Title: FILTRATION SYSTEMS AND MEMBRANES WITH ENHANCED FLUX AND METHOD FOR THEIR PREPARATION

Abstract: Membrane or filtration system comprising at least one membrane, wherein said membrane or at least one component or at least one part of a component of the filtration system has been obtained by a process comprising the following steps: A) oxidizing the surface of said component or part of a component B) treatment of the oxidized surface with a composition comprising at least one flux enhancing monomer, C) curing said composition to form a coating.
Filtration systems and Membranes with enhanced flux and method for their preparation

The present invention relates to filtration systems and membranes obtained by a process comprising the following steps:

A) oxidizing the surface of a base membrane
B) treatment of the oxidized surface with a composition comprising at least one flux enhancing monomer,
C) curing said composition to form a coating.

The invention further relates to novel membranes, processes for making such membranes, the use of such membranes and to a method of increasing the flux through a membrane.

Different types of membranes play an increasingly important role in many fields of technology. In particular, methods for treating water rely more and more on membrane technology.

An important issue with the application of membranes is fouling. The problem of biofouling is pronounced in semipermeable membranes used for separation purposes like reverse osmosis, forward osmosis, nanofiltration, ultrafiltration and micro filtration. Membranes may be classified according to their separation mechanism and/or pore sizes. For example, in water filtration applications ultrafiltration and microfiltration membranes (approximate pore diameter: 5 - 1000 nm) are used for wastewater treatment retaining organic and bioorganic material. In reverse osmosis and forward osmosis membranes, where monovalent ions and all components with larger diameter are rejected, the separation mechanism is based mainly on solution-diffusion mechanism.

In all applications where the ambient medium is an aqueous phase, potential blockage may occur by adhesion of microorganisms and biofilm formation. As a consequence, a membrane is desired, which reduces biofilm formation and thus requires fewer cleaning cycles. This can for example be achieved through membranes with anti-adhesive or antifouling properties.

Thus, fouling is currently one of the major remaining problems for filtration membranes. Fouling causes deterioration of the membrane performance and shortens membrane lifetime, limiting further application of membrane technology. It is thus desirable to improve antifouling and antibacterial properties to membranes without impairing their separation characteristics in order to enhance their resistance.

Several approaches have been tried to solve the problem of fouling and biofouling and to prevent the formation and deposition of organic materials from organisms.

Recent research has focused on three strategies to prevent biofouling of membranes: 1) blending of hydrophilic or amphiphilic copolymers for the manufacture of membranes; 2) surface modification of membranes and 3) bulk modification of membrane materials.
The following documents describe approaches undertaken in recent years:


US 4,277,344 discloses antifouling approaches on RO layers, formed by interfacial reaction.

Desalination 275 (2011) 252-259, describes the grafting of PEG on a polyamide layer.

US 6,280,853 and US 2010/043,733 disclose coatings of composite membranes with various polymers including polyalkylene oxide compounds or polyacrylamide compounds.


US 2010/1 12364 discloses substrates with biopassive coatings involving an oxidation step of a surface. US 2010/1 12364 does not disclose any membranes.

US 2008/269417 discloses a process for improving membranes by free radical graft polymerization.


It was an object of the invention to provide filtration systems and membranes that are less prone to fouling.
This objective has been solved by membranes or filtration systems comprising at least one membrane, wherein said membrane or at least one component or at least one part of a component of the filtration system has been obtained by a process comprising the following steps:

A) oxidizing the surface of said component or part of a component

B) treatment of the oxidized surface with a composition comprising at least one flux enhancing monomer,

C) curing said composition to form a coating.

In different embodiments of the invention, the component or part of the component in filtration systems according to the invention that is subjected to the above process steps is selected from a membrane, the separating layer of a membrane, a support layer of a membrane, a fabric layer of a membrane, the feed spacer of a membrane, the permeate spacer of a membrane, the casing of the filtration system, the piping of the filtration system, the joints of the filtration system, manifolds of the filtration system.

Normally the components or parts of a component suitable for the above process comprise an organic polymer as the main component.

In another aspect of the invention pertains to a process for making filtration systems, preferably comprising a membrane, comprising:

A) oxidizing the surface of said component or part of a component

B) treatment of the oxidized surface with a composition comprising at least one flux enhancing monomer,

C) curing said composition to form a coating.

It is an advantage of this process that it is not limited to certain parts or components of a filtration system. Rather, it can be applied to any component or part of a component of such filtration systems, if it comprises an organic polymer. Examples of suitable components or parts of components include a membrane, the separating layer of a membrane, a support layer of a membrane, a fabric layer of a membrane, the feed spacer of a membrane, the permeate spacer of a membrane, the casing of the filtration system, the piping of the filtration system, the joints of the filtration system, manifolds of the filtration system.

In another aspect of the invention pertains to membranes, obtained by a process comprising the following steps:

A) oxidizing the surface of a base membrane

B) treatment of the oxidized surface with a composition comprising at least one flux enhancing monomer,

C) curing said composition to form a coating.
The concept of a membrane is generally known in the art. In the context of this application a membrane shall be understood to be a thin, semipermeable structure capable of separating two fluids or separating molecular and/or ionic components or particles from a liquid. A membrane acts as a selective barrier, allowing some particles, substances or chemicals to pass through, while retaining others.

Membranes according to the invention can for example be microporous (average pore diameter smaller than 2 nm), mesoporous (average pore diameter from 2 nm to 50 nm) or macroporous (average pore diameter above 50 nm). Average pore diameters in this context are determined according to DIN 14652:2007-09 through correlation with the molecular weight cutoff of a membrane.

In this application the term "membrane" shall, depending on the context, refer to a membrane according to the invention that comprises a coating obtained in a grafting process, or to a membrane that is subjected to a coating process to obtain a membrane according to the invention, or both.

Optionally, a membrane or the layer of a membrane that is used as starting material for a coating process to obtain a membrane according to the invention is sometimes referred to as a "base membrane".

Thus, in case a membrane comprises more than one layer, the "base membrane" can refer to all layers of said membrane as a whole or to each of the layers of said membrane. The term "base membrane" usually refers to the layer that is subjected to the process steps A), B) and C), as defined above.

In one preferred embodiment, the base membrane refers to the separation layer of a membrane.

In another embodiment, the base membrane denotes the support membrane of a membrane, the protective layer or a nonwoven or woven support layer of a membrane.

Suitable membranes or the separation layer of suitable membranes can be made of at least one inorganic material like a ceramic or at least one organic polymer.

Examples of inorganic materials are clays, silicates, silicon carbide, aluminium oxide, zirconium oxide or graphite. Such membranes made of inorganic materials are normally made by applying pressure or by sintering of finely ground powder. Membranes made of inorganic materials may be composite membranes comprising two, three or more layers.

In one embodiment, membranes made from inorganic materials comprise a macroporous support layer, optionally an intermediate layer and a separation layer.

In a preferred embodiment, suitable membranes and/or the separation layer of a membrane comprise organic polymers, hereinafter referred to as polymers as the main components. A polymer shall be considered the main component of a membrane if it is comprised in said mem-
brane or in the separation layer of said membrane in an amount of at least 50 % by weight, preferably at least 60%, more preferably at least 70%, even more preferably at least 80% and particularly preferably at least 90% by weight.

Examples of suitable polymers are polyarylène ether, polysulfone, polyethersulfones (PES), polyphenylenesulfone (PPSU), polyamides (PA), polyvinylalcohol (PVA), cellulose acetate (CA), cellulose diacetate, cellulose triacetate (CTA), CA-triacetate blend, cellulose ester, cellulose nitrate, regenerated cellulose, aromatic, aromatic/aliphatic or aliphatic polyamide, aromatic, aromatic/aliphatic or aliphatic polyimide, polybenzimidazole (PBI), polybenzimidazolone (PBIL), polyacrylonitrile (PAN), polyetheretherketone (PEEK), sulfonated polyetheretherketone (SPEEK), PAN-poly(vinyl chloride) copolymer (PAN-PVC), PAN-methallyl sulfonate copolymer, poly(dimethylphenylène oxide) (PPO), polycarbonate, polyester, polytetrafluoroethylene PTFE, poly(vinyldene fluoride) (PVDF), polypropylene (PP), polyelectrolyte complexes, poly(methyl methacrylate) PMMA, polydimethylsiloxane (PDMS), aromatic, aromatic/aliphatic or aliphatic polyimide urethanes, aromatic, aromatic/aliphatic or aliphatic polyamidimides, crosslinked polyimides or mixtures thereof.

Preferably, membranes according to the invention comprise polysulfones, polyethersulfones (PES), polyamides (PA), polyvinylalcohols (PVA), Cellulose Acetate (CA), Cellulose Triacetate (CTA) Poly(vinyldiene fluoride) (PVDF) or mixtures thereof as main components.

Suitable polyethersulfones can for example be obtained from BASF SE under the brand name Ultrason<sup>R</sup>.

Preferred polyarylène ether sulfones (A) are composed of units of the general formula I

\[
\text{O} - \text{Ar} - \left( - \text{T} \begin{array}{c} \text{X} \end{array} \right)_t \text{O} - \text{Y} - \left( - \text{Ar}^1 \text{Q} \right)_q \text{Y} \]

where the definitions of the symbols \( t, q, Q, T, Y, \text{Ar} \) and \( \text{Ar}^1 \) are as follows:

- \( t, q \): independently of one another 0, 1, 2, or 3,
- \( Q, T, Y \): independently of one another in each case a chemical bond or group selected from -0-, -S-, -SO2-, S=0, C=0, -N=N-, and -CR=CR=CR=CR=CR-, where \( R^a \) and \( R^b \) independently of one another are in each case a hydrogen atom or a Cl-C12-alkyl, Cl-C12-alkoxy, or Cl-C6-C12-aryl group, and where at least one of \( Q, T, \) and \( Y \) is -SO2-, and
- \( \text{Ar} \) and \( \text{Ar}^1 \): independently of one another an arylenegroup having from 6 to 18 carbon atoms.

If, within the abovementioned preconditions, \( Q, T \) or \( Y \) is a chemical bond, this then means that the adjacent group on the left-hand side and the adjacent group on the right-hand side are pre-
sent with direct linkage to one another via a chemical bond.

However, it is preferable that Q, T, and Y in formula I are selected independently of one another from -O- and -SO2-, with the proviso that at least one of the group consisting of Q, T, and Y is -SO2-.

If Q, T, or Y is -CRaRb-, Ra and Rb independently of one another are in each case a hydrogen atom or a Cl-CI2-alkyl, Cl-CI2-alkoxy, or C6-C18 -aryl group.

Preferred Cl-CI2-alkyl groups comprise linear and branched, saturated alkyl groups having from 1 to 12 carbon atoms. The following moieties may be mentioned in particular: Cl-C6-alkyl moiety, e.g. methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, 2- or 3-methylpentyl, and longer chain moieties, e.g. unbranched heptyl, octyl, nonyl, decyl, undecyl, lauryl, and the singly branched or multibranched analogs thereof.

Preferred Cl-CI2-alkoxy groups can be used are the alkyl groups defined at an earlier stage above having from 1 to 12 carbon atoms. Cycloalkyl moieties that can be used with preference in particular comprise Ci3-CI2-cycloalkyl moieties, e.g. cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclopentyloxythyl, cyclopropylethyl, cyclopropylpropyl, cyclobutylmethyl, cyclobutylethyl, cyclopentyloxythyl, -propyl, -butyl, -pentyl, -hexyl, cyclohexylmethyl, -dimethyl, and -trimethyl.

Ar and Ar1 are independently of one another a C6-C18 -arylene group. On the basis of the starting materials described at a later stage below, it is preferable that Ar derives from an electron-rich aromatic substance that is very susceptible to electrophilic attack, preferably selected from the group consisting of hydroquinone, resorcinol, dihydroxynaphthalene, in particular 2,7-dihydroxynaphthalene, and 4,4'-bisphenol. Ar1 is preferably an unsubstituted C6- or Cl2-arylene group.

Particular C6-C18 -arylene groups Ar and Ar1 that can be used are phenylene groups, e.g. 1,2-, 1,3-, and 1,4-phenylene, naphthylene groups, e.g. 1,6-, 1,7-, 2,6-, and 2,7-naphthylene, and also the arylene groups that derive from anthracene, from phenanthrene, and from naphthacene.

In the preferred embodiment according to formula I, it is preferable that Ar and Ar1 are selected independently of one another from the group consisting of 1,4-phenylene, 1,3-phenylene, naphthylene, in particular 2,7-dihydroxynaphthalene, and 4,4'-bisphenylene.

Preferred polyarylene ether sulfones (A) are those which comprise at least one of the following repeat units 1a to 1d:
Other preferred units, in addition to the units la to lo that are preferably present, are those in which one or more 1,4-phenylene units deriving from hydroquinone have been replaced by 1,3-phenylene units deriving from resorcinol, or by naphthylene units deriving from dihydroxynaphthalene.

Particularly preferred units of the general formula I are the units la, Ig, and Ik. It is also particularly preferable that the polyarylene ether sulfones of component (A) are in essence composed of one type of unit of the general formula I, in particular of one unit selected from la, Ig, and Ik.

In one particularly preferred embodiment, Ar = 1,4-phenylene, t = 1, q = 0, T is a chemical bond, and Y = SO2. Particularly preferred polyarylene ether sulfones (A) composed of the abovementioned repeat unit are termed polyphenylene sulfone (PPSU) (formula Ig).

In another particularly preferred embodiment, Ar = 1,4-phenylene, t = 1, q = 0, T = C(CH3)2, and Y = SO2. Particularly preferred polyarylene ether sulfones (A) composed of the abovementioned repeat unit are termed polysulfone (PSU) (formula la).

In another particularly preferred embodiment, Ar = 1,4-phenylene, t = 1, q = 0, T = Y = SO2. Particularly preferred polyarylene ether sulfones (A) composed of the abovementioned repeat unit are termed polyether sulfone (PESU or PES) (formula Ik). This embodiment is very particularly preferred.

For the purposes of the present invention, abbreviations such as PPSU, PESU, and PSU are in accordance with DIN EN ISO 1043-1 :2001.
The weight-average molar masses $M_w$ of the polyarylene ether sulfones (A) of the present invention are preferably from 10 000 to 150 000 g/mol, in particular from 15 000 to 120 000 g/mol, particularly preferably from 18 000 to 100 000 g/mol, determined by means of gel permeation chromatography in dimethylacetamide as solvent against narrowly-distributed polymethyl methacrylate as standard.

In one embodiment of the invention, suitable polyarylene ether sulfones, particularly polysulfones or polyethersulfones comprise sulfonic acids, carboxylic acid, amino and/or hydroxy groups on some or all of the aromatic rings in the polymer.

Production processes that lead to the abovementioned polyarylene ethers are known to the person skilled in the art and are described by way of example in Herman F. Mark, "Encyclopedia of Polymer Science and Technology", third edition, volume 4, 2003, chapter "Polysulfones" pages 2 to 8, and also in Hans R. Kricheldorf, "Aromatic Polyethers " in: Handbook of Polymer Synthesis, second edition, 2005, pages 427 to 443.

Suitable membranes are for example membranes suitable as reverse osmosis (RO) membranes, forward osmosis (FO) membranes, nanofiltration (NF) membranes, ultrafiltration (UF) membranes or microfiltration (MF) membranes. These membrane types are generally known in the art.


Further suitable membranes are for example those disclosed in US6787216, col. 2, ln 54 to col 6, ln 19; US 6,454,943, col. 3; ln 25 to col. 6, ln 12; and WO 2006/012920, p. 3, last paragraph to p. 10, first paragraph.

FO membranes are normally suitable for treatment of seawater, brackish water, sewage or sludge streams. Thereby pure water is removed from those streams through a FO membrane into a so called draw solution on the back side of the membrane having a high osmotic pressure. Typically, FO type membranes, similar as RO membranes are separating liquid mixtures via a solution diffusion mechanism, where only water can pass the membrane whereas monovalent ions and larger components are rejected.

In a preferred embodiment, suitable FO membranes are thin film composite (TFC) FO membranes. Preparation methods and use of thin film composite membranes are principally known
and, for example described by R. J. Petersen in Journal of Membrane Science 83 (1993) 81-150.

In a further preferred embodiment, suitable FO membranes comprise a support layer, a separation layer and optionally a protective layer. Said protective layer can be considered an additional coating to smoothen and/or hydrophilize the surface.

Said fabric layer can for example have a thickness of 10 to 500 \( \mu \text{m} \). Said fabric layer can for example be a woven or nonwoven, for example a polyester nonwoven.

Said support layer of a TFC FO membrane normally comprises pores with an average pore diameter of for example 0.5 to 100 nm, preferably 1 to 40 nm, more preferably 5 to 20 nm. Said support layer can for example have a thickness of 5 to 100 \( \mu \text{m} \), preferably 10 to 200 \( \mu \text{m} \). Said support layer may for example comprise a main component a polysulfone, polyethersulfone, polyphenylenesulfone, PVDF, polyimide, polyimideurethane or cellulose acetate. Nano particles such as zeolites, particularly zeolite LTA, may be comprised in said support membrane. This can for example be achieved by including such nano particles in the dope solution for the preparation of said support layer.

Said separation layer can for example have a thickness of 0.05 to 1 \( \mu \text{m} \), preferably 0.1 to 0.5 \( \mu \text{m} \), more preferably 0.15 to 0.3 \( \mu \text{m} \). Preferably, said separation layer can for example comprise polyamide or cellulose acetate as the main component.

Optionally, TFC FO membranes can comprise a protective layer with a thickness of 30-500 nm, preferably 100-300 nm. Said protective layer can for example comprise polyvinylalcohol (PVA) as the main component. In one embodiment, the protective layer comprises a halamine like chloramine.

In one preferred embodiment, suitable membranes are TFC FO membranes comprising a support layer comprising polyethersulfone as main component, a separation layer comprising polyamide as main component and optionally a protective layer comprising polyvinylalcohol as the main component.

In a preferred embodiment suitable FO membranes comprise a separation layer obtained from the condensation of a polyamine and a polyfunctional acyl halide. Said separation layer can for example be obtained in an interfacial polymerization process.
RO membranes are normally suitable for removing molecules and ions, in particular monovalent ions. Typically, RO membranes are separating mixtures based on a solution/diffusion mechanism.

In a preferred embodiment, suitable membranes are thin film composite (TFC) RO membranes. Preparation methods and use of thin film composite membranes are principally known and, for example described by R. J. Petersen in Journal of Membrane Science 83 (1993) 81-150.

In a further preferred embodiment, suitable RO membranes comprise a fabric layer, a support layer, a separation layer and optionally a protective layer. Said protective layer can be considered an additional coating to smoothen and/or hydrophilize the surface.

Said fabric layer can for example have a thickness of 10 to 500 μm. Said fabric layer can for example be a woven or nonwoven, for example a polyester nonwoven. Said support layer of a TFC RO membrane normally comprises pores with an average pore diameter of for example 0.5 to 100 nm, preferably 1 to 40 nm, more preferably 5 to 20 nm. Said support layer can for example have a thickness of 5 to 1000 μm, preferably 10 to 200 μm. Said support layer may for example comprise a main component a polysulfone, polyethersulfone, PVDF, polyimide, polyimideurethane or cellulose acetate. Nano particles such as zeolites, particularly zeolite LTA, may be comprised in said support membrane. This can for example be achieved by including such nano particles in the dope solution for the preparation of said support layer.

Said separation layer can for example have a thickness of 0.02 to 1 μm, preferably 0.03 to 0.5 μm, more preferably 0.05 to 0.3 μm. Preferably, said separation layer can for example comprise polyamide or cellulose acetate as the main component. Optionally, TFC RO membranes can comprise a protective layer with a thickness of 5 to 500 preferable 10 to 300 nm. Said protective layer can for example comprise polyvinylalcohol (PVA) as the main component. In one embodiment, the protective layer comprises a halamine like chloramine.

In one preferred embodiment, suitable membranes are TFC RO membranes comprising a nonwoven polyester fabric, a support layer comprising polyethersulfone as main component, a separation layer comprising polyamide as main component and optionally a protective layer comprising polyvinylalcohol as the main component.
In a preferred embodiment suitable RO membranes comprise a separation layer obtained from the condensation of a polyamine and a polyfunctional acyl halide. Said separation layer can for example be obtained in an interfacial polymerization process.

Suitable polyamine monomers can have primary or secondary amino groups and can be aromatic (e.g. a diaminobenzene, a triminobenzene, m-phenylenediamine, p-phenylenediamine, 1,3,5-triaminobenzene, 1,3,4-triaminobenzene, 3,5-diaminobenzoic acid, 2,4-diaminotoluene, 2,4-diaminoanisole, and xylylenediamine) or aliphatic (e.g. ethylenediamine, propylenediamine, piperazine, and tris(2-diaminoethyl)amine).

Suitable polyfunctional acyl halides include trimesoyl chloride (TMC), trimellitic acid chloride, isophthaloyl chloride, terephthaloyl chloride and similar compounds or blends of suitable acyl halides. As a further example, the second monomer can be a phthaloyl halide.

In one embodiment of the invention, a separation layer of polyamide is made from the reaction of an aqueous solution of meta-phenylene diamine (MPD) with a solution of trimesoyl chloride (TMC) in an apolar solvent.

In another embodiment of the invention, the separation layer and optionally other layers of the membrane contain nanoparticles other than of vanadium pentoxide. Suitable nanoparticles normally have an average particle size of 1 to 1000 nm, preferably 2 to 100 nm, determined by dynamic light scattering. Suitable nanoparticles can for example be zeolites, silica, silicates or aluminium oxide. Examples of suitable nanoparticles include Aluminate, Alunite, Ammonia Alum, Alataxite, Apjohnite, Basaluminate, Bapatite, Bauxite, Beideilite, Boehmite, Cadwaladerite, Cardenite, Chalcoalumite, Chiolite, Chloraluminate, Cryolite, Dawsonite, Diaspore, Dickite, Gearsutite, Gibbsite, Hailosite, Hydrobasaluminate, Hydrocalumite, Hydrotalcite, Illite, Kalinite, Kaolinite, Mellite, Montmorillonite, Natroalumite, Nontronite, Pachnolite, Prehnite, Prosopite, Ralstonite, Ransomite, Saponite, Thomsenolite, Weberite, Woodhouseite, and Zinclusminit, kehoeite, pahasapaite and tiptopite; and the silicates: hsiaghualite, lovdarite, viselite, partheite, prehnite, rogganite, apophyllite, gyrolite, maricopaite, okenite, tacharanite and tobermorite.

Nanoparticles may also include a metallic species such as gold, silver, copper, zinc, titanium, iron, aluminum, zirconium, indium, tin, magnesium, or calcium or an alloy thereof or an oxide thereof or a mixture thereof. They can also be a nonmetallic species such as Si3N4, SiC, BN, B4C, or TIC or an alloy thereof or a mixture thereof. They can be a carbon-based species such as graphite, carbon glass, a carbon cluster of at least C-, buckminsterfullerene, a higher fullerene, a carbon nanotube, a carbon nanoparticle, or a mixture thereof.

In yet another embodiment the separation layer and optionally other layers of the membrane contain zeolites, zeolite precursors, amorphous aluminosilicates or metal organic frame works (MOFs) any preferred MOFs. Preferred zeolites include zeolite LTA, RHO, PAU, and KFI. LTA is especially preferred.
Preferably, the nanoparticles other than vanadium pentoxide comprised in the membrane have a polydispersity of less than 3.

In another embodiment of the invention the separation layer of the membrane contains a further additive increasing the permeability of the RO membrane. Said further additive can for example be a metal salt of a beta-diketonate compound, in particular an acetoacetate and/or an at least partially fluorinated beta-diketonate compound.

NF membranes are normally especially suitable for removing separate multivalent ions and large monovalent ions. Typically, NF membranes function through a solution/diffusion or/and filtration-based mechanism.

NF membranes are normally used in cross filtration processes.

NF membranes can for example comprise as the main component polyarylene ether, polysulfone, polyethersulfones (PES), polyphenylensulfone (PPSU), polyamides (PA), polyvinylalcohol (PVA), Cellulose Acetate (CA), Cellulose Triacetate (CTA), CA-triacetate blend, Cellulose ester, Cellulose Nitrate, regenerated Cellulose, aromatic, aromatic/aliphatic or aliphatic Polyamide, aromatic, aromatic/aliphatic or aliphatic Polyimide, Polybenzimidazole (PBI), Polybenzimidazole-trione (PBIL), polyetheretherketone (PEEK), sulfonated polyetheretherketone (SPEEK), Polyacrylonitrile (PAN), PAN-poly(vinyl chloride) copolymer (PAN-PVC), PAN-methallyl sulfonate copolymer, Polysulfone, Poly(dimethylphenylene oxide) (PPO), Polycarbonate, Polyester, Polytetrafluoroethylene (PTFE), Poly(vinylidene fluoride) (PVDF), Polypropylene (PP), Polyelectrolyte complexes, Poly(methyl methacrylate) PMMA, Polydimethylsiloxane (PDMS), aromatic, aromatic/aliphatic or aliphatic polyimide urethanes, aromatic, aromatic/aliphatic or aliphatic polyamidimides, crosslinked polyimides or mixtures thereof. In a preferred embodiment, said main components of NF membranes are positively or negatively charged.

Nanofiltration membranes often comprise charged polymers comprising sulfonic acid groups, carboxylic acid groups and/or ammonium groups.

preferably, NF membranes comprise as the main component polyamides, polyimides or polyimide urethanes, Polyetheretherketone (PEEK) or sulfonated polyetheretherketone (SPEEK).
UF membranes are normally suitable for removing suspended solid particles and solutes of high molecular weight, for example above 1000 Da. In particular, UF membranes are normally suitable for removing bacteria and viruses.

UF membranes normally have an average pore diameter of 0.5 nm to 50 nm, preferably 1 to 40 nm, more preferably 5 to 20 nm.

UF membranes can for example comprise as main component a polyarylene ether, polysulfone, polyethersulfones (PES), polyphenylensulfone (PPSU), polyamides (PA), polyvinylalcohol (PVA), Cellulose Acetate (CA), Cellulose Triacetate (CTA), CA-triacetate blend, Cellulose ester, Cellulose Nitrate, regenerated Cellulose, aromatic, aromatic/aliphatic or aliphatic Polyamide, aromatic, aromatic/aliphatic or aliphatic Polymide, Polybenzimidazole (PBI), Polybenzimidazolone (PBIL), Polyacrylonitrile (PAN), PAN-poly(vinyl chloride) copolymer (PAN-PVC), PAN-methallyl sulfonate copolymer, Polysulfone, Poly(dimethylphenylene oxide) (PPO), Polycarbonate, Polyester, Polytetrafluoroethylene PTFE, Poly(vinylidene fluoride) (PVDF), Polypropylene (PP), Polyelectrolyte complexes, Poly(methyl methacrylate) PMMA, Polydimethylsiloxane (PDMS), aromatic, aromatic/aliphatic or aliphatic polyimide urethanes, aromatic, aromatic/aliphatic or aliphatic polyamidimides, crosslinked polyamides or mixtures thereof.

Preferably, UF membranes comprise as main component polysulfone, polyethersulfone, polyphenylenesulfone (PPSU), PVDF, polyimide, polyamidimide, crosslinked polyimides, polyimide urethanes or mixtures thereof.

In one embodiment, UF membranes comprise further additives like polyvinyl pyrrolidones.

In one embodiment, UF membranes comprise further additives like block copolymers of polyarylene sulfones and alkyleneoxides like polyethyleneoxide.

In a preferred embodiment, UF membranes comprise as major components polysulfones or polyethersulfone in combination with further additives like polyvinylpyrrolidone.

In one preferred embodiment, UF membranes comprise 80 to 50% by weight of polyethersulfone and 20 to 50% by weight of polyvinylpyrrolidone.

In another embodiment UF membranes comprise 95 to 80% by weight of polyethersulfone and 5 to 15% by weight of polyvinylpyrrolidone.

In another embodiment UF membranes comprise 99.9 to 80% by weight of polyethersulfone and 0.1 to 15% by weight of polyvinylpyrrolidone.

In one embodiment of the invention, UF membranes are present as spiral wound membranes.

In another embodiment of the invention, UF membranes are present as tubular membranes.

In another embodiment of the invention, UF membranes are present as flat sheet membranes.
In another embodiment of the invention, UF membranes are present as hollow fiber membranes.
In yet another embodiment of the invention, UF membranes are present as single bore hollow fiber membranes.
In yet another embodiment of the invention, UF membranes are present as multi bore hollow fiber membranes.

MF membranes are normally suitable for removing particles with a particle size of 0.1 \( \mu \text{m} \) and above.

MF membranes normally have an average pore diameter of 0.1 \( \mu \text{m} \) to 10 nm, preferably 1.0 \( \mu \text{m} \) to 5 \( \mu \text{m} \).

Microfiltration can use a pressurized system but it does not need to include pressure.

Microfiltration systems are designed to remove suspended solids down to 0.1 micrometres in size, in a feed solution with up to 2-3% in concentration.

MF membranes can for example comprise as main component polyarylene ether, polysulfone, polyethersulfones (PES), polyphenylensulfone (PPSU), polyamides (PA), polyvinylalcohol (PVA), Cellulose Acetate (CA), Cellulose Triacetate (CTA), CA-triacetate blend, Cellulose ester, Cellulose Nitrate, regenerated Cellulose, aromatic, aromatic/aliphatic or aliphatic Polyamide, aromatic, aromatic/aliphatic or aliphatic Polyimide, Polybenzimidazole (PBI), Polybenzimidazole (PBIL), Polyacrylonitrile (PAN), PAN-poly(vinyl chloride) copolymer (PAN-PVC), PAN-methallyl sulfonate copolymer, Polysulfone, Poly(dimethylphenylene oxide) (PPO), Polycarbonate, Polyester, Polytetrafluoroethylene (PTFE), Poly(vinylidene fluoride) (PVDF), Polypropylene (PP), Polyelectrolyte complexes, Poly(methyl methacrylate) PMMA, Polydimethylsiloxane (PDMS), aromatic, aromatic/aliphatic or aliphatic polyimide urethanes, aromatic, aromatic/aliphatic or aliphatic polyamidimides, crosslinked polyimides or mixtures thereof.

The oxidation of the surface of the substrate (base membrane) can be performed, for example, by treatment with corona discharge, plasma, flame, ozone, electron-beam, X-ray or ultraviolet radiation.
Corona discharges can be electrical discharges characterized by a corona and occurring when one of two electrodes in a gas has a shape causing the electric field at its surface to be significantly greater than that between the electrodes. Air is usually used as gas. The substrate is usually located at ambient pressure in the discharge field between the two electrodes, for example by passing a film as substrate between two electrodes.

Plasma can be a gas where electrons and ions are present. Plasma can be generated by the treatment of gases with high temperatures or high electric fields. Plasma treatment is usually carried out in vacuum chambers at 10 to 100 Pa with a nonthermal plasma in a gas atmosphere consisting of an inert gas or reactive gas, for example oxygen or oxygen-containing gas such as air.

Flame can be flames that are formed when a flammable gas and an oxygen containing gas, for example atmospheric air, are combined and combusted. Examples of flammable gases are propane, butane or town gas. Flame treatment is usually carried out at ambient pressure.

Ozone can be generated from atmospheric oxygen in a corona discharge or by ultraviolet radiation.

Electron beam can be generated by electron beam accelerators, for example by cathode ray tubes.

X-rays can be generated by X-ray generators, for example by X-ray-tubes.

Preferably, the oxidation of the surface is performed by treatment with corona discharge, plasma or flame. More preferably, it is performed by corona discharge treatment or plasma treatment.

In one embodiment of the invention the surface of the base membrane is subjected to an oxidative process comprising treatment with oxidative immersion baths such as baths containing chromium sulfuric acid, sulfuric acid, hydrogen peroxide ammonium hydroxide, persulfuric acid, peroxo disulfuric acid, phosphoric acid, hypophosphorous acid, phosphorous acid, pyrophosphoric acid, triphosphoric acid, perphosphoric acid, permonophosphoric acid and mixtures thereof.

Membranes according to the invention comprise a coating that has been grafted on the surface of a base membrane after said surface has been subjected to an oxidative treatment. Said coating can also be described as a modified surface. Said coating can bind to the surface of the base membrane through adhesion or, preferably, through covalent bonds with the surface of the base membrane.
Said coating can be a monomer, oligomer or polymer. Said coating can be crosslinked or not be crosslinked.

Monomers that impart flux enhancing properties to the membrane are herein also referred to as "flux enhancing monomers" or "flux improving monomers". The term "flux" shall denote the flux of the medium that is subjected to a separation operation. In many cases, "flux" means the flux of water through the membrane. For example in the case of water treatment applications, "flux" means the amount of water that permeates through the specified membrane area in a certain period of time.

A "monomer", for example "biocidal monomers", "antiadhesive monomers" or "radically polymerizable monomers", in this application shall, depending on the context, refer to such monomer in unpolymerized (monomeric) form or in polymerized form. When the term "monomer" is for example used in the context of a formulation, it normally refers to the unpolymerized form. When the term "monomer" is for example used in the context of a polymer or a coating, it normally refers to the polymerized form, in which said monomer is comprised in the polymer or coating.

In the context of this application, "improving the flux" or "enhancing the flux" shall also be understood to mean "reducing the decrease of flux through a membrane over time".

Flux enhancing properties in the context of this invention refer in particular to the long term properties of membranes. While it is possible that through the application of a coating the flux may decrease over a short term, the flux over the long term will be improved (meaning that the decrease of flux is reduced) relative to a membrane to that no such coating has been applied.

The duration of a "short term" or "long term" may vary depending on the membrane or the application or the material subjected to that application, that is for example from the type of water treated. Thus, enhancing of flux in the context of this application shall mean that after at least one certain period of time and under at least one set of application conditions, the flux through a membrane according to the invention shall be improved or the decrease of flux be reduced over the flux through a membrane comprising no coating according to this invention or over membranes known from the art. For example, membranes according to the invention may show improved flux over prior art membranes after a period of 1 hour, 1 day, 3 days, 5 days, 1 week, 2 weeks, three weeks, one month, two months, three months, six months and/or one year. Sometimes the enhanced flux of membranes according to the invention only becomes observable after one or a certain number of cleaning cycles have been applied to the membrane.

It is also possible the membranes according to the invention show improved properties with respect to their ability to restore the flux after cleaning. Also membranes according to the invention can be easier to clean. Furthermore less cleaning agents may be requires for cleaning membranes according to the invention.
In particular, suitable flux enhancing monomers reduce fouling and in particular biofouling of the membrane.

In the context of this application, an effect of a polymer or the coating comprising a flux enhancing monomer is also sometimes referred to as the effect of the flux enhancing monomer.

Monomers bearing a charge, for example from ammonium groups or carboxylate groups, are accompanied by one or more counterions. If, in this application, a monomer bearing a charge is depicted or named without corresponding counterion, such monomers are to be understood to be accompanied by a suitable counterion (with the exception of betaines). Such counterions are for example chloride, bromide, iodide, carboxylates for monomers bearing a positive charge.

For monomers bearing negative charge, suitable counterions are for example sodium, potassium, magnesium, calcium, ammonium.

In a preferred embodiment, suitable flux enhancing monomers are antiadhesive monomers and/or biocidal monomers that impart biocidal and/or antiadhesive properties to the membrane.

An antiadhesive monomer in the context of this application shall mean a monomer that imparts antiadhesive properties to the coating, be it by itself or in combination with other components. Antiadhesive properties or antiadhesive coating means that for example particles or biological material or biological organisms or degradation products of biological material or biological organisms have a lower tendency to adhere to the surface of a membrane having such antiadhesive properties. The degree of fouling and in particular biofouling of a membrane is thus reduced.

Antiadhesive coatings are sometimes also referred to as anti-sticking coatings, 'stealth' coatings or biopassive coatings.

The concept of antiadhesive polymers and coatings is for example disclosed in the following pieces of literature, which are incorporated herein by reference:


In one embodiment of the invention, suitable antiadhesive monomers are those, whose polymerization leads to the formation of antiadhesive coatings that are characterized by the
presence of hydrophilic groups and preferentially the presence of hydrogen-bond-accepting groups, preferentially the absence of hydrogen-bond donating groups and preferentially the absence of net charge.

5 Suitable antiadhesive monomers are for example selected from
   a) esters of (meth)acrylic acid with polyols
   b) vinyl ethers of polyols
   c) hydrophilic macromonomers different from monomers a) and b)
   d) N-vinyl compounds
10 e) Low molecular weight hydrophilic (meth)acrylamides
   f) (meth)acrylates or (meth)acrylamides bearing epoxy groups
   g) monomers having a betain structure
   h) hydrophilic monomers different from those mentioned under a) to g).
   i) Ion pair comonomers

Suitable esters of (meth)acrylic acid with polyols a) are preferably esters with polyols that are hydrophilic and with which coatings can be prepared that show antiadhesive properties as described above.

20 In one embodiment, suitable esters of (meth)acrylic acid with polyols are polyols, in which each OH group is esterified with (meth)acrylic acid.
In one embodiment, suitable esters of (meth)acrylic acid with polyols are polyols, in which at least one OH group is esterified with (meth)acrylic acid and at least one OH group is not esterified.

25 In one embodiment, suitable esters of (meth)acrylic acid with polyols are polyols, in which at least one OH group is esterified with (meth)acrylic acid and at least one OH group is etherified with an alcohol like methanol, ethanol, propanol or a polyol like ethyleneglycol, neopentylglycol, trimethylolpropane, glycerol, trimethylolethane , pentaerythritol or dipentaerythritol, (poly)saccharide, in particular sorbitol.

Examples of suitable esters of (meth)acrylic acid with polyols are for example (meth)acrylates of alkoxylated polyols like ethyleneglycol, neopentylglycol, trimethylolpropane, glycerol, trimethylolethane, pentaerythritol, dipentaerythritol, or (poly)saccharide, in particular sorbitol bearing 1 to 100, preferably 1 to 50 ethoxy, propoxy, mixed ethoxy and propoxy, more preferably exclusively ethoxy groups per OH-group of the polyol.

More Preferably, suitable esters of (meth)acrylic acid with polyols are (meth)acrylates of, with respect to each OH group of the polyol, singly to hundred-fold, more preferably triply to 50-fold, in particular triply to vigintuply (20-fold) ethoxylated, propoxylated or mixedly ethoxylated and propoxylated, and more particularly exclusively ethoxylated, neopentylglycol, trimethylolpropane, glycerol, trimethylolethane , pentaerythritol, dipentaerythritol, or (poly)saccharide, in particular sorbitol.
Particularly preferred esters of (meth)acrylic acid with polyols are
- ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, oligoethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate,
- ethylene glycol mono(meth)acrylate, diethylene glycol mono(meth)acrylate, triethylene glycol mono(meth)acrylate, oligoethylene glycol mono(meth)acrylate, polyethylene glycol mono(meth)acrylate,
- ethylene glycol methyl ether (meth)acrylate, di(ethylene glycol) methyl ether (meth)acrylate, tri(ethylene glycol) methyl ether (meth)acrylate, oligo(ethylene glycol) methyl ether (meth)acrylate,
- glycerol tri(meth)acrylate, glycerol alkoxylate tri(meth)acrylate, preferentially glycerol ethoxylate tri(meth)acrylate
- trimethylolpropane tri(meth)acrylate, trimethylolpropane alkoxylate tri(meth)acrylate, preferentially trimethylolpropane ethoxylate tri(meth)acrylate
- pentaerythritol tetra(meth)acrylate, pentaerythritol alkoxylate tetra(meth)acrylate, preferentially pentaerythritol ethoxylate tetra(meth)acrylate
- pentaerythritol tri(meth)acrylate, pentaerythritol alkoxylate tri(meth)acrylate, preferentially pentaerythritol ethoxylate tri(meth)acrylate
- dipentaerythritol penta(meth)acrylate, dipentaerythritol alkoxylate penta(meth)acrylate, preferentially dipentaerythritol ethoxylate penta(meth)acrylate
- sorbitol hexa(meth)acrylate, sorbitol alkoxylate hexa(meth)acrylate, preferentially sorbitol ethoxylate hexa(meth)acrylate; sorbitol penta(meth)acrylate, sorbitol alkoxylate penta(meth)acrylate, sorbitol tetra(meth)acrylate, sorbitol alkoxylate tetra(meth)acrylate, preferentially sorbitol ethoxylate tetra(meth)acrylate; sorbitol tri(meth)acrylate, sorbitol alkoxylate tri(meth)acrylate, preferentially sorbitol ethoxylate tri(meth)acrylate

In one embodiment, suitable esters of (meth)acrylic acid with polyols do not include (meth)acrylic esters with polyalkyleneoxides like polyethylenoxides.

Suitable antiadhesive monomers b) are vinyl ethers of polyols or vinyl ethers of alkoxylated polyols.

Suitable vinyl ethers of polyols are preferably ethers with that are hydrophilic and with which coatings can be prepared that show antiadhesive properties as described above.

In one embodiment, suitable vinyl ethers of polyols are polyols, in which each OH group is etherified vinyl alcohol.
In one embodiment, suitable vinyl ethers of polyols are polyols, in which at least one OH group is etherified with vinyl alcohol and at least one OH group is not etherified.
In one embodiment, suitable vinyl ethers of polyols are polyols, in which at least one OH group is etherified with vinyl alcohol and at least one OH group is etherified with a saturated alcohol like methanol, ethanol, propanol or a polyol like ethyleneglycol, neopentylglycol, trimethylolpropane, glycerol, trimethylolethane, pentaerythritol, dipentaerythritol, (poly)saccharide like sorbitol.

Examples of suitable vinyl ethers of polyols are for example vinyl ethers of alkoxylated polyols like ethyleneglycol, neopentylglycol, trimethylolpropane, glycerol, trimethylolethane, pentaerythritol or dipentaerythritol bearing 1 to 100, preferably 1 to 50 ethoxy, propoxy, more preferably exclusively ethoxy groups per OH-group of the polyol.

Preferred vinyl ethers of polyols are ethylene glycol divinylether, diethylene glycol divinylether, triethylene glycol divinylether, oligoethylene glycol divinylether, polyethylene glycol divinyl ether, methoxyethylene glycol monovinylether, methoxy diethylene glycol monovinylether, methoxy triethylene glycol monovinylether, methoxy oligoethylene glycol monovinylether, methoxy polyethylene glycol monovinyl ether.

Suitable antiadhesive monomers c) are hydrophilic macromonomers such as (meth)acryloyl-, (meth)acrylamide- and vinyl ether-modified hydrophilic polymers, preferentially (meth)acryloyl-modified polyvinyl alcohol, (meth)acryloyl-modified partially hydrolyzed polyvinyl acetate, (meth)acryloyl-modified poly(2-alkyl-2-oxazoline), (meth)acrylamide-modified poly(2-alkyl-2-oxazoline), in particular (meth)acryloyl and (meth)acrylamide-modified poly(2-methyl-2-oxazoline) and (meth)acryloyl- and (meth)acrylamide-modified poly(2-ethyl-2-oxazoline), (meth)acryloyl- and (meth)acrylamide-modified polyvinyl pyrrolidone, (meth)acryloyl- and (meth)acrylamide-modified vinylpyrrolidone, (meth)acryloyl- and (meth)acrylamide-modified hydrophilic polypeptides, (meth)acryloyl- and (meth)acrylamide-modified polyphosphorylcholine, (meth)acryloyl- and (meth)acrylamide-modified polysulfobetain, (meth)acryloyl- and (meth)acrylamide-modified polycarbobetain, (meth)acryloyl- and (meth)acrylamide-modified polyampholyte.

Suitable antiadhesive monomers d) are N-vinyl compounds such as N-vinyl pyrrolidone, N-vinylcaprolactam, N-vinylcaprolactone or N-vinyl-2-piperidone.

In one embodiment, monomers d) do not include N-vinyl pyrrolidone.

Suitable antiadhesive monomers e) are low molecular weight (meth)acrylamides with a molecular weight below 200, preferably below 150.

Preferred low molecular weight (meth)acrylamides are those according to formula
with $R_1=H$ or CH3, $R_2, R_3$ independently from each other H, methyl, ethyl, 1-propyl, 2-propyl, 1-butyl, 2-butyl.

Preferred alkylated (meth)acrylamides are: $R_2=R_3=H$ (= (meth)acrylamide), $R_2=R_3$=methyl (=N, N-dimethyl (meth)acrylamide), $R_2=R_3$=ethyl (=N, N-diethyl (meth)acrylamide), $R_2=H$, $R_3$=2-propyl (=N-isopropyl (meth)acrylamide).

Suitable (meth)acrylates or (meth)acrylamides bearing epoxy groups f) are for example glycidyl (meth)acrylate.

Suitable monomers having a betain structure g) are for example sulfobetaines or carbobetaines of (meth)acrylates or (meth)acrylamides, sulfonyl- or carboxy-modified vinylimidazolium betains, sulfonyl- or carboxy-modified vinylpyridinium betains, sulfobetain- or carbobetain-modified styrenyls, phosphobetain(meth)acrylates or Phosphobetain(meth)acrylamides.

Suitable sulfobetaines or carbobetaines of (meth)acrylates or (meth)acrylamides are for example sulfobetain(meth)acrylates, sulfobetain(meth)acrylamides, carbobetain(meth)acrylates, carbobetain(meth)acrylamides of general formula

$$\text{CH}_2=\text{CH}-\text{X}-\text{L}-\text{N}^+\text{Z}^-\text{Y}^-$$

wherein

- $R_1=H$, Methyl;
- $R_2$, $R_3$ = alkyl, aryl, aralkyl, preferentially $R_2=R_3=$ Methyl;
- $X=O$, NH;
- $L$ = alkyl, aryl, aralkyl. L may contain heteroatoms in particular one or several groups of $(\text{CH}_2)_n\text{O}$, $(\text{CH}_2)_n\text{NH}$, $n$ is preferentially 2-3; preferably $L$ is methylene, ethylene or propylene; in particular ethylene or propylene.
- $Z=$ alkyl, aryl, aralkyl. $Z$ may contain heteroatoms in one or several groups of $(\text{CH}_2)_n\text{O}$, $(\text{CH}_2)_n\text{NH}$, $n$ is preferentially 2-3; preferably $Z$ is methylene, ethylene, propylene, butylene
- $Y=$ sulfonate or carboxylate
Examples of suitable sulfobetaines or carbobetaines of (meth)acrylates or (meth)acrylamides are:

Further suitable sulfobetaines or carbobetaines of (meth)acrylates or (meth)acrylamides are sulfobetain di(meth)acrylates, sulfobetain di(meth)acrylamides, carboxbetain di(meth)acrylates and carbobetain di(meth)acrylamides. Preferred sulfobetaines or carbobetaines of (meth)acrylates or (meth)acrylamides are of the general formula

\[
\begin{align*}
\text{R}_1, \text{R}_2 & = \text{H}, \text{Methyl} \\
\text{R}_3 & = \text{alkyl, aryl, aralkyl, preferably R}_3 = \text{Methyl} \\
\text{X} & = \text{O, NH} \\
\text{L}_{1,2} & = \text{independently from each other alkyl, aryl, aralkyl. L may contain heteroatoms in particular one or several groups of (CH}_2)_{n_1}\text{O, (CH}_2)_{n_2}\text{NH, n is preferentially 2-3; preferably L = methylene, ethylene, propylene; in particular ethylene and propylene;}}
\end{align*}
\]
L₃ = alkyl, aryl, aralkyl. L₃ may contain heteroatoms in particular one or several groups of (CH₂)ₙO, (CH₂)ₙNH, n is preferably 2-3; preferably L₃ = methylene, ethylene, propylene, butylene;

Y = sulfonate or carboxylate.

Further examples of suitable sulfobetaines or carbobetaines of (meth)acrylates or (meth)acrylamides are:

![Chemical Structures]

Examples of sulfonyle- or carboxy-modified vinylimidazolium betains are:

![Chemical Structures]
Suitable sulfonyl- or carboxy-modified vinylpyridinium betains are for example those according to the general formula
\[
\begin{align*}
Y & \quad \text{N-L'} \quad \text{N-L'} \\
\end{align*}
\]
wherein

- \( L = \text{alkyl, aryl, aralkyl}; \) L may contain heteroatoms in particular one or several groups of \((\text{CH}_2)_n\text{O}, (\text{CH}_2)_n\text{NH}, n \text{ is preferably } 2-3;\)
- preferably \( L = \text{methylene, ethylene, propylene, butylene}; \)
- \( Y = \text{sulfonate or carboxylate.} \)

Examples of sulfonyl- or carboxy-modified vinylpyridinium betains include

\[
\text{Suitable Sulfo- or Carbobetain-modified styrenyls are for example those according to the general formula}
\]
\[
\begin{align*}
\text{N-L'} \quad \text{N-L'} \\
\end{align*}
\]
wherein

- \( \text{R}_1, \text{R}_2 = \text{alkyl, aryl, aralkyl, preferably } \text{R}_1 = \text{R}_2 = \text{Methyl}, \)
- \( \text{L}_1, \text{L}_2 = \text{independently from each other alkyl, aryl, aralkyl}; \) L may contain heteroatoms in particular one or several groups of \((\text{CH}_2)_n\text{O}, (\text{CH}_2)_n\text{NH}, n \text{ is preferentially } 2-3;\)
- preferably \( L = \text{methylene, ethylene, propylene, butylene}; \) in particular ethylene and propylene,
- \( Y = \text{sulfonate or carboxylate.} \)

Examples of Sulfo- or Carbobetain-modified styrenyls include:

\[
\text{Suitable phosphobetain(meth)acrylates or phosphobetain(meth)acrylamides are those of the general formula}
\]
\[
\begin{align*}
\text{N-L'} \quad \text{N-L'} \\
\end{align*}
\]
wherein
R₁ = H, Methyl,
R₂, R₃, R₄ = alkyl, aryl, aralkyl, preferentially R₂ = R₃ = R₄ = Methyl,
X = O, NH,
L₁, L₂ = independently from each other alkyl, aryl, aralkyl. L₁, L₂ may independently from each other contain heteroatoms in particular one or several groups of (CH₂)ₙO,
(CH₂)ₙN H, n is preferably 2-3; preferably L₁, L₂ are independently from each other methylene, ethylene, propylene, butylene; in particular and independently from each other ethylene and propylene.

Examples of phosphobetain(meth)acrylates or phosphobetain(meth)acrylamides include

Suitable Ion pair comonomers are in particular ion pairs of ammonium-modified (meth)acrylates or (meth)acrylamides and sulfo-, carboxy-, phosphonyl or phosphoryl -modified (meth)acrylates or (meth)acrylamides. A preferred example is the combination

Suitable hydrophilic monomers h) different from those mentioned above are hydroxyethyl-(meth)acrylate, Vinyl alcohol, (Meth)acryloyl and (meth)acrylamide-modified mono- and oligo-saccharides.

Suitable Ion pair comonomers i) are in particular ion pairs of ammonium-modified (meth)acrylates or (meth)acrylamides and sulfo-, carboxy-, phosphonyl or phosphoryl -modified (meth)acrylates or (meth)acrylamides. A preferred example is the combination

In one embodiment of the invention the coating comprises only one antiadhesive monomer.
In one embodiment of the invention the coating comprises two or more antiadhesive monomers.

A biocidal monomer in the context of this application shall mean a monomer that imparts biocidal properties to the coating, be it by itself or in combination with other components. Biocidal properties or biocidal coating means that living biological organisms like plants, algae, bacteria, cyanobacteria, fungi, yeasts, molds, protozoa, viruses, mycoplasma, other microorganisms or higher organisms such as barnacles are deterred, controlled and/or inactivated by said coating. The degree of fouling and in particular biofouling of a membrane is thus reduced.

The mechanisms of such biocidal effects are not entirely understood. It is assumed the biocidal effect of biocidal monomers or coatings can for example be due to the interfering with the production of the bacterial plasma wall, interfering with protein synthesis, nucleic acid synthesis, or plasma membrane integrity, or to inhibiting critical biosynthetic pathways in the bacteria.

Suitable biocidal monomers are for example selected from

j) vinyl-imidazolium compounds
k) ethylenically unsaturated monomers bearing quarternary ammonium or phosphonium groups
l) diallyldialkylammoniumchlorides
m) alkylaminoalkyl (meth)acrylates and alkylaminoalkyl (meth)acrylamides
n) Polysine (meth)acrylamides or (meth)acrylates
o) alkyl-4-vinylpridinium and alkyl-2-vinyl-pyridinium salts, in particular bromides and iodides
p) ethylenically unsaturated monomers bearing guanide and biguanide groups
q) halamines


Suitable vinyl-imidazolium compounds j) are in particular 3-vinyl-imidazol-1-i um compounds. These are preferably selected from a 3-vinyl-imidazol-1-ium compounds having the formula (III)
in which $R^a$ is an organic radical having 1 to 22 C atoms, $R^b$, $R^c$ and $R^d$ independently of one another are an H atom or an organic radical having up to 22 C atoms and $A_\text{an}$ is an anion.

$R^a$ is an organic radical having 1 to 22 C atoms. The organic radical may also comprise further heteroatoms, more particularly oxygen atoms, nitrogen, sulfur or phosphorus atoms, or functional groups, as for example hydroxyl groups, ether groups, ester groups, or carbonyl groups.

More particularly $R^a$ is a hydrocarbon radical which apart from carbon and hydrogen may further comprise at most hydroxyl groups, ether groups, ester groups or carbonyl groups.

$R^a$ with particular preference is a hydrocarbon radical having 1 to 22 C atoms, more particularly having 4 to 20 C atoms, which comprises no other heteroatoms, e.g., oxygen or nitrogen. The hydrocarbon radical may be aliphatic (in which case unsaturated aliphatic groups are also included, but less preferred) or aromatic, or may comprise both aromatic and aliphatic groups. Preferably $R^a$ is an aliphatic hydrocarbon radical.

Examples of hydrocarbon radicals include the phenyl group, benzyl group, a benzyl group or phenyl group substituted by one or more $C\text{i}$ to $C_4$ alkyl groups, or the mesityl group, alkyl groups and alkenyl groups, more particularly the alkyl group.

With very particular preference $R^a$ is a $C_4$ to $C_22$ alkyl group, preferably a $C_4$ to $C_18$.

Examples for $R^a$ are methyl, ethyl, 1-propyl, 2-propyl, 1-butyl, 2-butyl, 2-methyl-1-propyl (isobutyl), 2-methyl-2-propyl (tert-butyl), 1-pentyl, 2-pentyl, 3-pentyl, 2-methyl-1-butyl, 3-methyl-1-butyl, 2-methyl-2-butyl, 3-methyl-2-butyl, 2,2-dimethyl-1-propyl, 1-hexyl, 2-hexyl, 3-hexyl, 2-methyl-1-pentyl, 3-methyl-1-pentyl, 4-methyl-1-pentyl, 2-methyl-2-pentyl, 3-methyl-2-pentyl, 4-methyl-2-pentyl, 2-methyl-3-pentyl, 3-methyl-3-pentyl, 2,2-dimethyl-1-butyl, 2,3-dimethyl-1-butyl, 3,3-dimethyl-1-butyl, 2-ethyl-1-butyl, 2,3-dimethyl-2-butyl, 3,3-dimethyl-2-butyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl,icosyl, phenylmethyl (benzyl), diphenylmethyl, triphenylmethyl, 2-phenylethyl, 3-phenylpropyl, cyclopentymethyl, 2-cyclopentylpropyl, cyclohexymethyl, 2-cyclohexylethyl, and 3-cyclohexylpropyl.

With very particular preference $R^a$ is a 1-butyl, 2-butyl, 2-methyl-1-propyl (isobutyl), 2-methyl-2-propyl (tert-butyl), 1-pentyl, 2-pentyl, 3-pentyl, 1-hexyl, 2-hexyl, 3-hexyl, 2-methyl-1-pentyl, 3-methyl-1-pentyl, 4-methyl-1-pentyl, 2-methyl-2-pentyl, 3-methyl-2-pentyl, 4-methyl-2-pentyl, 2-methyl-3-pentyl, 3-methyl-3-pentyl, 2,2-dimethyl-1-butyl, 2,3-dimethyl-1-butyl, 3,3-dimethyl-1-butyl, 2-ethyl-1-butyl, 2,3-dimethyl-2-butyl, 3,3-dimethyl-2-butyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, or icosyl group, with the butyl, pentyl, hexyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl, and octadecyl groups having particular importance.
In one preferred embodiment, \( R^b \) is an H atom.

In another preferred embodiment, \( R^b \) is an alkyl group, as for example a \( \text{Ci to Ci6} \) alkyl group, preferably a \( \text{Ci to C16} \), more preferably a \( \text{Ci to C14} \), very preferably \( \text{Ci to C12} \), and more particularly \( \text{Ci to C10} \) alkyl group. For the radical \( R^b \), a \( \text{Ci to C6} \) alkyl group represents one particular embodiment, and in a very particular embodiment the alkyl group is a \( \text{C1} \) to \( \text{C4} \) alkyl group.

\( R^c \) and \( R^d \) are preferably independently of one another a hydrogen atom or an organic radical having 1 to 10 C atoms. The organic radical may also comprise further heteroatoms, more particularly oxygen atoms, nitrogen, sulfur or phosphorus atoms, or functional groups, as for example hydroxyl groups, ether groups, ester groups, or carbonyl groups.

More particularly, \( R^c \) and \( R^d \) are a hydrocarbon radical which apart from carbon and hydrogen may further comprise at most hydroxyl groups, ether groups, ester groups or carbonyl groups.

\( R^c \) and \( R^d \) with particular preference are independently of one another a hydrocarbon radical having 1 to 20 C atoms, more particularly having 1 to 10 C atoms, which comprises no other heteroatoms, e.g., oxygen or nitrogen. The hydrocarbon radical may be aliphatic (in which case unsaturated aliphatic groups are also included) or aromatic, or may comprise both aromatic and aliphatic groups.

Examples of hydrocarbon radicals include the phenyl group, benzyl group, a benzyl group or phenyl group substituted by one or more \( \text{Ci to C4} \) alkyl groups, or the mesityl group, alkyl groups and alkenyl groups, more particularly the alkyl group.

With very particular preference, \( R^c \) and \( R^d \) are a hydrogen atom or a \( \text{Ci to C10} \) alkyl group. A particularly preferred alkyl group is a \( \text{C1 to C6} \) alkyl group, and in one particular embodiment the alkyl group is a \( \text{C1} \) to \( \text{C4} \) alkyl group.

With very particular preference, \( R^c \) and \( R^d \) are independently of one another a methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl or tert-butyl group, with the methyl, ethyl n-propyl, and n-butyl groups having particular importance.

In one particular embodiment, \( R^c \) and \( R^d \) are each H atoms.

In a very particular embodiment, \( R^b \), \( R^c \), and \( R^d \) are each H atoms.

Examples of imidazolium ions are:

- 1-butyl-3-vinyl-imidazol-1-iium, 1-pentyl-3-vinyl-imidazol-1-iium, 1-hexyl-3-vinyl-imidazol-1-iium,
- 1-octyl-3-vinyl-imidazol-1-iium, 1-decyl-3-vinyl-imidazol-1-iium, 1-dodecyl-3-vinyl-imidazol-1-iium,
- 1-tetradecyl-3-vinyl-imidazol-1-iium, 1-hexadecyl-3-vinyl-imidazol-1-iium, 1-octadecyl-3-vinyl-imidazol-1-iium,
- 1-hexyl-2-methyl-3-vinyl-imidazol-1-iium, 1-octyl-2-methyl-3-vinyl-imidazol-1-iium,
- 1-decyl-2-methyl-3-vinyl-imidazol-1-iium, 1-dodecyl-2-methyl-3-vinyl-imidazol-1-iium,
- 1-tetradecyl-2-methyl-3-vinyl-imidazol-1-iium, 1-hexadecyl-2-methyl-3-vinyl-imidazol-1-iium, and
- 1-octadecyl-2-methyl-3-vinyl-imidazol-1-iium.
Preferred imidazolium ions are 1-butyl-3-vinyl-imidazol-1-ium, 1-hexyl-3-vinyl-imidazol-1-ium, 1-octyl-3-vinyl-imidazol-1-ium, 1-decyl-3-vinyl-imidazol-1-ium, 1-dodecyl-3-vinyl-imidazol-1-ium, 1-tetradecyl-3-vinyl-imidazol-1-ium, 1-hexadecyl-3-vinyl-imidazol-1-ium, and 1-octadecyl-3-vinyl-imidazol-1-ium.

The anion An⁻ is any desired anion, preferably a halide or carboxylate anion, preferably a halide anion.

Anions other than carboxylate anion are described, for example, in WO 2007/090755, particularly from page 20 line 36 to page 24 line 37 therein, which is hereby made part of the present disclosure content by reference.

Suitable anions are more particularly those from

- the group of the halides and halogen-containing compounds of the following formulae: F⁻, Cl⁻, Br⁻, I⁻, BF₄⁻, PF₆⁻, AlCl₄⁻, Al₂Cl₇⁻, Al₃Cl₁₀⁻, AlBr₄⁻, FeCl₄⁻, BCIC₄⁻, SbF₆⁻, ZnCl₂⁻, SnCl₂⁻, CuCl₂⁻, CF₃SO₃⁻, (CF₃SO₂)₂N⁻, CF₃CO₂⁻, CCl₃CO₂⁻, CN⁻, SCN⁻, OCN⁻, NO₂⁻, NO₃⁻, N(CN)⁻, 1%;

- the group of the sulfates, sulfites, and sulfonates, of the following general formulae:

  S₀₄²⁻, HSO₃⁻, HSO₄⁻, R€OSO₃⁻, R€S₀₃⁻;

- the group of the phosphates, of the following general formulae:

  P₀₄³⁻, H₂P₀₄⁻, H₃P₀₄⁻, R€P₀₄⁻, R€R'P₀₄⁻;

- the group of the phosphonates and phosphinates, of the following general formula:

  R€HP₀₃⁻, R€R'R₀₂⁻, R€R'P₀₃⁻;

- the group of the phosphites, of the following general formulae:

  P₀₃³⁻, H₃P₀₃⁻, R€P₀₃⁻, R€R'R₀₃⁻, R€R'P₀₃⁻;

- the group of the phosphonites and phosphinites, of the following general formula:

  R€R'P₀₂⁻, R€HP₀₂⁻, R€R'PO⁻, R€HPO⁻;

- the group of the borates, of the following general formulae:

  B₀₃³⁻, H₂BO₃⁻, R€R'B₀₃⁻, R€HBO₃⁻, R€B₀₃²⁻, B(OR)₇(OR')(OR'')(OR'')⁻, B(HSO₄⁻)

- the group of the boronates, of the following general formulae:

  R€B₀₂⁻, R€R'B₀⁻;

- the group of the carbonates and carbonic esters, of the following general formulae:

  HCO₃⁻, CO₃²⁻, R€CO₃⁻;

- the group of the silicates and silicic acid esters, of the following general formulae:
$\text{Si}_4\text{O}_4^4$, $\text{HS}_1\text{O}_4^\text{3-}$, $\text{H}_2\text{S}_1\text{O}_4^\text{2-}$, $\text{H}_3\text{S}_1\text{O}_4^-$, $\text{R}_6\text{Si}_4^3\text{O}_4^4$, $\text{R}_6\text{R}_1^\text{R}_2^\text{Si}_4^3\text{O}_4^4$, $\text{HR}_6\text{Si}_4^2\text{O}_4^2$, $\text{H}_2\text{R}_6\text{Si}_4^4$.

the group of the alkyl silane and aryl silane salts, of the following general formulae:

\[ \text{R}_6\text{Si}_4^3\text{O}_4^4, \text{R}_6\text{R}_1^\text{R}_2^\text{Si}_4^3\text{O}_4^4, \text{R}_6\text{R}_1^\text{R}_2^\text{Si}_4^3\text{O}_4^4; \]

the group of the carboximides, bis(sulfonyl)imides, and sulfonylimides, of the following general formulae:

\[
\begin{align*}
\text{R}^\text{e} & \text{O} & \text{N}^- \\
\text{R}^\text{f} & \text{O} & \text{N}^- \\
\text{R}^\text{e} & \text{S} & \text{O} \\
\text{R}^\text{f} & \text{S} & \text{O} \\
\end{align*}
\]

the group of the methides, of the following general formula:

\[
\text{S}_2^2\text{O}_2^2\text{C} \text{R}^\text{g} \cdot \text{O} \cdot \text{S}_2^2\text{O}_2^2\text{R}^\text{f}
\]

the group of the alkoxydes and aryl oxides, of the following general formulae:

\[ \text{R}^\text{e}\text{O}^-; \]

the group of the halometallates, of the following general formula:

\[ [\text{M}, \text{Hal}]^s. \]

where M is a metal and Hal is fluorine, chlorine, bromine or iodine, r and t are positive integers, and indicate the stoichiometry of the complex, and s is a positive integer and indicates the charge of the complex;

the group of the sulfides, hydrogen sulfides, polysulfides, hydrogenpolysulfides, and thiolates, of the following general formulae:

\[ \text{S}^2, \text{HS}^-, [\text{Sv}]^2, [\text{HSv}], [\text{R}_6\text{S}]^-, \]

where v is a positive integer from 2 to 10; and

the group of the complex metal ions such as Fe(CN)$_6$$^{3-}$, Fe(CN)$_6$$^{4-}$, MnCV, Fe(CO)$_4$$^-$.

In the above anions, $\text{R}^\text{e}$, $\text{R}^\text{f}$, $\text{R}^\text{g}$, and $\text{R}^\text{h}$ independently of one another are in each case
hydrogen;
c1-c30 alkyl and its aryl-, heteroaryl-, cycloalkyl-, halogen-, hydroxyl-, amino-, carboxyl-, formyl-, -0-, -co- or -co -nh substituted components, such as, for example, methyl, ethyl, 1-propyl, 2-propyl, 1-buty1, 2-buty1, 2-methyl-1-propyl (isobutyl), 2-methyl-2-propyl (tert-butyl), 1-pentyl, 2-pentyl, 3-pentyl, 2-methyl-1-butyl, 2-methyl-2-butyl, 3-methyl-2-butyl, 2,2-dimethyl-1-propyl, 1-hexyl, 2-hexyl, 3-hexyl, 2-methyl-1-pentyl, 3-methyl-1-pentyl, 4-methyl-1-pentyl, 2-methyl-2-pentyl, 3-methyl-2-pentyl, 4-methyl-2-pentyl, 2-methyl-3-pentyl, 3-methyl-3-pentyl, 2,2-dimethyl-1-butyl, 2,3-dimethyl-1-butyl, 3,3-dimethyl-1-butyl, 2-ethyl-1-butyl, 2,3-dimethyl-2-butyl, 3,3-dimethyl-2-butyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, nonadecyl, icosyl, henicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, phenylmethyl (benzyl), diphenylmethyl, triphenylmethyl, 2-phenylethyl, 3-phenylpropyl, cyclopentylmethyl, 2-cyclopentylethyl, 3-cyclopentylpropyl, cyclohexylmethyl, 2-cyclohexylethyl, 3-cyclohexylpropyl, methoxy, ethoxy, formyl, acetyl or cₜF₂(qₜ-a)-(i-b)H₂a-b with q ≤ 30, 0 ≤ a ≤ q and b = 0 or 1 (for example, C₂F₃, C₂F₅, C₂H₂C₂C₂(q₂)F₂(q₂)₁, C₆F₃₇, C₈F₁₇, C₁₀F₂₁, C₁₂F₂₅);
c₃-c₁₂ cycloalkyl and its aryl-, heteroaryl-, cycloalkyl-, halogen-, hydroxyl-, amino-, carboxyl-, formyl-, -0-, -co- or -co-o -substituted components, such as, for example, cyclopentyl, 2-methy1-cyclopentyl, 3-methyl-1-cyclopentyl, cyclohexyl, 2-methyl-1-cyclohexyl, 3-methyl-1-cyclohexyl, 4-methyl-1-cyclohexyl or cₜF₂(qₜ-a)-(i-b)H₂a-b with q ≤ 30, 0 ≤ a ≤ q and b = 0 or 1;
c₂-c₃₀ alkenyl and its aryl-, heteroaryl-, cycloalkyl-, halogen-, hydroxyl-, amino-, carboxyl-, formyl-, -0-, -co- or -co-o -substituted components, such as, for example, 2-propenyl, 3-butenyl, cis-2-butenyl, trans-2-butenyl or cₜF₂(qₜ-a)-(i-b)H₂a-b with q ≤ 30, 0 ≤ a ≤ q and b = 0 or 1;
c₃-c₁₂ cycloalkenyl and its aryl-, heteroaryl-, cycloalkyl-, halogen-, hydroxyl-, amino-, carboxyl-, formyl-, -0-, -co- or -co-o -substituted components, such as, for example 3-cyclopentenyl, 2-cyclohexenyl, 3-cyclohexenyl, 2,5-cyclohexadienyl or cₜF₂(qₜ-a)-3(i-b)H₂a-3b with q ≤ 30, 0 ≤ a ≤ q and b = 0 or 1;
aryl or heteroaryl having 2 to 30 carbon atoms, and their alkyl-, aryl-, heteroaryl-, cycloalkyl-, halogen-, hydroxy-, amino-, carboxyl-, formyl-, -0-, -co- oder -co-o -substituted components, such as, for example, phenyl, 2-methylphenyl (2-tolyl), 3-methylphenyl (3-tolyl), 4-methylphenyl, 2-ethylphenyl, 3-ethylphenyl, 4-ethylphenyl, 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2,5-dimethylphenyl, 2,6-dimethylphenyl, 3,4-dimethylphenyl, 3,5-dimethylphenyl, 4-phenylphenyl, 1-naphthyl, 2-naphthyl, 1-pyrrolyl, 2-pyrrolyl, 3-pyrrolyl, 2-pyridinyl, 3-pyridinyl, 4-pyridinyl or C₆F₂₅ₐHa with 0 ≤ a ≤ 5; or
two radicals denote an unsaturated, saturated or aromatic ring which is unsubstituted or substituted by functional groups, aryl, alkyl, arylxy, alkyloxy, halogen, heteroatoms and/or heterocycles, and which is uninterrupted or interrupted by one or more oxygen and/or sulfur atoms and/or by one or more substituted or unsubstituted imino groups.

In the above anions, R⁰, R¹, R⁰, and Rʰ are preferably each independently of one another a hydrogen atom or a C₁ to C₁₂ alkyl group or a CF₃.

Examples of anions include chloride; bromide; iodide; thiocyanate; isothiocyanate; azide, hexafluorophosphate; trifluoromethanesulfonate; methanesulfonate; the carboxylates, especially formate; acetate; mandelate; carbonates, preferably methyl carbonate and n-butyl carbonate.
nitrate; nitrite; trifluoroacetate; sulfate; hydrogensulfate; methylsulfate; ethylsulfate; 1-propyl-
sulfate; 1-butylsulfate; 1-hexylsulfate; 1-octylsulfate; phosphate; dihydrogenphosphate; hydro-
gen-phosphate; C1-C4 dialkylphosphates; propionate; tetrachloroaluminate; Al2Cl7-; chlorozinc-
cate; chloroferrate; bis(trifluoromethylsulfonylimide); bis(pentafluoroethylsulfonylimide);
bis(methylsulfonfylimide); bis(p-tolylsulfonylimide); tris(trifluoromethylsulfonylmethide); bis(penta-
fluoroethylsulfonylmethide); p-tolylsulfonate; tetracarbonylcobaltate; dimethylene glycol mono-
methyl ether sulfate; olate; stearate; acrylate; methacrylate; maleate; hydrogencitrate; vinyl-
phosphonate; bis(pentafluoroethyl)phosphinate; borates such as bis[salicylato(2-)]borate, bis[oxalato(2-)]borate, bis[1,2-benzenediolato(2-)-0,0']borate, tetracyanoborate, tetrafluoro-
oborate; dicyanamide; tris(pentafluoroethyl)trifluorophosphate; tris(heptafluoropropyl)trifluoro-
ophosphate, cyclic arylphosphates such as pyrocathecol-phosphate (C6H402)P(0)-, and chlorocobaltate.

Particularly preferred anions are those from the group of the halides, especially chloride, bro-
mide, iodide, azide, thiocyanate, acetate, methyl carbonate, tetrafluoroborate, trifluoro-
thanesulfonate, methanesulfonate, bis(trifluoromethylsulfonylimide), ethylsulfate and diethyl
phosphate.

Examples of suitable vinyl-imidazolium compounds j) include:

Suitable flux enhancing monomers bearing quarternary ammonium or phosphonium groups k)
are for example selected from compounds of the general formula
An-, wherein
R₁ = H, methyl, preferably methyl,
X = O, NH preferably O,
Z = alkylene or polyoxyalkylene, preferably ethylene or polyoxyalkylene (polyalkylenglycol,
preferably poly(ethylene glycol), poly(propylene glycol); poly(2-alkyl-2-oxazoline), preferably poly(2-methyl-2-oxazoline), poly(2-ethyl-2-oxazoline));
L = N, P; preferably N;
R², R³, R⁴ = alkyl; preferably R² = R³ = methyl; R⁴ = preferably C₆ - C₂₂, more preferably C₈ - C₁₈, especially preferably C₆ - C₁₂, particularly preferably C₁₂;
A⁻: counterion, preferably bromide or iodide.

Examples of biocidal monomers bearing quaternary ammonium groups are for example

\[
\text{MAA-TMEA), (MAA-TMEA), (MA-DMP),}
\]

Further suitable flux enhancing monomers bearing quaternary ammonium groups are 3-methacryloyl aminopropyl-trimethyl ammoniumchloride, 2-methacryloyl oxyethyltrimethyl ammonium chloride, 2-Methacroyloxyethyl-trimethylammoniummethosulfate, 3-acrylamidopropyl trimethylammoniumchloride, trimethylvinylbenzyl-ammoniumchlorid, 2-acryloyloxyethyl-4-benzoylbenzyl-dimethyl ammoniumbromide, 2-acryloyloxyethyltrimethylammoniummethosulfate, N,N,N-Trimethylammonium-ethenebromide, 2- hydroxy N,N,N,N-trimethyl-3-[(2-methyl-1-oxo-2-propenyl)oxy]-ammoniumpropane chloride, N,N,N-Trimethyl-2-[(1-oxo-2-propenyl)oxy]-ammoniummethane-methylsulfate, N,N-Diethyl-N-methyl-2-[(1-oxo-2-propenyl)oxy]-ammoniummethane-methylsulfate,
Further suitable biocidal monomers bearing quaternary ammonium or phosphonium groups are for example selected from compounds of the general formula

\[
\begin{align*}
\text{R}_1 \quad \text{X} \quad \text{R}_2 \quad \text{X} \quad \text{R}_3 \\
\text{A}^n - 
\end{align*}
\]

wherein

- \(X = N, P\); preferably \(N\),
- \(\text{L}_1 = \text{alkylene or polyoxyalkylene, preferably ethylene or polyoxyalkylene (polyalkylenglycol, preferably poly(ethylene glycol), poly(propylene glycol); poly(2-alkyl-2-oxazoline), preferably poly(2-methyl-2-oxazoline), poly(2-ethyl-2-oxazoline))}\),
- \(\text{R}_i, \text{R}_2, \text{R}_3 = \text{independantly alkyl, aryl or aralkyl;}
\)
  - If \(X = N\): preferably \(\text{R}_1 = \text{R}_2 = \text{methyl}; \text{R}_3 = \text{preferably C}_6 - \text{C}_{22}\), more preferably \(\text{C}_6 - \text{C}_{12}\), especially preferably \(\text{C}_8 - \text{C}_{12}\), particularly preferably \(\text{C}_{12}\);
  - If \(X = P\): preferably \(\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{octyl, butyl or phenyl;}
\)
- \(\text{A}^n - \text{counterion, preferably halide, most preferably chloride, bromide or iodide.}\)

Examples of further suitable biocidal monomers bearing quaternary ammonium or phosphonium groups include:

Suitable diallyldialkylammoniumchlorides are for example diallyldimethylammoniumchloride (DADMAC).

Suitable alkylaminoalkyl (meth)acrylates and alkylaminoalkyl (meth)acrylamides are for example those according to formula (I)
wherein

\[ R_7 \text{ is } H \text{ or } CH_3, \]

\[ R_8 \text{ is } C_6 \text{alkyl bi-radical,} \]

\[ R_9 \text{ and } R_{10} \text{ are independently } H \text{ or } C_5 \text{alkyl radical which can be linear or branched,} \]

\[ X \text{ is a divalent radical of } -O-, \text{-NH-, or } -NR-n, \text{ wherein } R_{11} \text{ is } C_6 \text{alkyl.} \]

Preferred flux enhancing monomers according to formula (I) are 2-tert-butylaminoethyl (meth)acrylate (tBAEMA), 2-dimethylaminoethyl (meth)acrylate, 2-diethylaminoethyl (meth)acrylate, 3-dimethylaminopropyl (meth)acrylate, N-3-dimethylaminopropyl (meth)acrylamide, and N-3-diethylaminopropyl (meth)acrylamide with the most preferred being 2-tert-butylaminoethyl (meth)acrylate (tBAEMA).

Suitable Polylysine (meth)acrylamides or (meth)acrylates are for example epsilon-poly-L-lysine methacrylamide:

Suitable N-alkyl-4-vinylpridinium and alkyl-2-vinyl-pyridinium salts are for example the bromides and iodides of methyl in particular bromides and iodides N-methyl-4-vinylpridinium and N-methyl-2-vinyl-pyridinium.

Suitable biocidal monomers bearing guanide and biguanide groups are for example (Meth)acryloyl-modified Poly(hexamethylene biguanide)
wherein $R_1 = H$, methyl; $Y = H$, methyl.

Examples of suitable biocidal monomers bearing guanide and biguanide groups include:

\[
\text{wherein } R_1 = H, \text{ methyl; } Y = H, \text{ methyl.}
\]

Suitable halamines \(^1\) are for example chloramine
Flux enhancing monomers can be used alone, so that the coating is for example a homopolymer or homo oligomer.

Flux enhancing monomers can also be used in combination with other flux enhancing monomers.

In one embodiment of the invention, membranes comprise a coating comprising only antiadhesive monomers as flux enhancing monomers.

In one embodiment of the invention, membranes comprise a coating comprising only biocidal monomers as flux enhancing monomers.

In one embodiment of the invention, membranes comprise a coating comprising only one antiadhesive monomer and no biocidal monomer as flux enhancing monomer.

In one embodiment of the invention, membranes comprise a coating comprising only one biocidal monomer and no antiadhesive monomer as flux enhancing monomer.

In one embodiment of the invention, membranes comprise a coating comprising at least one antiadhesive and at least one biocidal monomers as flux enhancing monomers.

Flux enhancing monomers can also be used in combination with further monomers having no flux enhancing effect.

Suitable further monomers are monomers comprising an ethylenically unsaturated double bond that by themselves do not qualify as flux enhancing monomers a) to q) as defined above.

Examples of further monomers include acrylic acid, methacrylic acid, alkyl (meth)acrylate and alkyl (meth)acrylamide, in particular methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, lauryl (meth)acrylate, ethylhexyl (meth)acrylate, 4-hydroxy butyl (meth)acrylate, phenoxyethyl (meth)acrylate, styrene, alkyl vinyl ether, in particular, methyl vinyl ether, ethyl vinyl ether, n-butyl vinyl ether, 4-hydroxybutyl vinyl ether, vinyl acetate, acrylic nitrile, maleic anhydride.

When reference is made in this application to embodiments of membranes comprising certain flux enhancing monomers or combinations of flux enhancing monomers, this shall be understood to include membranes or filtration systems that have been obtained using a composition comprising the respective flux enhancing monomers or combinations of flux enhancing monomers.

In one embodiment of the invention, membranes according to the invention comprise at least one antiadhesive and/or biocidal monomer, with the proviso that said at least one antiadhesive and/or biocidal monomer is different from antiadhesive monomers a) as defined above.

In one embodiment of the invention, membranes according to the invention comprise at least one antiadhesive and/or biocidal monomer, with the proviso that said at least one antiadhesive and/or biocidal monomer is not an acrylic ester.
In one embodiment of the invention, membranes according to the invention comprise at least one antiadhesive monomer a) as defined above.

5 In one embodiment of the invention, membranes according to the invention comprise at least one antiadhesive monomer b)-i) as defined above.

In one embodiment of the invention, membranes according to the invention comprise at least one antiadhesive monomer a) as defined above in combination with at least one antiadhesive and/or biocidal monomer selected from monomers b) to q) as defined above.

10 In one embodiment of the invention, membranes according to the invention comprise at least one antiadhesive monomer b)-i) as defined above in combination with at least one antiadhesive and/or biocidal monomer selected from monomers c) to q) as defined above.

15 In one embodiment of the invention, membranes according to the invention comprise at least one antiadhesive monomer a) as defined above in combination with at least one antiadhesive and/or biocidal monomer selected from monomers b) to q) as defined above.

20 In one embodiment of the invention, membranes according to the invention comprise at least one antiadhesive monomer b) to i) as defined above.

25 In one embodiment, coatings comprised in membranes according to the invention comprise 5 to 95 % by weight of flux enhancing monomers and 95 to 5 % by weight of further monomers relative to the overall mass of the coating.

In one embodiment of the invention, membranes according to the invention comprise tBAEMA in combination with at least one flux enhancing monomer comprising at least one quaternary ammonium group.

In one embodiment of the invention, membranes according to the invention comprise tBAEMA in combination with at least one halamine.

In another embodiment, membranes according to the invention comprise at least one flux enhancing monomer comprising at least one quaternary ammonium group is used in combination with at least one halamine.

35 In one embodiment, membranes according to the invention comprise tBAEMA in combination with at least one flux enhancing monomer comprising at least one quaternary ammonium group and with at least one halamine.

40 In one embodiment, membranes according to the invention comprise HEMA (2-Hydroxyethyl methacrylate) and QAEMA ([2-(methacryloyloxy)ethyl] trimethylammonium chloride).
In another embodiment membranes according to the invention comprise HEMA (2-Hydroxyethyl methacrylate), QAEMA ([2-(methacryloyloxy)ethyl trimethylammonium chloride) and acrylic acid.

In a preferred embodiment, membranes according to the invention comprise vinyl pyrrolidone in combination with at least one biocidal monomer j), k), l), m), n), o), p) or q).

The at least one flux enhancing monomer can be applied on the base membrane neat or in solution with a solvent. Depending on the nature of the flux enhancing monomers and the further monomers used, different solvents can be used. Examples of suitable solvents are water, THF, dioxane, alcohols or mixtures thereof. Preferred solvents are water or alcohols, in particular water or isopropanol or mixtures thereof. In a preferred embodiment of the present invention, flux enhancing monomers and the further monomers are applied in solution at a concentration in the range of from 0.01 to 70 % by weight, more preferably in the range of from 0.5 to 60 % by weight, based on the overall content of flux enhancing and further monomers.

In one embodiment, the composition comprising the at least one flux enhancing monomer optionally comprises further additives like dispersants. Further additives that can be comprised are generally known in the art.

Said composition is then cured.

In one embodiment, said composition does not comprise a radical initiator.

In one embodiment, said composition comprises one or more radical initiators.

The one or more radical initiators can be thermal initiators such as 2,2-azobisisobutyronitrile or photoinitiators. Preferably, the one or more radical initiators are photoinitiators as they are for example disclosed in WO 08/132037A2 on p. 13, ln 5 to p.19, ln 13.

In another embodiment of the invention, said composition is cured in a radiation induced radical polymerization, for example using UV light.

In another embodiment of the invention, said composition is cured thermally.

The coating normally has a thickness of 1 nm to 100 µη, preferably 2 nm to 1 µη, more preferably 5 nm to 0.1 µη.
Membranes according to the invention are normally obtained by a process comprising the following steps:

A) oxidizing the surface of a base membrane,
B) treatment of the oxidized surface with a composition comprising at least one flux enhancing monomer,
C) curing said composition to form a coating.

Steps A), B) and C) are carried out as disclosed above. Normally, steps A), B) and C) are carried out consecutively.

In one embodiment, said composition comprises a solvent. In another embodiment, said composition does not comprise a solvent.

Preferred processes for oxidizing the surface are corona and oxygen containing plasma treatment.

Another aspect of the invention is a process for making membranes comprising the steps

A) oxidizing the surface of a base membrane,
B) treatment of the oxidized surface with a composition comprising at least one flux enhancing monomer,
C) curing said composition to form a coating.

Another aspect of the invention is a method of improving the flux through membranes, which comprises the following steps:

A) oxidizing the surface of a base membrane,
B) treatment of the oxidized surface with a composition comprising at least one flux enhancing monomer,
C) curing said composition to form a coating.

Another aspect of the invention is a composition comprising at least one flux enhancing monomer selected from

a) esters of (meth)acrylic acid polyols
b) vinyl ethers of polyols
c) hydrophilic macromonomers different from monomers a) and b)
d) N-vinyl compounds
e) Low molecular weight hydrophilic (meth)acrylamides
f) (meth)acrylates or (meth)acrylamides bearing epoxy groups
g) monomers having a betain structure
h) hydrophilic monomers different from those mentioned under a) to g).
i) ion pair comonomers
j) vinyl-imidazolium compounds
k) ethylenically unsaturated monomers bearing quarternary ammonium or phosphonium groups
l) diallyldialkylammonium chlorides
m) alkylaminoalkyl (meth)acrylates and alkylaminoalkyl (meth)acrylamides
n) Polylysine (meth)acrylamides or (meth)acrylates
o) alkyl-4-vinylpridinium and alkyl-2-vinyl-pyridinium salts, in particular bromides and iodides
p) ethylenically unsaturated monomers bearing guanide and biguanide groups
q) halamines.

For compositions according to the invention the same embodiments and preferred embodiments with respect to the choice of flux enhancing monomers apply as for membranes according to the invention.

In one embodiment of the invention, compositions according to the invention comprise at least one antiadhesive and/or biocidal monomer, with the proviso that said at least one antiadhesive and/or biocidal monomer is different from antiadhesive monomers a) as defined above.

In one embodiment of the invention, compositions according to the invention comprise at least one antiadhesive and/or biocidal monomer, with the proviso that said at least one antiadhesive and/or biocidal monomer is not an acrylic ester.

In one embodiment of the invention, compositions according to the invention comprise at least one antiadhesive monomer a) as defined above.

In one embodiment of the invention, compositions according to the invention comprise at least one antiadhesive monomer b)-i) as defined above.

In one embodiment of the invention, compositions according to the invention comprise at least one antiadhesive monomer from b)-g) as defined above.

In one embodiment of the invention, compositions according to the invention comprise at least one antiadhesive monomer a) as defined above in combination with at least one antiadhesive and/or biocidal monomer selected from monomers b) to q) as defined above.

In one embodiment of the invention, compositions according to the invention comprise at least one antiadhesive monomer a) as defined above in combination with at least one antiadhesive and/or biocidal monomer selected from monomers b) to g) and/or i) to q) as defined above.

In one embodiment of the invention, compositions according to the invention comprise at least one antiadhesive monomer b)-i) as defined above in combination with at least one antiadhesive and/or biocidal monomer selected from monomers c) to q) as defined above.
In one embodiment of the invention, compositions according to the invention comprise at least one antiadhesive monomer a) as defined above in combination with at least one antiadhesive and/or biocidal monomer selected from monomers b) to q) as defined above.

In one embodiment of the invention, compositions according to the invention comprise at least one antiadhesive monomer b) to i) as defined above.

In one embodiment, compositions according to the invention comprise 5 to 95 % by weight of flux enhancing monomers and 95 to 5 % by weight of further monomers relative to the overall mass of the coating.

In one embodiment of the invention, compositions according to the invention comprise tBAEMA in combination with at least one flux enhancing monomer comprising at least one quaternary ammonium group.

In one embodiment of the invention, compositions according to the invention comprise tBAEMA in combination with at least one halamine.

In another embodiment, compositions according to the invention comprise at least one flux enhancing monomer comprising at least one quaternary ammonium group in combination with at least one halamine.

In one embodiment, compositions according to the invention comprise tBAEMA in combination with at least one flux enhancing monomer comprising at least one quaternary ammonium group and with at least one halamine.

In one embodiment, compositions according to the invention comprise HEMA (2-Hydroxyethyl methacrylate) and QAEMA ([2-(methacryloyloxy)ethyl] trimethylammonium chloride).

In another embodiment compositions according to the invention comprise HEMA (2-Hydroxyethyl methacrylate), QAEMA ([2-(methacryloyloxy)ethyl] trimethylammonium chloride) and acrylic acid.

In a preferred embodiment, compositions according to the invention comprise vinyl pyrrolidone in combination with at least one biocidal monomer j), k), l), m), n), o), p) or q).

Another aspect of the invention is the use of a composition comprising at least one flux enhancing monomer for improving the flux of membranes, or for imparting biocidal and/or antiadhesive properties to a membrane.
Filtration systems and membranes according to the invention show improved properties with respect to the decrease of flux over time and their fouling and particularly biofouling properties. Filtration systems and membranes according to the invention are easy and economical to make. Filtration systems and membranes according to invention can be made using aqueous or alcoholic systems and are thus environmentally friendly. Furthermore, leaching of toxic substances is not problematic with membranes according to the invention. Membranes according to the invention have a long lifetime and allow for the treatment of water. Membranes according to the invention can be cleaned more easily and with lower amounts of cleaning agents.

Membranes according to the invention have longer cleaning cycles meaning that they need to be cleaned less often than membranes known from the art.

In a preferred embodiment, membranes according to the invention are used for the treatment of sea water or brackish water.

In one preferred embodiment of the invention, membranes according to the invention, particularly RO, FO or NF membranes are used for the desalination of sea water or brackish water.

Membranes according to the invention, particularly RO, FO or NF membranes are used for the desalination of water with a particularly high salt content of for 3 to 8 % by weight. For example membranes according to the invention are suitable for the desalination of water from mining and oil/gas production and fracking processes, to obtain a higher yield in these applications.

Different types of membrane according to the invention can also be used together in hybrid systems combining for example RO and FO membranes, RO and UF membranes, RO and NF membranes, RO and NF and UF membranes, NF and UF membranes.

In another preferred embodiment, membranes according to the invention, particularly NF, UF or MF membranes are used in a water treatment step prior to the desalination of sea water or brackish water.

In another preferred embodiment membranes according to the invention, particularly NF, UF or MF membranes are used for the treatment of industrial or municipal waste water.

Membranes according to the invention, particularly RO and/or FO membranes can be used in food processing, for example for concentrating, desalting or dewatering food liquids (such as fruit juices), for the production of whey protein powders and for the concentration of milk, the UF permeate from making of whey powder, which contains lactose, can be concentrated by RO, wine processing, providing water for car washing, making maple syrup, during electrochemical production of hydrogen to prevent formation of minerals on electrode surface, for supplying water to reef aquaria.
Membranes according to the invention, particularly UF membranes can be used in medical applications like dialysis and other blood treatments, food processing, concentration for making cheese, processing of proteins, desalting and solvent-exchange of proteins, fractionation of proteins, clarification of fruit juice, recovery of vaccines and antibiotics from fermentation broth, laboratory grade water purification, drinking water disinfection (including removal of viruses), removal of endocrines and pesticides combined with suspended activated carbon pretreatment.

Membranes according to the invention, particularly RO, FO, NF membranes can be used for rehabilitation of mines, homogeneous catalyst recovery, desalting reaction processes.

Membranes according to the invention, particularly NF membranes, can be used for separating divalent ions or heavy and/or radioactive metal ions, for example in mining applications, homogeneous catalyst recovery, desalting reaction processes.
Examples

Example 1
A reverse osmosis membrane comprising a polyamide separation layer is subjected for 2 min to oxygen plasma pre-treatment using a Honle UVACUBE 100 plasma generator equipped with a mercury irradiation source and a quartz filter. Then, a 1% by weight solution of polyethylene glycol (600) diacrylate, sold as SR-610 by Sartomer Company, in isopropanol is applied to the oxidized surface of the membrane using a 30 µm draw-down bar. The membrane is stored until the isopropanol has evaporated. The dry treated membrane is irradiated under nitrogen atmosphere with approximately 1400 mJ/cm² at an 1ST irradiation unit.

Example 2
The process of example 1 is repeated, except that instead of the 1% by weight solution of polyethylene glycol (600) diacrylate, a 1% by weight solution of an equimolar mixture of polyethylene glycol (600) diacrylate and polyethylene glycol (600) di(phenylglyoxylate), which is prepared as described in example 3 of WO 06/067061, is used.
Claims

1. Filtration system comprising at least one membrane, wherein at least one component or at least one part of a component of the filtration system has been obtained by a process comprising the following steps:
   A) oxidizing the surface of said component or part of a component
   B) treatment of the oxidized surface with a composition comprising at least one flux enhancing monomer,
   C) curing said composition to form a coating,

wherein said at least one flux enhancing monomer is an antiadhesive monomer selected from
a) esters of (meth)acrylic acid polyols, wherein (meth)acrylic esters with polyalkylene-oxides are excluded;
b) vinyl ethers of polyols;
c) hydrophilic macromonomers different from monomers a) and b);
d) N-vinyl compounds;
e) Low molecular weight hydrophilic (meth)acrylamides;
f) (meth)acrylates or (meth)acrylamides bearing epoxy groups;
g) monomers having a betain structure;
h) hydrophilic monomers selected from hydroxyethyl-(meth)acrylate, vinyl alcohol, (Meth)acryloyl and (meth)acrylamide-modified mono- and oligosaccharides,

```
R1
    O
|   X
\---S==O
```

with \( R_1 = \text{H, Methyl}; X = 0, \text{NH}; \)

i) Ion pair comonomers;

   and/or a biocidal monomer selected from
j) vinyl-imidazolium compounds;
k) ethylenically unsaturated monomers bearing quarternary ammonium or phosphonium groups;
l) diallyldialkylammoniumchlorides;
m) alkylaminoalkyl (meth)acrylates and alkylaminoalkyl (meth)acrylamides;
n) Polysine (meth)acrylamides or (meth)acrylates;
o) alkyl-4-vinylpirdinium and alkyl-2-vinyl-pyridinium salts, in particular bromides and iodides;
p) ethylenically unsaturated monomers bearing guanide and biguanide groups;
q) Halamines.

2. Filtration system according to claim 1, wherein said composition comprises at least one monomer according to formula (I)
wherein

\[
R_7 \text{ is } H \text{ or } CH_3, \\
R_s \text{ is } C_1-C_5 \text{alkyl bi-radical,} \\
R_g \text{ and } R_{io} \text{ are independently } H \text{ or } d-C_5 \text{alkyl radical which can be linear or branched,} \\
\text{and } X \text{ is a divalent radical of } -O-, \text{-NH- or } -NR_n, \text{ wherein } R_n \text{ is } C_1-C_6 \text{alkyl.}
\]

3. Filtration system according to any of 1 to 2, wherein said composition comprises 2-tert-butylaminoethyl (meth)acrylate or a combination of 2-Hydroxyethyl methacrylate and [2-(methacryloyloxy)ethyl] trimethylammonium chloride.

4. Filtration system according to any of 1 to 3, wherein said component or part of a component is selected from a membrane, the separating layer of a membrane, a support layer of a membrane, a fabric layer of a membrane, the feed spacer of a membrane, the permeate spacer of a membrane, the casing of the filtration system, the piping of the filtration system, the joints of the filtration system, manifolds of the filtration system.

5. Membrane, obtained by a process comprising the following steps:

A) oxidizing the surface of a base membrane
B) treatment of the oxidized surface with a composition comprising at least one flux enhancing monomer,
C) curing said composition to form a coating,
wherein said at least one flux enhancing monomer is an antiadhesive monomer selected from
a) esters of (meth)acrylic acid polyols, wherein (meth)acrylic esters with polyalkylene-oxides are excluded;
b) vinyl ethers of polyols;
c) hydrophilic macromonomers different from monomers a) and b);
d) N-vinyl compounds;
e) Low molecular weight hydrophilic (meth)acrylamides;
(meth)acrylates or (meth)acrylamides bearing epoxy groups;
monomers having a betain structure;
hydrophilic monomers selected from hydroxyethyl-(meth)acrylate, vinyl alcohol, (Meth)acyroyl and (meth)acrylamide-modified mono- and oligosaccharides,

\[
\begin{align*}
\text{R}_1 \bigg(\text{X} \bigg(\text{L} \bigg) \text{SO}_3^- \bigg),
\end{align*}
\]
with \(R_1 = \text{H}, \text{Methyl}; \text{X} = \text{O}, \text{NH};\)
ion pair comonomers;

and/or a biocidal monomer selected from
vinyl-imidazolium compounds;
ethylenically unsaturated monomers bearing quarternary ammonium or phosphonium groups;
diallyldialkylammoniumchlorides;
alkylaminoalkyl (meth)acrylates and alkylaminoalkyl (meth)acrylamides;
Polylysine (meth)acrylamides or (meth)acrylates;
alkyl-4-vinylpridinium and alkyl-2-vinyl-pyridinium salts, in particular bromides and iodides;
ethylenically unsaturated monomers bearing guanide and biguanide groups;
halamines.

6. Membrane according to claim 5, wherein said composition comprises at least one monomer according to formula (I)

\[
\begin{align*}
\text{R}_7 \bigg(\text{X} \bigg(\text{R}_8 \bigg) \text{R}_9 \bigg) \text{N} \bigg(\text{R}_{10} \bigg),
\end{align*}
\]
wherein
\(R_7\) is \(\text{H}\) or \(\text{CH}_3\),
\(R_s\) is \(\text{C}_1-\text{C}_2\)alkyl bi-radical,
\(R_9\) and \(R_{10}\) are independently \(\text{H}\) or \(\text{d-}\text{Csalkyl}\) radical which can be linear or branched, and \(X\) is a divalent radical of \(-\text{O-}, -\text{NH-} or -\text{NR}_n\), wherein \(R_n\) is \(\text{C}_1-\text{C}_6\)alkyl.
7. Membrane according to any of 5 to 6, wherein said composition comprises 2-tert-
butylaminoethyl (meth)acrylate or a combination of 2-Hydroxyethyl methacrylate and [2-
(methacryloyloxy)ethyl] trimethylammonium chloride.

8. Membrane according to any of 5 to 7, wherein the oxidizing of the surface is carried out
by treatment of the surface with corona discharge, plasma, flame, ozone, electron beam,
actinic irradiation in particular X-ray, UV or gamma radiation, preferably by treatment
with corona discharge or plasma, particularly oxygen containing plasma.

9. Membrane according to any of 5 to 8, wherein the oxidizing of the surface is carried out
by treatment of the surface with an oxidative immersion bath such as a bath containing
chromium sulfuric acid, sulfuric acid, hydrogen peroxide, ammonium hydroxide, persulfu-
rac acid, peroxo disulfuric acid, phosphoric acid, hypophosphorous acid, phosphorous
acid, pyrophosphoric acid, triphosphoric acid, perphosphoric acid, permonophosphoric
acid or mixtures thereof.

10. Membrane according to any of 5 to 9, wherein said composition comprises at least one
antiadhesive monomer and at least one biocidal monomer.

11. Membrane according to any of 5 to 10, wherein said base membrane or the separating
layer of said base membrane comprises as main component a polymer selected from
polyarylene ether, polysulfone, polyethersulfones (PES), polyphenylenesulfone, polyam-
ides (PA), polyvinylalcohol (PVA), Cellulose Acetate (CA), Cellulose Triacetate (CTA),
CA-triacetate blend, Cellulose ester, Cellulose Nitrate, regenerated Cellulose, aromatic
aromatic/aliphatic or aliphatic Polyamide, aromatic, aromatic/aliphatic or aliphatic Poly-
mide, Polybenzimidazole (PBI), Polybenzimidazolone (PBIL), Polyacrylonitrile (PAN),
PAN-poly(vinyl chloride) copolymer (PAN-PVC), PAN-methallyl sulfonate copolymer,
Polysulfone, Poly(dimethylphenylene oxide) (PPO), Polycarbonate, Polyester, Polytetra-
fluoroethylene PTFE, Poly(vinylidene fluoride) (PVDF), Polypropylene (PP), Polyelectro-
lyte complexes, Poly(methyl methacrylate) PMMA, Polydimethylsiloxane (PDMS), aro-
matic, aromatic/aliphatic or aliphatic polyimide urethanes, aromatic, aromatic/aliphatic or
aliphatic polyamidimides, crosslinked polyimides or mixtures thereof.

12. Membrane according to any of 5 to 11, wherein the membrane is a thin film composite
membrane.
13. Membrane according to any of 5 to 12, in which said membrane is suitable as a reverse osmosis membrane, forward osmosis membrane, nanofiltration membrane, ultrafiltration membrane and/or microfiltration membrane.

14. Process for making a membrane according to any of 5 to 13, comprising the following steps:
   A) oxidizing the surface of a base membrane,
   B) treatment of the oxidized surface with a composition comprising at least one flux enhancing monomer,
   C) curing said composition to form a coating.

   wherein said at least one flux enhancing monomer is an antiadhesive monomer selected from
   a) esters of (meth)acrylic acid polyols, wherein (meth)acrylic esters with polyalkylene-oxides are excluded;
   b) vinyl ethers of polyols;
   c) hydrophilic macromonomers different from monomers a) and b);
   d) N-vinyl compounds;
   e) Low molecular weight hydrophilic (meth)acrylamides;
   f) (meth)acrylates or (meth)acrylamides bearing epoxy groups;
   g) monomers having a betain structure;
   h) hydrophilic monomers selected from hydroxyethyl-(meth)acrylate, vinyl alcohol,
      (Meth)acryloyl and (meth)acrylamide-modified mono- and oligosaccharides,
      \[
      \begin{align*}
      &R_1= \text{H, Methyl; } X=0, \text{ NH;} \\
      &\text{with } R_1= \text{H, Methyl; } X=0, \text{ NH;} \\
      &\text{and/or a biocidal monomer selected from} \\
      &\text{j) vinyl-imidazolium compounds;} \\
      &k) \text{ethylenically unsaturated monomers bearing quarternary ammonium or phosphonium groups;} \\
      &l) \text{diallyldialkylammoniumchlorides;} \\
      &m) \text{alkylaminoalkyl (meth)acrylates and alkylaminoalkyl (meth)acrylamides;} \\
      &n) \text{Polylsine (meth)acrylamides or (meth)acrylates;} \\
      &o) \text{alkyl-4-vinylpridinium and alkyl-2-vinyl-pyridinium salts, in particular bromides and iodides;} \\
      &p) \text{ethylenically unsaturated monomers bearing guanide and biguanide groups;} \\
      &q) \text{halamines.}
      \end{align*}
\]
15. Process according to claim 12, wherein said composition comprises at least one monomer according to formula (I)

\[
\begin{align*}
\text{R}_7 \quad \text{O} \\
\text{X} \quad \text{R}_8 \\
\text{N} \quad \text{R}_9 \quad \text{R}_{10}
\end{align*}
\]

wherein
\(\text{R}_7\) is H or CHs,
\(\text{R}_8\) is C1-Csalkyl bi-radical,
\(\text{R}_9\) and \(\text{R}_{10}\) are independently H or d-Csalkyl radical which can be linear or branched,
and \(X\) is a divalent radical of -O-, -NH- or -NR\(n\), wherein \(R_n\) is C1-C6alkyl.

16. Process according to any of claims 12 to 13, wherein said composition comprises 2-tert-butylaminoethyl (meth)acrylate or a combination of 2-Hydroxyethyl methacrylate and [2-(methacryloyloxy)ethyl] trimethylammonium chloride.

17. Use of membranes according to at least one of the preceding claims or of membranes made according to at least one of the preceding claims for the treatment of water, for the desalination of sea water or brackish water, for the treatment of industrial or municipal wastewater, in food processing or in medical applications like dialysis.
INTERNATIONAL SEARCH REPORT

INTERNATIONAL APPLICATION No
PCT/EP2013/076743

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01D67/00 B01D69/12 B01D71/52 B01D71/56 B01D65/08

ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C. See patent family annex.

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Date of the actual completion of the international search: 21 March 2014

Date of mailing of the international search report: 01/04/2014

Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040;  
Fax: (+31-70) 340-3016

Authorized officer: Verissimo, Sonia
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<td>Zou L ET AL: &quot;Surface hydrophilic modification of R0 membranes by plasma polymerization for low organic fouling&quot;, JOURNAL OF MEMBRANE SCIENCE, ELSEVIER SCI ENTI FIC PUBL. COMPANY, AMSTERDAM, NL, vol. 369, no. 1, 10 December 2010 (2010-12-10), pages 420-428, XP028134477, ISSN: 0376-7388, DOI: 10.1016/J.MEMSCI.2010.12.023 [retrieved on 2010-12-17] cited in the application on abstract page 421, column 1, paragraph 4 paragraphs [02.1] - [2.2.2], [03.2] the whole document</td>
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