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(71) Applicant: **DOW GLOBAL TECHNOLOGIES LLC**
[US/US]; 2040 Dow Center, Midland, MI 48674 (US).(72) Inventors: **ROY, Abhishek**; 6701 Indian Hills Road, Edina, MN 55439 (US). **MAEDA, Yasushi**; 889-13, Niihashi, Gotemba-shi, Shizuoka, 412-0043 (JP). **PAUL, Mou**; 6701 Indian Hills Road, Edina, MN 55439 (US). **ROSENBERG, Steven**; 5725 Brentridge Drive, Shorewood, MN 55331 (US). **TOMLINSON, Ian, A.**; 4415 Andre Street, Midland, MI 48642 (US).(74) Agent: **BLACK, Edward, W.**; The Dow Chemical Company, Intellectual Property, P. O. Box 1967, Midland, MI 48641-1967 (US).

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(54) Title: COMPOSITE POLYAMIDE MEMBRANE INCLUDING TRI-HYDROCARBYL PHOSPHATE

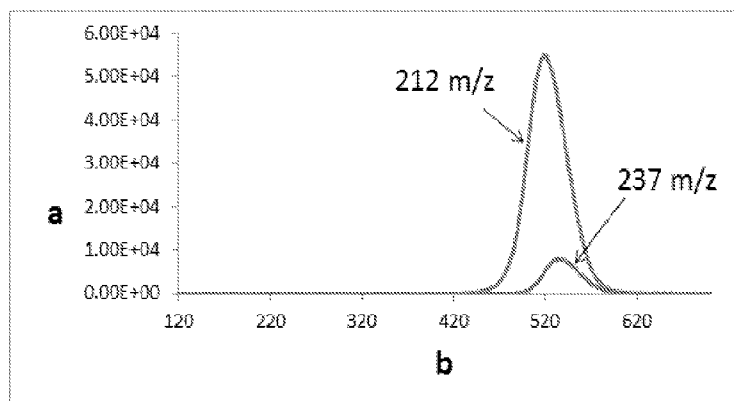


Fig. 1

(57) Abstract: A method for making a composite polyamide membrane comprising a porous support and a thin film polyamide layer, wherein the method includes: i) applying a polar solution including a polyfunctional amine monomer and a non-polar solution including a polyfunctional acylhalide monomer to a surface of a porous support and interfacially polymerizing the monomers to form a thin film polyamide layer, and wherein at least one or both of the solutions further includes a tri-hydrocarbyl phosphate compound and ii) exposing the thin film polyamide layer to nitrous acid.

COMPOSITE POLYAMIDE MEMBRANE INCLUDING TRI-HYDROCARBYL PHOSPHATE FIELD

The present invention is generally directed toward composite polyamide membranes along
5 with methods for making and using the same.

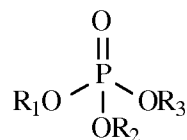
INTRODUCTION

Composite polyamide membranes are used in a variety of fluid separations. One common
class of membranes includes a porous support coated with a “thin film” polyamide layer. The thin
10 film layer may be formed by an interfacial polycondensation reaction between polyfunctional amine
(e.g. m-phenylenediamine) and polyfunctional acyl halide (e.g. trimesoyl chloride) monomers which
are sequentially coated upon the support from immiscible solutions, see for example US 4277344 to
Cadotte. Various constituents may be added to one or both of the coating solutions to improve
membrane performance. For example, US 4259183 to Cadotte describes the use of combinations of
15 bi- and tri-functional acyl halide monomers, e.g. isophthaloyl chloride or terephthaloyl chloride
with trimesoyl chloride. WO2012/102942, WO2012/102943, WO2012/102944, WO2013/048765
and WO2013/103666 describe the addition of various monomers including carboxylic acid and
amine-reactive functional groups in combination with the addition of a tri-hydrocarbyl phosphate
compound as described in US 6878278 to Mickols. US 2011/0049055 describes the addition of
20 moieties derived from sulfonyl, sulfinyl, sulfenyl, sulfuryl, phosphoryl, phosphonyl, phosphinyl,
thiophosphoryl, thiophosphonyl and carbonyl halides. US 2009/0272692, US 2012/0261344 and
US 8177978 describe the use of various polyfunctional acyl halides and their corresponding partially
hydrolyzed counterparts. US 4812270 and US 4888116 to Cadotte (see also WO 2013/047398,
US2013/0256215, US2013/0126419, US2012/0305473, US2012/0261332 and US2012/0248027)
25 describe post-treating the membrane with phosphoric or nitrous acid. The search continues for new
combinations of monomers, additives and post-treatments that further improve membrane
performance.

SUMMARY

30 The invention includes a method for making a composite polyamide membrane including a
porous support and a thin film polyamide layer. The method includes the steps of: i) applying a polar
solution including a polyfunctional amine monomer and a non-polar solution including a
polyfunctional acyl halide monomer to a surface of a porous support and interfacially polymerizing
the monomers to form a thin film polyamide layer, and wherein at least one or both of the solutions
35 further includes a tri-hydrocarbyl phosphate compound represented by Formula I:

Formula (I):



wherein R₁, R₂ and R₃ are independently selected from hydrogen and hydrocarbyl groups comprising from 1 to 10 carbon atoms, with the proviso that no more than one of R₁, R₂ and R₃ are hydrogen; and ii) exposing the thin film polyamide layer to nitrous acid.

In another preferred embodiment, non-polar solution further comprises an acid-containing monomer comprising a C₂-C₂₀ hydrocarbon moiety substituted with at least one carboxylic acid functional group or salt thereof and at least one amine-reactive functional group selected from: acyl halide, sulfonyl halide and anhydride, wherein the acid-containing monomer is distinct from the polyfunctional acyl halide monomer.

Many additional embodiments are described including applications for such membranes.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a plot of pyrolysis GC-MS response (a) for a representative thin film polyamide layer as a function of temperature (b) corresponding to a representative thin film polyamide layer.

DETAILED DESCRIPTION

The invention is not particularly limited to a specific type, construction or shape of composite membrane or application. For example, the present invention is applicable to flat sheet, tubular and hollow fiber polyamide membranes useful in a variety of applications including forward osmosis (FO), reverse osmosis (RO), nano filtration (NF), ultra filtration (UF), micro filtration (MF) and pressure retarded fluid separations. However, the invention is particularly useful for membranes designed for RO and NF separations. RO composite membranes are relatively impermeable to virtually all dissolved salts and typically reject more than about 95% of salts having monovalent ions such as sodium chloride. RO composite membranes also typically reject more than about 95% of inorganic molecules as well as organic molecules with molecular weights greater than approximately 100 Daltons. NF composite membranes are more permeable than RO composite membranes and typically reject less than about 95% of salts having monovalent ions while rejecting more than about 50% (and often more than 90%) of salts having divalent ions - depending upon the species of divalent ion. NF composite membranes also typically reject particles in the nanometer range as well as organic molecules having molecular weights greater than approximately 200 to 500 Daltons (AMU).

Examples of composite polyamide membranes include FilmTec Corporation FT-30™ type membranes, i.e. a flat sheet composite membrane comprising a bottom layer (back side) of a

nonwoven backing web (e.g. PET scrim), a middle layer of a porous support having a typical thickness of about 25-125 μm and top layer (front side) comprising a thin film polyamide layer having a thickness typically less than about 1 micron, e.g. from 0.01 micron to 1 micron but more commonly from about 0.01 to 0.1 μm . The porous support is typically a polymeric material having pore sizes which are of sufficient size to permit essentially unrestricted passage of permeate but not large enough so as to interfere with the bridging over of a thin film polyamide layer formed thereon. For example, the pore size of the support preferably ranges from about 0.001 to 0.5 μm . Non-limiting examples of porous supports include those made of: polysulfone, polyether sulfone, polyimide, polyamide, polyetherimide, polyacrylonitrile, poly(methyl methacrylate), polyethylene, polypropylene, and various halogenated polymers such as polyvinylidene fluoride. For RO and NF applications, the porous support provides strength but offers little resistance to fluid flow due to its relatively high porosity.

Due to its relative thinness, the polyamide layer is often described in terms of its coating coverage or loading upon the porous support, e.g. from about 2 to 5000 mg of polyamide per square meter surface area of porous support and more preferably from about 50 to 500 mg/m^2 . The polyamide layer is preferably prepared by an interfacial polycondensation reaction between a polyfunctional amine monomer and a polyfunctional acyl halide monomer upon the surface of the porous support as described in US 4277344 and US 6878278. More specifically, the polyamide membrane layer may be prepared by interfacially polymerizing a polyfunctional amine monomer with a polyfunctional acyl halide monomer, (wherein each term is intended to refer both to the use of a single species or multiple species), on at least one surface of a porous support. As used herein, the term "polyamide" refers to a polymer in which amide linkages ($-\text{C}(\text{O})\text{NH}-$) occur along the molecular chain. The polyfunctional amine and polyfunctional acyl halide monomers are most commonly applied to the porous support by way of a coating step from solution, wherein the polyfunctional amine monomer is typically coated from an aqueous-based or polar solution and the polyfunctional acyl halide from an organic-based or non-polar solution. Although the coating steps need not follow a specific order, the polyfunctional amine monomer is preferably first coated on the porous support followed by the polyfunctional acyl halide. Coating can be accomplished by spraying, film coating, rolling, or through the use of a dip tank among other coating techniques. Excess solution may be removed from the support by air knife, dryers, ovens and the like.

The polyfunctional amine monomer comprises at least two primary amine groups and may be aromatic (e.g., m-phenylenediamine (mPD), p-phenylenediamine, 1,3,5-triaminobenzene, 1,3,4-triaminobenzene, 3,5-diaminobenzoic acid, 2,4-diaminotoluene, 2,4-diaminoanisole, and xylylenediamine) or aliphatic (e.g., ethylenediamine, propylenediamine, cyclohexane-1,3-diamine and tris (2-diaminoethyl) amine). One particularly preferred polyfunctional amine is m-phenylene

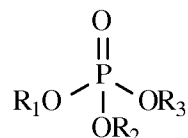
diamine (mPD). The polyfunctional amine monomer may be applied to the porous support as a polar solution. The polar solution may contain from about 0.1 to about 10 wt% and more preferably from about 1 to about 6 wt% polyfunctional amine monomer. In one set of embodiments, the polar solutions includes at least 2.5 wt% (e.g. 2.5 to 6 wt %) of the polyfunctional amine monomer. Once coated on the porous support, excess solution may be optionally removed.

The polyfunctional acyl halide monomer comprises at least two acyl halide groups and preferably no carboxylic acid functional groups and may be coated from a non-polar solvent although the polyfunctional acyl halide may be alternatively delivered from a vapor phase (e.g., for polyfunctional acyl halides having sufficient vapor pressure). The polyfunctional acyl halide is not particularly limited and aromatic or alicyclic polyfunctional acyl halides can be used along with combinations thereof. Non-limiting examples of aromatic polyfunctional acyl halides include: trimesic acyl chloride, terephthalic acyl chloride, isophthalic acyl chloride, biphenyl dicarboxylic acyl chloride, and naphthalene dicarboxylic acid dichloride. Non-limiting examples of alicyclic polyfunctional acyl halides include: cyclopropane tri carboxylic acyl chloride, cyclobutane tetra carboxylic acyl chloride, cyclopentane tri carboxylic acyl chloride, cyclopentane tetra carboxylic acyl chloride, cyclohexane tri carboxylic acyl chloride, tetrahydrofuran tetra carboxylic acyl chloride, cyclopentane dicarboxylic acyl chloride, cyclobutane dicarboxylic acyl chloride, cyclohexane dicarboxylic acyl chloride, and tetrahydrofuran dicarboxylic acyl chloride. One preferred polyfunctional acyl halide is trimesoyl chloride (TMC). The polyfunctional acyl halide may be dissolved in a non-polar solvent in a range from about 0.01 to 10 wt%, preferably 0.05 to 3% wt% and may be delivered as part of a continuous coating operation. In one set of embodiments wherein the polyfunctional amine monomer concentration is less than 3 wt %, the polyfunctional acyl halide is less than 0.3 wt %. Suitable solvents are those which are capable of dissolving the polyfunctional acyl halide and which are immiscible with water; e.g. paraffins (e.g. hexane, cyclohexane, heptane, octane, dodecane), isoparaffins (e.g. ISOPARTM L), aromatics (e.g. SolvessoTM aromatic fluids, VarsolTM non-dearomatized fluids, benzene, alkylated benzene (e.g. toluene, xylene, trimethylbenzene isomers, diethylbenzene)) and halogenated hydrocarbons (e.g. FREONTM series, chlorobenzene, di and trichlorobenzene) or mixtures thereof. Preferred solvents include those which pose little threat to the ozone layer and which are sufficiently safe in terms of flashpoints and flammability to undergo routine processing without taking special precautions. A preferred solvent is ISOPARTM available from Exxon Chemical Company. The non-polar solution may include additional constituents including co-solvents, phase transfer agents, solubilizing agents, complexing agents and acid scavengers wherein individual additives may serve multiple functions. Representative co-solvents include: benzene, toluene, xylene, mesitylene, ethyl benzene--- diethylene glycol dimethyl ether, cyclohexanone, ethyl acetate, butyl carbitolTM acetate, methyl laurate and acetone. A representative

acid scavenger includes N, N-diisopropylethylamine (DIEA). The non-polar solution may also include small quantities of water or other polar additives but preferably at a concentration below their solubility limit in the non-polar solution.

One or both of the polar and non-polar solutions additionally includes a tri-hydrocarbyl phosphate compound as represented by Formula I.

Formula (I):



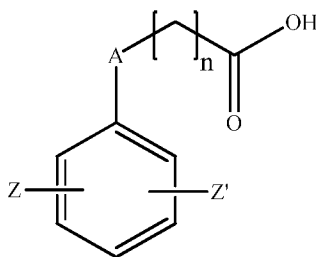
wherein "P" is phosphorous, "O" is oxygen and R₁, R₂ and R₃ are independently selected from hydrogen and hydrocarbyl groups comprising from 1 to 10 carbon atoms, with the proviso that no more than one of R₁, R₂ and R₃ are hydrogen. R₁, R₂ and R₃ are preferably independently selected from aliphatic and aromatic groups. Applicable aliphatic groups include both branched and unbranched species, e.g. methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, 2-pentyl, 3-pentyl. Applicable cyclic groups include cyclopentyl and cyclohexyl. Applicable aromatic groups include phenyl and naphthyl groups. Cyclo and aromatic groups may be linked to the phosphorous atom by way of an aliphatic linking group, e.g., methyl, ethyl, etc. The aforementioned aliphatic and aromatic groups may be unsubstituted or substituted (e.g., substituted with methyl, ethyl, propyl, hydroxyl, amide, ether, sulfone, carbonyl, ester, cyanide, nitrile, isocyanate, urethane, beta-hydroxy ester, etc); however, unsubstituted alkyl groups having from 3 to 10 carbon atoms are preferred. Specific examples of tri-hydrocarbyl phosphate compounds include: tripropyl phosphate, tributyl phosphate, tripentyl phosphate, trihexyl phosphate, triphenyl phosphate, propyl biphenyl phosphate, dibutyl phenyl phosphate, butyl diethyl phosphate, dibutyl hydrogen phosphate, butyl heptyl hydrogen phosphate and butyl heptyl hexyl phosphate. The specific compound selected should be at least partially soluble in the solution from which it is applied. Additional examples are as such compounds are described in US 6878278, US 6723241, US 6562266 and US 6337018.

When combined within the non-polar solution, the solution preferably includes from 0.001 to 10 wt% and more preferably from 0.01 to 1 wt% of the tri-hydrocarbyl phosphate compound. In another embodiment, the non-polar solution includes the tri-hydrocarbyl phosphate compound in a molar (stoichiometric) ratio of 1:5 to 5:1 and more preferably 1:1 to 3:1 with the polyfunctional acyl halide monomer. When combined within the polar solution, the solution preferably includes from 0.001 to 10 wt% and more preferably from 0.1 to 1 wt% of the tri-hydrocarbyl phosphate compound. A preferred species for addition to the polar phase includes triethylphosphate.

In a preferred subset of embodiments, the non-polar solution further comprises an acid-containing monomer comprising a C₂-C₂₀ hydrocarbon moiety substituted with at least one carboxylic

acid functional group or salt thereof and at least one amine-reactive functional group selected from: acyl halide, sulfonyl halide and anhydride, wherein the acid-containing monomer is distinct from the polyfunctional acyl halide monomer. In one set of embodiments, the acid-containing monomer comprises an arene moiety. Non-limiting examples include mono and di-hydrolyzed counterparts of the aforementioned polyfunctional acyl halide monomers including two to three acyl halide groups and mono, di and tri-hydrolyzed counterparts of the polyfunctional halide monomers that include at least four amine-reactive moieties. A preferred species includes 3,5-bis(chlorocarbonyl)benzoic acid (i.e. mono-hydrolyzed trimesoyl chloride or “mhTMC”). Additional examples of monomers are described in WO 2012/102942 and WO 2012/102943 (see Formula III wherein the amine-reactive groups (“Z”) are selected from acyl halide, sulfonyl halide and anhydride). Specific species including an arene moiety and a single amine-reactive group include: 3-carboxylbenzoyl chloride, 4-carboxylbenzoyl chloride, 4-carboxy phthalic anhydride and 5-carboxy phthalic anhydride, and salts thereof. Additional examples are represented by Formula II.

Formula (II):

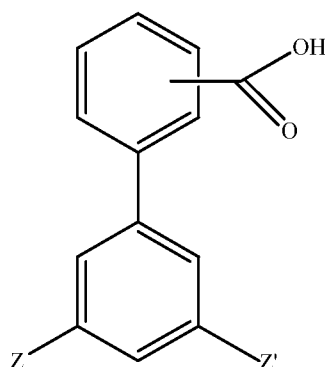


wherein A is selected from: oxygen (e.g. -O-); amino (-N(R)-) wherein R is selected from a hydrocarbon group having from 1 to 6 carbon atoms, e.g. aryl, cycloalkyl, alkyl – substituted or unsubstituted but preferably alkyl having from 1 to 3 carbon atoms with or without substituents such as halogen and carboxyl groups); amide (-C(O)N(R)-) with either the carbon or nitrogen connected to the aromatic ring and wherein R is as previously defined; carbonyl (-C(O)-); sulfonyl (-SO₂-); or is not present (e.g. as represented in Formula III); n is an integer from 1 to 6, or the entire group is an aryl group; Z is an amine reactive functional group selected from: acyl halide, sulfonyl halide and anhydride (preferably acyl halide); Z' is selected from the functional groups described by Z along with hydrogen and carboxylic acid. Z and Z' may be independently positioned meta or ortho to the A substituent on the ring. In one set of embodiments, n is 1 or 2. In yet another set of embodiments, both Z and Z' are both the same (e.g. both acyl halide groups). In another set of embodiments, A is selected from alkyl and alkoxy groups having from 1 to 3 carbon atoms. Non-limiting representative species include: 2-(3,5-bis(chlorocarbonyl)phenoxy)acetic acid, 3-(3,5-bis(chlorocarbonyl)phenyl)propanoic acid, 2-((1,3-dioxo-1,3-dihydroisobenzofuran-5-yl)oxy)acetic acid, 3-(1,3-dioxo-1,3-dihydroisobenzofuran-5-yl)propanoic acid, 2-(3-(chlorocarbonyl) phenoxy)acetic acid, 3-(3-

(chlorocarbonyl)phenyl)propanoic acid, 3-((3,5-bis(chlorocarbonyl)phenyl) sulfonyl) propanoic acid, 3-((3-(chlorocarbonyl)phenyl)sulfonyl)propanoic acid, 3-((1,3-dioxo-1,3-dihydroisobenzofuran-5-yl)sulfonyl)propanoic acid, 3-((1,3-dioxo-1,3-dihydroisobenzofuran-5-yl)amino) propanoic acid, 3-((1,3-dioxo-1,3-dihydroisobenzofuran-5-yl)(ethyl)amino)propanoic acid, 3-((3,5-bis(chlorocarbonyl) phenyl)amino) propanoic acid, 3-((3,5-bis(chlorocarbonyl) phenyl)(ethyl)amino) propanoic acid, 4-(4-(chlorocarbonyl)phenyl)-4-oxobutanoic acid, 4-(3,5-bis(chlorocarbonyl)phenyl)-4-oxobutanoic acid, 4-(1,3-dioxo-1,3-dihydroisobenzofuran-5-yl)-4-oxobutanoic acid, 2-(3,5-bis(chlorocarbonyl) phenyl)acetic acid, 2-(2,4-bis(chlorocarbonyl)phenoxy) acetic acid, 4-((3,5-bis(chlorocarbonyl) phenyl)amino)-4-oxobutanoic acid, 2-((3,5-bis(chloro carbonyl)phenyl)amino)acetic acid, 2-(N-(3,5-bis(chlorocarbonyl)phenyl)acetamido)acetic acid, 2,2'-((3,5-bis(chlorocarbonyl)phenylazanediyl) diacetic acid, N-[(1,3-dihydro-1,3-dioxo-5-isobenzofuranyl)carbonyl]-glycine, 4-[[[(1,3-dihydro-1,3-dioxo-5-isobenzofuranyl)carbonyl]amino]-benzoic acid, 1,3-dihydro-1,3-dioxo-4-isobenzofuran propanoic acid, 5-[[[(1,3-dihydro-1,3-dioxo-5-isobenzofuranyl)carbonyl]amino]-1,3-benzenedicarboxylic acid and 3-[(1,3-dihydro-1,3-dioxo-5-isobenzofuranyl)sulfonyl]- benzoic acid.

Another embodiment is represented by Formula III.

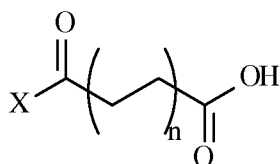
Formula (III):



wherein the carboxylic acid group may be located meta, para or ortho upon the phenyl ring.

Representative examples where the hydrocarbon moiety is an aliphatic group are represented by Formula IV.

Formula (IV):



wherein X is a halogen (preferably chlorine) and n is an integer from 1 to 20, preferably 2 to 10. Representative species include: 4-(chlorocarbonyl) butanoic acid, 5-(chlorocarbonyl) pentanoic acid, 6-(chlorocarbonyl) hexanoic acid, 7-(chlorocarbonyl) heptanoic acid, 8-(chlorocarbonyl) octanoic acid, 9-(chlorocarbonyl) nonanoic acid, 10-(chlorocarbonyl) decanoic acid, 11-chloro-11-

oxoundecanoic acid, 12-chloro-12-oxododecanoic acid, 3-(chlorocarbonyl)cyclobutanecarboxylic acid, 3-(chlorocarbonyl)cyclopentane carboxylic acid, 2,4-bis(chlorocarbonyl)cyclopentane carboxylic acid, 3,5-bis(chlorocarbonyl) cyclohexanecarboxylic acid, and 4-(chlorocarbonyl) cyclohexanecarboxylic acid. While the acyl halide and carboxylic acid groups are shown in terminal positions, one or both may be located at alternative positions along the aliphatic chain. While not shown in Formula (IV), the acid-containing monomer may include additional carboxylic acid and acyl halide groups.

Representative examples of acid-containing monomers include at least one anhydride group and at least one carboxylic acid groups include: 3,5-bis(((butoxycarbonyl)oxy)carbonyl)benzoic acid, 1,3-dioxo-1,3-dihydroisobenzofuran-5-carboxylic acid, 3-(((butoxycarbonyl)oxy)carbonyl)benzoic acid, and 4-(((butoxycarbonyl)oxy)carbonyl)benzoic acid.

The upper concentration range of acid-containing monomer may be limited by its solubility within the non-polar solution and is dependent upon the concentration of the tri-hydrocarbyl phosphate compound, i.e. the tri-hydrocarbyl phosphate compound is believed to serve as a solubilizer for the acid-containing monomer within the non-polar solvent. In most embodiments, the upper concentration limit is less than 1 wt %. In one set of embodiments, the acid-containing monomer is provided in the non-polar solution at concentration of at least 0.01 wt%, 0.02 wt%, 0.03 wt%, 0.04 wt%, 0.05 wt%, 0.06 wt%, 0.07 wt%, 0.08 wt%, 0.1wt% or even 0.13wt % while remaining soluble in solution. In another set of embodiments, the non-polar solution comprises from 0.01 to 1 wt %, 0.02 to 1 wt %, 0.04 to 1 wt % or 0.05 to 1 wt% of the acid-containing monomer. The inclusion of the acid-containing monomer during interfacial polymerization between the polyfunctional amine and acyl halide monomers results in a membrane having improved performance. And, unlike post hydrolysis reactions that may occur on the surface of the thin-film polyamide layer, the inclusion of the acid-containing monomer during interfacial polymerization is believed to result in a polymer structure that is beneficially modified throughout the thin-film layer.

In a preferred embodiment, the thin film polyamide layer is characterized by having a dissociated carboxylate content of at least 0.18, 0.20, 0.22, 0.3, 0.4 and in some embodiments at least 0.45moles/kg of polyamide at pH 9.5 as measured by a Rutherford Backscattering (RBS) measurement technique. More specifically, samples membranes (1 inch x 6 inch) are boiled for 30 minutes in deionized water (800 mL), then placed in a 50/50 w/w solution of methanol and water (800 mL) to soak overnight. Next, 1 inch x 1 inch size sample of these membranes are immersed in a 20 mL 1 x 10⁻⁴ M AgNO₃ solution with pH adjusted to 9.5 for 30 minutes. Vessels containing silver ions are wrapped in tape and to limit light exposure. After soaking with the silver ion solution, the unbound silver is removed by soaking the membranes in 2 clean 20 mL aliquots of dry methanol for 5 minutes each. Finally, the membranes are allowed to dry in a nitrogen atmosphere

for a minimum of 30 minutes. Membrane samples are mounted on a thermally and electrically conductive double sided tape, which was in turn mounted to a silicon wafer acting as a heat sink. The tape is preferably Chromerics Thermattach T410 or a 3M copper tape. RBS measurements are obtained with a Van de Graff accelerator (High Voltage Engineering Corp., Burlington, MA); A 2 MeV He^+ room temperature beam with a diameter of 3 mm at an incident angle of 22.5° , exit angle of 52.5° , scattering angle of 150° , and 40 nanoamps (nAmps) beam current. Membrane samples are mounted onto a movable sample stage which is continually moved during measurements. This movement allows ion fluence to remain under $3 \times 10^{14} \text{ He}^+/\text{cm}^2$. Analysis of the spectra obtained from RBS is carried out using SIMNRA[®], a commercially available simulation program. A description of its use to derive the elemental composition from RBS analysis of RO/NF membranes is described by; Coronell, *et. al. J. of Membrane Sci.* 2006, 282, 71-81 and *Environmental Science & Technology* 2008, 42(14), 5260-5266. Data can be obtained using the SIMNRA[®] simulation program to fit a two layer system, a thick polysulfone layer beneath a thin polyamide layer, and fitting a three-layer system (polysulfone, polyamide, and surface coating) can use the same approach. The atom fraction composition of the two layers (polysulfone before adding the polyamide layer, and the surface of final TFC polyamide layer) is measured first by XPS to provide bounds to the fit values. As XPS cannot measure hydrogen, an H/C ratio from the proposed molecular formulas of the polymers were used, 0.667 for polysulfone and a range of 0.60 – 0.67 was used for polyamide. Although the polyamides titrated with silver nitrate only introduces a small amount of silver, the scattering cross section for silver is substantially higher than the other low atomic number elements (C, H, N, O, S) and the size of the peak is disproportionately large to the others despite being present at much lower concentration thus providing good sensitivity. The concentration of silver is determined using the two layer modeling approach in SIMNRA[®] by fixing the composition of the polysulfone and fitting the silver peak while maintaining a narrow window of composition for the polyamide layer (layer 2, ranges predetermined using XPS). From the simulation, a molar concentration for the elements in the polyamide layer (carbon, hydrogen, nitrogen, oxygen and silver) is determined. The silver concentration is a direct reflection of the carboxylate molar concentration available for binding silver at the pH of the testing conditions. The moles of carboxylic acids groups per unit area of membrane is indicative of the number of interactions seen by a species passing through the membrane, and a larger number will thus favorably impact salt passage. This value may be calculated by multiplying the measured carboxylate content by a measured thickness and by the polyamide density. Alternatively, the carboxylate number per unit area of membrane (moles/m²) may be determined more directly by methods that measure the total complexed metal within a known area. Approaches using both Uranyl acetate and toluidine blue O dye are described in: Tiraferri, *et. al., Journal of Membrane Science*, 2012, 389, 499-508. An approach to determine the complexed cation

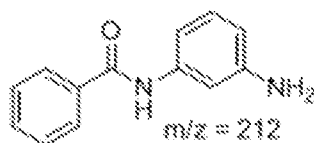
(sodium or potassium) content in membranes by polymer ashing is described in (Wei Xie, et al., *Polymer*, Volume 53, Issue 7, 22 March 2012, Pages 1581-1592).

A preferred method to determine the dissociated carboxylate number at pH 9.5 per unit area of membrane for a thin film polyamide membrane is as follows. A membrane sample is boiled for 30 minutes in deionized water, then placed in a 50 wt% solution of methanol in water to soak overnight. Next, the membrane sample is immersed in a 1×10^{-4} M AgNO_3 solution with pH adjusted to 9.5 with NaOH for 30 minutes. After soaking in the silver ion solution, the unbound silver is removed by soaking the membranes twice in dry methanol for 30 minutes. The amount of silver per unit area is preferably determined by ashing, as described by Wei, and redissolving for measurement by ICP.

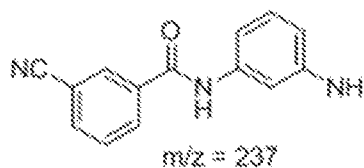
Preferably, the dissociated carboxylate number at pH 9.5 per square meter of membrane is greater than 6×10^{-5} , 8×10^{-5} , 1×10^{-4} , 1.2×10^{-4} , 1.5×10^{-4} , 2×10^{-4} , or even 3×10^{-4} moles/ m^2 .

In another preferred embodiment, pyrolysis of the thin film polyamide layer at 650°C results in a ratio of responses from a flame ionization detector for fragments produced at 212 m/z and 237 m/z of less than 2.8, and more preferably less than 2.6. The fragments produced at 212 and 237 m/z are represented by Formula V and VI, respectively.

Formula (V):



Formula (VI):



This ratio of fragments is believed to be indicative of polymer structures that provide improved flux, salt passage or integrity (particularly for membranes having relatively high carboxylic acid content, e.g. a dissociated carboxylate content of at least 0.18, 0.20, 0.22, 0.3, and in some embodiments at least 0.4 moles/kg of polyamide at pH 9.5). With reference to Figure 1, investigation has shown that dimer fragment 212 m/z forms predominantly during pyrolysis temperatures below 500°C whereas dimer fragment 237 m/z predominantly forms at pyrolysis temperatures above 500°C . This indicates that dimer fragment 212 originates from end groups where only single bond cleavage prevails and that dimer fragment 237 originates substantially from the bulk material where multiple bond cleavages and reduction occurs. Thus, the ratio of dimer fragment 212 to 237 can be used as a measure of relative conversion.

A preferred pyrolysis methodology is conducted using gas chromatography mass spectrometry with mass spectral detection, e.g. a Frontier Lab 2020iD pyrolyzer mounted on an Agilent 7890 GC with detection using a LECO time of flight (TruTOF) mass spectrometer. Peak area detection is made using a flame ionization detector (FID). Pyrolysis is conducted by dropping the polyamide sample cup into pyrolysis oven set at 650°C for 6 seconds in single shot mode. Separation is performed using a 30M X 0.25mm id column from Varian (FactorFour VF-5MS CP8946) with a 1

um 5% phenyl methyl silicone internal phase. Component identification is made by matching the relative retention times of the fragment peaks to that of the same analysis performed with a LECO time of flight mass spectrometer (or optionally by matching mass spectra to a NIST database or references from literature). Membrane samples are weighed into Frontier Labs silica lined stainless steel cups using a Mettler E20 micro-balance capable of measuring to 0.001 mg. Sample weight targets were 200 ug +/- 50 ug. Gas chromatograph conditions are as follows: Agilent 6890 GC (SN: CN10605069), with a 30M X 0.25 mm, 1 μ m 5% dimethyl polysiloxane phase (Varian FactorFour VF-5MS CP8946); injection port 320°C, Detector port: 320°C, Split injector flow ratio of 50:1, GC Oven conditions: 40°C to 100°C at 6°C per min., 100°C to 320°C at 30°C/min, 320°C for 8 min; Helium carrier gas with constant flow of 0.6 mL/min providing a back pressure of 5.0 psi. LECO TruTOF Mass Spectrometer Parameters are as follows: electron ionization source (positive EI mode), Scan Rate of 20 scans per second, Scan range: 14 – 400 m/z; Detector voltage = 3200 (400V above tune voltage); MS acquisition delay = 1 min; Emission Voltage – 70V. The peak area of the fragment 212 m/z and fragment 237 m/z are normalized to the sample weight. The normalized peak areas are used to determine the ratio of fragments 212 m/z to 237 m/z. Further the normalize peak area of fragment 212 m/z is divided by the sum of the normalized peak areas for all other fragments providing a fraction of the m/z 212 fragment relative to the polyamide and is commonly noted as a percent composition by multiplying by 100. Preferably this value is less than 12 %.

In yet another preferred embodiment, the thin film layer has an isoelectric point (IEP) of less than or equal to 4.3, 4.2, 4.1, 4, 3.8, 3.6 or in some embodiments 3.5. The isoelectric point can be determined using a standard Zeta-Potential technique with a quartz cell by electrophoretic light scattering (ELS) using Desal Nano HS instrument. For example, membrane samples (2 inch x 1 inch) are first boiled for 20 minutes in DI water, then rinsed well with room temperature DI water and stored at room temperature in a fresh DI solution overnight. The samples are then loaded as per reference: 2008 “User’s Manual for the Delsa™ Nano Submicron Particle Size and Zeta Potential,” and the “Pre-Course Reading” for the same instrument presented by Beckmann Coulter. pH titration is completed over a range from pH 10 to pH 2 and isoelectric point is determined at the pH where the zeta potential becomes zero.

Once brought into contact with one another, the polyfunctional acyl halide and polyfunctional amine monomers react at their surface interface to form a polyamide layer or film. This layer, often referred to as a polyamide “discriminating layer” or “thin film layer,” provides the composite membrane with its principal means for separating solute (e.g. salts) from solvent (e.g. aqueous feed). The reaction time of the polyfunctional acyl halide and the polyfunctional amine monomer may be less than one second but contact times typically range from about 1 to 60 seconds. The removal of the excess solvent can be achieved by rinsing the membrane with water and then drying at elevated

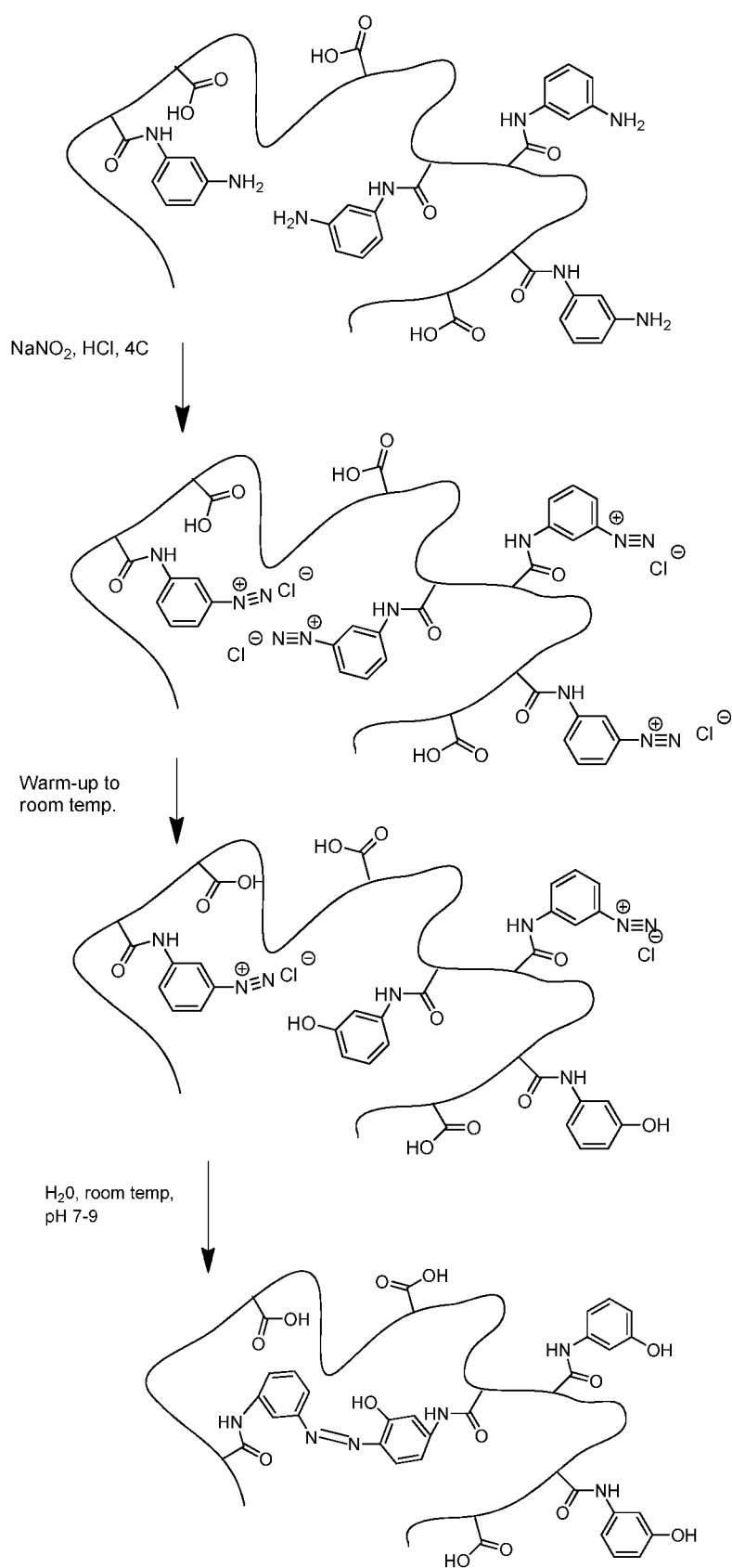
temperatures, e.g. from about 40°C to about 120°C, although air drying at ambient temperatures may be used. However, for purposes of the present invention, the membrane is preferably not permitted to dry and is simply rinsed (e.g. dipped) with water and optionally stored in a wet state. Once formed, the polyamide layer is exposed to nitrous acid. A variety of techniques are described in US 4888116 and are incorporated herein by reference. It is believed that the nitrous acid reacts with the residual primary amine groups present in the polyamide discrimination layer to form diazonium salt groups. At least a portion of these diazonium salt groups hydrolyze to form phenol groups or azo crosslinks via diazo-coupling. Although the aqueous solution may include nitrous acid, it preferably includes reagents that form nitrous acid in situ, e.g. an alkali metal nitrite in an acid solution or nitrosyl sulfuric acid. Because nitrous acid is volatile and subject to decomposition, it is preferably formed by reaction of an alkali metal nitrite in an acidic solution in contact with the polyamide discriminating layer. Generally, if the pH of the aqueous solution is less than about 7, (preferably less than about 5), an alkali metal nitrite will react to liberate nitrous acid. Sodium nitrite reacted with hydrochloric or sulfuric acid in an aqueous solution is especially preferred for formation of nitrous acid. The aqueous solution may further include wetting agents or surfactants. The concentration of the nitrous acid in the aqueous solution is preferably from 0.01 to 1 wt%. Generally, the nitrous acid is more soluble at 5° than at 20° C and somewhat higher concentrations of nitrous acid are operable at lower temperatures. Higher concentrations are operable so long as the membrane is not deleteriously affected and the solutions can be handled safely. In general, concentrations of nitrous acid higher than about one-half (0.5) percent are not preferred because of difficulties in handling these solutions. Preferably, the nitrous acid is present at a concentration of about 0.1 weight percent or less because of its limited solubility at atmospheric pressure. The temperature at which the membrane is contacted can vary over a wide range. Inasmuch as the nitrous acid is not particularly stable, it is generally desirable to use contact temperatures in the range from about 0° to about 30° C, with temperatures in the range from 0° to about 20° C being preferred. Temperatures higher than this range can increase the need for ventilation or super-atmospheric pressure above the treating solution. Temperatures below the preferred range generally result in reduced reaction and diffusion rates.

The reaction between the nitrous acid and the primary amine groups occurs relatively quickly once the nitrous acid has diffused into the membrane. The time required for diffusion and the desired reaction to occur will depend upon the concentration of nitrous acid, any pre-wetting of the membrane, the concentration of primary amine groups present and the temperature at which contact occurs. Contact times may vary from a few minutes to a few days. The optimum reaction time can be readily determined empirically for a particular membrane and treatment.

One preferred application technique involves passing the aqueous nitrous acid solution over the surface of the membrane in a continuous stream. This allows the use of relatively low

concentrations of nitrous acid. When the nitrous acid is depleted from the treating medium, it can be replenished and the medium recycled to the membrane surface for additional treatment. Batch treatments are also operable. The specific technique for applying aqueous nitrous acid is not particularly limited and includes spraying, film coating, rolling, or through the use of a dip tank among other application techniques. Once treated the membrane may be washed with water and stored either wet or dry prior to use. For RO and NF applications, membranes treated with nitrous acid preferably have a NaCl rejection of at least 2 % when tested using an aqueous NaCl solution (250 ppm) at 25°C and 70 psi.

A representative reaction scheme illustrating the treatment of the polyamide with nitrous acid is provided below.



The thin film polyamide layer may optionally include hygroscopic polymers upon at least a portion of its surface. Such polymers include polymeric surfactants, polyacrylic acid, polyvinyl acetate, polyalkylene oxide compounds, poly(oxazoline) compounds, polyacrylamides and related reaction products as generally described in US 6280853; US 7815987; US 7918349 and US 7905361.

5 In some embodiments, such polymers may be blended and/or reacted and may be coated or otherwise applied to the polyamide membrane from a common solution, or applied sequentially.

Many embodiments of the invention have been described and in some instances certain embodiments, selections, ranges, constituents, or other features have been characterized as being “preferred.” Characterizations of “preferred” features should in no way be interpreted as deeming
10 such features as being required, essential or critical to the invention.

EXAMPLES

Sample membranes were prepared using a pilot scale membrane manufacturing line. Polysulfone supports were cast from 16.5 wt % solutions in dimethylformamide (DMF) and
15 subsequently soaked in an aqueous solution meta-phenylene diamine (mPD). The resulting support was then pulled through a reaction table at constant speed while a thin, uniform layer of a non-polar coating solution was applied. The non-polar coating solution included a isoparaffinic solvent (ISOPAR L), a combination of trimesoyl acid chloride (TMC), and/or 1-carboxy-3,5-dichloroformyl benzene (mhTMC) in varying ratios and/or tri butyl phosphate (TBP). Excess non-polar solution was
20 removed and the resulting composite membrane was passed through water rinse tanks and drying ovens. Sample membrane sheets were then either (i) stored in deionized water until testing; or (ii) soaked for approximately 15 minutes in a solution at 0-10 °C prepared by combining 0.05% w/v NaNO₂ and 0.1 w/v% HCl and thereafter rinsed and stored in deionized water until testing.

25 Example 1: In order to illustrate the synergistic impact of preparing composite polyamide membranes with a tri-hydrocarbyl compound along with post-treatment with nitrous acid, a series of membrane were prepared using various quantities (expressed as wt %) of mPD and TMC, both with and without TBP (expressed as a stoichiometric ratio with TMC). Samples subjected to post-treatment with nitrous acid are designed with an asterisk (*). Testing was conducted with a 2000 ppm
30 NaCl solution at room temperature and 150 psi. “SP” refers to NaCl passage. As shown by the test results summarized in Table 1, post-treatment of samples including tri-hydrocarbyl compound had an unexpected improvement in flux over comparable post-treated membranes without a tri-hydrocarbyl compound.

Table 1:

Sample	mPD (wt%)	TMC (wt%)	TBP (stoich)	Mean (AvgFlux) GFD	Mean (Avg SP)	Std Dev (Avg Flux)	Std Dev (Avg SP)	% change in Flux
1-1a	2.5	0.20	0	11.8	1.83%	0.27	0.36	
*1-1b	2.5	0.20	0	11.7	2.19%	0.69	0.92	-1.0
1-1c	2.5	0.20	1.5	52.1	1.50%	1.39	0.24	
*1-1d	2.5	0.20	1.5	68.1	1.77%	2.55	0.13	30.6
1-2a	2.5	0.25	0	8.2	1.98%	0.04	0.04	
*1-2b	2.5	0.25	0	7.9	1.99%	0.73	0.11	-3.1
1-2c	2.5	0.25	1.5	45.7	2.02%	0.98	0.35	
*1-2d	2.5	0.25	1.5	50.4	2.19%	4.35	0.92	10.2
1-3a	2.5	0.30	0	6.3	1.86%	0.24	0.08	
*1-3b	2.5	0.30	0	6.6	2.38%	0.37	0.46	5.3
1-3c	2.5	0.30	1.5	37.0	3.69%	1.26	0.46	
*1-3d	2.5	0.30	1.5	38.6	4.73%	0.53	0.27	4.4
1-4a	3.5	0.20	0	20.7	0.74%	0.36	0.08	
*1-4b	3.5	0.20	0	24.0	0.95%	0.36	0.08	15.8
1-4c	3.5	0.20	1.5	36.2	0.63%	0.72	0.02	
*1-4d	3.5	0.20	1.5	48.3	0.73%	1.63	0.01	33.6
1-5a	3.5	0.25	0	13.9	0.97%	0.44	0.07	
*1-5b	3.5	0.25	0	14.9	1.11%	0.56	0.03	6.6
1-5c	3.5	0.25	1.5	40.7	0.75%	1.39	0.13	
*1-5d	3.5	0.25	1.5	52.7	0.92%	1.92	0.02	29.3
1-6a	3.5	0.30	0	11.9	1.18%	1.16	0.03	
*1-6b	3.5	0.30	0	11.9	1.21%	1.57	0.17	-0.6
1-6c	3.5	0.30	1.5	40.3	0.94%	0.84	0.08	
*1-6d	3.5	0.30	1.5	52.6	1.22%	1.94	0.09	30.5
1-7a	4.5	0.20	0	22.6	0.65%	0.54	0.01	
*1-7b	4.5	0.20	0	27.6	0.63%	0.14	0.02	21.8
1-7c	4.5	0.20	1.5	23.9	0.57%	0.49	0.06	
*1-7d	4.5	0.20	1.5	32.6	0.51%	0.39	0.01	36.3

Example 2: In order to illustrate the synergistic impact of preparing composite polyamide membranes with both a tri-hydrocarbyl compound and an acid-containing monomer along with post-treatment with nitrous acid, a series of membrane were prepared using various quantities of mPD and TMC, with and without TBP and mh TMC. Samples subjected to post-treatment with nitrous acid are designed with an asterisk (*). Testing was conducted with a 2000 ppm NaCl solution at room temperature and 150 psi. As shown by the test results summarized in Tables 2-1 and 2-2, post-treatment of samples including a tri-hydrocarbyl compound (TBP) and an acid-containing monomer (mhTMC) had an unexpected improvement in flux as compared with membranes without post-

treatment, or those with post treatment but without a tri-hydrocarbyl compound an acid-containing monomer.

Table 2-1:

Sample	mPD (wt%)	TMC (wt%)	TBP (Stoich)	mhTMC (wt%)	Mean (Avg Flux) GFD	Mean (Avg SP)	Std Dev (Avg Flux)	Std Dev (Avg SP)	% change in Flux
2-1a	2.5	0.20	0	0	11.8	1.83%	0.27	0.36	
*2-1b	2.5	0.20	0	0	11.7	2.19%	0.69	0.92	-1.0
2-1c	2.5	0.16	1.5	0.04	51.1	1.63%	0.79	0.11	
*2-1d	2.5	0.16	1.5	0.04	74.8	1.47%	0.66	0.11	46.4
2-2a	2.5	0.25	0	0	8.2	1.98%	0.04	0.04	
*2-2b	2.5	0.25	0	0	7.9	1.99%	0.73	0.11	-3.1
2-2c	2.5	0.21	1.5	0.04	51.9	0.86%	1.07	0.06	
*2-2d	2.5	0.21	1.5	0.04	63.8	0.96%	0.69	0.04	22.9
2-3a	3.5	0.20	0	0	20.7	0.74%	0.36	0.08	
*2-3b	3.5	0.20	0	0	24.0	0.95%	0.36	0.08	15.8
2-3c	3.5	0.16	1.5	0.04	26.3	2.28%	0.80	0.75	
*2-3d	3.5	0.16	1.5	0.04	40.4	1.52%	0.93	0.12	53.6
2-4a	3.5	0.25	0	0	13.9	0.97%	0.44	0.07	
*2-4b	3.5	0.25	0	0	14.9	1.11%	0.56	0.03	6.6
2-4c	3.5	0.21	1.5	0.04	40.2	0.37%	1.36	0.03	
*2-4d	3.5	0.21	1.5	0.04	57.4	0.60%	0.70	0.07	42.9
2-5a	3.5	0.30	0	0	11.9	1.18%	1.16	0.03	
*2-5b	3.5	0.30	0	0	11.9	1.21%	1.57	0.17	-0.6
2-5c	3.5	0.26	1.5	0.04	45.5	0.52%	0.24	0.03	
*2-5d	3.5	0.26	1.5	0.04	59.4	0.73%	0.86	0.08	30.4
2-5a	4.5	0.20	0	0	22.6	0.65%	0.54	0.01	
*2-5b	4.5	0.20	0	0	27.6	0.63%	0.14	0.02	21.8
2-5c	4.5	0.16	1.5	0.04	20.1	0.36%	0.24	0.01	
*2-5d	4.5	0.16	1.5	0.04	29.6	0.36%	0.56	0.02	47.2

5 Table 2-2

Sample	mPD (wt%)	TMC (wt%)	TBP (Stoich)	mhTMC (wt%)	Dissociated Carboxylate (moles/kg)	212:237 m/z ratio
2-3c	3.5	0.16	1.5	0.04	0.375	2.1
2-4c	3.5	0.21	1.5	0.04	0.35	1.8
2-5c	3.5	0.26	1.5	0.04	0.31	1.7

Example 3: In order to illustrate the effect of preparing composite polyamide membranes with both a tri-hydrocarbyl compound and increasing quantities of acid-containing monomer along with post-treatment with nitrous acid, a series of membranes were prepared using various quantities of mPD, TMC, and TBP, with and without mh TMC. Samples subjected to post-treatment with nitrous acid are designed with an asterisk (*). Testing was conducted with a 250 ppm NaCl solution at room temperature and 70 psi. As shown by the test results summarized in Table 3, post-treatment of samples including a tri-hydrocarbyl compound (TBP) and an acid-containing monomer (mhTMC) had an unexpected improvement in salt passage (SP) for membranes prepared with increasing quantities of the acid-containing monomer.

Table 3:

Sample	mPD (wt%)	TMC (wt%)	TBP (stoich)	mhTMC (wt%)	Mean (Avg Flux) GFD	Mean (Avg SP)	Std Dev (Avg Flux)	Std Dev (Avg SP)
3-1a	3.5	0.26	1.1	0	21.4	0.80%	0.82	0.09
*3-1b	3.5	0.26	1.1	0	26.3	1.33%	0.46	0.07
3-1c	3.5	0.24	1.1	0.03	22.3	0.53%	0.60	0.16
*3-1d	3.5	0.24	1.1	0.03	29.4	0.79%	0.11	0.06
3-1e	3.5	0.21	1.1	0.05	21.6	0.48%	0.57	0.01
*3-1f	3.5	0.21	1.1	0.05	28.8	0.57%	0.88	0.06
3-1g	3.5	0.16	1.1	0.10	23.9	0.51%	0.57	0.12
*3-1h	3.5	0.16	1.1	0.10	29.6	0.45%	0.50	0.05
3-1i	3.5	0.12	1.1	0.14	26.3	1.11%	0.11	0.03
*3-1j	3.5	0.12	1.1	0.14	29.7	0.46%	1.06	0.00
3-2a	3	0.26	1.5	0	24.5	0.70%	1.07	0.11
*3-2b	3	0.26	1.5	0	33.9	1.11%	2.60	0.29
3-2c	3	0.24	1.5	0.03	26.3	0.46%	0.83	0.01
*3-2d	3	0.24	1.5	0.03	35.1	0.61%	0.55	0.12
3-2e	3	0.21	1.5	0.05	24.6	0.52%	1.59	0.12
*3-2f	3	0.21	1.5	0.05	31.8	0.35%	1.27	0.03
3-2g	3	0.13	1.5	0.13	27.2	4.27%	4.79	1.03
*3-2h	3	0.13	1.5	0.13	25.6	0.88%	0.98	0.07
3-3a	2.5	0.26	1.5	0	25.8	1.76%	4.02	0.24
*3-3b	2.5	0.26	1.5	0	31.9	1.81%	2.14	0.08
3-3c	2.5	0.24	1.5	0.03	27.8	0.58%	0.75	0.12
*3-3d	2.5	0.24	1.5	0.03	32.0	0.83%	0.56	0.11
3-3e	2.5	0.21	1.5	0.05	26.5	0.72%	4.11	0.17
*3-3f	2.5	0.21	1.5	0.05	33.1	0.63%	1.84	0.03
3-3g	2.5	0.13	1.5	0.13	29.5	5.97%	4.97	1.98
*3-3h	2.5	0.13	1.5	0.13	22.9	1.29%	1.55	0.05

Example 4: In order to further illustrate the effect of preparing composite polyamide membranes with both a tri-hydrocarbyl compound and increasing quantities of an acid-containing monomer, (3-(chlorocarboynyl)benzoic acid, i.e. “mono hydrolyzed isophthaloyl chloride” or “mhIPC”) along with post-treatment with nitrous acid, a series of membranes were prepared using various quantities of mPD and TMC, with TBP and mhIPC. Samples subjected to post-treatment with nitrous acid are designed with an asterisk (*). Testing was conducted with a 2000 ppm NaCl solution at room temperature and 150 psi. As shown by the test results summarized in Table 4, post-treatment of samples including a tri-hydrocarbyl compound (TBP) and an acid-containing monomer (mhIPC) showed improved flux along with improved salt passage (SP) for membranes including increasing quantities of carboxylic acid functionality (i.e. due to incorporation of the acid-containing monomer).

Table 4:

Sample	mPD (wt%)	TMC (wt%)	mhIPC (wt%)	TBP (stoich)	Mean (Avg Flux) GFD	Mean (Avg SP)	Std Dev (Avg Flux)	Std Dev (Avg SP)
4-1a	3.5	0.26	0.00	1.3	46.9	0.76%	2.4	0.04%
4-1b*					55.3	1.21%	3.39	0.12%
4-2a	3.5	0.26	0.01	1.3	45.6	0.58%	1.11	0.02%
4-2b*					48	0.93%	0.82	0.03%
4-3a	3.5	0.25	0.01	1.3	43.2	0.53%	2.59	0.02%
4-3b*					49.3	0.72%	0.22	0.06%
4-4a	3.5	0.25	0.03	1.3	43.2	0.52%	4.73	0.07%
4-4b*					48.7	0.68%	2.02	0.07%
4-5a	3.5	0.24	0.04	1.3	41.6	0.63%	1.89	0.10%
4-5b*					45.9	0.53%	2.63	0.02%
4-6a	3.5	0.22	0.08	1.3	41.8	1.57%	0.69	0.18%
4-6b*					46.1	0.99%	1.24	0.09%

Example 5: In order to illustrate the effect of preparing composite polyamide membranes with both a tri-hydrocarbyl compound and increasing quantities of an acid-containing monomer, 6-chloro-6-oxohexanoic acid, ("mono hydrolyzed adipoyl chloride" or mh adipoyl chloride) along with post-treatment with nitrous acid, a series of membranes were prepared using various quantities of mPD and TMC, with TBP and mh adipoyl chloride. Samples subjected to post-treatment with nitrous acid are designed with an asterisk (*). Testing was conducted with a 2000 ppm NaCl solution at room temperature and 150 psi. As shown by the test results summarized in Table 5, post-treatment of samples including a tri-hydrocarbyl compound (TBP) and an acid-containing monomer (mh adipoyl chloride) showed improved flux

Table 5:

Sample	mPD (wt%)	TMC (wt%)	mh adipoyl chloride (wt%)	TBP	Mean (Avg Flux) GFD	Mean (Avg SP)	Std Dev (Avg Flux)	Std Dev (Avg SP)
5-1a	3.5	0.26	0	1.3	42	0.99%	1.87	0.17%
5-1b*					50.2	1.30%	2.56	0.17%
5-2a	3.5	0.26	0.01	1.3	40.4	0.81%	0.37	0.05%
5-2b*					49.1	0.99%	2.58	0.01%
5-3a	3.5	0.25	0.01	1.3	40.3	0.71%	1.36	0.07%
5-3b*					49.3	0.79%	0.44	0.02%
5-4a	3.5	0.25	0.03	1.3	39.9	0.62%	0.16	0.03%
5-4b*					49.1	0.74%	1.18	0.04%
5-5a	3.5	0.24	0.04	1.3	39.7	0.57%	1.15	0.04%
5-5b*					51.6	0.90%	2.32	0.05%
5-6a	3.5	0.23	0.05	1.3	35.2	0.55%	1.88	0.03%
5-6b*					42.1	0.76%	0.77	0.08%
5-7a	3.5	0.23	0.06	1.3	39.1	0.67%	0.44	0.04%
5-7b*					48.1	0.89%	1.13	0.06%

Example 6: In order to illustrate the synergistic impact of preparing composite polyamide membranes with a tri-hydrocarbyl compound added in the polar phase (along with amine) and post-treatment with nitrous acid, a series of membrane were prepared using increasing amount of tri ethyl phosphate in water phase (expressed as wt %). mPD was kept fixed at 3.5 wt % and TMC at 0.26 wt % in the organic phase. Samples subjected to post-treatment with nitrous acid are designed with an asterisk (*). Testing was conducted with a 2000 ppm NaCl solution at room temperature and 150 psi. “SP” refers to NaCl passage. As shown by the test results summarized in Table 1, post-treatment of samples including tri-hydrocarbyl compound had an unexpected improvement in flux over comparable post-treated membranes without a tri-hydrocarbyl compound.

Table 6:

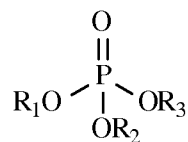
Sample	mPD (wt%)	TMC (wt%)	TEP (wt %)	Mean (Avg Flux) GFD	Mean (Avg SP)	Std Dev (Avg Flux)	Std Dev (Avg SP)
6-1a	3.5	0.26	0	13.82	0.93%	0.35	0.11%
6-1b*				15.38	1.79%	0.66	0.27%
6-2a	3.5	0.26	0.03	18.64	0.87%	0.55	0.12%
6-2b*				21.88	1.45%	1.24	0.20%
6-3a	3.5	0.26	0.1	22.24	0.73%	0.48	0.17%
6-3b*				27.11	1.13%	0.54	0.15%
6-4a	3.5	0.26	0.3	31.94	0.63%	0.43	0.09%
6-4b*				41.04	0.87%	0.86	0.04%
6-5a	3.5	0.26	0.5	32.39	0.70%	0.52	0.14%
6-5b*				43.37	1.01%	1.50	0.36%
6-6a	3.5	0.26	0.75	32.43	0.60%	0.28	0.08%
6-6b*				43.72	0.94%	1.56	0.06%
6-7a	3.5	0.26	1	30.83	0.62%	0.32	0.00%
6-7b*				41.75	1.20%	1.11	0.14%
6-8a	3.5	0.26	2	19.04	5.18%	0.81	0.53%
6-8b*				26.98	6.14%	2.27	0.88%

CLAIMS:

1. A method for making a composite polyamide membrane comprising a porous support and a thin film polyamide layer, wherein the method comprises:

5 i) applying a polar solution comprising a polyfunctional amine monomer and a non-polar solution comprising a polyfunctional acyl halide monomer to a surface of a porous support and interfacially polymerizing the monomers to form a thin film polyamide layer, and wherein at least one of the solutions further comprises a tri-hydrocarbyl phosphate compound represented by Formula I:

Formula (I):



10 wherein R₁, R₂ and R₃ are independently selected from hydrogen and hydrocarbyl groups comprising from 1 to 10 carbon atoms, with the proviso that no more than one of R₁, R₂ and R₃ are hydrogen; and

15 ii) exposing the thin film polyamide layer to nitrous acid.

2. The method of claim 1 wherein the non-polar solutions further comprises an acid-containing monomer comprising a C₂-C₂₀ hydrocarbon moiety substituted with at least one carboxylic acid functional group or salt thereof and at least one amine-reactive functional group selected from: acyl halide, sulfonyl halide and anhydride, wherein the acid-containing monomer is distinct from the polyfunctional acyl halide monomer.

3. The method of claim 2 wherein the acid-containing monomer comprises an arene moiety.

25 4. The method of claim 2 wherein the acid-containing monomer comprises an aliphatic moiety.

5. The method of claim 2 wherein the acid-containing monomer comprises at least two amine-reactive functional groups.

30 6. The method of claim 1 wherein the thin film polyamide layer has a dissociated carboxylic acid content of at least 0.18 moles/kg at pH 9.5 as measured by RBS prior to the step of applying the aqueous solution of nitrous acid.

7. The method of claim 2 wherein the thin film polyamide layer has a dissociated carboxylic acid content of at least 0.3 moles/kg at pH 9.5 prior to the step of applying the aqueous solution of nitrous acid.

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8. The method of claim 2 wherein the thin film polyamide layer has a dissociated carboxylic acid content of at least 0.45 moles/kg at pH 9.5 prior to the step of applying the aqueous solution of nitrous acid.

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9. The method of claim 2 wherein pyrolysis of the thin film polyamide layer at 650⁰C results in a ratio of responses from a flame ionization detector for fragments produced at of 212 m/z and 237 m/z of less than 2.6.

10. The method of claim 2 wherein the thin film polyamide layer has an isoelectric point (IEP) of less than or equal to 4.3 prior to the step of applying the aqueous solution of nitrous acid.

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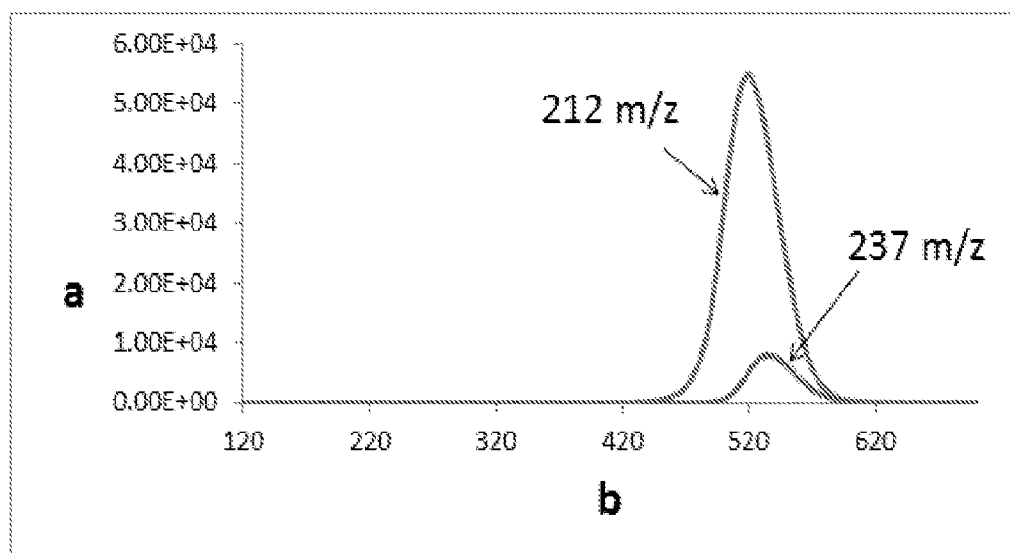


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US14/10121

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01D 67/00, 71/56, 69/12 (2014.01)

USPC - 427/246; 210/654, 500.38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8): B01D 67/00, 71/56, 69/12 (2014.01)

USPC: 427/246; 210/654, 500.38

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

MicroPatent (US-G, US-A, EP-A, EP-B, WO, JP-bib, DE-C,B, DE-A, DE-T, DE-U, GB-A, FR-A); ProQuest; Google/Google Scholar; IP.com; KEYWORDS: polyamide*, poly-amide*, "poly amide", "poly amides", nylon*, aramid*, layer*, film*, sheet*, ply, plies, lamina*, support*, substrate*, amine*, monomer*, acyl, acid, halide*, fluoride*, chloride*, bromide*, iodide*, phosphate*, "nitrous acid", nitrous

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2012/102942 A1 (JONS, SD et al.) 02 August 2012; page 4, line 11 to page 5, line 27; page 6, lines 30-33; page 9, lines 13-19; Claims 1, 4, 7, 9	1-8, 10
Y	US 4,888,116 A (CADOTTE, JE et al.) 19 December 1989; column 8, lines 32-51	1-8, 10
Y	WO 2012/102944 A1 (ROY, A et al.) 02 August 2012; page 6, lines 10-24	4
Y	US 6,406,626 B1 (MURAKAMI, M et al.) 18 June 2002; column 3, line 58 to column 4, line 33	5
Y	US 6,777,488 B1 (ARAKI, E et al.) 17 August 2004; column 2, lines 59-67; column 3, lines 28-67	6-8
Y	TIRAFERRI, A et al. "Direct quantification of negatively charged functional groups on membrane surfaces" Journal of Membrane Science, 20 November 2012, Volume 389; pages 499-508; page 505, paragraphs 3-4; figure 6	6-8
Y	ARIZA, MA et al. "Effect of pH on electrokinetic and electrochemical parameters of both sub-layers of composite polyamide/polysulfone membranes" Desalination 2002, Volume 148; pages 377-382;	10
Y	NIETO, OC. "Quantitative characterization of physico-chemical properties of the active layers of reverse osmosis and nanofiltration membranes, and their relation to membrane performance". Publication [online]. 2010 [retrieved 25 March 2014]. Retrieved from the Internet: <URL: https://www.ideals.illinois.edu/bitstream/handle/2142/15596/2_Coronell%20Nieto_Orlando.pdf?sequence=3 >; pages 104-105 only	6

☒ Further documents are listed in the continuation of Box C.


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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search

08 April 2014 (08.04.2014)

Date of mailing of the international search report

25 APR 2014

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450
Facsimile No. 571-273-3201

Authorized officer:

Shane Thomas

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US14/10121

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	STRAUS, S et al. "Pyrolysis of Polyamides" Journal of Research of the National Bureau of Standards, 01 January 1958, Volume 60, Number 1, pages 39-45; table 1; page 45, paragraph 4	9
A	US 4,401,590 A (YOSHIMURA, S et al.) 30 August 1983; column 13, lines 38-52	9
A	US 2012/0003440 A1 (OKUZU, T et al.) 05 January 2012; abstract; paragraph [0069]	9
A	WO 2012/102943 A1 (PAUL, M et al.) 02 August 2012; entire document	1-10