

CLAIMS

1. A polymeric semipermeable membrane comprising a non-cross-linked base polymer having reactive pendant moieties, said base polymer being modified by forming a cross-linked skin onto a surface thereof, said skin being formed by a cross-linking reaction of reactive pendant moieties on said surface with an oligomer or another polymer; wherein at least one portion of said cross-linked skin is covalently bonded to a nanofiltration (NF) layer, wherein said nanofiltration layer comprises:

a. at least one di-, tri- or tetra-halo substituted diazine or triazine-containing monomer, oligomer or polymer, and

a.b.at least one multifunctional amine having a molecular weight in the range of 400 to 750,000,

provided that at least one of the di-, tri- or tetra-halo substituted diazine or triazine-containing monomer, oligomer or polymer is not a di- or triazine monomer which is substituted only by Cl.;

2. The polymeric semipermeable membrane according to claim 1, wherein additionally comprising a woven or non-woven textile substrate underlying said base polymer.

~~3. The polymeric semipermeable membrane according to claim 1, wherein at least one portion of said cross-linked skin is hydrophilic, hydrophobic and a combination thereof.~~

~~4. The polymeric semipermeable membrane according to claim 1, wherein said reactive pendant moieties are a species selected from the group consisting of halogen, nitrile and a combination thereof.~~

~~5.3. The polymeric semipermeable membrane according to claim 1, wherein said base polymer is selected from the group consisting of polyvinylidene fluoride, polyacrylonitrile polymer and any copolymers thereof.~~

~~6.4. The polymeric semipermeable membrane according to claim 1, wherein said base polymer preferably comprises polyacrylonitrile.~~

~~7. The polymeric semipermeable membrane according to claim 1, wherein said reactive pendant moieties are added to the outer surface of said base polymer by a chemical process selected from the group consisting of oxidation reaction, ozonation reaction, chlorosulfonation reaction and any combination thereof.~~

~~8. The polymeric semipermeable membrane according to claim 1, wherein said base polymer comprises a plurality of repeating sulfone groups.~~

~~9. The polymeric semipermeable membrane according to claim 1, wherein said base polymer is selected from a group consisting of polysulfones, polyether sulfones, polyphenylene sulfones and any combination thereof.~~

~~10. The polymeric semipermeable membrane according to claim 1, wherein said base polymer is preferably polyether sulfone.~~

~~11. The polymeric semipermeable membrane according to claim 7, wherein said chlorosulfonation reaction is carried out in a solvent comprising glacial acetic acid or a mixture of acetic acid with at least one non-polar solvent.~~

~~12.5. The polymeric semipermeable membrane according to claim 1, wherein said another polymer is selected from the group consisting of polyethylenimine, polyvinyl alcohol and a combination thereof.~~

~~13.6. The polymeric semipermeable membrane according to claim 1, wherein said another polymer is preferably polyethylenimine.~~

~~14.7. The polymeric semipermeable membrane according to claim 1, wherein said polymeric semipermeable membrane is an ultrafiltration (UF) membrane or a microfiltration (MF) membrane.~~

~~15. The polymeric semipermeable membrane according to claim 1, wherein said cross-linking reaction is effected at elevated temperature utilizing a solution of said oligomer or another polymer, optionally followed by a drying step at elevated temperature.~~

~~16. The polymeric semipermeable membrane according to claim 15, wherein said drying step is effected by air drying at elevated temperature.~~

~~17.8. The polymeric semipermeable membrane according to claim 1, wherein said polymeric semipermeable membrane is preferably a polyacrylonitrile ultrafiltration membrane and said another polymer is preferably polyethylenimine.~~

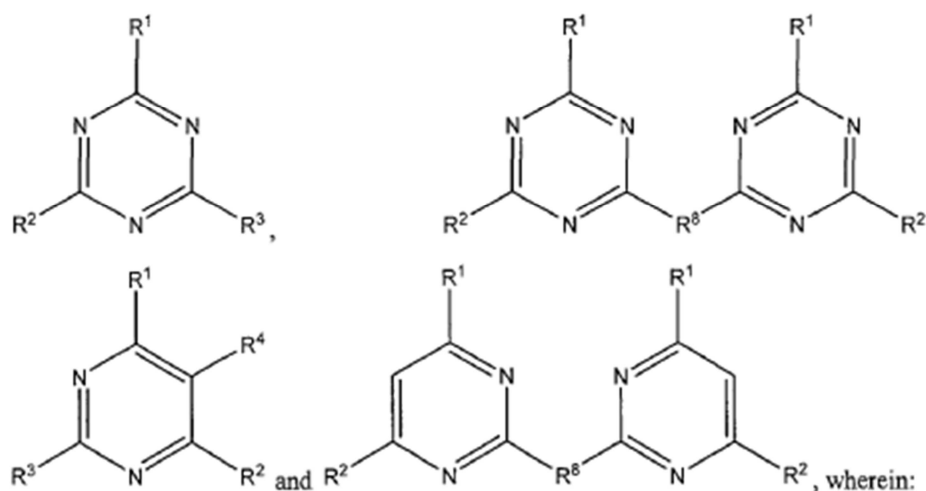
~~18. The polymeric semipermeable membrane according to claim 1, wherein said polymeric semipermeable membrane is a polyvinylidene fluoride ultrafiltration membrane and said another polymer is polyethylenimine.~~

~~19. The polymeric semipermeable membrane according to claim 1, characterized by having improved stability compared to the non-modified membrane in an aggressive environment including at least one of the group consisting of acid media, basic media, organic solvents, oxidizing species, elevated temperatures and elevated pressure.~~

~~20. The polymeric semipermeable membrane according to claim 1, wherein said nanofiltration (NF) layer is formed from:~~

- ~~(i) — at least one di-, tri- or tetra-halo-substituted diazine or triazine-containing monomer, oligomer or polymer, and~~
- ~~(ii) — at least one multifunctional amine having a molecular weight in the range of 400 to 750,000, provided that at least one of the di-, tri- or tetra-halo-substituted diazine or triazine-containing monomer, oligomer or polymer is not a di- or triazine monomer which is substituted only by chloro.~~

~~21.9.~~ The polymeric semipermeable membrane of claim ~~20~~ 1, wherein said diazine or triazine-containing monomer or oligomer is selected from the group consisting of



R¹ is independently selected at each occurrence from bromo, chloro, iodo, fluoro, -NHR⁵, -OR⁵ and SR⁵, wherein R⁵ is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl;

R² is independently selected at each occurrence from bromo, chloro and fluoro;

R³ is independently selected at each occurrence from bromo, chloro, fluoro,

-NHR⁵, -OR⁵ and SR⁵, wherein R⁵ is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl;

R⁴ is selected from H, bromo, chloro, fluoro, -NHR⁵, -OR⁵ and SR⁵, wherein R⁵ is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl; and

R⁸ is independently at each occurrence -NH-A-NH-, wherein A is selected from C₁₋₂₀ aliphatic moieties, C₆₋₁₀ aromatic moieties, and combinations thereof; provided that at least two occurrences, R¹, R², R³ and R⁴, taken together, are selected from bromo, chloro and fluoro, and further provided that when both R¹ and R² on a single ring are Cl, at least one of R³ and R⁴ is not Cl.

~~22.10.~~ The polymeric semipermeable membrane of claims ~~20 to 21~~ 1, wherein said multifunctional amine has a molecular weight of in the range of 400 to 250,000.

~~23.11.~~ The polymeric semipermeable membrane of ~~any of claims 20 to 22~~ 1, wherein said multifunctional amine is selected from the group consisting of polyethylenimine, polyvinylamine, polyvinylanilines, polybenzylamines, polyvinylimidazolines, and amine-modified polyepihalohydrins.

~~24.12.~~ The polymeric semipermeable membrane of any of claims 1 to ~~1123~~ 1, wherein further comprising supplemental cross-linker selected from the group consisting of 2,4,6-trichloro-s-triazine, 4,6-dichloro-2-sodium p-sulfoanile-s-triazine (4,6-dichloro-2-p-

anilinesulfonic acid sodium salt-s-triazine), 4,6-dichloro-2-diethanolamine-s-triazine and 4,6-dichloro-2-~~athine~~amino-s-triazine.

~~25.13.~~ A method of forming a polymeric semipermeable membrane comprising the steps of: providing a non-cross-linked base polymer having reactive pendant moieties; and effecting a cross-linking reaction between the reactive pendant moieties on a surface of said base polymer with an oligomer or another polymer, thereby forming a cross-linked skin on said surface of said base polymer; wherein said method additionally comprising steps of forming a nanofiltration (NF) layer over at least a portion of said cross-linked skin~~2~~, wherein said nanofiltration layer comprises:

a. at least one di-, tri- or tetra-halo substituted diazine or triazine-containing monomer, oligomer or polymer, and

a.b.at least one multifunctional amine having a molecular weight in the range of 400 to 750,000,

provided that at least one of the di-, tri- or tetra-halo substituted diazine or triazine-containing monomer, oligomer or polymer is not a di- or triazine monomer which is substituted only by Cl.

~~26.14.~~ The method according to claim ~~25~~13, wherein said step of forming further comprising step of covalently bonding said NF layer to said cross-linked skin.

~~27. The method according to claim 25, wherein said method additionally comprising step of providing said reactive pendant moieties selected from the group consisting of halogen, nitrile and a combination thereof.~~

~~28.15.~~ The method according to claim ~~25~~13, wherein said method additionally comprising step of providing said base polymer selected from the group consisting of ~~polyvinylidene fluoride,~~ polyacrylonitrile polymer and any copolymers thereof.

~~29.16.~~ The method according to claim ~~25~~13, wherein said method additionally comprising step of providing said base polymer comprising polyacrylonitrile.

~~30. The method according to claim 25, wherein said method additionally comprising step of adding reactive pendant moieties to the outer surface of said base polymer by a chemical process in order to provide said non cross linked base polymer having reactive pendant moieties.~~

~~31. The method according to claim 25, wherein said method additionally comprising step of providing base polymer selected from the group consisting of polysulfones, polyether sulfones, polyphenylene sulfones and a combination thereof.~~

~~32. The method according to claim 25, wherein said method additionally comprising step of providing base polymer comprising polyether sulfone.~~

~~33.17.~~ The method according to claim ~~2513~~, wherein said method additionally comprising step of providing said another polymer selected from polyethylenimine and polyvinyl alcohol.

~~34.18.~~ The method according to claim ~~2513~~, wherein said method additionally comprising step of providing said another polymer comprising polyethylenimine.

~~35.19.~~ The method according to claim ~~2513~~, wherein said step of effecting said cross-linking reaction at a first elevated temperature utilizing a solution of said oligomer or another polymer.

~~36.20.~~ The method ~~of according to~~ claim ~~3518~~, wherein said ~~step of effecting at a first elevated temperature~~ is in the range of 50 - 100 °C.

~~37.21.~~ The method ~~of according to~~ claim ~~3518~~, wherein said ~~step of effecting at a first elevated temperature~~ in the range of 70 - 90 °C.

~~38.22.~~ The method ~~of according to~~ claim ~~2513~~, wherein said step of effecting said cross-linking reaction is carried out for 5 - 32 hours.

~~39.23.~~ The method ~~of according to~~ claim ~~2513~~, wherein said step of effecting said cross-linking reaction is carried out for 10 - 20 hours.

~~40.24.~~ The method ~~of according to~~ claim ~~2513~~, wherein said method additionally comprising step of providing said oligomer or another polymer in said solution with the concentration in the range of 2 - 10%.

~~41.25.~~ The method ~~of according to~~ claim ~~2513~~, wherein said method additionally comprising step of providing said oligomer or another polymer in said solution having concentration of preferably 4%.

~~42.26.~~ The method ~~of according to~~ claim ~~2513~~, wherein said method additionally comprising step of a drying step at a second elevated temperature in the range of 70 – 120°C.

~~43.~~ The method ~~of claim 25~~, wherein said method additionally comprising ~~step of providing said cross-linking reaction comprising reacting amine groups with nitrile groups to form amidine groups.~~

~~44.27.~~ The method according to claim ~~2513~~, wherein said method additionally comprising step of providing said polymeric semipermeable membrane comprising polyacrylonitrile ultrafiltration membrane and said another polymer is polyethylenimine.

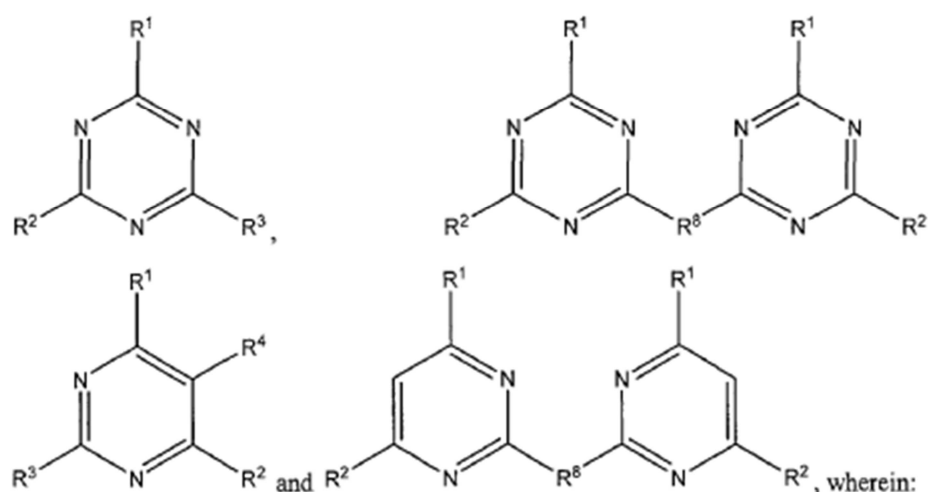
~~45.~~ The method according to claim 25, wherein said method additionally comprising ~~step of providing said cross-linking reaction comprising reacting primary and secondary amino groups with halocarbon groups to form imine and tertiary amino groups.~~

~~46.~~ The method according to claim 25, wherein said method additionally comprising ~~step of providing polymeric semipermeable membrane comprising polyvinylidene fluoride ultrafiltration membrane and said another polymer is polyethylenimine.~~

47. The method according to claim 25, wherein said step of forming nanofiltration (NF') layer comprising:

- (iii) ~~at least one di-, tri- or tetra-halo substituted diazine or triazine containing monomer, oligomer or polymer, and~~
- (iv) ~~at least one multifunctional amine having a molecular weight in the range of 400 to 750,000, provided that at least one of the di-, tri- or tetra-halo substituted diazine or triazine containing monomer, oligomer or polymer is not a di- or triazine monomer which is substituted only by chloro.~~

48.28. The method according to claim 47.13, wherein additionally comprising step of selecting said diazine or triazine-containing monomer or oligomer is from the group consisting of



R¹ is independently selected at each occurrence from bromo, chloro, iodo, fluoro, -NHR⁵, -OR⁵ and SR⁵, wherein R⁵ is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl;

R² is independently selected at each occurrence from bromo, chloro and fluoro;

R³ is independently selected at each occurrence from bromo, chloro, fluoro, -NHR⁵, -OR⁵ and SR⁵, wherein R⁵ is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl;

R⁴ is selected from H, bromo, chloro, fluoro, -NHR⁵, -OR⁵ and SR⁵, wherein

R⁵ is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl; and

R⁸ is independently at each occurrence -NH-A-NH-, wherein A is selected from C₁₋₂₀ aliphatic moieties, C₆₋₁₀ aromatic moieties, and combinations thereof; provided that at least two occurrences, R¹, R², R³ and R⁴, taken together, are selected from bromo, chloro, iodo, fluoro, -NHR⁵, -OR⁵ and SR⁵.

chloro and fluoro, and further provided that when both R¹ and R² on a single ring are Cl, at least one of R³ and R⁴ is not Cl.

- | ~~49.29.~~ The method according to ~~claims 47 to 48~~13, wherein additionally comprising step of providing said multifunctional amine having a molecular weight of in the range of 400 to 250,000.
- | ~~50.30.~~ The method according to ~~claims 23 to 46~~13-, wherein additionally comprising step of selecting said multifunctional amine from the group consisting of ~~polyethylenimine~~polyethylenimine, polyvinylamine, polyvinylanilines, polybenzylamines, polyvinylimidazolines, and amine-modified polyepihalohydrins.
- | ~~51.31.~~ The method according to ~~claims 25 to 50~~any of claims 13 to 30, wherein additionally comprising step of providing supplemental cross-linker selected from the group consisting of 2,4,6-trichloro-s-triazine, 4,6-dichloro-2-sodium p-sulfoanile-s-triazine (4,6-dichloro-2-p-anilinesulfonic acid sodium salt-s-triazine), 4,6-dichloro-2-diethanolamine-s-triazine and 4,6-dichloro-2-amino-s-triazine.