

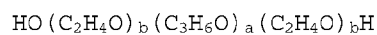
WATER WETTABLE FILTRATION MEMBRANES AND THEIR MANUFACTURE

TECHNICAL FIELD

The invention relates to durable filtration membranes, filter membrane assemblies comprising such membranes, and their use in recovering water from feed streams. In particular, the invention relates to durable filtration membranes and their use in recovering water from feed streams where periodic *in situ* cleaning of the membrane is required.

BACKGROUND ART

The publication of Schmolka (1973) discloses the preparation of polyoxyethylene-polyoxypropylene block polymers represented by the formula:



where *a* is an integer such that the hydrophobic base represented by $(\text{C}_3\text{H}_6\text{O})_a$ has a molecular weight of at least 2,250 and *b* is an integer from about 8 to 180 or higher. These block polymers are used to prepare solid or semisolid colloids containing considerable quantities of liquid - 'gels' or 'hydrosols' (where the liquid is water) that are particularly useful in the formulation of topically applied cosmetic and pharmaceutical compositions. Referred to as poloxamers, these nonionic triblock copolymers are supplied under a number of trade names, including ACCLAIM™, ADEKANOL™, ANTAROX™, BASOROL™, BLAUNON™, ETHOX™, KOLLIPHOR™, LUTROL™, MEROXAPOL™, PLURIOL™, PLURONIC™ and SYNPERONIC™. The properties of the poloxamer are determined by both the ratio and size of the integers *a* and *b*. Triblock copolymers in which the order of the polyoxyethylene and polyoxypropylene blocks is reversed are also supplied under these trade names. These "reverse" triblock copolymers may be identified by the use of the letter "R" and should not be referred to as "poloxamers".

The publication of Wang *et al* (2006) discloses the formation of membranes from blends of polyether sulfone and different triblock copolymers by a phase inversion method. Water fluxes determined for the membranes were observed to be dependent on the triblock copolymer structure rather than content. For example, the water flux (50.161 LMH) of a membrane formed from a blend with PLURONIC™ 123 was observed to be less than that (109.081 LMH) observed for the polyether sulfone control membrane. The water flux (218.28 LMH) of a membrane formed from a blend with PLURONIC™ F68 was observed to be higher than that of the control membrane.

The publication (machine translation) of Liu *et al* (2014) discloses the preparation of a microporous membrane with a microstructured surface for use in the separation of oil from water in oil/water emulsions. In the method of

preparing the membrane polyoxyethylene-polyoxypropylene-polyoxyethylene (F127) is used as an additive in the preparation of a homogenous solution of polymer in solvent. The polymer is selected from a group consisting of polyvinylidene fluoride (PVDF), polysulfone (PSf), polyether sulfone (PES), polyacrylonitrile (PAN), polyvinyl chloride (PVC), polylactic acid (PLA), polyimide (PI), polypropylene (PP) or cellulose acetate and the solvent is selected from a group consisting of chloroform (CHCl₃), N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide (DMAc), phosphoric acid triethyl ester (TEP), trimethyl phosphate (TMP), N-methyl pyrrolidone (NMP), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), dibutyl phthalate (DBP), dioxane, propiophenone, diphenyl ether in one or more mixtures thereof.

The publication of Yang *et al* (2014) discloses a composite polymer electrolyte for use in lithium-polymer batteries. The composite was composed of mesoporous modified silica fillers dispersed in poly(vinylidene fluoride-hexafluoropropylene) matrix. The triblock copolymer PLURONIC™ 123 (Aldrich) was used in the preparation of the mesoporous silica fillers.

The publication of Guo *et al* (2015) discloses a microporous material used in micro- and ultrafiltration membranes. The microporous material comprises finely divided particles, such as water insoluble silica filler, distributed throughout a matrix, such as poly(ethylene). The material further comprises a network of interconnecting pores and may be further processed depending on the desired application. In such further processing triblock copolymers based on poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) may be used as a hydrophilic coating, although polymers comprising tertiary amine functional groups are preferred. Without intending to be bound by theory, it is stated that components of the coating may interact with the silica particles in the fill of the microporous material and adjust the surface energy, affecting wettability. No covalent binding of the hydrophilic coating, such as that achievable by grafting, is disclosed.

The publication (machine translation) of Cheng *et al* (2017) discloses the use of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer as a "structure directing agent" in the preparation of a mesoporous composite film. The structure directing agent is used with a catalyst and precursor compound such as tetraethyl orthosilicate, titanium tetrachloride, titanium n-butyl acetate, isopropyl titanium, phthalic acid di-zinc acetate, tin ester and one or more of niobate to provide the mesoporous composite film.

The publication of Carter *et al* (2018) discloses the evaluation of the triblock copolymer PLURONIC™ L64 as a solvent for pore filling regenerated

cellulose membranes during initiator immobilisation. Glycerol was determined to be a more efficient pore filling solvent in this context.

The fouling by non-specific adsorption or deposition of proteins necessitates periodic cleaning of filtration membranes. Efficiencies in plant operation are realised if the filtration membranes can be cleaned *in situ*. Filtration membranes that are tolerant to the agents (acid, alkali, hypochlorite) used in these clean-in-place (CIP) protocols are desired.

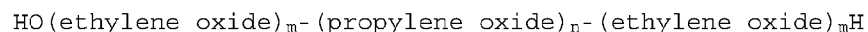
It is an object of the present invention to provide filtration membranes suitable for use in these and other circumstances or at least to provide a useful choice in the selection of filtration membranes for use in these and other circumstances.

STATEMENT OF INVENTION

In a **first** aspect a water-wettable filtration membrane comprising a poloxamer adhered to a substrate consisting of a microporous sheet of polyolefin is provided. The poloxamer is adhered to a preformed microporous sheet of the polyolefin. The poloxamer is adhered to the polyolefin matrix of the preformed microporous sheet by the formation of covalent bonds between the two polymers. The covalent bonds may be formed directly between the poloxamer and the polyolefin or indirectly via a crosslinking agent.

Preferably, the poloxamer is adhered to the matrix by grafting. Most preferably, the poloxamer is adhered to the matrix by photoinitiated grafting. In this context, the photoinitiated grafting will be understood to encompass the formation of covalent bonds initiated by irradiation with ultraviolet (UV) light in the presence of a suitable photoinitiator. Suitable photoinitiators are type II photoinitiators such as benzophenone (diphenylmethanone; BP). The photoinitiated grafting is advantageously performed in the presence of a crosslinking agent. Suitable crosslinking agents are low molecular weight diethenyl compounds. Low molecular weight diethenyl compounds are those with a molecular weight below 150 g mol^{-1} , such as divinylbenzene (DVB).

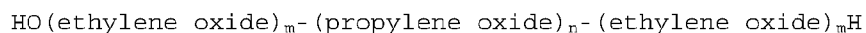
Preferably, the poloxamer is a polymer of the structure



where m is in the range 15 to 25 and n is in the range 50 to 90. Most preferably, the poloxamer is equivalent to the triblock copolymer supplied under the trade name PLURONIC™ P-123 (Sigma-Aldrich). It is understood that m is 20 and n is 70 for the polymer sold under the trade name PLURONIC™ P-123 (Sigma-Aldrich).

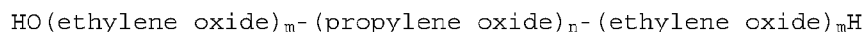
Preferably, the polyolefin is poly(ethylene) or poly(propylene). More preferably, the polyolefin is poly(ethylene). Most preferably, the polyolefin is a virgin poly(ethylene).

5 In a first embodiment of the first aspect a water-wettable filtration membrane consisting of a microporous sheet of grafted poly(ethylene) is provided where the graft comprises a poloxamer of the structure:



where m is in the range 15 to 25 and n is in the range 50 to 90.

10 In a second embodiment of the first aspect a water-wettable filtration membrane consisting of a microporous sheet of grafted poly(ethylene) is provided where the graft comprises divinylbenzene and a poloxamer of the structure:



where m is in the range 15 to 25 and n is in the range 50 to 90.

15 It is anticipated that poly(propylene) may be substituted for poly(ethylene) in either of the first or second embodiments of the first aspect.

Preferably, the filtration membrane is a semipermeable membrane.

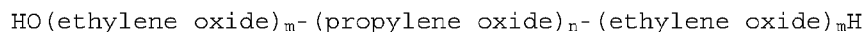
In a **second** aspect a method of preparing a water-wettable filtration membrane is provided where the method comprises:

- 20
1. Contacting a microporous sheet of polyolefin with a solution in a solvent of a poloxamer to provide a contacted sheet;
 2. Irradiating the contacted sheet with ultraviolet light in the presence of a photoinitiator to provide an irradiated sheet; and then
 3. Washing and drying the irradiated sheet to provide the membrane.

25 Preferably, the polyolefin is poly(ethylene) or poly(propylene). More preferably, the polyolefin is poly(ethylene). Most preferably, the polyolefin is virgin poly(ethylene).

Preferably, the solution comprises the photoinitiator. More preferably, the solution additionally comprises a crosslinking agent.

30 Preferably, the poloxamer is a polymer of the structure



where m is in the range 15 to 25 and n is in the range 50 to 90. Most

preferably, the poloxamer is equivalent to the triblock copolymer supplied under the trade name PLURONIC™ P-123 (Sigma-Aldrich). It is understood that m is 20 and n is 70 for the polymer sold under the trade name PLURONIC™ P-123 (Sigma-Aldrich).

5 Preferably, the solvent is water-alcohol or water-acetone where the ratio (v/v) of water to the alcohol or acetone is in the range 1:1 to 3:1. More preferably, the ratio (v/v) of water to the alcohol or acetone is in the range 1:1 to 2:1. Most preferably, the solvent is water-ethanol.

10 Preferably, the photoinitiator is a Type II photoinitiator. Most preferably, the photoinitiator is benzophenone (diphenylmethanone; BP).

Preferably, the crosslinking agent is a diethenyl compound with a molecular weight below 150 g mol⁻¹. Most preferably, the crosslinking agent is divinylbenzene (DVB).

15 Preferably, the wavelength of the ultraviolet light in the range 250 to 360 nm. More preferably, the wavelength of the ultraviolet light is in the range 250 to 280 nm. Most preferably, the wavelength of the ultraviolet light is 250 nm.

20 Preferably, the irradiating is for a period of time between one and a half minutes and two and a half minutes. More preferably, the irradiating is for a period of time of two minutes plus or minus 10 seconds.

25 In an embodiment of the second aspect a method of preparing a water wettable membrane is provided comprising irradiating at a wavelength of 250 nm a microporous sheet of poly(ethylene) impregnated with a solution in 30 to 50 % (v/v) ethanol in water of 3 to 5 % (w/v) of the poloxamer supplied as PLURONIC™ P-123, 0.5 to 1 % (w/v) benzophenone, and 0 to 0.5 % (w/v) divinylbenzene.

It is anticipated that poly(propylene) may be substituted for poly(ethylene) in this embodiment of the second aspect.

30 In a **third** aspect a water-wettable filtration membrane prepared according to the second aspect is provided.

In a **fourth** aspect a method of recovering water from a feed stream is provided comprising contacting a first side of a filtration membrane of the first or third aspects with the feed stream at a pressure sufficient to provide a permeate.

35 Preferably, the feed stream is selected from the group consisting of: milk and waste water. More preferably, the feed stream is selected from the group

consisting of: skim milk and wastewater containing particulates. Most preferably, the feed stream is selected from the group consisting of wastewater containing particulates in suspension. The particulates may be of abiotic or biotic origin.

- 5 Preferably, the filtration membrane is in the form of a filtration membrane assembly or filter element. More preferably, the membrane is in the form of a spiral wound filtration membrane assembly or filter element.

Preferably, the method comprises at least periodically contacting the filtration membrane with acid, alkali or chlorite.

- 10 In a **fifth** aspect the invention provides a spiral wound filtration membrane assembly or filter element comprising a filtration membrane of the first or third aspects.

- In the description and claims of this specification the following abbreviations, acronyms, phrases and terms have the meaning provided: "block"
- 15 means portion of a macromolecule comprising many constitutional units, that has at least one constitutional or configurational feature which is not present in the adjacent portions; "CAS RN" means Chemical Abstracts Service (CAS, Columbus, Ohio) Registry Number; "comprising" means "including", "containing" or "characterized by" and does not exclude any additional
- 20 element, ingredient or step; "consisting essentially of" means excluding any element, ingredient or step that is a material limitation; "consisting of" means excluding any element, ingredient or step not specified except for impurities and other incidentals; "crosslinking" means a reaction involving sites or groups on existing macromolecules or an interaction between existing
- 25 macromolecules that results in the formation of a small region, such as a crosslinking bridge, in a macromolecule from which at least four chains emanate; "crosslinking agent" means a material that is incorporated into the crosslinking bridge of a crosslinked polymer network; "curing" means chemical process of converting a prepolymer or a polymer into a polymer of higher
- 30 molecular mass and connectivity and finally into a network; "filter" means to remove particles from a fluid by passing through a porous substrate and "filtration" has a corresponding meaning; "graft molecule" or "graft polymer molecule" means a macromolecule with one or more species of block connected to the main chain as side chains having constitutional or configurational
- 35 features that differ from those in the main chains; "grafting" means a reaction in which one or more species of block are connected to the main chain of a macromolecule by side chains having constitutional configurational features that differ from those in the main chain and "grafted" has a corresponding meaning; "LMH" means litres per hour per square metre;
- 40 "impregnating" means permeating a substrate, e.g. with a solution of reagents

in a solvent; "macromolecule" or "polymer" means a molecule of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass; "monomer molecule" means a molecule which can
5 undergo polymerisation, thereby contributing constitutional units to the essential structure of a macromolecule; "monomeric unit", "monomer unit" or "mer" means the largest constitutional unit contributed by a single monomer molecule to the structure of a macromolecule; "permeable" means allowing the passage of a solvent, e.g. water; "permeate" means to spread throughout;
10 "poloxamer" means a symmetrical non-ionic triblock copolymer composed of a central chain of poly(propylene oxide) flanked by two chains of poly(ethylene oxide); "semipermeable" means allowing certain substances to pass through, but not others, especially allowing the passage of a solvent, e.g. water, but not of certain solutes, e.g. proteins, salts or sugars; "wetttable" means
15 becoming permeated with solvent, e.g. water, on being contacted with the solvent under standard laboratory conditions (i.e. 25 °C at 100 kPa) and "water-wetttable" means wetttable with water.

A paronym of any of the defined terms has a corresponding meaning. Where there is uncertainty in respect of the meaning of an undefined abbreviation,
20 acronym, phrase or term relating to polymer terminology and nomenclature the meaning provided in the publication of Jones *et al* (2008) is to take precedent.

It is recognised that the porosity determined for a substrate will depend at least in part on the method employed to determine the porosity. In the
25 present description the term "microporous" is being used to refer to the porosity of a sheet of polyolefin that is equivalent to the porosity of TARGRAY™ wet process polyethylene separators, item no. SW320H (Targray, Kirkland QC, Canada). In this context the term "equivalent" means the porosity determined for the sheet of polyolefin is 75 to 125% of the porosity
30 determined for TARGRAY™ wet process polyethylene separators, item no. SW320H (Targray, Kirkland QC, Canada) by the same method.

The terms "first", "second", "third", etc. used with reference to aspects, elements, features or integers of the subject matter described in the
Statement of Invention or defined in the Claims, or when used with reference
35 to alternative aspects or embodiments of the invention, are not intended to imply an order of preference.

Where concentrations or ratios of reagents are specified, the concentration or ratio specified is the initial concentration or ratio of the reagents. Where values are expressed to one or more decimal places standard rounding
40 applies. For example, 1.7 encompasses the range 1.650 recurring to 1.749

recurring.

The invention will now be described with reference to embodiments or examples and the figures of the accompanying drawings pages. In the Brief Description of Drawings and elsewhere in the following description, reference to the "top" (Ctop, Etop, etc.) of the filtration membrane or microporous sheet of polyolefin prepared according to a laboratory method refers to the face or side of the membrane or sheet with which the working solution is contacted. Reference to the "back" (Cback, Eback, etc.) or "backing layer" refers to the opposite face or side. It will be understood that due to the mounting of the membrane or sheet in the filtration membrane assembly the entire face or side is not exposed to the feed stream. A description of this filtration membrane assembly (Sterlitech Corp.) and its use is provided at page 24, line 24 onwards of the specification accompanying international application no. PCT/NZ2015/050034 [publ. no. WO 2015/147657 A1].

BRIEF DESCRIPTION OF DRAWINGS

Figure 1. Exploded view of the filtration membrane assembly (Sterlitech Corp.) used in the flux testing of samples of sheets of filtration membrane.

Figure 2. A comparison of the spectra (3800 cm^{-1} to 525 cm^{-1}) recorded for the untreated microporous poly(ethylene) (TARGRAY™ wet process polyethylene separators, item no. SW320H (Targray, Kirkland QC, Canada)) (PE virgin), the triblock copolymer (PLURONIC™ P-123; lot #MKCC2305, Sigma-Aldrich) used in the preparation of the samples (P123), and the top (Etop) and backing layer (Eback) side of each of the samples designated 040918Wiv, 040918Wv and 040918Wvi.

Figure 3. A comparison of the spectra expanded over the 'fingerprint region' (1800 cm^{-1} to 600 cm^{-1}) recorded for the untreated microporous poly(ethylene) (TARGRAY™ wet process polyethylene separators, item no. SW320H (Targray, Kirkland QC, Canada)) (PE virgin), the triblock copolymer (PLURONIC™ P-123; lot #MKCC2305, Sigma-Aldrich) used in the preparation of the samples (P123), and the top (Etop) and backing layer (Eback) side of each of the samples designated 040918Wiv, 040918Wv and 040918Wvi.

Figure 4. A comparison of the spectra (3800 cm^{-1} to 525 cm^{-1}) recorded for regions of the sample designated 040918Wvi with (Ctop and Cback) and without (Etop and Eback) exposure to the feed stream.

Figure 5. Scanning electron micrographs of the top (Etop) side the sample designated 040918Wiv at magnifications of 250,000x (A), 35,000x (B) and 10,000x (C).

Figure 6. Scanning electron micrographs of two regions of the top (Etop) side the sample designated 040918Wiv at a magnification of 100,000x.

Figure 7. Comparison of the flux (LMH) maintained for samples of filtration membrane (180419Wi and 230419Wii (■); 180419Wii and 230419Wiii (●)) prepared with (solid line) and without (broken line) a crosslinking agent (DVB).

Figure 8. Schematic representation of the prototype production line used in the preparation of the water-wettable filtration membrane according to Example C.

DESCRIPTION

Filtration membranes are used in a range of industrial processes, including food processing, to recover or remove water from a feed stream. In one application the objective may be to separate the water from contaminating particulates. In another application the objective may be to concentrate high value solutes.

In either application efficiency is increased by contacting the feed stream with a large surface area of the filter membrane. To this end the filtration membrane will often be assembled into a spiral wound filter element, which is then installed in the industrial plant. Such spiral wound membrane assemblies - or "filter elements" - are supplied by manufacturers such as Synder Filtration (Vacaville, California, USA).

Further efficiencies are realised if cleaning can be performed in place without the need for removal and reinstallation of the filter element. Clean-in-place protocols use chemically aggressive solutions such as acid, alkali and hypochlorite. Alternatively, the feed streams to which the membrane is exposed may be chemically aggressive and durability under these conditions reduces the frequency with which the filter element needs to be replaced.

Microporous sheets of polyolefin, such as poly(ethylene) are available commercially from suppliers such as Celgard (Charlotte, North Carolina, USA) and Targray (Kirkland, Quebec, Canada). One impediment to the use of these substrates as filtration membranes in the applications alluded to above is there inherent hydrophobicity. Where the objective is to provide a semipermeable membrane for use in concentrating high value solutes the required rejection properties may also be lacking.

It has now been determined that the grafting of a microporous sheet of poly(ethylene) with the poloxamer supplied under the trade name PLURONIC-P123 provides a filtration membrane that is readily wetted with water and provides high flux rates at relatively low pressures (5 bar). The filtration membranes

so produced have also been demonstrated to have the desired durability when exposed to chemically aggressive liquids.

The retention of these desirable properties - attributable to the graft - is enhanced by the inclusion of a crosslinking agent in the working solution used in the method of preparation. Without wishing to be bound by theory low molecular weight crosslinking agents are favoured so as not to disrupt the favourable rejection properties also demonstrated for the membranes.

The method of preparing the filtration membrane is readily adaptable to a continuous production process. In accordance with the methods described, working solutions of the following composition are used to impregnate the microporous substrate before it is irradiated with ultraviolet light at a wavelength in the range 250 nm to 360 nm, wavelengths at or toward the lower end of this range (250 nm) being preferred.

Working solution:

3 to 5 % (w/v) poloxamer

0.5 to 1 % (w/v) photoinitiator

0 to 0.5 % (w/v) crosslinking agent

30 to 50 % (v/v) in alcohol or acetone in water

The preferred poloxamer for use in the working solution is that supplied under the trade name PLURONIC P-123. The preferred photoinitiator for use in the working solution is benzophenone. The preferred crosslinking agent for use in the working solution is divinylbenzene.

EXAMPLE A

Preparation of filtration membrane (laboratory method)

A volume of 5 mL of a solution in water of 10% (w/v) triblock copolymer (PLURONIC™ P-123; lot #MKCC2305, Sigma-Aldrich) was mixed with an equal volume of deionised water. A quantity of 0.1 g of the photoinitiator benzophenone (diphenylmethanone; Ph₂O) was dissolved in a separate volume of 5 mL of ethanol before being added to the diluted solution of the triblock copolymer. The working solution was stored in the dark until use.

Samples (13.5 x 18.5 cm) were cut from a sheet of microporous poly(ethylene) (TARGRAY™ wet process polyethylene separators, item no. SW320H (Targray, Kirkland QC, Canada)) and each sample coated with a volume of 5 mL of the working solution. The coated samples were then irradiated with ultraviolet (UV) light in the range 250 to 360 nm for a period of time of two minutes before rinsing with water and air-drying on top of a warm oven.

The four replicate samples prepared according to this method were designated 040918Wiv, 040918Wv, 040918Wvi and 151018Wi. A small piece of the sample designated 040918Wiv was excised from the edge of the sample and submitted to scanning electronic microscopy (SEM).

- 5 Each of the samples was readily wetted with water, being observed to become uniformly translucent when contacted with this solvent.

Durability, flux and protein rejection

A filtration membrane assembly (Sterlitech) as illustrated in Figure 1 was used to determine flux (LMH) for each of the samples designated 040918Wiv,
10 040918Wv and 040918Wvi. Samples were individually mounted in the filtration membrane assembly and the flux determined at 0 and 5 bar. The time to collect a predetermined volume of permeate at the specified pressure and temperature was recorded and the flux (J) was calculated according to the following equation:

15
$$J = \frac{V}{t \times A}$$

where V was the volume of permeate (L), t was the time (h) for the collection of V and A was area of the sample (m²) exposed to the feed stream (water or skim milk). The results are summarised in Table 1.

Sample	Temperature 0 bar/5 bar	Flux	
		0 bar	5 bar
040918Wiv	9/9	10	367
040918Wv	15/11	33	476
040918Wvi	10/9	32	428

20 **Table 1.** Fluxes (LMH) determined at 0 and 5 bar with water as the feed stream at the temperatures (°C) specified.

To assess durability fluxes were also determined after repeated clean-in-place (CIP) protocols. The CIP protocol was based on that employed in a commercial processing operation for reverse osmosis (RO) membranes (Anon (2014)) and is summarised in Table 2.

Step	Feed stream	Time (min)	Temperature (°C)
1	water	5	Ambient
2	water	5	35
3	alkali	5	35
4	water	5	35
5	acid	10	35
6	water	5	Ambient
7	hypochlorite	5	35
8	water	5	Ambient

Table 2. Clean-in-place (CIP) protocol adapted from Anon (2014). The 'alkali' was 2% (w/v) sodium hydroxide (NaOH). The 'acid' was 1.9% (w/v) nitric acid (H_2NO_3) and 0.6 (w/v) phosphoric acid (H_3PO_4).

For each sample a number of CIP protocols were repeated alternating with the use of water or skim milk as the feed stream. The fluxes and percentage protein rejection (with skim milk as the feed stream) determined for the samples designated 040918Wv and 040918Wvi are provided in Table 3. Total protein concentrations in permeate were calculated on the basis of HPLC analysis with UV absorbance monitoring.

Sample	Feed stream	CIP protocols	Temperature (°C) 0 bar/5 bar	Flux (LMH)		Protein rejection (%)
				0 bar	5 bar	
040918Wiv	water	0	9/9	10	367	
040918Wv	water	0	15/11	33	476	
040918Wv	water	1	10/10	6	139	
040918Wv	water	2	-/12	-	195	
040918Wv	water	3	-/11	-	171	
040918Wv	water	6	-/10	-	476	
040918Wv	water	10	11/10	46	494	
040918Wv	milk	3	-/11	-	21	
040918Wv	water	6	-/10	-	476	
040918Wv	water	10	11/10	46	494	
040918Wv	milk	10	11/12	4	21	99.4
040918Wvi	water	0	10/9	32	428	
040918Wvi	water	1	19/10	43	642	
040918Wvi	water	2	13/12	40	714	
040918Wvi	water	3	10/10	38	644	
040918Wvi	milk	3	9/11	3	24	
040918Wvi	water	4	-/9	-	56 (dry)	
040918Wvi	milk	4	-/10	-	9	99.71
040918Wvi	water	5	10/9	38	234	
040918Wvi	water	7	9/9	60	803	
040918Wvi	water	10	11/10	64	188	
040918Wvi	milk	10	-/12	-	9	99.76

Table 3. Fluxes (LMH) and protein rejection determined at 0 and 5 bar with water or skim milk as the feed stream at the temperatures (°C) specified. Determinations were made for each of the samples following repeated clean-in-place (CIP) protocols.

The durability of the filtration membranes was further evaluated by contacting the sample designated 151018Wi with 2% (w/v) sodium hydroxide (NaOH) for 7 days. The fluxes and percentage protein rejection (with skim milk as the feed stream) determined for these samples are provided in Table 4.

Sample	Feed stream	Temperature (°C) 0 bar/5 bar	Flux (LMH)		Protein rejection (%)
			0 bar	5 bar	
151018Wi	water	9/9	54	257	
151018Wi	milk	10/10	-	8	99.65

Table 4. Fluxes (LMH) and protein rejection determined at 0 and 5 bar with water or skim milk as the feed stream at the temperatures (°C) specified. Determinations were made for the samples following exposure to 2% (w/v) sodium hydroxide (NaOH) for 7 days.

Fourier transform infrared (FTIR) spectroscopy

Spectra were recorded for each of the samples designated 040918Wiv, 040918Wv and 040918Wvi using a Thermo Electron Nicolet 8700 FTIR spectrometer equipped with a single bounce ATR and diamond crystal. Thirty-two scans at a resolution of 4 cm⁻¹ were averaged for each sample. A comparison of the spectra (3800 cm⁻¹ to 525 cm⁻¹) recorded for: (i) the untreated microporous poly(ethylene) (TARGRAY™ wet process polyethylene separators, item no. SW320H (Targray, Kirkland QC, Canada)) ('PE virgin'); (ii) the triblock copolymer (PLURONIC™ P-123; lot #MKCC2305, Sigma-Aldrich) used in the preparation of the samples ('P123'); and (iii) the top (Etop) and back (Eback) sides of each of the samples designated 040918Wiv, 040918Wv and 040918Wvi is provided in Figure 2.

Signals corresponding to the symmetrical stretch mode of C-O-C fragments (1108 cm⁻¹) and the C-H stretch mode of CH₃ (2970 cm⁻¹) present in the spectrum of the triblock copolymer (PLURONIC™ P-123) were also present in the spectra recorded for each of the samples. Many signals characteristic of the triblock copolymer (PLURONIC™ P-123) were also observed at low intensity in the 'fingerprint' region of the spectra provided in Figure 3. Signals characteristic of the triblock copolymer (PLURONIC™ P-123) were retained in spectra recorded for regions of the sample designated 040918Wiv following exposure to the feed stream (water) as shown in Figure 4.

- *SEM*

Scanning electron micrographs of the small piece excised from the edge of the sample designated 040918Wiv are provided in Figure 5 and Figure 6. The fibres of poly(ethylene) of the microporous sheet appear to be coated.

The observations from FTIR spectroscopy and SEM appeared to demonstrate the grafting of the poloxamer to the polyolefin matrix of the microporous sheet. The conversion of the inherently hydrophobic microporous sheet of polyolefin to a water-wettable permeable membrane is attributed to this grafting.

5 **EXAMPLE B**

Preparation of filtration membrane (laboratory method)

A volume of 10 mL of a solution in water of 10% (w/v) triblock copolymer (PLURONIC™ P-123; lot #MKCC2305, Sigma-Aldrich) was mixed with an equal volume of deionised water. Quantities of 0.2 g of the photoinitiator
10 benzophenone (diphenylmethanone; Ph₂O) and 0 or 0.1 g of the crosslinking agent divinylbenzene (DVB) were dissolved in separate volumes of 10 mL of ethanol (methylated spirits) before being added to a volume of 10 mL of the diluted solution of the triblock copolymer. These working solutions -
15 excluding or including the crosslinking agent DVB - were stored in the dark until use.

Samples (13.5 x 18.5 cm) were cut from a sheet of microporous poly(ethylene) (TARGRAY™ wet process polyethylene separators, item no. SW320H (Targray, Kirkland QC, Canada)) and each sample coated with a volume of one of the working solutions. The coated samples were then irradiated with ultraviolet
20 (UV) light in the range 250 to 360 nm for a period of time of two minutes before rinsing with water and air-drying in open air.

The three replicate samples prepared according to this method using the working solution excluding DVB were designated 110419Wi, 180419Wi and 180419Wii. The three replicate samples prepared according to this method with
25 the working solution including DVB were designated 230419Wi, 230419Wii and 230419Wiii. Each of the samples was readily wetted with water, being observed to become uniformly translucent when contacted with this solvent.

The water flux was determined for each of the samples with deionised water as the feed stream (DI1). The samples were then completely dried before again
30 determining the water flux with deionised water as the feed stream (DI2). Each of the samples were then subjected to a clean-in-place (CIP) protocol before twice more determining the water flux with deionised water as the feed stream (DI3 and DI4) and an intervening drying of the samples. Each of the samples remained readily wettable with water. The results are summarised in
35 Table 5 and Table 6 and compared in Figure 7.

Sample	DI#	Flux	
		0 bar	5 bar
110419Wi	1	61	964
	2	32	771
	3	38	964
	4	95	1446*
180419Wi	1	70	890
	2	35	723
	3	48	964
	4	-	76
180419Wii	1	62	964
	2	34	643
	3	86	890
	4	-	26

Table 5. Average fluxes (LMH) determined at room temperature (22 to 24 °C) at 0 and 5 bar with water as the feed stream (*membrane failure).

Sample	DI#	Flux	
		0 bar	5 bar
230419Wi	1	43	680
	2	15	321
	3	24	609
	4	15	399
230419Wii	1	345	826
	2	28	642
	3	34	826
	4	17	1285
230419Wiii	1	26	723
	2	33	642
	3	56	723
	4	26	964

Table 6. Average fluxes (LMH) determined at room temperature (22 to 24 °C) at 0 and 5 bar with water as the feed stream.

5 **EXAMPLE C**

Preparation of filtration membrane (prototype method)

A volume of 300 mL of a solution of 10% (w/v) triblock copolymer (PLURONIC™ P-123; lot #MKCC2305, Sigma-Aldrich) in distilled water was dispensed into a reservoir protected from exposure to light. A further volume of 300 mL of distilled water was then added to provide an initial solution of 5% (w/v) triblock copolymer (PLURONIC™ P-123; lot #MKCC2305, Sigma-Aldrich) in the reservoir. A solution of 1.5% (w/v) benzophenone in ethanol (methylated spirits) was prepared separately and a volume of the crosslinking agent divinylbenzene (DVB) added to provide a final concentration of 0.75% (v/v) DVB. A volume of 400 mL of this separately prepared solution was then mixed with the solution of triblock copolymer (PLURONIC™ P-123; lot #MKCC2305, Sigma-Aldrich) in a reservoir to provide the working solution.

Referring to Figure 7 of the accompanying drawings pages, peristaltic pumps (1,2) were used to deliver the working solution from the reservoirs (3,4) to the two hemicylindrical troughs (5,6) of a prototype production line. The reservoirs were periodically replenished with the working solution during the operation of the prototype production line.

The width of a continuous microporous sheet (7) of microporous poly(ethylene) was fed from a dispensing roll of stock into a first impregnation station comprising an idler roller (8) co-axially mounted in the first of the two hemicylindrical troughs (5). The difference between the radii of the roller (8) and trough (5) was sufficient to permit free passage of the sheet (7) around the roller and through the trough, but not so great as to promote evaporation of the working solution in the trough. The surface of the roller (8) over which the sheet (7) passes may be spiral engraved to promote passage of the working solution across the length of the surface.

The sheet (7) exiting the first impregnation station was then fed vertically into a first irradiating station comprising a slotted chamber (9) containing two opposed arrays (10,11) of ultraviolet light sources. The sheet (7) passed between the opposed arrays (10,11) so that both sides were irradiated. The rate at which the sheet (7) was fed was regulated to provide the required residence time within the slotted chamber (9).

The irradiated sheet (7) was then passed through a second impregnation station (12) and second irradiating station (13) of the same configuration as the first impregnation station and first irradiating station. Following these repeated steps, the irradiated sheet (7) was fed around a plurality of idler rollers (14,15,16) immersed in water in a washing station (17). The water in the washing station (17) was circulated by an external pump (18) and the depth of the water controlled by a combination of level transmitter and solenoid valve (19). The combination of a plurality of idler rollers (14,15,16) and depth of water ensured sufficient residence time before the water washed sheet (7) was fed into the drying station.

The drying station was a forced air dryer comprising two plenum chambers (20,21) having opposed perforated face plates between which the sheet of substrate passed. Hot air blowers (22,23) mounted in the wall of each chamber forced air through the perforated face plates. The dried sheet (7) of substrate was then rewound onto a receiving roll (not shown).

Filter elements

The membrane may be used in the manufacture of assemblies of various configurations. In one embodiment the membrane is used in the manufacture of a spiral wound filter element. The manufacture of such filter elements is well known in the art.

Although the invention has been described with reference to embodiments or examples it should be appreciated that variations and modifications may be made to these embodiments or examples without departing from the scope of the invention. Where known equivalents exist to specific elements, features or integers, such equivalents are incorporated as if specifically referred to in this specification. Variations and modifications to the embodiments or examples that include elements, features or integers disclosed in and selected from the referenced publications are within the scope of the invention unless specifically disclaimed. The advantages provided by the invention and discussed in the description may be provided in the alternative or in combination in these different embodiments of the invention.

INDUSTRIAL APPLICABILITY

Methods of preparing filtration membranes and their use in recovering or removing water from feed streams are provided. The filtration membranes are advantageously used in recovering or removing water from feed streams where cleaning of the membranes *in situ* is desirable to increase efficiency of plant operations.

INCORPORATION BY REFERENCE

Where the claims, description or drawings of this specification are missing in their entirety or part, the corresponding portion of the specification accompanying the most recently filed application from which priority is claimed is to be incorporated by reference so as to complete this specification in accordance with Rules 4.18, 20.5 and 20.6 of the PCT Regulations (as in force from 1 July 2015 or subsequently amended).

For the purposes of 37 C.F.R. 1.57 of the United States Code of Federal Regulations the disclosures of the following publications (as more specifically identified under the heading 'Referenced Publications') are incorporated by reference: Jones *et al* (2008) and Schmolka (1973).

REFERENCED PUBLICATIONS

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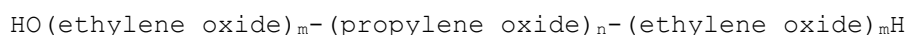
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CLAIMS

- 1) A water-wettable filtration **membrane** consisting of a microporous sheet of grafted polyolefin where the graft comprises a poloxamer of the structure



where m is in the range 15 to 25 and n is in the range 50 to 90.

- 2) The membrane of claim 1 where the polyolefin is poly(ethylene).
- 3) The membrane of claim 1 or 2 where m is 20 and n is 70.
- 4) The membrane of any one of claims 1 to 3 where the graft comprises a crosslinking agent.
- 5) The membrane of claim 4 where the crosslinking agent has a molecular weight below 150 g mol^{-1} .
- 6) The membrane of claim 5 where the crosslinking agent is divinylbenzene.
- 7) A filter **assembly** comprising the membrane of any one of claims 1 to 6.
- 8) The assembly of claim 7 where the membrane is spiral wound.
- 9) A **method** of preparing a water-wettable filtration membrane comprising:
- (a) Contacting a microporous sheet of polyolefin with a solution of a poloxamer in a solvent to provide a contacted sheet;
 - (b) Irradiating the contacted sheet with ultraviolet light in the presence of a photoinitiator to provide an irradiated sheet; and
 - (c) Drying and washing the irradiated sheet to provide the membrane,
- where the poloxamer is a polymer of the structure
- $$\text{HO(ethylene oxide)}_m\text{-(propylene oxide)}_n\text{-(ethylene oxide)}_m\text{H}$$
- where m is in the range 15 to 25 and n is in the range 50 to 90.
- 10) The method of claim 9 where the polyolefin is poly(ethylene).
- 11) The method of claim 9 or 10 where m is 20 and n is 70.
- 12) The method of any one of claims 9 to 11 where the solution comprises the photoinitiator.
- 13) The method of any one of claims 9 to 12 where the photoinitiator is a Type II photoinitiator.

- 14) The method of any one of claims 9 to 13 where the photoinitiator is benzophenone.
- 15) The method of any one of claims 9 to 14 where the solution comprises a low molecular weight crosslinking agent.
- 16) The method of claim 15 where the crosslinking agent is divinylbenzene.
- 17) The method of any one of claims 9 to 16 where the solvent is 30 to 50 % (v/v) alcohol or acetone in water.
- 18) The method of any one of claims 9 to 14 where the solvent is 30 to 50 % (v/v) ethanol in water.
- 19) A **method** of recovering or removing water from a feed stream comprising the step of contacting a first side of a membrane of any one of claims 1 to 6 with the feed stream at a pressure sufficient to provide a permeate.
- 20) The method of claim 19 where the pressure is less than 10 bar and the flux is greater than 500 LMH.