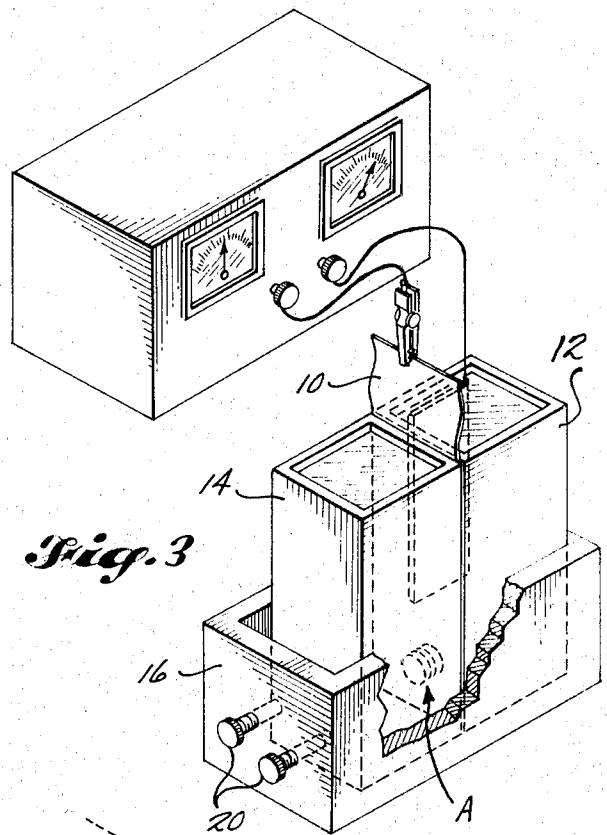
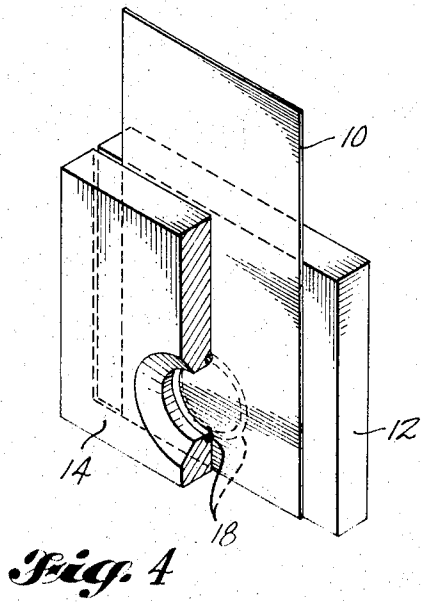
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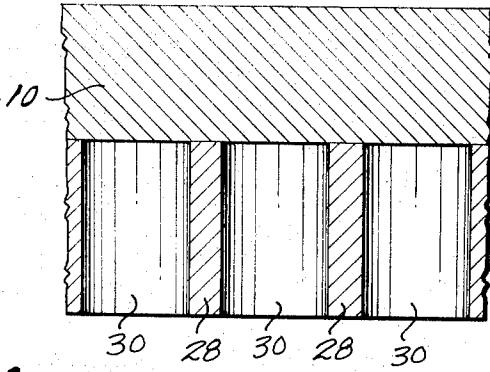
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PORES AS  
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REMOVE  
ALUMINUM AND  
BARRIER LAYER  
OF  $Al_2O_3$

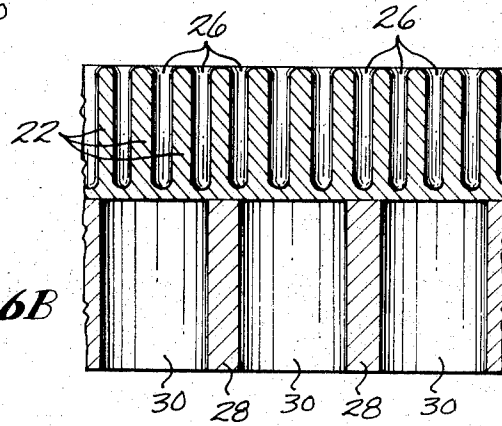
*Fig. 1*



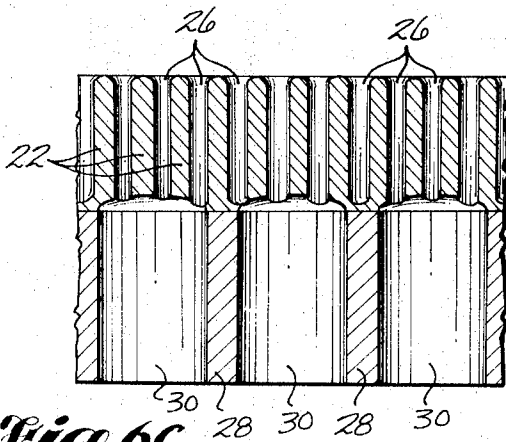




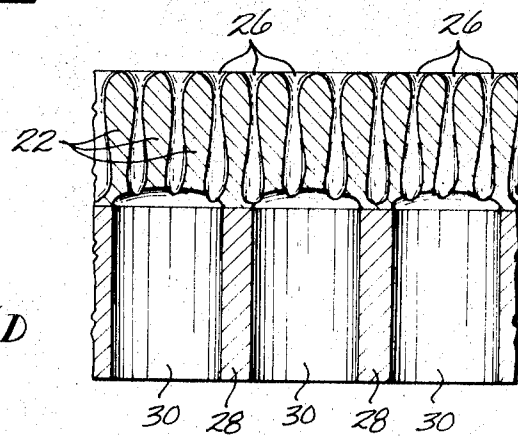
*Fig. 6A*



*Fig. 6B*



*Fig. 6C*



*Fig. 6D*

# PROCESS FOR PRODUCING AN ANODIC ALUMINUM OXIDE MEMBRANE

## BACKGROUND OF THE INVENTION

### a. Field of the Invention

The present invention relates to porous membranes and more specifically to a method for making porous membranes for hyperfiltration (reverse osmosis) and ultrafiltration.

### b. Description of the Prior Art

Membranes are used for the purpose of allowing or excluding the passage of various constituents of a fluid. The membranes contain pores or holes. Particles smaller than the pore size will pass through. Particles larger than the pore size cannot pass through and are trapped as with a sieve. For purposes of reference to size, the particles are designed by the size pore or hole which will trap them. The pores themselves are treated as being cylindrical about a longitudinal axis substantially perpendicular to the surface of the membrane. Thus, the pore is referred to as having a diameter and this "diameter" is in reality the diameter of a cylinder representing the effective cross sectional area of the pore at its most constricted point. When a pore is "closed," the material containing the pore is made to swell or a precipitate is deposited within the pore (or both) to make the size of the effective cross sectional area less so that smaller particles will be blocked or trapped.

In one mode of use, the solvent is forced through the membrane and dissolved or suspended particles remain behind. The term ultrafiltration refers to membranes with pores of the order of 50A to 10  $\mu$ m in diameter. The term reverse osmosis refers to filtering small solutes, less than a hundred angstroms, which have appreciable osmotic pressures. Thus, several hundred psi is needed in water desalinization just to counterbalance the osmotic pressure before filtration can take place. In another mode, the particles diffuse through the membrane. This is called dialysis. In one form of dialysis, an electric field is used to draw either positive or negative ions through the membrane. To prevent reverse flow of

the ions of opposite charge an ion-exchange membrane is used which allows only ions of one electrical charge (positive or negative) to pass.

Membranes have been used or proposed in many fields to effect separations. Table I covers the application of membranes of different classes to separations in various fields which are in use or have been proposed.

The structure of a membrane is a great importance. It should have a thin uniform pore size layer for separation, backed by a high permeability layer for mechanical support. The success of cellulose acetate membranes for reverse osmosis has come from the development of this structure.

The actual separation layer of these membranes is formed by the packing of roughly spherical particles. The permeability is less than that of cylindrical channels of equivalent pore size.

Almost all currently used membranes are based on organic polymers. Porous glass membranes have been studied but do not seem to be competitive at the present time.

Specific problems associated with areas of membrane use are:

#### 1. Water Desalinization

There are two disadvantages of present organic membranes of the cellulose acetate type used in reverse osmosis water desalinization: These disadvantages are the limitations on pressure which may be applied and the decrease in throughput with time. Since the water flow and salt rejection both increase with pressure, this limitation is most important. The decrease in throughput with time goes beyond problems due to clogging by materials in solution. Both problems seem to be due to the compaction of the membrane which closes the pores.

#### 2. Waste Treatment

Waste water treatment of both household or industrial wastes may involve several steps. One is removal of solids by conventional filtration. Removal of biological materials requires ultrafiltration. Removal and possible recovery of salts requires reverse osmosis. Solvents must be used to clean the membrane and/or sterilization must be carried out at elevated temperatures.

TABLE I

Membrane Pore Size	Separation	Processes	Applications	Examples
50A	SALTS FROM WATER	REVERSE OSMOSIS	WATER PURIFICATION	SEA WATER
			CHEMICAL RECOVERY	SPENT COBALT CALAYST
			WASTE TREATMENT	RESIDENTIAL
50-100A	WATER + SALTS FROM MACROMOLECULES	ELECTRO-DIALYSIS	INDUSTRIAL (RADIO-ACTIVE WASTE)	
			PULP MILL	
			WASTE TREATMENT	RESIDENTIAL
			FOOD CONCENTRATION	EGG WHITE, WHEY
50-500A	MACROMOLECULE	ELECTRO-DIALYSIS	PHARMACEUTICAL PURIFICATIONS	ENZYMES
			MEDICAL TREATMENTS	KIDNEY MACHINE
		ULTRA-FILTRATION DIALYSIS	MEDICINE PHARMACEUTICAL FOOD	PROTEIN - VIRUS SERUMS MILK PROTEIN-SUGARS

Salt removal is subject to the same considerations as mentioned in water desalinization.

### 3. Ultrafiltration of Biological and Food Products

In all these cases one is dealing with relatively large molecules which may need to be separated from each other, from salts, or from water. The most important factor besides having precise pore sizes is the ability to clean and sterilize the membranes. There are often wide limits to temperatures and solvents used.

### 4. Medical Usage

One of the problems in medical processing such as in the artificial kidney machine is the desire to keep the volume of the system as small as possible. Since this is a dialysis rather than filtration, the flow of salts through the membrane is slow and a high area of membrane is needed. Here, rigidity of the membrane would allow more closely spaced structures to be built to keep the volume of solution smaller than with present organic membranes.

The development of polymeric membranes for the above uses has been extensive in recent years and sophisticated techniques to optimizing their properties have been applied. Clearly, the development of a new membrane must give promise of superior properties. Present membranes are produced by casting a polymeric film which becomes granular with the space around the granules becoming the pores. These membranes lack rigidity, are subject to compaction under pressure and are limited in temperature and solvents which may be used.

It has, however, been demonstrated that hydrous oxides including aluminum oxides, when deposited in the pores of filters do have the ability to separate salt from water. It is the teaching of this invention to form a porous membrane of desired characteristics of aluminum oxide alone by forming a porous layer of aluminum oxide on metallic aluminum through anodization, closing the pore diameter as necessary, and removing all undesired metal and oxide by an etching process to leave only the desired membrane remaining.

Therefore, an object of the present invention is to provide a method for the production of a membrane where pore size can be controlled such that they may be small enough so that the membrane can be used in hyperfiltration, such as in desalinization of salt water, or large enough for ultrafiltration such as the dewatering of whey, or of a size suitable for dialysis such as in the artificial kidney machine.

Another object of the present invention is to provide a method for the production of a membrane that is rigid, thus allowing it to be made in thin sections with good flow and separation characteristics. Rigidity also allows close tolerances to be maintained in the operating cell and the use of a high pressure environment.

Another object of the present invention is to provide a method for the production of an inorganic membrane so that it can be used or cleaned in solvents or under conditions that are not accessible to organic membranes.

Other objects and many of the attendant advantages of this invention will be appreciated as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings.

## DESCRIPTION OF THE DRAWINGS

The present invention will be described in relation to the accompanying drawings, wherein:

FIG. 1 is a block diagram of the steps involved in the preferred embodiment of the present invention.

FIG. 2A is a cross section showing an anodized layer on an aluminum sheet corresponding to the first step in FIG. 1.

FIG. 2B is a cross section showing an anodized layer on an aluminum sheet with the pores constricted after a hydration (closing) process corresponding to the second step in FIG. 1.

FIG. 2C is a cross section showing an anodized layer of pores after the aluminum sheet and barrier layer have been removed corresponding to the third step in FIG. 1. The resultant membrane layer of pores is shown supported by a large pored support layer.

FIG. 3 shows the apparatus used for making the present invention under laboratory conditions so as to allow testing.

FIG. 4 is a detail drawing of the membrane formation area of the apparatus at A in FIG. 3.

FIG. 5 shows the apparatus of FIG. 3 as setup for testing the present invention after manufacture.

FIG. 6A is a cross section showing an aluminum sheet with a support structure adjacent prior to anodizing.

FIG. 6B is a cross section showing the structure of FIG. 6A after the aluminum sheet has been entirely anodized leaving only an oxide coating and the support structure.

FIG. 6C is a cross section showing the structure of FIG. 6B after the barrier layer has been etched away adjacent to the large pores in the support structure.

FIG. 6D is a cross section showing the structure of FIG. 6C after the pores have been closed by a hydration process. This represents a portion of the membrane which is the subject of the present invention as supported and ready for operation after commercial manufacture in a typical manner.

NOTE: The drawings of FIGS. 2A, 2B, 2C, 6A, 6B, 6C and 6D are not meant to be to scale, but rather, they are a representation of the process which takes place.

## DESCRIPTION AND OPERATION OF THE INVENTION

The present invention will be described with respect to making a membrane wherein the pore diameter must be closed to attain the desired membrane characteristics. It is important to note that the steps of pore closing and etching can be accomplished in various orders and combinations because of the nature of the materials involved and their reaction to the various processes described. A clearer understanding of the ways in which the disclosed process can be accomplished will be found by an inspection of the examples which follow hereinafter.

Referring to FIG. 3 and FIG. 4, a sheet of aluminum 10 is mounted such that separate solutions can be brought into contact with the surface of the aluminum sheet 10 individually or simultaneously in the area to be the foundation for the membrane. In the apparatus depicted in FIG. 3 this was accomplished by placing the aluminum sheet 10 between a first box 12 and a second box 14 contained in an outer box 16. The two boxes 12 and 14 contained matching holes with O-ring seals 18

such that when the boxes 12 and 14 were placed inside outer box 16 and screws 20 were tightened, the aluminum sheet 10 would be contained between the two O-ring seals 18 under pressure so as to form a liquid tight seal while exposing the portion of the aluminum sheet 10 to any solutions in first box 12 and second box 14 within the area bounded by O-ring seals 18.

Having thus described the apparatus used to make samples of the present invention, the process can be described with reference to FIG. 1 and FIGS. 2A, 2B and 2C.

The present invention is founded on the discovery that, by anodizing an aluminum foil in certain acids such as sulfuric, chromic, oxalic, and phosphoric and then etching away the unanodized metal and "barrier layer" oxide, a membrane of controlled porosity will result. The key to the present invention contained in the discovery is the repeatability of the porosity resulting from the anodization process. The porous oxide layer formed on aluminum by anodizing in solutions such as sulfuric acid has been studied in detail. Layers from 0.1 to 100  $\mu\text{m}$  thick have been produced. Pore diameters vary from 100–500 Å with pore spacings of 300–2,000 Å. The pore diameter and pore spacing are largely controlled by the voltage used during anodization. The oxide is amorphous or microcrystalline, contains about 10 percent of the anodizing ion and variable amounts of moisture. Between the porous layer and the metal remaining after anodization is a layer, the so-called barrier layer, whose thickness is about 10 Å per anodizing volt. This is depicted as the first step in FIG. 2A. Based on the desired membrane structure for the application, the aluminum sheet 10 is anodized with sulphuric acid in the standard manner so as to produce an oxide layer 22 of desired thickness containing a barrier layer 24 and pores 26 of the proper diameter.

It is important to remember that the anodization process consumes the aluminum sheet 10 to some degree to form the oxide layer 22. As depicted in the drawing and described herein, a portion of the aluminum sheet 10 remains after the anodization process. The drawing is illustrative of the basic process only. As will be further seen from the examples that follow hereinafter, if the aluminum sheet 10 is in the form of a very thin foil or formed layer, the entire aluminum sheet 10 may be consumed in the anodization process. This will be re-examined later in relation to supporting the resultant membrane which is the subject of the present invention.

The second step shown in FIG. 2B, that of closing the pores 26 is an optional step to be applied as necessary to cause a reduction in the pore size. If the oxide layer 22 is heated in water the pores 26 will be constricted due to the swelling of the surrounding material of the oxide layer 12. This is a pure hydration process. As an alternative, the pores 26 can also be closed by subjecting the oxide layer 22 to an alkaline solution. In this case part of the oxide layer 22 is removed and immediately precipitated within the pores 26 as a hydrated oxide. As used herein, both types of hydration are referred to as "hydration." If desired, the hydration process can be delayed until after the removal of the barrier layer 24 and aluminum sheet 10 in step 3. That is, step 2 and step 3 can be interchanged. Once the size of the pores 26 is established, with or without hydration, the oxide layer 22 can be stabilized to prevent inadvertent hydration from taking place during use or other-

wise by heating the oxide layer 22 in an acid phosphate solution.

The third step is that of removing the barrier layer 24 and any remaining aluminum sheet 10 leaving only the membrane which consists of only that portion of the oxide layer 22 containing the pores 26. This is shown in FIG. 2C. The aluminum sheet 10 and the barrier layer 24 of FIG. 2B are removed by etching away the aluminum sheet 10 with hydrochloric acid containing a copper salt followed by etching away the barrier layer 24 with either the same acid solution or by an alkaline solution such as sodium hydroxide. The choice of etchant is determined by the thickness of the materials to be removed in each instance. The object is to remove material as evenly as possible so as to eliminate both areas of incomplete removal wherein the membrane is incomplete and areas of excessive removal where the membrane is weak.

The resultant membrane is rigid over small areas but must be supported with a support structure 28 containing large pores 30 as shown in FIG. 2C when used over large areas and under high pressures. There are a number of ways the membrane could be supported as shown in FIG. 2C. The membrane portion of the oxide layer 22 could be formed first and then placed adjacent to a supporting structure 28. For particular applications, manufacturing of commercially usable membranes could take advantage of the ability of the anodization process to totally consume a thin foil or layer of the aluminum sheet 10. For example, FIGS. 6A, 6B, 6C and 6D depict a possible commercial manufacturing sequence supported by experiments with the present invention.

FIG. 6A depicts the placing of a thin aluminum sheet 10 adjacent to a support 28 containing large pores 30. The aluminum sheet 10 could be a layer of aluminum formed by evaporation of aluminum adjacent to an existing support structure 28. The support structure 28 could also be formed by slip casting a structure adjacent to an existing aluminum sheet 10. Having once formed the composite structure shown in FIG. 6A comprising the aluminum sheet 10 and the support structure 28, the aluminum sheet 10 could be processed as hereinbefore described according to the following optional sequence of operations to form a supported porous membrane. The thin aluminum sheet 10 would be anodized completely so as to virtually replace all of aluminum sheet 10 with oxide layer 22 containing pores 26 and a thin barrier layer 24 as shown in FIG. 6B.

The barrier layer 24 would next be removed adjacent to the large pores 30 of the support structure 28 by placing the sodium hydroxide etching solution into large pores 30 to form the porous supported membrane shown in FIG. 6C. At this point the porous membrane structure of FIG. 6C could be tested for performance characteristics. If necessary, the oxide layer 22 could be hydrated using hot water or sodium hydroxide solution to cause the closing of the membrane pores 26. The testing and hydrating process can be repeated until desired performance characteristics are met. At that point future hydration can be inhibited by heating the oxide layer 22 in phosphoric acid or phosphoric acid and metal phosphate buffer solution. The inhibiting of hydration was not done in the laboratory tests but would be highly desirable in membranes to be used commercially.

## EXAMPLES OF THE PRESENT INVENTION

All examples were manufactured and tested using the apparatus previously described and depicted in FIGS. 3, 4 and 5.

### EXAMPLE NO. 1

Aluminum foil 0.0005 inches thick was anodized by placing a solution of 15 percent  $\text{H}_2\text{SO}_4$  (by weight) containing 1.5 percent  $\text{Na}_2\text{Cr}_2\text{O}_7$  in the first box 12 of FIG. 3. The anodization process was at 15 volts for a period of 37 minutes. At this time the foil was translucent. After rinsing, the sample was etched with a 15 percent solution of  $\text{H}_2\text{SO}_4$  on the unanodized side in second box 14 and pure water on the anodized side in first box 12 until the sample became transparent (50 minutes). After rinsing, the sample was placed in distilled water to hydrate for 20 minutes at  $50^\circ - 60^\circ\text{C}$  and allowed to cool slowly.

The osmotic flow of the resultant membrane was determined by placing a 5 molar NaCl solution in the second box 14 and pure water in the first box 12. A value of 3  $\text{mg}/\text{cm}^2/\text{hr}$  was obtained for water flow and a ratio of 3:1 for water/salt flow.

A 15 percent  $\text{H}_2\text{SO}_4$ , 1.5 percent  $\text{Na}_2\text{Cr}_2\text{O}_7$  solution was then placed in the second box 14 and a moderately concentrated  $\text{K}_2\text{CrO}_4$  solution was placed in the first box 12. The  $\text{K}_2\text{CrO}_4$  gives a buffered basic solution. After 30 minutes the sample was rinsed and the membrane as modified was again tested. A water flow of 33  $\text{mg}/\text{cm}^2/\text{hr}$  was obtained and a water/salt flow ratio of 3:1. In this case the barrier layer had not been removed completely by the first etching.

The sample pores were then closed further by placing a 1 molar  $\text{Na}_2\text{Cr}_2\text{O}_7$  solution (buffered base) in the second box 14 and a 1 molar  $\text{Na}_2\text{Cr}_2\text{O}_7$  solution in the first box 12 for 20 min. This membrane produced a water flow of 110  $\text{mg}/\text{cm}^2/\text{hr}$  with a water/salt flow ratio of 8.5:1. When measured with a 1 molar salt solution the water flow was 70  $\text{mg}/\text{cm}^2/\text{hr}$  and the water/salt flow ratio was 23:1.

### EXAMPLE NO. 2

A 0.0005 inch thick aluminum foil was anodized in 10 percent chromic acid in first box 12 at 50 volts until the sample became fairly transparent (58 minutes). After rinsing, an osmotic flow with 1 molar NaCl was determined. The water flow was 5  $\text{mg}/\text{cm}^2/\text{hr}$  and the water/salt flow ratio was 7:1. In this example the barrier layer was etched toward the end and as part of the anodizing process itself. The quantity of water flow and water/salt flow ratio were too small for the resultant membrane to be of value.

### EXAMPLE NO. 3

Aluminum foil 0.0005 inches thick was anodized in concentrated  $\text{Na}_2\text{Cr}_2\text{O}_7$  with a small amount of concentrated  $\text{H}_2\text{SO}_4$  added in first box 12. The sample was anodized at 50 volts until the sample became transparent after 36 minutes. Then the sample was etched with 15 percent  $\text{H}_2\text{SO}_4$  plus 1.5 percent  $\text{Na}_2\text{Cr}_2\text{O}_7$  solution in second box 14 and a buffered  $\text{NaCrO}_4$  plus  $\text{Na}_2\text{Cr}_2\text{O}_7$  solution in first box 12 for 205 minutes. After rinsing, the osmotic flow was measured with a 1 percent NaCl solution. The water flow was 16  $\text{mg}/\text{cm}^2/\text{hr}$  and the water/salt flow ratio was 32:1. In this example the buffered solution in box 12 probably caused some hydrate

to precipitate in the pores giving a moderate desalination membrane.

### EXAMPLE NO. 4

Aluminum foil 0.002 inches thick was anodized in a 10 percent chromic acid and 1 percent sulfuric acid solution at 1 volt for 20 minutes (to inhibit pitting) and then slowly raised to 100 volts with the solution cooled to  $5^\circ\text{C}$ . It was anodized at 100 volts for 142 minutes. The sample was then placed in a solution of  $\text{HgCl}_2$  in 0.1 molar HCl until it became translucent to remove the unanodized metal and barrier layer in one step. The sample was rinsed and tested with a 1 molar NaCl solution. A water flow of 80  $\text{mg}/\text{cm}^2/\text{hr}$  and a water/salt flow ratio of 7:1 was obtained.

### EXAMPLE NO. 5

A 0.002 inch thick aluminum foil was anodized in 10 percent chromic acid plus 1 percent sulphuric acid at 80 volts for 165 minutes. Then a solution of 40 percent HCl (by volume) plus a small amount of copper chloride was placed in the second box 14 and pure water was placed in the first box 12. The sample quickly became transparent and was then rinsed. Then a  $5 \times 10^{-2}$  mole NaOH solution was placed in the second box 14 and a 1 molar solution of  $\text{Na}_2\text{Cr}_2\text{O}_7$  (acid buffer) was placed in the first box 12. The effect of this was to remove the barrier layer and cause a hydration through precipitation of hydrated oxide in the same step. After 140 minutes the sample was rinsed. The osmotic water flow into 1 molar NaCl was 95  $\text{mg}/\text{cm}^2/\text{hr}$  and the water/salt flow ratio was 84:1.

### EXAMPLE NO. 6

A sample was prepared as in Example No. 5 with the exception that the anodization was to 50 volts and the NaOH solution was left in 50 minutes. A water flow of 77  $\text{mg}/\text{cm}^2/\text{hr}$  was obtained with a corresponding water/salt flow ratio of 90:1. Note: Examples 5 and 6 give both high water flow and water/salt ratio. They represent the best practice for producing a desalination membrane.

Having thus described the present invention, what is claimed is:

1. The method of making a porous membrane for water desalination comprising the steps of:
  - a. forming an oxide coating on a sheet of aluminum in an anodizing solution which produces an oxide, said oxide comprising a generally porous layer and a non-porous layer;
  - b. removing any of said sheet of aluminum remaining after said anodization of said sheet of aluminum;
  - c. removing said non-porous layer of oxide; and,
  - d. treating said generally porous layer so that it allows the flow of water but restricts the flow of salts.
2. The method of making a porous membrane for water desalination as claimed in claim 1 wherein:
  - said generally porous layer is protected by the application of a buffered solution to said generally porous layer while said non-porous layer is removed by the application of a solution selected from the group consisting of acids and alkalines.
3. The method of making a porous membrane for water desalination as claimed in claim 1 wherein:
  - said step of treating said generally porous layer so that it allows the flow of water but restricts the flow



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of salts is accomplished by the application of hot water to said generally porous layer.

4. The method of making a porous membrane for water desalination as claimed in claim 1 wherein:

said step of treating said generally porous layer so that it allows the flow of water but restricts the flow of salts is accomplished by the simultaneous application of an alkaline solution to one side of said membrane and a buffered solution to the other side of said membrane.

5. The method of making a porous membrane for

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water desalination as claimed in claim 1 wherein:

said steps of removing said non-porous layer of oxide and of treating said generally porous layer so that it allows the flow of water but restricts the flow of salts are accomplished at one time by the simultaneous application of an alkaline solution to the non-porous layer side of said oxide coating and a buffered solution to the generally porous layer side of said oxide coating.

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