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(54) **Titre : MEMBRANE DE FILTRAGE COMPORTANT UN MATERIAU MICROPOREUX ENDUIT DE POLYOLEFINE ET DE PARTICULES DE SILICE**

(54) **Title: FILTRATION MEMBRANE COMPRISING COATED MICROPOROUS MATERIAL OF POLYOLEFIN AND PARTICULATE SILICA**

(57) **Abrégé/Abstract:**
The present invention is directed to microfiltration and ultrafiltration membranes comprising a microporous material. The microporous material comprises: (a) a polyolefin matrix present in an amount of at least 2 percent by weight, (b) finely divided, particulate, substantially water-insoluble silica filler distributed throughout said matrix, said filler constituting from about 10 percent to about 90 percent by weight of said coated microporous material substrate, (c) at least 20 percent by volume of a network of interconnecting pores communicating throughout the coated microporous material, and (d) at least one coating composition applied to at least one surface of the membrane to adjust the surface energy of the membrane.

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(54) Title: COATED MICROPOROUS MATERIALS HAVING FILTRATION AND ADSORPTION PROPERTIES AND THEIR USE IN FLUID PURIFICATION PROCESSES

(57) Abstract: The present invention is directed to microfiltration and ultrafiltration membranes comprising a microporous material. The microporous material comprises: (a) a polyolefin matrix present in an amount of at least 2 percent by weight, (b) finely divided, particulate, substantially water-insoluble silica filler distributed throughout said matrix, said filler constituting from about 10 percent to about 90 percent by weight of said coated microporous material substrate, (c) at least 20 percent by volume of a network of interconnecting pores communicating throughout the coated microporous material, and (d) at least one coating composition applied to at least one surface of the membrane to adjust the surface energy of the membrane.

FILTRATION MEMBRANE COMPRISING COATED MICROPOROUS MATERIAL OF POLYOLEFIN AND PARTICULATE SILICA

FIELD OF THE INVENTION

[0001] The present invention relates to coated microporous materials useful in filtration and adsorption membranes and their use in fluid purification processes.

BACKGROUND OF THE INVENTION

[0002] Accessibility to clean and potable water is a concern throughout the world, particularly in developing countries. The search for low-cost, effective filtration materials and processes is ongoing. Filtration media that can remove both macroscopic, particulate contaminants and molecular contaminants are particularly desired, including those that can remove both hydrophilic and hydrophobic contaminants at low cost and high flux rate.

[0003] It would be desirable to provide novel membranes suitable for use on liquid or gaseous streams that serve to remove contaminants via both chemisorption and physisorption.

SUMMARY OF THE INVENTION

[0004] The present invention is directed to microfiltration and ultrafiltration membranes comprising a microporous material. The microporous material comprises:

(a) a polyolefin matrix present in an amount of at least 2 percent by weight,

(b) finely divided, particulate, substantially water-insoluble silica filler distributed throughout said matrix, said filler constituting from about 10 percent to about 90 percent by weight of said coated microporous material substrate,

(c) at least 20 percent by volume of a network of interconnecting pores communicating throughout the coated microporous material, and

(d) at least one coating composition applied to at least one surface of the membrane to adjust the surface energy of the membrane.

DETAILED DESCRIPTION OF THE INVENTION

[0005] Other than in any operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0006] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

[0007] Also, it should be understood that any numerical range recited herein is intended to include all sub-ranges subsumed therein. For example, a range of "1 to 10" is intended to include all sub-ranges between (and including) the recited minimum value of 1 and the recited maximum value of 10, that is, having a minimum value equal to or greater than 1 and a maximum value of equal to or less than 10.

[0008] As used in this specification and the appended claims, the articles "a," "an," and "the" include plural referents unless expressly and unequivocally limited to one referent.

[0009] The various embodiments and examples of the present invention as presented herein are each understood to be non-limiting with respect to the scope of the invention.

[0010] As used in the following description and claims, the following terms have the meanings indicated below:

[0011] By "polymer" is meant a polymer including homopolymers and copolymers, and oligomers. By "composite material" is meant a combination of two or more differing materials.

[0012] As used herein, "formed from" denotes open, e.g., "comprising," claim language. As such, it is intended that a composition "formed from" a list of recited components be a composition comprising at least these recited components, and can further comprise other, nonrecited components, during the composition's formation.

[0013] As used herein, the term "polymeric inorganic material" means a polymeric material having a backbone repeat unit based on an element or elements other than carbon. For more information see James Mark et al., Inorganic Polymers, Prentice Hall Polymer Science and Engineering Series, (1992) at page 5. Moreover, as used herein, the term "polymeric organic materials" means synthetic polymeric materials, semisynthetic polymeric materials and natural polymeric materials, all of which have a backbone repeat unit based on carbon.

[0014] An "organic material," as used herein, means carbon containing compounds wherein the carbon is typically bonded to itself and to hydrogen, and often to other elements as well, and excludes binary compounds such as the carbon oxides, the carbides, carbon disulfide, etc.; such ternary compounds as the metallic cyanides, metallic carbonyls, phosgene, carbonyl sulfide, etc.; and carbon-containing ionic compounds such as metallic carbonates, for example calcium carbonate and sodium carbonate. See R. Lewis, Sr., Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at pages 761-762, and M. Silberberg, Chemistry The Molecular Nature of Matter and Change (1996) at page 586.

[0015] As used herein, the term "inorganic material" means any material that is not an organic material.

[0016] As used herein, a "thermoplastic" material is a material that softens when exposed to heat and returns to its original condition when cooled to room temperature. As used

herein, a "thermoset" material is a material that solidifies or "sets" irreversibly when heated.

[0017] As used herein, "microporous material" or "microporous sheet material" means a material having a network of interconnecting pores, wherein, on a coating-free, printing ink-free, impregnant-free, and pre-bonding basis, the pores have a volume average diameter ranging from 0.001 to 0.5 micrometer, and constitute at least 5 percent by volume of the material as discussed herein below.

[0018] By "plastomer" is meant a polymer exhibiting both plastic and elastomeric properties.

[0019] As noted above, the present invention is directed to microfiltration and ultrafiltration membranes comprising a microporous material. Microporous materials used in the membranes of the present invention comprise a polyolefin matrix (a). The polyolefin matrix is present in the microporous material in an amount of at least 2 percent by weight. Polyolefins are polymers derived from at least one ethylenically unsaturated monomer. In certain embodiments of the present invention, the matrix comprises a plastomer. For example, the matrix may comprise a plastomer derived from butene, hexene, and/or octene. Suitable plastomers are available from ExxonMobil Chemical under the tradename "EXACT".

[0020] In certain embodiments of the present invention, the matrix comprises a different polymer derived from at least one ethylenically unsaturated monomer, which may be used in place of or in combination with the plastomer. Examples include polymers derived from ethylene, propylene, and/or butene, such as polyethylene, polypropylene, and polybutene. High density and/or ultrahigh molecular weight polyolefins such as high density polyethylene are also suitable.

[0021] In a particular embodiment of the present invention, the polyolefin matrix comprises a copolymer of ethylene and butene.

[0022] Non-limiting examples of ultrahigh molecular weight (UHMW) polyolefin can include essentially linear UHMW polyethylene or polypropylene. Inasmuch as UHMW polyolefins are not thermoset polymers having an infinite molecular weight, they are technically classified as thermoplastic materials.

[0023] The ultrahigh molecular weight polypropylene can comprise essentially linear ultrahigh molecular weight isotactic polypropylene. Often the degree of isotacticity of such polymer is at least 95 percent, e.g., at least 98 percent.

[0024] While there is no particular restriction on the upper limit of the intrinsic viscosity of the UHMW polyethylene, in one non-limiting example, the intrinsic viscosity can range from 18 to 39 deciliters/gram, e.g., from 18 to 32 deciliters/gram. While there is no particular restriction on the upper limit of the intrinsic viscosity of the UHMW polypropylene, in one non-limiting example, the intrinsic viscosity can range from 6 to 18 deciliters/gram, e.g., from 7 to 16 deciliters/gram.

[0025] For purposes of the present invention, intrinsic viscosity is determined by extrapolating to zero concentration the reduced viscosities or the inherent viscosities of several dilute solutions of the UHMW polyolefin where the solvent is freshly distilled decahydronaphthalene to which 0.2 percent by weight, 3,5-di-tert-butyl-4-hydroxyhydrocinnamic acid, neopentanetetrayl ester [CAS Registry No. 6683-19-8] has been added. The reduced viscosities or the inherent viscosities of the UHMW polyolefin are ascertained from relative viscosities obtained at 135 °C using an Ubbelohde No. 1 viscometer in accordance with the general procedures of ASTM D 4020-81, except that several dilute solutions of differing concentration are employed.

[0026] The nominal molecular weight of UHMW polyethylene is empirically related to the intrinsic viscosity of the polymer in accordance with the following equation:

$$M=5.37 \times 10^4 [\acute{\eta}]^{1.37}$$

[0027] wherein M is the nominal molecular weight and [ή] is the intrinsic viscosity of the UHMW polyethylene expressed in deciliters/gram. Similarly, the nominal molecular weight of UHMW polypropylene is empirically related to the intrinsic viscosity of the polymer according to the following equation:

$$M=8.88 \times 10^4 [ή]^{1.25}$$

wherein M is the nominal molecular weight and [ή] is the intrinsic viscosity of the UHMW polypropylene expressed in deciliters/gram.

[0028] A mixture of substantially linear ultrahigh molecular weight polyethylene and lower molecular weight polyethylene can be used. In certain embodiments, the UHMW polyethylene has an intrinsic viscosity of at least 10 deciliters/gram, and the lower molecular weight polyethylene has an ASTM D 1238-86 Condition E melt index of less than 50 grams/10 minutes, e.g., less than 25 grams/10 minutes, such as less than 15 grams/10 minutes, and an ASTM D 1238-86 Condition F melt index of at least 0.1 gram/10 minutes, e.g., at least 0.5 gram/10 minutes, such as at least 1.0 gram/10 minutes. The amount of UHMW polyethylene used (as weight percent) in this embodiment is described in column 1, line 52 to column 2, line 18 of U.S. Patent 5,196,262. More particularly, the weight percent of UHMW polyethylene used is described in relation to Figure 6 of U.S. 5,196,262; namely, with reference to the polygons ABCDEF, GHCI or JHCK of Figure 6.

[0029] The nominal molecular weight of the lower molecular weight polyethylene (LMWPE) is lower than that of the UHMW polyethylene. LMWPE is a thermoplastic material and many different types are known. One method of classification is by density, expressed in grams/cubic centimeter and rounded to the nearest thousandth, in accordance with ASTM D 1248-84 (Reapproved 1989). Non-limiting examples of the densities of LMWPE are found in the following Table 1.

TABLE 1

Type	Abbreviation	Density, g/cm^3
Low Density Polyethylene	LDPE	0.910-0.925
Medium Density Polyethylene	MDPE	0.926-0.940
High Density Polyethylene	HDPE	0.941-0.965

[0030] Any or all of the polyethylenes listed in Table 1 above may be used as the LMWPE in the matrix of the microporous material. HDPE may be used because it can be more linear than MDPE or LDPE. Processes for making the various LMWPE's are well known and well documented. They include the high pressure process, the Phillips Petroleum Company process, the Standard Oil Company (Indiana) process, and the Ziegler process. The ASTM D 1238-86 Condition E (that is, 190° C. and 2.16 kilogram load) melt index of the LMWPE is less than about 50 grams/10 minutes. Often the Condition E melt index is less than about 25 grams/10 minutes. The Condition E melt index can be less than about 15 grams/10 minutes. The ASTM D 1238-86 Condition F (that is, 190° C. and 21.6 kilogram load) melt index of the LMWPE is at least 0.1 gram/10 minutes. In many cases the Condition F melt index is at least 0.5 gram/10 minutes such as at least 1.0 gram/10 minutes.

[0031] The UHMWPE and the LMWPE may together constitute at least 65 percent by weight, e.g., at least 85 percent by weight, of the polyolefin polymer of the microporous material. Also, the UHMWPE and LMWPE together may constitute substantially 100 percent by weight of the polyolefin polymer of the microporous material.

[0032] In a particular embodiment of the present invention, the microporous material can comprise a polyolefin comprising ultrahigh molecular weight polyethylene, ultrahigh

molecular weight polypropylene, high density polyethylene, high density polypropylene, or mixtures thereof.

[0033] If desired, other thermoplastic organic polymers also may be present in the matrix of the microporous material provided that their presence does not materially affect the properties of the microporous material substrate in an adverse manner. The amount of the other thermoplastic polymer which may be present depends upon the nature of such polymer. In general, a greater amount of other thermoplastic organic polymer may be used if the molecular structure contains little branching, few long side chains, and few bulky side groups, than when there is a large amount of branching, many long side chains, or many bulky side groups. Non-limiting examples of thermoplastic organic polymers that optionally may be present in the matrix of the microporous material include low density polyethylene, high density polyethylene, poly(tetrafluoroethylene), polypropylene, copolymers of ethylene and propylene, copolymers of ethylene and acrylic acid, and copolymers of ethylene and methacrylic acid. If desired. all or a portion of the carboxyl groups of carboxyl-containing copolymers can be neutralized with sodium, zinc or the like. Generally, the microporous material comprises at least 70 percent by weight of UHMW polyolefin, based on the weight of the matrix. In a non-limiting embodiment, the above-described other thermoplastic organic polymer are substantially absent from the matrix of the microporous material.

[0034] The microporous materials used in the membranes of the present invention further comprise finely divided, particulate, substantially water-insoluble silica filler (b) distributed throughout the matrix.

[0035] The particulate filler typically comprises precipitated silica particles. It is important to distinguish precipitated silica from silica gel inasmuch as these different materials have different properties. Reference inthis regard is made to R. K. Iler, The Chemistry of Silica, John Wiley & Sons, New York (1979). Library of Congress Catalog No. QD 181.S6144. Note especially pages 15-29, 172-176, 218-233, 364-365, 462-465, 554-564, and 578-

579. Silica gel is usually produced commercially at low pH by acidifying an aqueous solution of a soluble metal silicate, typically sodium silicate, with acid. The acid employed is generally a strong mineral acid such as sulfuric acid or hydrochloric acid although carbon dioxide is sometimes used. Inasmuch as there is essentially no difference in density between gel phase and the surrounding liquid phase while the viscosity is low, the gel phase does not settle out, that is to say, it does not precipitate. Silica gel, then, may be described as a nonprecipitated, coherent, rigid, three-dimensional network of contiguous particles of colloidal amorphous silica. The state of subdivision ranges from large, solid masses to submicroscopic particles, and the degree of hydration from almost anhydrous silica to soft gelatinous masses containing on the order of 100 parts of water per part of silica by weight.

[0036] Precipitated silica is usually produced commercially by combining an aqueous solution of a soluble metal silicate, ordinarily alkali metal silicate such as sodium silicate, and an acid so that colloidal particles will grow in weakly alkaline solution and be coagulated by the alkali metal ions of the resulting soluble alkali metal salt. Various acids may be used, including the mineral acids, but the preferred acid is carbon dioxide. In the absence of a coagulant, silica is not precipitated from solution at any pH. The coagulant used to effect precipitation may be the soluble alkali metal salt produced during formation of the colloidal silica particles, it may be added electrolyte such as a soluble inorganic or organic salt, or it may be a combination of both.

[0037] Precipitated silica, then, may be described as precipitated aggregates of ultimate particles of colloidal amorphous silica that have not at any point existed as macroscopic gel during the preparation. The sizes of the aggregates and the degree of hydration may vary widely.

[0038] Precipitated silica powders differ from silica gels that have been pulverized in ordinarily having a more open structure, that is, a higher specific pore volume. However,

the specific surface area of precipitated silica as measured by the Brunauer, Emmet, Teller (BET) method using nitrogen as the adsorbate, is often lower than that of silica gel.

[0039] Many different precipitated silicas may be employed in the present invention, but the preferred precipitated silicas are those obtained by precipitation from an aqueous solution of sodium silicate using a suitable acid such as sulfuric acid, hydrochloric acid, or carbon dioxide. Such precipitated silicas are themselves known and processes for producing them are described in detail in the U.S. Pat. No. 2,940,830 and in West German Offenlegungsschrift No. 35 45 615, including especially the processes for making precipitated silicas and the properties of the products.

[0040] The precipitated silicas used in the present invention can be produced by a process involving the following successive steps:

(a) an initial stock solution of aqueous alkali metal silicate having the desired alkalinity is prepared and added to (or prepared in) a reactor equipped with means for heating the contents of the reactor,

(b) the initial stock solution within the reactor is heated to the desired reaction temperature,

(c) acidifying agent and additional alkali metal silicate solution are simultaneously added with agitation to the reactor while maintaining the alkalinity value and temperature of the contents of the reactor at the desired values,

(d) the addition of alkali metal silicate to the reactor is stopped, and additional acidifying agent is added to adjust the pH of the resulting suspension of precipitated silica to a desired acid value,

(e) the precipitated silica in the reactor is separated from the reaction mixture, washed to remove by-product salts, and

(f) dried to form the precipitated silica.

[0041] The washed silica solids are then dried using conventional drying techniques. Non-limiting examples of such techniques include oven drying, vacuum oven drying,

rotary dryers, spray drying or spin flash drying. Non-limiting examples of spray dryers include rotary atomizers and nozzle spray dryers. Spray drying can be carried out using any suitable type of atomizer, in particular a turbine, nozzle, liquid-pressure or twin-fluid atomizer.

[0042] The washed silica solids may not be in a condition that is suitable for spray drying. For example, the washed silica solids may be too thick to be spray dried. In one aspect of the above-described process, the washed silica solids, e.g., the washed filter cake, are mixed with water to form a liquid suspension and the pH of the suspension adjusted, if required, with dilute acid or dilute alkali, e.g., sodium hydroxide, to from 6 to 7, e.g., 6.5, and then fed to the inlet nozzle of the spray dryer.

[0043] The temperature at which the silica is dried can vary widely but will be below the fusion temperature of the silica. Typically, the drying temperature will range from above 50 °C to less than 700 °C, e.g., from above 100 °C, e.g., 200 °C, to 500 °C. In one aspect of the above-described process, the silica solids are dried in a spray dryer having an inlet temperature of approximately 400 °C and an outlet temperature of approximately 105 °C. The free water content of the dried silica can vary, but is usually in the range of from approximately 1 to 10 wt.%, e.g., from 4 to 7 wt.%. As used herein, the term free water means water that can be removed from the silica by heating it for 24 hours at from 100 °C to 200 °C, e.g., 105 °C.

[0044] In one aspect of the process described herein, the dried silica is forwarded directly to a granulator where it is compacted and granulated to obtain a granular product. Dried silica can also be subjected to conventional size reduction techniques, e.g., as exemplified by grinding and pulverizing. Fluid energy milling using air or superheated steam as the working fluid can also be used. The precipitated silica obtained is usually in the form of a powder.

[0045] Most often, the precipitated silica is rotary dried or spray dried. Rotary dried silica particles have been observed to demonstrate greater structural integrity than spray dried

silica particles. They are less likely to break into smaller particles during extrusion and other subsequent processing during production of the microporous material than are spray dried particles. Particle size distribution of rotary dried particles does not change as significantly as does that of spray dried particles during processing. Spray dried silica particles are more friable than rotary dried, often providing smaller particles during processing. It is possible to use a spray dried silica of a particular particle size such that the final particle size distribution in the membrane does not have a detrimental effect on water flux. In certain embodiments, the silica is reinforced; i.e., has a structural integrity such that porosity is preserved after extrusion. More preferred is a precipitated silica in which the initial number of silica particles and the initial silica particle size distribution is mostly unchanged by stresses applied during membrane fabrication. Most preferred is a silica reinforced such that a broad particle size distribution is present in the finished membrane. Blends of different types of dried silica and different sizes of silica may be used to provide unique properties to the membrane. For example, a blend of silicas with a bimodal distribution of particle sizes may be particularly suitable for certain separation processes. It is expected that external forces applied to silica of any type may be used to influence and tailor the particle size distribution, providing unique properties to the final membrane.

[0046] The surface of the particle can be modified in any manner well known in the art, including, but not limited to, chemically or physically changing its surface characteristics using techniques known in the art. For example, the silica may be surface treated with an anti-fouling moiety such as polyethylene glycol, carboxybetaine, sulfobetaine and polymers thereof, mixed valence molecules, oligomers and polymers thereof and mixtures thereof. Another embodiment may be a blend of silicas in which one silica has been treated with a positively charged moiety and the other silica has been treated with a negatively charged moiety. The silica may also be surface modified with functional groups that allow for targeted removal of specific contaminants in a fluid stream to be purified using the microfiltration membrane of the present invention. Untreated particles

may also be used. Silica particles coated with hydrophilic coatings reduce fouling and may eliminate pre-wetting processing. Silica particles coated with hydrophobic coatings also reduce fouling and may aid degassing and venting of a system.

[0047] Precipitated silica typically has an average ultimate particle size of 1 to 100 nanometers.

[0048] The surface area of the silica particles, both external and internal due to pores, can have an impact on performance. High surface area fillers are materials of very small particle size, materials having a high degree of porosity or materials exhibiting both characteristics. Usually the surface area of the filler itself is in the range of from about 125 to about 700 square meters per gram (m^2/g) as determined by the Brunauer, Emmett, Teller (BET) method according to ASTM C 819-77 using nitrogen as the adsorbate but modified by outgassing the system and the sample for one hour at 130°C. Often the BET surface area is in the range of from about 190 to 350 m^2/g, more often, the silica demonstrates a BET surface area of 351 to 700 m^2/g.

[0049] The BET/CTAB quotient is the ratio of the overall precipitated silica surface area including the surface area contained in pores only accessible to smaller molecules, such as nitrogen (BET), to the external surface area (CTAB). This ratio is typically referred to as a measure of microporosity. A high microporosity value, i.e., a high BET/CTAB quotient number, is a high proportion of internal surface – accessible to the small nitrogen molecule (BET surface area) but not to larger particles - to the external surface (CTAB).

[0050] It has been suggested that the structure, i.e., pores, formed within the precipitated silica during its preparation can have an impact on performance. Two measurements of this structure are the BET/CTAB surface area ratio of the precipitated silica noted above, and the relative breadth (γ) of the pore size distribution of the precipitated silica. The relative breadth (γ) of pore size distribution is an indication of how broadly the pore sizes are distributed within the precipitated silica particle. The lower the γ value, the narrower is the pore size distribution of the pores within the precipitated silica particle.

[0051] The silica CTAB values may be determined using a CTAB solution and the hereinafter described method. The analysis is performed using a Metrohm 751 Titrino™ automatic titrator, equipped with a Metrohm Interchangeable "Snap-In" 50 milliliter buret and a Brinkmann Probe Colorimeter Model PC 910 equipped with a 550 nm filter. In addition, a Mettler Toledo HB43 or equivalent is used to determine the 105 °C moisture loss of the silica and a Fisher Scientific Centrific™ Centrifuge Model 225 may be used for separating the silica and the residual CTAB solution. The excess CTAB can be determined by auto titration with a solution of Aerosol OT® until maximum turbidity is attained, which can be detected with the probe colorimeter. The maximum turbidity point is taken as corresponding to a millivolt reading of 150. Knowing the quantity of CTAB adsorbed for a given weight of silica and the space occupied by the CTAB molecule, the external specific surface area of the silica is calculated and reported as square meters per gram on a dry-weight basis.

[0052] Solutions required for testing and preparation include a buffer of pH 9.6, cetyl [hexadecyl] trimethyl ammonium bromide (CTAB), dioctyl sodium sulfosuccinate (Aerosol OT) and 1N sodium hydroxide. The buffer solution of pH 9.6 can be prepared by dissolving 3.101 g of orthoboric acid (99%; Fisher Scientific, Inc., technical grade, crystalline) in a one-liter volumetric flask, containing 500 milliliters of deionized water and 3.708 grams of potassium chloride solids (Fisher Scientific, Inc., technical grade, crystalline). Using a buret, 36.85 milliliters of the 1N sodium hydroxide solution was added. The solution is mixed and diluted to volume.

[0053] The CTAB solution is prepared using 11.0 g ± 0.005 g of powdered CTAB (cetyl trimethyl ammonium bromide, also known as hexadecyl trimethyl ammonium bromide, Fisher Scientific Inc., technical grade) onto a weighing dish. The CTAB powder is transferred to a 2-liter beaker and the weighing dish rinsed with deionized water. Approximately 700 milliliters of the pH 9.6 buffer solution and 1000 milliliters of distilled or deionized water is added to the 2-liter beaker and stirred with a magnetic stir bar. The beaker may be covered and stirred at room temperature until the CTAB powder is totally

dissolved. The solution is transferred to a 2-liter volumetric flask, rinsing the beaker and stir bar with deionized water. The bubbles are allowed to dissipate, and the solution diluted to volume with deionized water. A large stir bar can be added and the solution mixed on a magnetic stirrer for approximately 10 hours. The CTAB solution can be used after 24 hours and for only 15 days. The Aerosol OT® (dioctyl sodium sulfosuccinate, Fisher Scientific Inc., 100% solid) solution may be prepared using 3.46 g ± 0.005 g, which is placed onto a weighing dish. The Aerosol OT on the weighing dish is rinsed into a 2-liter beaker, which contains about 1500 milliliter deionized water and a large stir bar. The Aerosol OT solution is dissolved and rinsed into a 2-liter volumetric flask. The solution is diluted to the 2-liter volume mark in the volumetric flask. The Aerosol OT® solution is allowed to age for a minimum of 12 days prior to use. The shelf life of the Aerosol OT solution is 2 months from the preparation date.

[0054] Prior to surface area sample preparation, the pH of the CTAB solution should be verified and adjusted as necessary to a pH of 9.6 ± 0.1 using 1N sodium hydroxide solution. For test calculations a blank sample should be prepared and analyzed. 5 milliliters of the CTAB solution are pipetted and 55 milliliters deionized water added into a 150-milliliter beaker and analyzed on a Metrohm 751 Titrino automatic titrator. The automatic titrator is programmed for determination of the blank and the samples with the following parameters: Measuring point density = 2, Signal drift = 20, Equilibrium time = 20 seconds, Start volume = 0 ml, Stop volume = 35 ml, and Fixed endpoint = 150 mV. The buret tip and the colorimeter probe are placed just below the surface of the solution, positioned such that the tip and the photo probe path length are completely submerged. Both the tip and photo probe should be essentially equidistant from the bottom of the beaker and not touching one another. With minimum stirring (setting of 1 on the Metrohm 728 stirrer) the colorimeter is set to 100 %T prior to every blank and sample determination and titration initiated with the Aerosol OT® solution. The end point can be recorded as the volume (ml) of titrant at 150 mV.

[0055] For test sample preparation, approximately 0.30 grams of powdered silica was weighed into a 50-milliliter container containing a stir bar. Granulated silica samples, were riffled (prior to grinding and weighing) to obtain a representative sub-sample. A coffee mill style grinder was used to grind granulated materials. Then 30 milliliters of the pH adjusted CTAB solution was pipetted into the sample container containing the 0.30 grams of powdered silica. The silica and CTAB solution was then mixed on a stirrer for 35 minutes. When mixing was completed, the silica and CTAB solution were centrifuged for 20 minutes to separate the silica and excess CTAB solution. When centrifuging was completed, the CTAB solution was pipetted into a clean container minus the separated solids, referred to as the "centrifugate". For sample analysis, 50 milliliters of deionized water was placed into a 150-milliliter beaker containing a stir bar. Then 10 milliliters of the sample centrifugate was pipetted for analysis into the same beaker. The sample was analyzed using the same technique and programmed procedure as used for the blank solution.

[0056] For determination of the moisture content, approximately 0.2 grams of silica was weighed onto the Mettler Toledo HB43 while determining the CTAB value. The moisture analyzer was programmed to 105 ° C with the shut-off 5 drying criteria. The moisture loss was recorded to the nearest + 0.1%.

[0057] The external surface area is calculated using the following equation,

$$\text{CTAB Surface Area (dried basis) } [m^2/g] = \frac{(2V_o - V) \times (4774)}{(V_o W) \times (100 - Vol)}$$

wherein,

V_o = Volume in ml of Aerosol OT® used in the blank titration.

V = Volume in ml of Aerosol OT® used in the sample titration.

W = sample weight in grams.

Vol = % moisture loss (Vol represents "volatiles").

[0058] Typically, the CTAB surface area of the silica particles used in the present invention ranges from 120 to 500 m^2/g. Often, the silica demonstrates a CTAB surface area of 170-280 m^2/g. More often, the silica demonstrates a CTAB surface area of 281-500 m^2/g.

[0059] In certain embodiments of the present invention, the BET value of the precipitated silica will be a value such that the quotient of the BET surface area in square meters per gram to the CTAB surface area in square meters per gram is equal to or greater than 1.0. Often, the BET to CTAB ratio is 1.0-1.5. More often, the BET to CTAB ratio is 1.5-2.0.

[0060] The BET surface area values reported in the examples of this application were determined in accordance with the Brunauer-Emmet-Teller (BET) method in accordance with ASTM D1993-03. The BET surface area can be determined by fitting five relative-pressure points from a nitrogen sorption isotherm measurement made with a Micromeritics TriStar 3000™ instrument. A flow Prep-060™ station provides heat and a continuous gas flow to prepare samples for analysis. Prior to nitrogen sorption, the silica samples are dried by heating to a temperature of 160 °C in flowing nitrogen (P5 grade) for at least one (1) hour.

[0061] The filler particles can constitute from 10 to 90 percent by weight of the microporous material. For example, such filler particles can constitute from 25 to 90 percent by weight of the microporous material, such as from 30 percent to 90 percent by weight of the microporous material, or from 40 to 90 percent by weight of the microporous material, or from 50 to 90 percent by weight of the microporous material and even from 60 percent to 90 percent by weight of the microporous material. The filler is typically present in the microporous material of the present invention in an amount of 50 percent to about 85 percent by weight of the microporous material. Often the weight ratio of silica to polyolefin in the microporous material is 0.5:1 to 10:1, such as 1.7:1 to 3.5:1. Alternatively the weight ratio of filler to polyolefin in the microporous material may be greater than 4:1.

[0062] The microporous material used in the membrane of the present invention further comprises a network of interconnecting pores (c) communicating throughout the microporous material.

[0063] On an impregnant-free basis, such pores can comprise at least 15 percent by volume, e.g. from at least 20 to 95 percent by volume, or from at least 25 to 95 percent by volume, or from 35 to 70 percent by volume of the microporous material. Often the pores comprise at least 35 percent by volume, or even at least 45 percent by volume of the microporous material. Such high porosity provides higher surface area throughout the microporous material, which in turn facilitates removal of contaminants from a fluid stream and higher flux rates of a fluid stream through the membrane.

[0064] As used herein and in the claims, the porosity (also known as void volume) of the microporous material, expressed as percent by volume, is determined according to the following equation:

$$\text{Porosity}=100[1-d_1/d_2]$$

wherein d_1 is the density of the sample, which is determined from the sample weight and the sample volume as ascertained from measurements of the sample dimensions, and d_2 is the density of the solid portion of the sample, which is determined from the sample weight and the volume of the solid portion of the sample. The volume of the solid portion of the same is determined using a Quantachrome stereopycnometer (Quantachrome Corp.) in accordance with the accompanying operating manual.

[0065] The volume average diameter of the pores of the microporous material can be determined by mercury porosimetry using an Autopore™ III porosimeter (Micromeretics, Inc.) in accordance with the accompanying operating manual. The volume average pore radius for a single scan is automatically determined by the porosimeter. In operating the porosimeter, a scan is made in the high pressure range (from 138 kilopascals absolute to 227 megapascals absolute). If approximately 2 percent or less of the total intruded volume occurs at the low end (from 138 to 250 kilopascals absolute) of the high pressure

range, the volume average pore diameter is taken as twice the volume average pore radius determined by the porosimeter. Otherwise, an additional scan is made in the low pressure range (from 7 to 165 kilopascals absolute) and the volume average pore diameter is calculated according to the equation:

$$d = 2 [v_1r_1/w_1 + v_2r_2/w_2] / [v_1/ w_1 + v_2/ w_2]$$

wherein d is the volume average pore diameter, v_1 is the total volume of mercury intruded in the high pressure range, v_2 is the total volume of mercury intruded in the low pressure range, r_1 is the volume average pore radius determined from the high pressure scan, r_2 is the volume average pore radius determined from the low pressure scan, w_1 is the weight of the sample subjected to the high pressure scan, and w_2 is the weight of the sample subjected to the low pressure scan. For ultrafiltration membranes, the volume average diameter of the pores (mean pore size) is typically less than 0.1 micrometers (microns), and can be in the range of from 0.001 to 0.70 micrometers, e.g., from 0.30 to 0.70 micrometers. For microfiltration membranes, the mean pore size is typically greater than 0.1 micrometers (microns),

[0066] In the course of determining the volume average pore diameter of the above procedure, the maximum pore radius detected is sometimes noted. This is taken from the low pressure range scan, if run; otherwise it is taken from the high pressure range scan. The maximum pore diameter is twice the maximum pore radius. Inasmuch as some production or treatment steps, e.g., coating processes, printing processes, impregnation processes and/or bonding processes, can result in the filling of at least some of the pores of the microporous material, and since some of these processes irreversibly compress the microporous material, the parameters in respect of porosity, volume average diameter of the pores, and maximum pore diameter are determined for the microporous material prior to the application of one or more of such production or treatment steps.

[0067] To prepare the microporous materials of the present invention, filler, polymer powder (polyolefin polymer), processing plasticizer, and minor amounts of lubricant and

antioxidant are mixed until a substantially uniform mixture is obtained. The weight ratio of filler to polymer powder employed in forming the mixture is essentially the same as that of the microporous material substrate to be produced. The mixture, together with additional processing plasticizer, is introduced to the heated barrel of a screw extruder. Attached to the extruder is a die, such as a sheeting die, to form the desired end shape.

[0068] In an exemplary manufacturing process, when the material is formed into a sheet or film, a continuous sheet or film formed by a die is forwarded to a pair of heated calender rolls acting cooperatively to form continuous sheet of lesser thickness than the continuous sheet exiting from the die. The final thickness may depend on the desired end-use application. The microporous material may have a thickness ranging from 0.7 to 18 mil (17.8 to 457.2 microns), such as 0.7 to 15 mil (17.8 to 381 microns), or 1 to 10 mil (25.4 to 254 microns), or 5 to 10 mil (127 to 254 microns), and demonstrates a bubble point of 10 to 80 psi based on ethanol.

[0069] Optionally, the sheet exiting the calendar rolls may then be stretched in at least one stretching direction above the elastic limit, depending on whether the membrane being formed is to be for microfiltration or ultrafiltration. Stretching may alternatively take place during or immediately after exiting from the sheeting die or during calendaring, or multiple times, but it is typically done prior to extraction. Stretched microporous material substrate may be produced by stretching the intermediate product in at least one stretching direction above the elastic limit. Usually the stretch ratio is at least about 1.5. In many cases the stretch ratio is at least about 1.7. Preferably it is at least about 2. Frequently the stretch ratio is in the range of from about 1.5 to about 15. Often the stretch ratio is in the range of from about 1.7 to about 10. Usually the stretch ratio is in the range of from about 2 to about 6. However, care should be taken that stretching does not result in pore sizes too large for ultrafiltration.

[0070] The temperatures at which stretching is accomplished may vary widely. Stretching may be accomplished at about ambient room temperature, but usually elevated

temperatures are employed. The intermediate product may be heated by any of a wide variety of techniques prior to, during, and/or after stretching. Examples of these techniques include radiative heating such as that provided by electrically heated or gas fired infrared heaters, convective heating such as that provided by recirculating hot air, and conductive heating such as that provided by contact with heated rolls. The temperatures which are measured for temperature control purposes may vary according to the apparatus used and personal preference. For example, temperature-measuring devices may be placed to ascertain the temperatures of the surfaces of infrared heaters, the interiors of infrared heaters, the air temperatures of points between the infrared heaters and the intermediate product, the temperatures of circulating hot air at points within the apparatus, the temperature of hot air entering or leaving the apparatus, the temperatures of the surfaces of rolls used in the stretching process, the temperature of heat transfer fluid entering or leaving such rolls, or film surface temperatures. In general, the temperature or temperatures are controlled such that the intermediate product is stretched about evenly so that the variations, if any, in film thickness of the stretched microporous material are within acceptable limits and so that the amount of stretched microporous material outside of those limits is acceptably low. It will be apparent that the temperatures used for control purposes may or may not be close to those of the intermediate product itself since they depend upon the nature of the apparatus used, the locations of the temperature-measuring devices, and the identities of the substances or objects whose temperatures are being measured.

[0071] In view of the locations of the heating devices and the line speeds usually employed during stretching, gradients of varying temperatures may or may not be present through the thickness of the intermediate product. Also because of such line speeds, it is impracticable to measure these temperature gradients. The presence of gradients of varying temperatures, when they occur, makes it unreasonable to refer to a singular film temperature. Accordingly, film surface temperatures, which can be measured, are best used for characterizing the thermal condition of the intermediate product.

[0072] These are ordinarily about the same across the width of the intermediate product during stretching although they may be intentionally varied, as for example, to compensate for intermediate product having a wedge-shaped cross-section across the sheet. Film surface temperatures along the length of the sheet may be about the same or they may be different during stretching.

[0073] The film surface temperatures at which stretching is accomplished may vary widely, but in general they are such that the intermediate product is stretched about evenly, as explained above. In most cases, the film surface temperatures during stretching are in the range of from about 20°C to about 220°C. Often such temperatures are in the range of from about 50°C to about 200°C. From about 75°C to about 180°C is preferred.

[0074] Stretching may be accomplished in a single step or a plurality of steps as desired. For example, when the intermediate product is to be stretched in a single direction (uniaxial stretching), the stretching may be accomplished by a single stretching step or a sequence of stretching steps until the desired final stretch ratio is attained. Similarly, when the intermediate product is to be stretched in two directions (biaxial stretching), the stretching can be conducted by a single biaxial stretching step or a sequence of biaxial stretching steps until the desired final stretch ratios are attained. Biaxial stretching may also be accomplished by a sequence of one of more uniaxial stretching steps in one direction and one or more uniaxial stretching steps in another direction. Biaxial stretching steps where the intermediate product is stretched simultaneously in two directions and uniaxial stretching steps may be conducted in sequence in any order. Stretching in more than two directions is within contemplation. It may be seen that the various permutationes of steps are quite numerous. Other steps, such as cooling, heating, sintering, annealing, reeling, unreeling, and the like, may optionally be included in the overall process as desired.

[0075] Various types of stretching apparatus are well known and may be used to accomplish stretching of the intermediate product. Uniaxial stretching is usually accomplished by stretching between two rollers wherein the second or downstream roller rotates at a greater peripheral speed than the first or upstream roller. Uniaxial stretching can also be accomplished on a standard tentering machine. Biaxial stretching may be accomplished by simultaneously stretching in two different directions on a tentering machine. More commonly, however, biaxial stretching is accomplished by first uniaxially stretching between two differentially rotating rollers as described above, followed by either uniaxially stretching in a different direction using a tenter machine or by biaxially stretching using a tenter machine. The most common type of biaxial stretching is where the two stretching directions are approximately at right angles to each other. In most cases where continuous sheet is being stretched, one stretching direction is at least approximately parallel to the long axis of the sheet (machine direction) and the other stretching direction is at least approximately perpendicular to the machine direction and is in the plane of the sheet (transverse direction).

[0076] Stretching the sheets prior to extraction of the processing plasticizer allows for larger pore sizes than in microporous materials conventionally processed, thus making the microporous material particularly suitable for use in the microfiltration membranes of the present invention. It is also believed that stretching of the sheets prior to extraction of the processing plasticizer minimizes thermal shrinkage after processing.

[0077] The product passes to a first extraction zone where the processing plasticizer is substantially removed by extraction with an organic liquid which is a good solvent for the processing plasticizer, a poor solvent for the organic polymer, and more volatile than the processing plasticizer. Usually, but not necessarily, both the processing plasticizer and the organic extraction liquid are substantially immiscible with water. The product then passes to a second extraction zone where the residual organic extraction liquid is substantially removed by steam and/or water. The product is then passed through a forced air dryer for substantial removal of residual water and remaining residual organic

extraction liquid. From the dryer the microporous material may be passed to a take-up roll, when it is in the form of a sheet.

[0078] The processing plasticizer has little solvating effect on the thermoplastic organic polymer at 60°C, only a moderate solvating effect at elevated temperatures on the order of about 100°C, and a significant solvating effect at elevated temperatures on the order of about 200°C. It is a liquid at room temperature and usually it is processing oil such as paraffinic oil, naphthenic oil, or aromatic oil. Suitable processing oils include those meeting the requirements of ASTM D 2226-82, Types 103 and 104. Those oils which have a pour point of less than 22°C, or less than 10°C, according to ASTM D 97-66 (reapproved 1978) are used most often. Examples of suitable oils include Shellflex® 412 and Shellflex® 371 oil (Shell Oil Co.) which are solvent refined and hydrotreated oils derived from naphthenic crude. It is expected that other materials, including the phthalate ester plasticizers such as dibutyl phthalate, bis(2-ethylhexyl) phthalate, diisodecyl phthalate, dicyclohexyl phthalate, butyl benzyl phthalate, and ditridecyl phthalate will function satisfactorily as processing plasticizers.

[0079] There are many organic extraction liquids that can be used. Examples of suitable organic extraction liquids include 1,1,2-trichloroethylene, perchloroethylene, 1,2-dichloroethane. 1,1,1-trichloroethane, 1,1,2-trichloroethane, methylene chloride, chloroform, isopropyl alcohol, diethyl ether and acetone.

[0080] In the above described process for producing microporous material substrate, extrusion and calendering are facilitated when the filler carries much of the processing plasticizer. The capacity of the filler particles to absorb and hold the processing plasticizer is a function of the surface area of the filler. Therefore the filler typically has a high surface area as discussed above. Inasmuch as it is desirable to essentially retain the filler in the microporous material substrate, the filler should be substantially insoluble in the processing plasticizer and substantially insoluble in the organic extraction liquid when microporous material substrate is produced by the above process.

[0081] The residual processing plasticizer content is usually less than 15 percent by weight of the resulting microporous material and this may be reduced even further to levels such as less than 5 percent by weight, by additional extractions using the same or a different organic extraction liquid.

[0082] The resulting microporous materials may be further processed depending on the desired application. In the present invention, a hydrophilic coating may be applied to the surface of the microporous material to adjust the surface energy of the material. Though not intending to be bound by theory, it is believed that components of the coating interact with the silica particles in the filler of the microporous material and adjust the surface energy, affecting wettability. Application of the coating may occur before, during, or after the stretching step described above, but is usually done simultaneously with stretching to maximize coating coverage on additional surface area created during the stretching process.

[0083] Hydrophilic coatings may comprise one or more of a polyoxazoline, including polyalkyloxazolines such as poly(2-ethyl-2-oxazoline), poly(2-methyl-2-oxazoline), and poly(2-methyl/ethyl-2-oxazoline); triblock copolymers based on poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol); polyethyleneimine; polyamide; oxidized polyethylene or its derivatives; polyethyleneoxide; polyethyleneglycol; polyvinylpyrrolidone; polyacrylic acid; polymethacrylic acid; polyethylene glycol derivatives; polypropylene oxide or its derivatives; a copolymer of poly(ethylene glycol) and polyethyleneoxide; polyvinyl alcohol; ethylene vinyl acetate; cellulose or its derivatives; polyimide; hydrogels such as collagen, polypeptides, guar and pectin; polypeptoids; poly(meth)acrylates such as poly(2-hydroxyethylmethacrylate); poly(meth)acrylamide; polysaccharides; zwitterionic polymers such as poly(phosphorylcholine) derivatives, polysulfobetaines, and polycarbobetaines; polyampholytes, and polyethylenimine. The hydrophilic coating preferably comprises at least one polymer having tertiary amine functional groups, such as poly(2-ethyl-2-oxazoline).

[0084] In certain embodiments, the coating compositions used in the methods of the present invention comprise one or more suitable surfactants to reduce surface tension. Surfactants include materials otherwise known as wetting agents, anti-foaming agents, emulsifiers, dispersing agents, leveling agents etc. Surfactants can be anionic, cationic and nonionic, and many surfactants of each type are available commercially. Some coating compositions include at least a wetting agent. Still other coating compositions may have additional surfactants to perform additional effects.

[0085] Other suitable surfactants may also be selected. The amount and number of surfactants added to the coating compositions will depend on the particular surfactant(s) selected, but should be limited to the minimum amount of surfactant that is necessary to achieve wetting of the substrate while not compromising the performance of the dried coating. In certain embodiments, the coating compositions comprise 0.01 up to 10 percent by weight of surfactant, in some embodiments, 0.05 up to 5 percent by weight, or, in yet other embodiments, 0.1 up to 3 percent by weight of surfactant. The amount of surfactant present in the coating compositions can range between any combination of these values inclusive of the recited values. The use of coating compositions in the membranes of the present invention allows for their use in separation systems without the need for pre-wetting of the membrane such as with isopropanol.

[0086] The microporous material may be adhered to a support layer such as a fiberglass layer to provide additional structural integrity, depending on the particular end use. Additional optional stretching of the continuous sheet in at least one stretching direction may also be done during or immediately after any of the steps upon extrusion in step (ii). For example, in the production of an ultrafiltration membrane of the present invention, preparation of the microporous material may include stretching of the continuous sheet during calendering, to allow for pore sizes in the upper range of ultrafiltration. Typically, however, in the production of an ultrafiltration membrane of the present invention, preparation of the microporous material does not include stretching steps.

[0087] The microporous materials prepared as described above are suitable for use in the microfiltration and ultrafiltration membranes of the present invention, capable of removing particulates from a fluid stream ranging in size from 0.005 to 0.1 microns (ultrafiltration) and capable of removing particulates from a fluid stream ranging in size from 0.05 to 1.5 microns (microfiltration). The membranes also serve to remove molecular contaminants from a fluid stream by adsorption or by physical rejection due to molecular size.

[0088] The membranes of the present invention may be used in a method of separating suspended or dissolved materials from a fluid stream, such as removing one or more contaminants from a fluid (liquid or gaseous) stream, or concentrating desired components in a depleted stream. The method comprises contacting the stream with the membrane, typically by passing the stream through the membrane. Examples of contaminants include toxins, such as neurotoxins; heavy metal; hydrocarbons; oils; dyes; neurotoxins; pharmaceuticals; and/or pesticides. The fluid stream (such as a water stream, but it may be liquid or gas) is usually passed through the membrane at a flux rate of at least 1, for example, 1 to 10000 gal/(ft^2 day) (GFD), at 25 psi, without the use of pre-wetting agents. Ultrafiltration membranes may demonstrate a water flux rate of greater than 100 GFD, preferably greater than 150 GFD, and a molecular weight cut-off of 100 to 500,000, while microfiltration membranes may demonstrate a water flux rate of greater than 300 GFD, preferably greater than 500 GFD. The membranes of the present invention demonstrate a Gurley number of less than 2000 seconds.

[0089] Coated membranes comprising microporous material coated with hydrophilic coating compositions demonstrate a water contact angle less than 70°, often less than 30°, more often less than 10°.

EXAMPLES

In Part I of the following examples, the materials and methods used to prepare the microporous sheet materials are described. In Part II, the methods and conditions

used to stretch the microporous sheet materials are described. Part III describes the coating formulations and methods used to coat the microporous sheet materials. The physical properties of the Examples (coated) and Comparative Examples (uncoated) are presented in Part IV.

Part I – Preparation of Microporous Sheet Materials

The dry ingredients of Example 1 were separately weighed into a FM-130D Littleford plough blade mixer with one high intensity chopper style mixing blade in the order and amounts specified in Table 1. The dry ingredients were premixed for 15 seconds using the plough blades only. The process oil was then pumped in via a double diaphragm pump through a spray nozzle at the top of the mixer over a period of about 45-60 seconds, with only the plough blades running. The high intensity chopper blade was then turned on, along with the plough blades, and mixing continued for 30 seconds. The mixer was shut off and the internal sides of the mixer were scraped down to ensure all ingredients were evenly mixed. The mixer was turned back on with both the high intensity chopper and plough blades in use, and the mixing continued for an additional 30 seconds. The resulting mixture of dry ingredients was extruded and calendered into sheet form as follows. A gravimetric loss in weight feed system (K-tron model # K2MLT35D5) was used to feed the mix into a 27 millimeter twin screw extruder (Leistritz Micro-27 mm). The extruder barrel was comprised of eight temperature zones and a heated adaptor to the sheet die. The extrusion mixture feed port was located just prior to the first temperature zone. An atmospheric vent was located in the third temperature zone. A vacuum vent was located in the seventh temperature zone.

The mixture was fed into the extruder at a rate of 90 grams/minute. Additional processing oil also was injected at the first temperature zone, as required, to achieve the desired total oil content in the extruded sheet.

Examples 2 and 3 were prepared, extruded and calendered into final sheet form using an extrusion system that was production sized. The version of the system is

similar to the equipment and procedures described above for Example 1 except for the size of the equipment. The oil contained in the extruded sheet (extrudate) being discharged from the extruder is referenced herein as the extrudate oil weight fraction, which is based on the total weight of the sample. The arithmetic average of the extrudate oil weight fraction for all of the samples was 0.57.Residual oil in each of Examples 1, 2 and 3 was removed using a 1,1,2-trichloroethylene oil extraction process.

Table 1: Formulation of the microporous membrane sheet

Ingredient	Example 1	Example 2	Example 3
GUR® 4150[1]	1.44	144	136
FINA® 1288[2]	1.44	144	136
Hi-Sil® 135[3]	5.00	500	500
SYNPRO® 1580[4]	0.05	4	4
IRGANOX® B215[5]	0.03	4	4
TUFFLO® 6056[6]	8.39	835	835

[1]An Ultra High Molecular Weight Polyethylene (UHMWPE), obtained commercially from Ticona Corp and reported to have a molecular weight of about 9.2 million grams per mole.
[2]A High Density Polyethylene (HDPE), obtained commercially from Total Petrochemicals.
[3]A precipitated silica available from PPG Industries, Inc.
[4]Reported to be a calcium-zinc stearate lubricant, obtained commercially from Ferro
[5]A processing and thermal stabilizing blend of antioxidants, obtained commercially from BASF.
[6]A process oil, obtained commercially from PPC Lubricants.

Part II – Preparation of Stretched Sheet Microporous Materials

Stretching was conducted by Parkinson Technologies, Inc. using the Marshall and Williams Biaxial Orientation Plastic Processing System. The Machine Direction Oriented (MDO) stretching of the material from Part II was accomplished by heating the microporous sheet of Examples 2 and 3 and stretching it in the machine direction over a series of rollers maintained at the temperatures listed in Table 2.

Transverse Direction Orientation (TDO) stretching was conducted after MDO stretching by heating the resultant sheets according to the temperature conditions listed in Table 2, and stretching in the transverse (or cross) direction on a tenter frame,

consisting of two horizontal chain tracks, on which clip and chain assemblies held the material in place. The combination of MDO and TDO conditions provided biaxial stretching of the material.

Table 2: Microporous sheet stretching conditions:

Example		4	5	6
Microporous sheet material		Ex. 2	Ex. 3	Ex. 3
MCO	Stretch roll (°C)	132	132	132
	Anneal roll (°C)	141	141	141
	Cooling (°C)	25	25	25
	Slow draw speed, FPM	10.4	10.4	10.4
	Fast Roll Speed, FPM	35	35	40
TDO	Stretch ratio	2	3	NA
	Preheat (°C)	132	132	NA
	Stretching (°C)	132	132	NA
	Anneal (°C)	141	141	NA

Part III – Hydrophilic coating formulations:

a) Preparation of hydrophilic coatings:

The hydrophilic coating Examples A, B and C were prepared according to the ingredients and quantities listed in Table 3. The first ingredient of the corresponding Example was dissolved in the specified quantity of deionized water with vigorous stirring. Upon complete dissolution, Pluronic™ 17R2 was added, followed by butoxyethanol. The coating solutions were stirred gently for a minimum of 30 minutes before proceeding.

Table 3: Hydrophilic coating formulation

Example	A	B	C
Polyethyleneoxazoline[1] (g)	7.5		
Chitosan[2] (g)		10	
PVP-K90[3] (g)			5
Deionized Water (g)	457	480	480
PLURONIC® 17R2[4] (g)	5	5	5
Butoxyethanol (g)	30	5	10

[1]Molecular weight 50,000, available from SigmaAldrich.
[2]Chitosan from shrimp shells, practial grade, available from SigmaAldrich.
[3]Polyvinylpyrrolidone with average Mw 360,000, available from SigmaAldrich.
[4]Block copolymer surfactant, available from BASF Corporation.

b) Procedure for coating microporous materials:

The microporous materials described in the previous Examples were cut into sheets 12 inches square. The hydrophilic coating compositions were applied by dipping the microporous materials of the previous examples into a Pyrex dish containing sufficient hydrophilic coating to completely submerge the sheet. The sheet was submerged in the hydrophilic coating for about 5 minutes. The sheet was then removed from the solution and excess coating solution was allowed to drip off. The coated microporous material was then clamped in an aluminum frame which was fitted with a gasket to prevent the film from shrinking during drying. The frame with film then was dried in an oven at 95°C for 15 minutes. The stretched microporous material of Example 4 was coated with each of the coating solutions of Examples A, B and C in this manner. The stretched microporous materials of Examples 5 and 6 and the unstretched microporous material of Example 1 were coated with the coating formulation of Example A.

Part IV – Properties:

The stretched microporous materials of Examples 4, 5 and 6 and the unstretched microporous material of Example 1 were tested for properties and water permeability with and without a hydrophilic coating applied.

Table 6 demonstrates the differences between the microporous material of Example 4 with and without a hydrophilic coating composition. Tables 7 and 8 illustrate the water permeability of various microporous materials with and without a hydrophilic coating composition. Properties were determined using the methods described below:

a) Thickness was determined by using an Ono Sokki thickness gauge EG-225. The thickness reported is the average of 9 measurements.

b) Porosity was determined using a Gurley Precision Densometer, model 4340, manufactured by GPI Gurley Precision Instruments of Troy, New York.

c) The maximum elongation or tensile energy to break the samples was determined following the procedure of ASTM D-882-02. Samples were tested oriented such that the stress was applied in the machine direction ("MD") and the transverse direction ("TD") as described in Part II.

d) Contact angle was measured on a VCA 2500XE video contact angle system, available from AST Products, Inc. using 1 microliter of ultrapure water.

e) Water flux testing was carried out on a Sepa™ CF II cross flow test cell apparatus provided by Sterlitech Corp, Kent WA at 20 psi and 25°C, with an effective membrane area of 140cm^2.

f) Water intrusion pressure was determined on a circular sample with an area of 90cm^2. The sample was sandwiched in a dead end filter provided by Sterlitech Corp, Kent WA. 100mL of water was placed on top of the sample. Pressure was applied in 5 psi increments, holding 15 minutes between pressure increments. The test pressure was recorded when the first drop water was visible passing through the sample.

g) Pore volume: The pore volume, expressed as percent by volume, is determined according to the following equation

$$Porosity = 100(1 - \frac{d1}{d2})$$

Where, d_1 is the density of the sample, which is determined from the same weight and the sample dimensions, and d_2 is the density of the solid portion of the sample, which is determined from the sample weight and the volume of the solid portion of the sample. The volume of the solid portion of the same is determined using a Stereopycnometer (Quantachrome Corp.) in accordance with the accompanying operating manual.

Table 6: Physical properties of uncoated and hydrophilically coated microporous material

Example	CE-4	4A
Microporous Material	Example 4	Example 4
Hydrophilic coating	None	Example A
Thickness (micron)	110	115
Gurley (sec)	36	35
Contact angle	>100°	<20°
MD Maximum elongation	15	14
MD Maximum tension	3550	2970
TD Maximum elongation	63	85
TD Maximum tension	279	175

Table 7: Water permeability of uncoated microporous materials:

Comparative Example	CE-1	CE-4	CE-5	CE-6

Microporous Material	Ex. 1	Ex. 4	Ex. 5	Ex. 6
Water flux @ 20psi (GFD)	<1*	<1*	<1*	<1*
Water intrusion pressure (psi)	>60	>40	>40	>45
Pore volume (%)	>60	>80	>80	>80

* No detectable volume observed after 30 minutes @ 20psi.

Table 8: Water permeability of microporous materials with hydrophilic coating:

Example	1A	4A	4B	4C	5A	6A
Microporous Material	Ex. 1	Ex. 4	Ex. 4	Ex. 4	Ex. 5	Ex. 6
Hydrophilic Coating	Ex. A	Ex. A	Ex. B	Ex. C	Ex. A	Ex. A
Water flux @ 20psi (GFD)	283	884	990	1060	1308	707
Water intrusion pressure (psi)	<5	<5	<5	<5	<5	<5
Water wetable time (sec)	<5	<5	<5	<5	<5	<5
Pore Volume (%)	>60	>80	>80	>80	>80	>80

[0090] Whereas particular embodiments of this invention have been described above for purposes of illustration, it will be evident to those skilled in the art that numerous variations of the details of the present invention may be made without departing from the scope of the invention as defined in the appended claims.

CLAIMS:

1. A coated filtration membrane comprising:

a microporous material substrate comprising:

(a) a polyolefin matrix present in an amount of at least 2 percent by weight based on the microporous material substrate,

(b) particulate, substantially water-insoluble silica filler distributed throughout said matrix, said filler constituting from about 10 percent to about 90 percent by weight based on the microporous material substrate; wherein said filler comprises precipitated silica having a Brunauer, Emmett, Teller (BET) surface area ranging from 125 to 700 m^2/g, an external surface area (CTAB) ranging from 120 to 500 m^2/g, and a BET to CTAB ratio of greater than or equal to 1; and

(c) at least 20 percent by volume of a network of interconnecting pores, and

at least one coating composition applied to at least one surface of the microporous material substrate such that the coated filtration membrane demonstrates a water contact angle of less than 30°,

wherein the coating composition applied to at least one surface of the microporous material substrate comprises one or more of a polyoxazoline, a polyvinylpyrrolidone, or chitosan.

2. The coated filtration membrane of claim 1 which demonstrates a water contact angle of less than 10°.

3. The coated filtration membrane of claim 1 which demonstrates an initial water flux of at least 1 gal/(ft^2 day) at 20 psi at 25°C.

4. The coated filtration membrane of claim 1, wherein the polyolefin matrix comprises a linear ultrahigh molecular weight polyethylene, a linear ultrahigh molecular weight polypropylene, and mixtures thereof.

5. The coated filtration membrane of claim 4, wherein the polyolefin matrix further comprises high density polyethylene and/or low density polyethylene.

6. The coated filtration membrane of claim 1, wherein the membrane is an ultrafiltration membrane and the volume average pore diameter is less than 0.1 microns.

7. The coated filtration membrane of claim 6, which demonstrates a molecular weight cut-off of 100-500,000.

8. The coated filtration membrane of claim 1, wherein the membrane is a microfiltration membrane and the volume average pore diameter is greater than 0.1 microns.

9. The coated filtration membrane of claim 1, which has a thickness ranging from 0.7 mil to 18 mil (17.8 to 457.2 microns).

10. The coated filtration membrane of claim 1, wherein the coating composition comprises at least one polymer having tertiary amine functional groups.

11. The coated filtration membrane of claim 1, wherein the silica filler (b) has been surface treated with at least one of polyethylene glycol, carboxybetaine, sulfobetaine and polymers thereof.

12. The coated filtration membrane of claim 1, wherein the silica filler (b) has been surface modified with functional groups.

13. The coated filtration membrane of claim 1, further comprising a support layer to which the microporous material substrate is adhered.

14. The coated filtration membrane of claim 1, wherein the weight ratio of silica to polyolefin present in the microporous material substrate is in the range of 0.5:1 to 10:1.

15. The coated filtration membrane of claim 1, which demonstrates a Gurley number of < 2000sec.