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,~~ poly~~acrylonitrile 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.~~

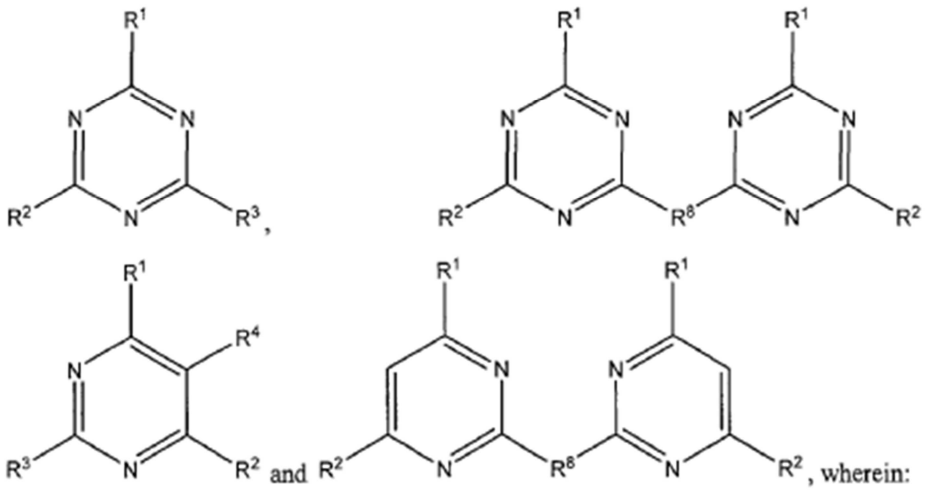
~~19. The polymeric semipermeable membrane according to claim 1, characterized by having improved stability compared to the non-modified membrane in an aggressive environment including at least one of the group consisting of acid media, basic media, organic solvents, oxidizing species, elevated temperatures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



R^1 is independently selected at each occurrence from bromo, chloro, iodo, fluoro, -NHR^5, -OR^5 and SR^5, wherein R^5 is is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl;

R^2 is independently selected at each occurrence from bromo, chloro and fluoro;

R^3 is independently selected at each occurrence from bromo, chloro, fluoro,

-NHR^5, -OR^5 and SR^5, wherein R^5 is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl;

R^4 is selected from H, bromo, chloro, fluoro, -NHR^5, -OR^5 and SR^5, wherein R^5 is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl; and

R^8 is independently at each occurrence -NH-A-NH-, wherein A is selected from C_{1-20} aliphatic moieties, C_{6-10} aromatic moieties, and combinations thereof; provided that at at least two occurrences, R^1, R^2, $R^3$and R^4, taken together, are selected from bromo, chloro and fluoro, and further provided that when both R^1 and R^2 on a single ring are Cl, at least one of R^3 and R^4 is not Cl.

~~22.~~10. The polymeric semipermeable membrane of ~~any of~~ claim~~s 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~~ claim~~s 20 to 22~~ 1, wherein said multifunctional amine is selected from the group consisting of polyethylenemine, polyvinylamine, polyvinylanilines, polybenzylamines, polyvinylimidazolines, and amine-modified polyepihalohydrins.

~~24.~~12. The polymeric semipermeable membrane of any of claims 1 to 11~~23~~, 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-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~~,~~, 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 ~~25~~13, wherein said method additionally comprising step of providing said another polymer selected from polyethylenimine and polyvinyl alcohol.

~~34.~~18. The method according to claim ~~25~~13, wherein said method additionally comprising step of providing said another polymer comprising polyethylenimine.

~~35.~~19. The method according to claim ~~25~~13, 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 according to claim ~~35~~18, wherein said ~~step of effecting at a~~ first elevated temperature is in the range of 50 - 100 ^{0}C.

~~37.~~21. The method according to claim ~~35~~18, wherein said ~~step of effecting at a~~ first elevated temperature in the range of 70 - 90 ^{0}C.

~~38.~~22. The method according to claim ~~25~~13, wherein said step of effecting said cross-linking reaction is carried out for 5 - 32 hours.

~~39.~~23. The method according to claim ~~25~~13, wherein said step of effecting said cross-linking reaction is carried out for 10 - 20 hours.

~~40.~~24. The method according to claim ~~25~~13, 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 according to claim ~~25~~13, 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 according to claim ~~25~~13, wherein said method additionally comprising step of a drying step at a second elevated temperature in the range of 70 – 120^{0}C.

~~43. The method according to 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 ~~25~~13, 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.~~

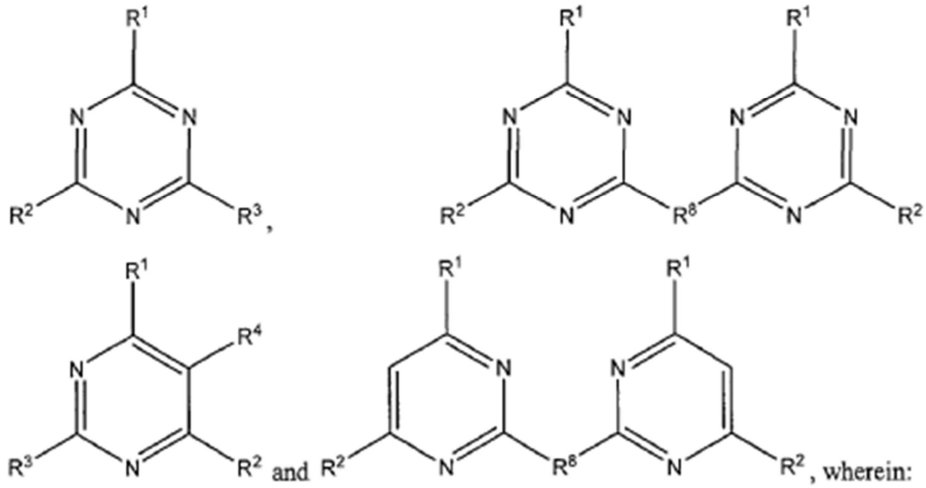
~~46. The method according to claim 25, wherein said method additionally comprising step of providing polymeric semipermeable membrane comprising polyvinylidene fluoride ultrafiltration membrane and said another polymer is polyethylenimine.~~

~~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



R^1 is independently selected at each occurrence from bromo, chloro, iodo, fluoro, $-NHR^5$, $-OR^5$ and SR^5, wherein R^5 is is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl;

R^2 is independently selected at each occurrence from bromo, chloro and fluoro;

R^3 is independently selected at each occurrence from bromo, chloro, fluoro,

$-NHR^5$, $-OR^5$ and SR^5, wherein R^5 is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl;

R^4 is selected from H, bromo, chloro, fluoro, $-NHR^5$, $-OR^5$ and SR^5, wherein R^5 is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl; and

R^8 is independently at each occurrence -NH-A-NH-, wherein A is selected from C_{1-20} aliphatic moieties, C_{6-10} aromatic moieties, and combinations thereof; provided that at at least two occurrences, R^1, R^2, $R^3$and R^4, taken together, are selected from bromo, chloro and

fluoro, and further provided that when both R^1 and R^2 on a single ring are Cl, at least one of R^3 and R^4 is not Cl.

~~49.~~29. The method according to claim~~s 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 claim~~s 47 to 49~~13, wherein additionally comprising step of selecting said multifunctional amine from the group consisting of polyethylenemine, 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.