613781

COMMONWEALTH of AUSTRALIA
Patents Act 1952

APPLICATION FOR A STANDARD PATENT

I/We

Hydranautics Corporation

of

Suite E, 11111 Flintkote Avenue, San Diego, California, 92121, United States of America

hereby apply for the grant of a Standard Patent for an invention entitled:

Interfacially synthesized reverse osmosis membrane containing an amine salt and processes for preparing the same

which is described in the accompanying complete specification.

Details of basic application(s):-

Number	Convention Country	Date
250,190	United States of America	28 September 1988

The address for service is care of DAVIES & COLLISON, Patent Attorneys, of 1 Little Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia.

DATED this TENTH day of AUGUST 1989

To: THE COMMISSIONER OF PATENTS

.....
a member of the firm of
DAVIES & COLLISON for
and on behalf of the
applicant(s)

M 011427 100889

Davies & Collison, Melbourne

F-858

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

DECLARATION IN SUPPORT OF CONVENTION OR NON-CONVENTION APPLICATION FOR A PATENT

In support of the Application made for a patent for an invention

Insert title of invention.

entitled: INTERFACIALLY SYNTHESIZED REVERSE OSMOSIS MEMBRANE CONTAINING AN AMINE SALT AND PROCESSES FOR PREPARING THE SAME

Insert full name(s) and address(es) of declarant(s) being the applicant(s) or person(s) authorized to sign on behalf of an applicant company.

I ~~We~~ Minoru Ohishi, of
Hydranautics Corporation
Suite E
11111 Flintkote Avenue
San Diego, California 92121, USA

do solemnly and sincerely declare as follows :-

Cross out whichever of paragraphs 1(a) or 1(b) does not apply

1(a) relates to application made by individual(s)

1(b) relates to application made by company; insert name of applicant company.

1. (a) ~~I am / We are the applicant for the patent~~

or (b) I am authorized by

Hydranautics Corporation

the applicant..... for the patent to make this declaration on ~~their~~ its behalf.

Cross out whichever of paragraphs 2(a) or 2(b) does not apply

2(a) relates to application made by inventor(s)

2(b) relates to application made by company(s) or person(s) who are not inventor(s); insert full name(s) and address(es) of inventors.

2. (a) ~~I am / We are the actual inventor of the invention~~

or (b)

John E. Tomaschke
8979 Revelstoke Terrace
San Diego, California 92126, USA

~~is / are~~ the actual inventor..... of the invention and the facts upon which the applicant..... ~~is / are~~ entitled to make the application are as follows :-

State manner in which applicant(s) derive title from inventor(s)

by Assignment dated October 5, 1988, the actual inventor assigned the invention to the said applicant.

Cross out paragraphs 3 and 4 for non-convention applications. For convention applications, insert basic country(s) followed by date(s) and basic applicant(s).

3. The basic application..... as defined by Section 141 of the Act ~~were~~ was made

in the United States of America on the 28th September 1988

by John E. Tomaschke

in ..... on the .....

by .....

in ..... on the .....

by .....

4. The basic application..... referred to in paragraph 3 of this Declaration ~~were~~ was the first application..... made in a Convention country in respect of the invention the subject of the application.

Insert place and date of signature.

Declared at Santa Barbara, CA USA this 30 day of June 1989

Hydranautics Corporation

Signature of declarant(s) (no attestation required)

.....

.....
Minoru Ohishi, Chief Executive Officer

Note: Initial all alterations.

DAVIES & COLLISON, MELBOURNE and CANBERRA.

(12) PATENT ABRIDGMENT (11) Document No. AU-B-39483/89
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 613781

(54) Title
INTERFACIALLY SYNTHESIZED REVERSE OSMOSIS MEMBRANE CONTAINING AN AMINE SALT AND PROCESSES FOR PREPARING THE SAME

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(56) Prior Art Documents
US 4769148
US 4277344

(57) Claim

1. A water permeable membrane prepared by interfacially polymerizing, on a microporous support, (1) an essentially monomeric, aromatic polyamine reactant having at least two primary or secondary amine functional groups, and (2) an essentially monomeric, aromatic, amine-reactive reactant comprising a polyfunctional acyl halide or mixture thereof, wherein the amine-reactive reactant has, on the average, at least about 2.2 acyl halide groups per reactant molecule, in the presence of (3) a monomeric amine salt.

2. The water permeable membrane as claimed in claim 1, wherein said water permeable membrane is produced by the process comprising the steps of:

(a) coating a microporous support with an aqueous solution comprising (i) the polyamine reactant and (ii) the monomeric amine salt, to form a liquid layer on said microporous support;

(b) contacting said liquid layer with an organic solvent solution of the amine-reactive reactant; and

(c) drying the product of step (b) so as to form said water permeable membrane.

.../2

30. A process for producing a water permeable membrane comprising interfacially polymerizing, on a microporous support, (1) an essentially monomeric, aromatic polyamine reactant having at least two primary or secondary amine functional groups, and (2) an essentially monomeric, aromatic, amine-reactive reactant comprising a polyfunctional acyl halide or mixture thereof, wherein the amine-reactive reactant has, on the average, at least 2.2 acyl halide groups per reactant molecule, in the presence of (3) a monomeric amine salt.

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PATENTS ACT 1952

COMPLETE SPECIFICATION

NAME & ADDRESS
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NAME(S) OF INVENTOR(S):

John E. Tomaschke

ADDRESS FOR SERVICE:

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1 Little Collins Street, Melbourne, 3000.

COMPLETE SPECIFICATION FOR THE INVENTION ENTITLED:

Interfacially synthesized reverse osmosis membrane containing an amine salt and processes for preparing the same

The following statement is a full description of this invention, including the best method of performing it known to me/us:-

INTERFACIALLY SYNTHESIZED REVERSE OSMOSIS MEMBRANE CONTAINING AN AMINE SALT AND PROCESSES FOR PREPARING THE SAME

Field of the Invention

The present invention relates to an interfacially synthesized reverse osmosis membrane useful for the separation of fluid mixtures and solutions. In particular, the present invention relates to an aromatic polyamide water permeable membrane containing an amine salt therein, which is useful for desalination of an aqueous solution. The present invention also relates to processes for preparing the membrane.

Background of the Invention

It is known that dissolved substances can be separated from their solvents by use of selective membranes. For example, of great practical interest is the removal of salt from water by reverse osmosis. The efficiency and economy of such removal is of tremendous economic significance in order to provide potable water from brackish or sea water for household or agricultural use. A critical factor in desalination is the performance of the membrane in terms of salt rejection, i.e., the reduction in salt concentration across the membrane, and flux, i.e., the flow rate across the membrane. For practical applications, the flux should be on the order of greater than about 10 gallons/ft^2-day (gfd) at a pressure of about 55 atmospheres for sea water and about 15 gfd at a pressure of about 15 atmospheres for brackish water. The continuing goal of research and development in this area is to develop membranes having increased flux and/or salt rejection which are useful in desalination.

Among the known membranes used in desalination are included a large number of various types of polyamides which are prepared by a variety of methods.

Of particular interest within this broad group of polyamide membranes are crosslinked aromatic polyamide membranes. The crosslinked aromatic polyamide membranes include, for example, those disclosed in the following U.S. Patents.

U.S. Patent 3,904,519, issued to McKinney et al, discloses reverse osmosis membranes of improved flux prepared by crosslinking aromatic polyamide membranes using crosslinking agents and/or irradiation. The polyamides are prepared, for example, by the interfacial polymerization of amine groups and carboxyl groups followed by crosslinking.

U.S. Patent 3,996,318, issued to van Heuven, teaches the production of aromatic polyamide membranes, wherein crosslinking is achieved using a reactant having a functionality of three or greater.

U.S. Patent 4,277,344, issued to Cadotte, describes a reverse osmosis membrane which is the interfacial reaction product of an aromatic polyamine having at least two primary amine substituents with an aromatic acyl halide having at least three acyl halide substituents. The preferred membrane is made of a poly(phenylenediamine trimesamide) film on a porous polysulfone support.

U.S. Patent 4,529,646, issued to Sundet, shows a similar membrane in which all or a portion of the trifunctional aromatic acyl halide is replaced by cyclohexane - 1,3,5-tricarbonyl chloride. Similar membranes are disclosed in U.S. Patents 4,520,044, 4,544,484 and 4,626,468, each issued to Sundet.

U.S. Patent 4,661,254, issued to Zupanic et al, discloses a reverse osmosis composite membrane formed

by the interfacial polymerization of a triaryl triamine with an aromatic carboxylic acid chloride.

While some of the above referenced membranes are commercially useable, the goal of the industry continues to be to develop membranes that have better flux and salt rejection characteristics in order to reduce costs and increase efficiency of operation.

Summary of the Invention

Accordingly, an object of the present invention is to provide an interfacially synthesized reverse osmosis membrane which has high salt rejection and excellent flux.

This and other objects of the present invention, which will be apparent from the detailed description of the present invention provided hereinafter, have been met by a water permeable membrane prepared by interfacially polymerizing, on a microporous support, (1) an essentially monomeric, aromatic polyamine reactant having at least two amine functional groups, and (2) an essentially monomeric, aromatic, amine-reactive reactant comprising a polyfunctional acyl halide or mixture thereof, wherein the amine-reactive reactant has, on the average, at least about 2.2 acyl halide groups per reactant molecule, in the presence of (3) ~~an~~ a monomeric amine salt.

In one embodiment of the present invention, a solution containing an amine salt and an aromatic polyamine is coated on a microporous support prior to coating with a solution of an aromatic polyfunctional acyl halide.

In a second embodiment of the present invention, an amine salt solution is coated on a microporous support prior to coating with an aromatic polyamine solution and an aromatic polyfunctional acyl halide solution.

The resulting membrane consists of an ultrathin membrane on the microporous support. This membrane has excellent salt rejection and flux and is suitable for desalination applications.

Detailed Description of the Invention

In one embodiment, the objects of the present invention have been met by a water permeable membrane produced by the process comprising the steps of:

(a) coating a microporous support with an aqueous solution comprising (i) an essentially monomeric, aromatic, polyamine reactant having at least two amine functional groups and (ii) an amine salt, to form a liquid layer on said microporous support;

(b) contacting said liquid layer with an organic solvent solution of an essentially monomeric, aromatic, amine-reactive reactant comprising a polyfunctional acyl halide or mixture thereof, wherein the amine-reactive reactant has, on the average, at least about 2.2 acyl halide groups per reactant molecule; and

(c) drying the product of step (b) so as to form said water permeable membrane.

In a second embodiment, the water permeable membrane is produced by the process comprising the steps of:

(a) coating a microporous support with a first aqueous solution comprising an amine salt to form an amine salt layer on said microporous support;

(b) coating said amine salt layer with a second aqueous solution comprising an essentially monomeric, aromatic, polyamine reactant having at least two amine functional groups to form a liquid layer on said amine salt layer;

(c) coating said liquid layer with an organic solvent solution of an essentially monomeric, aromatic, amine-reactive reactant, comprising a polyfunctional acyl halide or mixture thereof, wherein the amine-reactive reactant has, on the average, at least about 2.2 acyl halide groups per reactant molecule; and

(d) drying the product of step (c) so as to form said water permeable membrane.

The particular microporous support employed in the present invention is not critical thereto. Examples of such microporous supports useful in the present invention include those made of a polyarylether sulfone, such as a polysulfone and a polyether sulfone; a polyimide; and a polyvinylidene fluoride. The microporous support is preferably made of a polyarylether sulfone.

The thickness of the microporous support is not critical to the present invention. Generally, the thickness of the microporous support is about 25 to 125 μm, preferably about 40 to 75 μm.

The essentially monomeric, aromatic, polyamine reactant employed in the present invention has at least two amine functional groups, preferably 2 to 3 amine functional groups. The amine functional group is a primary or secondary amine functional group, preferably a primary amine functional group.

The particular polyamine reactant employed in the present invention is not critical thereto. Examples of such polyamine reactants include aromatic primary diamines, such as m-phenylenediamine and p-phenylenediamine and substituted derivatives thereof, wherein the substituent includes, e.g., an alkyl group, such as a methyl group or an ethyl group; an alkoxy group, such as a methoxy group or an ethoxy group; a hydroxy alkyl group; a hydroxy group

or a halogen atom; cycloaliphatic primary diamines, such as cyclohexane diamine; cycloaliphatic secondary diamines, such as piperizine and trimethylene dipiperidine; aromatic secondary diamines, such as N,N'-diphenylethylene diamine; and xylylene diamine. The preferred polyamine reactants employed in the present invention are aromatic primary diamines, more preferably m-phenylenediamine.

The essentially monomeric, aromatic, amine-reactive reactant has, on the average, at least 2.2 polyfunctional acyl halide groups, preferably 2.2 to 3.0 polyfunctional acyl halide groups per reactant molecule.

The particular amine-reactive reactant employed in the present invention is not critical thereto. Examples of such amine-reactive reactants include isophthaloyl halide, trimesoyl Halide, terephthaloyl halide and mixtures thereof. The preferred amine-reactive reactants employed in the present invention are isophthaloyl chloride (IPC) and trimesoyl chloride (TMC).

The amine salt employed in the present invention maybe a salt of an amine and an acid, and is preferably a salt of a tertiary amine and a strong acid.

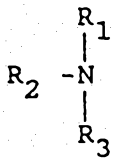
As used herein, a strong acid is an acid which reacts essentially completely with water to give a hydronium ion.

Examples of such strong acids include an aromatic sulfonic acid; an aliphatic sulfonic acid; a cycloaliphatic sulfonic acid, such as camphorsulfonic acid; trifluoroacetic acid; nitric acid; hydrochloric acid; and sulfuric acid.

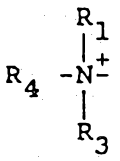
The particular amine salt employed in the present invention is not critical thereto and may be

any aliphatic, alkoxy, cycloaliphatic, heterocyclic or alkanol amine salt.

Preferred amine salts employed in the invention are represented by formula (I) and (II) below:

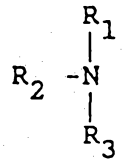


(I)



(II)

wherein R_1, R_2, R_3 and R_4, which may be the same or different, each represents a hydrocarbon; X represents a member selected from the group consisting of a halide, a nitrate, a sulfate, a phosphate, a sulfonate, a carboxylate, a halogenated carboxylate and an oxygenated haloacid derivative; and HX represents a strong acid which forms a water soluble salt with



In formula (I), the hydrocarbons represented by R_1, R_2 and R_3 preferably have a total number of carbon atoms of 3 to 9, more preferably, 3 to 6. In formula (II), the hydrocarbons represented by R_1, R_2, R_3 and R_4, preferably have a total number of carbon atoms of 4 to 16, more preferably, 4 to 13. The hydrocarbon may be, e.g., a straight or branched chain substituted or unsubstituted alkyl group, alkoxy group, alkanol group or benzyl group. Further, in formula (I), two or more of R_1, R_2 and R_3 may combine together to form a ring.

More preferably, the amine salt employed in the present invention is a water soluble salt of a strong acid and a tertiary amine selected from the group consisting of a trialkylamine, such as trimethylamine, triethylamine, tripropylamine; an N-alkylcycloaliphatic amine, such as 1-methylpiperidine; an N,N-dialkylamine, such as N,N-dimethylethylamine and N,N-diethylmethylamine; an N,N-dialkyl ethanolamine, such as N,N-dimethylethanolamine; a bicyclic tertiary amine, such as 3-quinuclidinol and mixtures thereof, or a quaternary amine selected from at least one member of the group consisting of a tetraalkylammonium hydroxide, such as, tetramethylammonium hydroxide, tetraethylammonium hydroxide, and tetrapropylammonium hydroxide; a benzyltrialkylammonium hydroxide, such as benzyltrimethylammonium hydroxide, benzyltriethylammonium hydroxide, and benzyltripropylammonium hydroxide; and mixtures thereof.

The amine salt is employed either as a solid, which is water soluble, or as an aqueous solution having dissolved therein the amine salt. The amine salt is preferably employed as an aqueous solution thereof.

The amine used to prepare the amine salt preferably has a pKa of more than about 8 more preferably about 8 to 13, most preferably about 9 to 13.

In one embodiment of the present invention, the microporous support is coated with a first aqueous solution containing generally about 0.25 to 10.0 wt% of an amine salt, preferably about 1.0 to 8.0 wt% of an amine salt. The first aqueous solution is preferably adjusted to a pH of about 5.5 to 9, more preferably about 7 to 8, by controlling the

concentration of the acid or the amine salt. In this case, the second aqueous solution containing the polyamine reactant generally has a pH of about 5 to 10, preferably about 7 to 9. Further, in this case, where the amine salt and the polyamine reactant are separately coated on the microporous support, the coating amount is generally adjusted so that the molar ratio of the amine salt to the polyamine reactant is about 0.1 to 4.0, preferably about 0.6 to 1.4.

In order to save a step in the process of the present invention, the above aqueous solution of the amine salt can also contain the polyamine reactant. In this case the aqueous solution is generally adjusted to a pH of about 5.5 to 9, preferably about 7 to 8. Further, in this case, the molar ratio of the amine salt to the polyamine reactant is also generally adjusted to about 0.1 to 4.0, preferably about 0.6 to 1.4.

The above aqueous solutions are coated by any well know means, such as dipping, spraying, roller coating or rod coating, and allowed to remain in place generally for about 5 seconds to 10 minutes, preferably about 20 seconds to 4 minutes.

If desired, the aqueous solutions may contain a surfactant for more improved results. The particular surfactant employed in the present invention is not critical thereto. Examples of such surfactants include sodium dodecyl benzene sulfonate (SDBS), sodium dodecyl sulfate (SDS), sodium lauryl sulfate (SLS) or mixtures thereof. The surfactants are generally employed at a concentration of about 0.01 to 0.5 wt%, preferably about 0.1 to 0.25 wt%.

After forming a liquid layer containing the amine salt and the polyamine reactant, a second layer of an organic solvent solution containing the

essentially monomeric, aromatic, amine-reactive reactant is coated thereon.

Generally, the organic solvent solution contains about 0.05 to 5.0 wt/vol%, preferably about 0.1 to 0.5 wt/vol% of the amine-reactive reactant.

The organic solvent employed in the present invention is generally one which is non-miscible with water. The particular organic solvent employed in the present invention is not critical thereto. Examples of such organic solvents include alkanes, such as hexane and nonane; cycloalkanes, such as cyclohexane; and halogenated derivatives thereof, such as Freon® (DuPont deNemours), including 1,1,2-trichlorotrifluoroethane; and mixtures thereof. The preferred organic solvents employed in the present invention are alkanes having from 8 to 12 carbon atoms.

The organic solvent containing the amine-reactive reactant is coated by any well known means, such as dipping or spraying and allowed to remain in place generally for about 5 seconds to 10 minutes, preferably about 20 seconds to 4 minutes.

It is preferable to employ an about 5 to 50, more preferably an about 10 to 30 molar excess of the polyamine reactant to the amine-reactive reactant.

After each step of coating the aqueous and organic solvent solutions, the excess solutions are drained off if necessary or otherwise removed. Then, after the last coating and draining step, the resulting product is dried to form a water permeable membrane. The resulting product is generally dried in an oven at about 60 to 110°C, preferably about 70 to 100°C for about 1 to 10 minutes, preferably about 2 to 8 minutes.

In this manner, a polyamide layer is formed on the microporous support. The thickness of the

resulting polyamide layer is generally about 0.05 to 1.0 μm, preferably about 0.15 to 0.5 μm.

The following examples are provided for illustrative purposes only and are in no way intended to limit the scope of the present invention.

Example 1

An aqueous solution containing, at a final concentration, 2.0 wt% of m-phenylenediamine (MPD), 2.0 wt% of tetramethylammonium hydroxide (TMAH), and 0.1 wt% of sodium dodecyl benzyl sulfonate (SDBS) in water was prepared. The pH of the final solution was adjusted to 5.7 with acetic acid. The solution was coated on a 60-70 μm thick microporous polysulfone support by pouring the aqueous solution on the microporous polysulfone support to form a liquid layer thereon. After coating the aqueous solution on the microporous polysulfone support and allowing it to remain thereon for 2 minutes, the support was drained to remove the excess aqueous solution. Then, an organic solvent solution containing, at a final concentration, 0.05 wt% of trimesoyl chloride (TMC) and 0.075 wt% of isophthaloyl chloride (IPC), in Isopar® (Exxon Corp.), was coated on the liquid layer by pouring the organic solvent solution on the liquid layer and allowing it to remain for 1 minute before the support was drained to remove the excess organic solvent solution. Next, the microporous polysulfone layer coated with the above-described solutions was dried in an oven at 95°C for 6 minutes.

The performance of the resulting water permeable membrane was measured by passing an aqueous solution containing 2,000 ppm of NaCl, pH 7.0, through the membrane at 225 psig.

The salt rejection was 99.69% and the flux was 20.1 gfd.

Example 2

The procedure of Example 1 was repeated, except that the pH of the final solution was adjusted to 8.0 with acetic acid.

The salt rejection was 99.84% and the flux was 19.8 gfd under the same test conditions as in Example 1.

Comparative Examples A-D and Examples 3-19

The procedure of Example 1 was repeated, except that the amine salt was omitted or the amine salts set forth in Table 1 below were substituted for TMAH in the amounts indicated in Table 1 and the strong acids in Table 1 were substituted for acetic acid so as to achieve the final pH shown in Table 1. For ease of consideration, Examples 1 and 2 are also shown in Table 1.

Table 1

Example	Amine Salt			pH
	Amine			
		Concentration wt%	Acid	
1	tetramethylammonium hydroxide	2	AA	5.7
2	tetramethylammonium hydroxide	2	AA	8.0
3	tetramethylammonium hydroxide	2	CSA	9.3
4	dipropylamine	2	CSA	7.8
5	triethylamine	2	CSA	7.8
Comp. A	--	--	CSA	7.4
6	tripropylamine	2	CSA	8.0
7	1-methylpiperidine	2	CSA	8.0
8	N,N-diethylmethylamine	2	CSA	8.0
9	N,N-dimethylethylamine	2	CSA	8.0
10	N,N-dimethylethanolamine	2	CSA	8.0
Comp. B	--	--	CSA	9.0
11	N,N-dimethyl 4-amino-pyridine	0.32	CSA	5.7
Comp. C	--	--	CSA	5.7
12	benzyltrimethylammonium chloride	2	HCl	7.5
13	tetramethylammonium hydroxide	2	HCl	7.4
14	triethylamine	2	HCl	8.5
15	trimethylamine	2	HCl	5.7
Comp. D	--	--	HCl	5.7
16	3-quinuclidinol	0.5	HCl	9.0
17	1-methylpiperidine	2	MSA	7.8
18	tetramethylammonium hydroxide	2	TFAA	7.35
19	triethylamine	2	TFAA	7.8

AA = acetic acid
CSA = camphorsulfonic acid
MSA = methanesulfonic acid
TFAA = trifluoroacetic acid

The resulting water permeable membranes were evaluated as in Example 1 and the results are shown in Table 2 below. For ease of consideration, the results for the water permeable membranes of Examples 1 and 2 are also shown in Table 2.

Table 2

Example	Salt Rejection (%)	Flux (gfd)
1	99.69	20.1
2	99.84	19.8
3	99.90	16.3
4	99.88	15.8
5	99.87	22.1
Comp. A	99.81	5.6
6	99.84	19.8
7	99.88	20.8
8	99.86	22.3
9	99.91	19.8
10	99.87	20.7
Comp. B	99.46	6.2
11	99.64	17.8
Comp. C	99.82	15.3
12	99.76	18.5
13	99.90	16.8
14	99.64	18.9
15	99.66	16.6
Comp. D	99.76	13.4
16	99.82	15.5
17	99.26	15.1
18	99.90	15.9
19	99.87	21.8

As shown in Table 2 above, there is a significant (up to three fold or more) increase in flux using the amine salt as per the present invention without adversely effecting the salt rejection regardless of the amine salt, acid employed in the aqueous solution, or pH thereof.

Examples 20-34 and Comparative Examples E-M

An aqueous solution was prepared containing, at a final concentration, 2.0 wt% of MPD; 6.6 wt% of amine salt of triethylamine and camphorsulfonic acid and 0.1 wt% of SDBS in water. For comparison, a similar solution was prepared without the amine salt. The pH of the final solutions was adjusted to the

values as indicated in Table 3 below with camphorsulfonic acid.

The resulting aqueous solutions were coated on a 60-70 μm thick microporous polysulfone supports by pouring and allowing such to remain for 2 minutes before draining off the excess aqueous solutions.

After coating the aqueous solutions, organic solvent solutions containing, at the final concentrations set forth in Table 3, the acid chlorides set forth in Table 3, were coated thereon by pouring, allowing such to remain for 1 minute and then draining the excess organic solvent solutions. Next, the microporous polysulfone supports coated with the above-described solutions were dried in an oven under the conditions indicated in Table 3.

Table 3

Example	TEACSA (wt%)	pH	Acid Chloride	Acid Chloride Concentration (wt%)	Solvent	Drying	
						Time (min.)	Temp (°C)
20	6.6	8.7	TMC	0.10	Freon	3.5	70
Comp. E	-	8.7	TMC	0.10	Freon	3.5	70
21	6.6	8.7	TMC	0.10	Isopar	6.0	95
Comp. F	-	8.7	TMC	0.10	Isopar	6.0	95
22	6.6	8.6	Mixture A	0.125	Isopar	6.0	95
Comp. G	-	8.6	Mixture A	0.125	Isopar	6.0	95
23	6.6	8.7	Mixture B	0.125	Isopar	6.0	95
24	6.6	8.7	Mixture B	0.125	Freon	3.5	70
Comp. H	-	8.7	Mixture B	0.125	Freon	3.5	70
25	6.6	8.7	TMC	0.125	Freon	3.5	70
Comp. I	-	8.7	TMC	0.125	Freon	3.5	70
26	6.6	7.0	Mixture B	0.125	Freon	6.0	95
27	6.6	7.0	Mixture B	0.25	Freon	6.0	95
28	6.6	7.0	Mixture B	0.25	Freon	3.5	70
29	6.6	7.0	Mixture C	0.125	Freon	3.5	70
Comp. J	-	7.0	Mixture C	0.125	Freon	3.5	70
30	6.6	7.0	Mixture C	0.125	Isopar	6.0	95
Comp. K	-	7.0	Mixture C	0.125	Isopar	6.0	95
31	6.6	7.0	Mixture B	0.125	Freon	3.5	70
Comp. L	-	7.0	Mixture B	0.125	Freon	3.5	70
32	6.6	7.0	Mixture B	0.125	Isopar	6.0	95
Comp. M	-	7.0	Mixture B	0.125	Isopar	6.0	95

TEACSA = amine salt of triethylamine and camphorsulfonic acid.
Mixture A = a mixture of 70wt% IPC and 30wt% TMC.
Mixture B = a mixture of 60wt% IPC and 40wt% TMC.
Mixture C = a mixture of 50wt% IPC and 50wt% TMC.

The resulting water permeable membranes were evaluated as in Example 1 and the results are shown in Table 4 below.

Table 4

Example	Salt Rejection (%)	Flux (gfd)
20	99.78	18.4
Comp. E	99.37	14.2
21	99.80	19.4
Comp. F	99.84	5.7
22	99.58	14.1
Comp. G	99.16	2.6
23	99.85	26.3
24	99.25	20.0
Comp. H	98.35	10.2
25	99.69	19.3
Comp. I	99.63	16.3
26	99.79	20.1
27	99.81	22.6
28	99.78	18.8
29	99.83	20.7
Comp. J	99.72	5.0
30	99.84	25.8
Comp. K	99.75	7.7
31	99.60	21.9
Comp. L	99.50	12.2
32	99.45	21.2
Comp. M	99.63	6.2

As shown in Table 4 above, there is a significant (up to three fold or more) increase in flux using the amine salt as per the present invention without adversely effecting the salt rejection, regardless of the particular organic solvent solution and pH of the aqueous solution employed.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A water permeable membrane prepared by interfacially polymerizing, on a microporous support, (1) an essentially monomeric, aromatic polyamine reactant having at least two primary or secondary amine functional groups, and (2) an essentially monomeric, aromatic, amine-reactive reactant comprising a polyfunctional acyl halide or mixture thereof, wherein the amine-reactive reactant has, on the average, at least about 2.2 acyl halide groups per reactant molecule, in the presence of (3) a monomeric amine salt.

2. The water permeable membrane as claimed in claim 1, wherein said water permeable membrane is produced by the process comprising the steps of:

(a) coating a microporous support with an aqueous solution comprising (i) the polyamine reactant and (ii) the monomeric amine salt, to form a liquid layer on said microporous support;

(b) contacting said liquid layer with an organic solvent solution of the amine-reactive reactant; and

(c) drying the product of step (b) so as to form said water permeable membrane.

3. The water permeable membrane as claimed in claim 1, wherein said water permeable membrane is produced by the process comprising the steps of:

(a) coating a microporous support with a first aqueous solution comprising the monomeric amine salt to form an amine salt layer on said microporous support;

(b) coating said monomeric amine salt layer with a second aqueous solution comprising the polyamine reactant to form a liquid layer on said monomeric amine salt layer;

(c) coating said liquid layer with an organic

solvent solution of the amine-reactive reactant; and

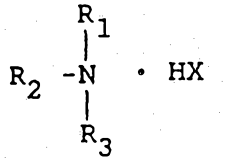
(d) drying the product of step (c) so as to form said water permeable membrane.

4. The water permeable membrane as claimed in any preceding claim, wherein the amine used to prepare said monomeric amine salt has a pKa of at least 8.

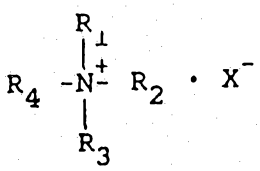
5. The water permeable membrane as claimed in claim 4, wherein the amine used to prepare said monomeric amine salt has a pKa in the range 8 to 13.

6. The water permeable membrane as claimed in claim 5, wherein the amine used to prepare said monomeric amine salt has a pKa in the range 9 to 13.

7. The water permeable membrane as claimed in any preceding claim, wherein said monomeric amine salt is represented by formula (I) or (II)

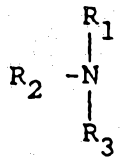


(I)



(II)

wherein R_1, R_2, R_3 and R_4, which may be the same or different, each represents a hydrocarbon; X represents a member selected from the group consisting of a halide, a nitrate, a sulfate, a phosphate, a sulfonate, a carboxylate, a halogenated carboxylate and an oxygenated haloacid derivative; and HX represents a strong acid which forms a water soluble salt with



8. The water permeable membrane as claimed in claim 7, wherein said strong acid is selected from the group consisting of an aromatic sulfonic acid; an aliphatic sulfonic acid; a cycloaliphatic sulfonic acid, trifluoroacetic acid; nitric acid; hydrochloric acid; and sulfuric acid.

9. The water permeable membrane as claimed in any one of claims 1 to 6, wherein said monomeric amine salt is a water soluble salt of a strong acid and a tertiary amine selected from at least one member of the group consisting of a trialkylamine; an N-alkyl cycloaliphatic amine; an N,N-dialkylamine; N,N-dialkylethanolamine and a bicyclic tertiary amine, or a quaternary amine selected from at least one member of the group consisting of a tetraalkylammonium hydroxide; and a benzyltrialkyl-ammonium hydroxide; and mixtures thereof.

10. The water permeable water membrane as claimed in claim 9, wherein said monomeric amine salt is a water soluble salt of a strong acid and triethylamine.

11. The water permeable membrane as claimed in any preceding claim, wherein said amine-reactive reactant is at least one member selected from the group consisting of isophthaloyl halide, trimesoyl halide and terephthaloyl halide.

12. The water permeable membrane as claimed in any preceding claim, wherein said amine functional groups are primary amine functional groups.

13. The water permeable membrane as claimed in any preceding claim, wherein said polyamine reactant is at leat one member selected from the group consisting of an aromatic primary diamine and substituted derivatives thereof; a cycloaliphatic primary diamine; a cycloaliphatic secondary diamine; an aromatic secondary diamine and xylylene diamine.

14. The water permeable membrane as claimed in claim 2 or any preceding claim dependent thereon, wherein said aqueous solution has a pH of 5.5 to 9.

15. The water permeable membrane as claimed in claim 14, wherein said aqueous solution has a pH of 7 to 8.

16. The water permeable membrane as claimed in claim 3 or any preceding claim dependent thereon, wherein said first aqueous solution has a pH of 5.5 to 9.

17. The water permeable membrane as claimed in claim 16, wherein said first aqueous solution has a pH of 7 to 8.

18. The water permeable membrane as claimed in claim 3 or any preceding claim dependent thereon, wherein said second aqueous solution has a pH of 5 to 10.

19. The water permeable membrane as claimed in claim 18, wherein said second aqueous solution has a pH of 7 to 9.

20. The water permeable membrane as claimed in claim 3 or any preceding claim dependent thereon, wherein said first aqueous solution contains 0.25 to 10.0 wt% of said monomeric amine salt.

21. The water permeable membrane as claimed in claim 20, wherein said first aqueous solution contains 1.0 to

8.0 wt% of said monomeric amine salt.

22. The water permeable membrane as claimed in any preceding claim, wherein the molar ratio of the monomeric amine salt to the polyamine reactant is 0.1 to 4.0.

23. The water permeable membrane as claimed in claim 22, wherein the molar ratio of the monomeric amine salt to the polyamine reactant is 0.6 to 1.4.

24. The water permeable membrane as claimed in claim 2 or any preceding claim dependent thereon, wherein the concentration of the amine-reactive reactant in the organic solvent solution is 0.05 to 5 wt/vol%.

25. The water permeable membrane as claimed in claim 24, wherein the concentration of the amine-reactive reactant in the organic solvent solution is 0.1 to 0.5 wt/vol%.

26. The water permeable membrane as claimed in claim 3 or any preceding claim dependent thereon, wherein the concentration of the amine-reactive reactant in the organic solvent solution is 0.05 to 5.0 wt/vol%.

27. The water permeable membrane as claimed in claim 26, wherein the concentration of the amine-reactive reactant in the organic solvent solution is 0.1 to 0.5 wt/vol%.

28. The water permeable membrane as claimed in any preceding claim, wherein a 5 to 50 molar excess of the polyamine reactant to the amine-reactive reactant is employed.

29. The water permeable membrane as claimed in claim 28, wherein a 10 to 30 molar excess of the polyamine reactant to the amine-reactive reactant is employed.

30. A process for producing a water permeable membrane comprising interfacially polymerizing, on a microporous support, (1) an essentially monomeric, aromatic polyamine reactant having at least two primary or secondary amine functional groups, and (2) an essentially monomeric, aromatic, amine-reactive reactant comprising a polyfunctional acyl halide or mixture thereof, wherein the amine-reactive reactant has, on the average, at least 2.2 acyl halide groups per reactant molecule, in the presence of (3) a monomeric amine salt.

31. The process as claimed in claim 30, comprising the steps of:

(a) coating a microporous support with an aqueous solution comprising (i) the polyamine reactant and (ii) the monomeric amine salt, to form a liquid layer on said microporous support;

(b) contacting said liquid layer with an organic solvent solution of the amine-reactive reactant; and

(c) drying the product of step (b) so as to form said water permeable membrane.

32. The process as claimed in claim 30, comprising the steps of:

(a) coating a microporous support with a first aqueous solution comprising the monomeric amine salt to form a monomeric amine salt layer on said microporous support;

(b) coating said monomeric amine salt layer with a second aqueous solution comprising the polyamine reactant to form a liquid layer on said monomeric amine salt layer;

(c) coating said liquid layer with an organic solvent solution of the amine-reactive reactant; and

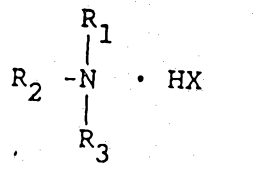
(d) drying the product of step (c) so as to form said water permeable membrane.

33. The process as claimed in claim 30, 31 or 32, wherein the amine used to prepare said monomeric amine salt has a pKa of at least 8.

34. The process as claimed in claim 33, wherein the amine used to prepare said monomeric amine salt has a pKa of at least 8 to 13.

35. The process as claimed in claim 34, wherein the amine used to prepare said monomeric amine salt has a pKa of at least 9 to 13.

36. The process as claimed in any one of claims 30 to 35, wherein said monomeric amine salt is represented by formula (I) or (II)



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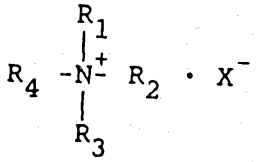
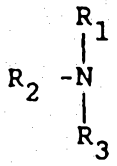


(II)

wherein R_1, R_2, R_3 and R_4, which may be the same or different, each represents a hydrocarbon; X represents a member selected from the group consisting of a halide, a nitrate, a sulfate, a phosphate, a sulfonate, a carboxylate, a halogenated carboxylate and an oxygenated haloacid derivative; and HX represents a strong acid which forms a water soluble salt with



37. The process as claimed in claim 36, wherein said

strong acid is selected from the group consisting of an aromatic sulfonic acid; an aliphatic sulfonic acid; a cycloaliphatic sulfonic acid; trifluoroacetic acid; nitric acid; hydrochloric acid; and sulfuric acid.

38. The process as claimed in any one of claims 30 to 35, wherein said monomeric amine salt is a water soluble salt of a strong acid and a tertiary amine selected from at least one member of the group consisting of a trialkylamine; an N-alkyl cycloaliphatic amine; an N,N-dialkylamine; N,N-dialkylethanolamine and a bicyclic tertiary amine, or a quaternary amine selected from at least one member of the group consisting of a tetraalkylammonium hydroxide, and a benzyl trialkylammonium hydroxide; and mixtures thereof.

39. The process as claimed in claim 38, wherein said monomeric amine salt is a water soluble salt of a strong acid and triethylamine.

40. The process as claimed in any one of claims 30 to 39, wherein said amine-reactive reactant is at least one member selected from the group consisting of isophthaloyl halide, trimesoyl halide, and terephthaloyl halide.

41. ~~The water permeable membrane~~ The process as claimed in any one of claims 30 to 40, wherein said amine functional groups are primary amine functional groups.

42. The process as claimed in any one of claims 30 to 41, wherein said polyamine reactant is at least one member selected from the group consisting of an aromatic primary diamine and substituted derivatives thereof; a cycloaliphatic primary diamine; a cycloaliphatic secondary diamine; an aromatic secondary diamine and xylylene diamine.

43. The process as claimed in claim 31 or any one of claims 32 to 42 when dependent thereon, wherein said aqueous solution has a pH of 5.5 to 9.

44. The process as claimed in claim 43, wherein said aqueous solution has a pH of 7 to 8.

45. The process as claimed in claim 32 or any one of claims 33 to 42 when dependent thereon, wherein said first aqueous solution has a pH of 5.5 to 9.

46. The process as claimed in claim 45, wherein said first aqueous solution has a pH of 7 to 8.

47. The process as claimed in claim 32 or any one of claims 33 to 42 when dependent thereon, wherein said second aqueous solution has a pH of 5 to 10.

48. The process as claimed in claim 47, wherein said second aqueous solution has a pH of 7 to 9.

49. The process as claimed in claim 32 or any one of claims 33 to 42 when dependent thereon, wherein said first aqueous solution contains 0.25 to 10.0 wt% of said monomeric amine salt.

50. The process as claimed in claim 49, wherein said first aqueous solution contains 1.0 to 8.0 wt% of said monomeric amine salt.

51. The process as claimed in any one of claims 30 to 50, wherein the molar ratio of the monomeric amine salt to the polyamine reactant is 0.1 to 4.0.

52. The process as claimed in claim 51, wherein the molar ratio of the monomeric amine salt to the polyamine

reactant is 0.6 to 1.4.

53. The process as claimed in claim 31 or any one of claims 32 to 52 when dependent thereon, wherein the concentration of the amine-reactive reactant in the organic solvent solution is 0.05 to 5 wt/vol%.

54. The process as claimed in claim 53, wherein the concentration of the amine-reactive reactant in the organic solvent solution is 0.1 to 0.5 wt/vol%.

55. The process as claimed in claim 32 or any one of claims 33 to 54 when dependent thereon, wherein the concentration of the amine-reactive reactant in the organic solvent solution is 0.05 to 5 wt/vol%.

56. The process as claimed in claim 55, wherein the concentration of the amine-reactive reactant in the organic solvent solution is 0.1 to 0.5 wt/vol%.

57. The process as claimed in any one of claims 30 to 56, wherein a 5 to 50 molar excess of the polyamine reactant to the amine-reactive reactant is employed.

58. The process as claimed in claim 57, wherein a 10 to 30 molar excess of the polyamine reactant to the amine-reactive reactant is employed.

59. Water permeable membranes or methods for their manufacture or use, substantially as hereinbefore described with reference to the examples.

60. A method of desalination of an aqueous solution, the method comprising passing the aqueous solution through a membrane as defined in any one of claims 1 to 29, thereby removing dissolved salts from the aqueous solution.

DATED this 14th day of May, 1991.

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By Its Patent Attorneys
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