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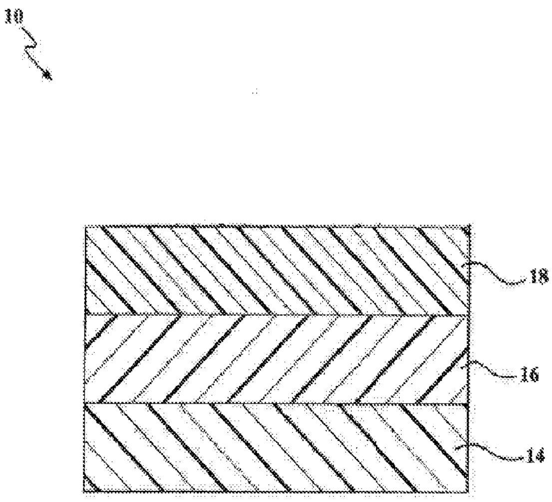

FIG. 1

(57) **Abstract:** A treated substrate comprise a substrate, an adhesion promoter layer disposed on the substrate, and a topcoat layer disposed on the adhesion layer such that the adhesion layer is between the topcoat layer and the substrate. The adhesion promoter layer is formed from an adhesion promoter composition, with the adhesion promoter composition comprising a polyhedral oligomeric silsesquioxane or a linear organosilane polymer. The topcoat layer is formed from a topcoat composition, with the topcoat composition comprising at least one fluorinated organic silicon compound which contains no etheric oxygen atom and at least one fluorinated organic silicon compound which contains an etheric oxygen atom.

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TREATED SUBSTRATE HAVING HYDROPHOBIC AND DURABILITY PROPERTIES

RELATED APPLICATION

[0001] This application claims priority to and all advantages of United States Provisional Patent Application No. 62/549,764, which was filed on August 24, 2017, entitled "POSS Adhesion Promoters and Their Use", and United States Provisional Patent Application No. ______________, which was filed on August 19, 2018 and entitled "Adhesion Promoters and Their Use", the disclosures of which are specifically incorporated by reference in their entirety.

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0002] The invention generally relates to treated substrates and, more particularly, to treated substrates having hydrophobic and durability properties.

2. Description of Related Art

[0003] Treated substrates are used in various fields to provide enhanced physical properties to untreated substrates. For example, in certain industries, such as the transportation industry or electronics industry, the application or disposition of one or more layers of a composition or compositions to an untreated substrate to form a treated substrate and associated articles may improve a particular physical property or properties as compared to the untreated substrate. For example, the application or disposition of an adhesion promoter layer in combination with a topcoat layer to a glass substrate to form a treated glass substrate may provide an increase in hydrophobicity that allows the treated glass substrate to more easily repel water (i.e., has increased water repellency properties) or be cleaned as compared with the corresponding untreated glass substrate.

[0004] However, in many applications, the enhanced property or properties, such as hydrophobicity, provided by the addition of the one or more layers to the untreated substrate decrease over time due to environmental conditions or the like that adversely impact the durability of such applied layers. It would thus be desirable to form treated substrates that have enhanced durability while providing other desired physical properties such as increased hydrophobicity and associated water repellent properties.

SUMMARY OF THE INVENTION AND ADVANTAGES

[0005] The subject invention relates to a treated substrate that comprises a substrate, an adhesion promoter layer disposed on the substrate, and a topcoat layer disposed on the adhesion promoter layer. The adhesion promoter layer is formed from an adhesion promoter composition, with the adhesion promoter composition comprising a polyhedral oligomeric silsesquioxane or a linear organosilane polymer. The topcoat layer is formed from a topcoat composition, with the topcoat composition comprising at least one fluorinated organic silicon compound which contains no etheric oxygen atom and at least one fluorinated organic silicon compound which contains an etheric oxygen atom.

[0006] The treated substrate has excellent initial hydrophobic properties and related water repellent properties, and retains such hydrophobic properties under a wide variety of test conditions intended to simulate environmental conditions, which evidences the durability of the treated substrates, particularly as compared with other treated substrates that include only one of adhesion promoter layers and topcoat layers as described above, or alternatively as compared with treated substrates utilizing a different adhesion promoter composition or topcoat composition to form its respective adhesion promoter and topcoat layers.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Advantages of the subject invention will be readily appreciated as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawing.

[0008] Figure 1 is perspective side view of a treated substrate in accordance with one embodiment of the subject invention.

DETAILED DESCRIPTION OF THE INVENTION

[0009] Referring to Figure 1, a treated substrate 10 is provided that includes a substrate 14, an adhesion promoter layer 16 disposed on the substrate 14, and a topcoat layer 18 disposed on the adhesion promoter layer 16.

I. Substrate

[0010] The substrate 14 (i.e., an untreated substrate) may be rigid or flexible material. In certain embodiments, the rigid or flexible material is also substantially transparent. As defined herein, the term “substantially transparent”, as used with respect to the substrate 14, refers to a material that allows 70% or more of light transmission in a predefined wavelength range, such as the visible light range to travel therethrough.

[0011] Examples of suitable rigid substrates include inorganic materials, such as glass plates or panels. The panes of glass are preferably automotive glass and, more specifically, soda-lime-silica glass. In another embodiment, the glass panel is a tempered glass panel, which is a single layer glass panel that has been processed by controlled thermal or chemical treatments to increase its strength compared to normal glass (i.e., untempered glass such as the soda-lime-silica glass or annealed glass).

[0012] In other embodiments, it may be desirable for the substrate 14 to be flexible (i.e., a flexible substrate). In these embodiments, specific examples of the flexible substrate include those comprising various organic polymers. From the view point of transparency, refractive index, heat resistance and durability, specific examples of the flexible substrate include those comprising polyolefins (polyethylene, polypropylene, etc.), polyesters (poly(ethylene terephthalate), poly(ethylene naphthalate), etc.), polyamides (nylon 6, nylon 6,6, etc.), polystyrene, poly(vinyl chloride), polyimides, polycarbonates, polynorbornenes, polyurethanes, poly(vinyl alcohol), poly(ethylene vinyl alcohol), polyacrylics, celluloses (triacetylcellulose, diacetylcellulose, cellophane, etc.), or interpolymers (e.g. copolymers) of such organic polymers.

[0013] In certain embodiments, the substrate 14 is in the form of a laminated glass panel assembly that includes an inner transparent sheet and an outer transparent sheet and an interlayer disposed between the inner transparent sheet and the outer transparent sheet. In certain embodiments, the inner and outer transparent sheets are panes of glass that are substantially transparent. However, in other embodiments, the inner and outer transparent sheets may be plastic, fiberglass, or any other suitable substantially transparent material. In other embodiments, the inner and outer transparent sheets are panes of glass that are less transparent. For example, wherein the glass assembly is a privacy glass, the transparency of the glass assembly is substantially reduced, and thus allows less than 70% light transmission in a predefined wavelength range, such as from greater than 0 to 70% light transmission at the predefined wavelength range.

[0014] In certain embodiments, the laminated glass panel assembly also includes an interlayer disposed between the inner and outer transparent sheets. Preferably, the interlayer bonds the inner and outer transparent sheets and allows the laminated glass panel assembly to retain glass panel pieces upon impact or breakage.

[0015] The interlayer typically is typically substantially transparent to light and includes a polymer or thermoplastic resin, such as polyvinyl butyral (PVB). However, other suitable materials for implementing the interlayer may be utilized. Similar to the inner and outer transparent sheets, the interlayer is also substantially transparent or otherwise transparent to light, and accordingly the laminated glass panel assembly that includes the interlayer between the inner and outer transparent sheets is also substantially transparent or otherwise transparent to light.

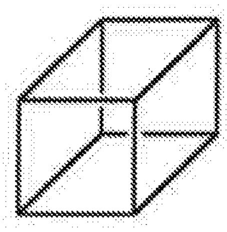
[0016] Further, in certain embodiments, the substrate 14 may be reinforced, e.g. with fillers and/or fibers.

II. Adhesion Promoter Layer

[0017] As noted above, the treated substrate 10 also includes an adhesion promoter layer 16 disposed on the substrate 14.

[0018] The adhesion promoter layer 16, in certain embodiments, is formed from an adhesion promoter composition. In certain preferred embodiments, the adhesion promoter composition comprises a polyhedral oligomeric silsesquioxane.

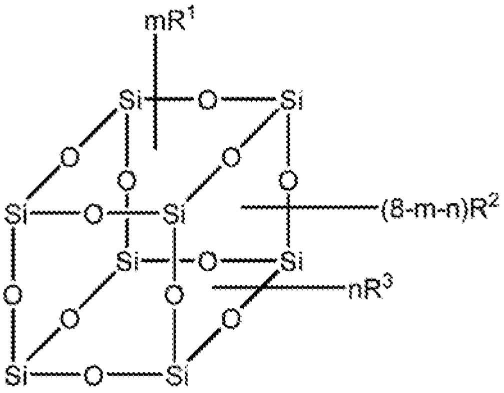
[0019] Silsesquioxanes have a cage-like structure, which is most commonly a cube, hexagonal prism, octagonal prism, decagonal prism, or dodecagonal prism. In exemplary embodiments, of the various possible polyhedral oligomeric silsesquioxane cage molecular structures, the cube-like ("T8") cage structure is formed. As used herein, the cube-like ("T8") cage structure is represented by the shorthand:



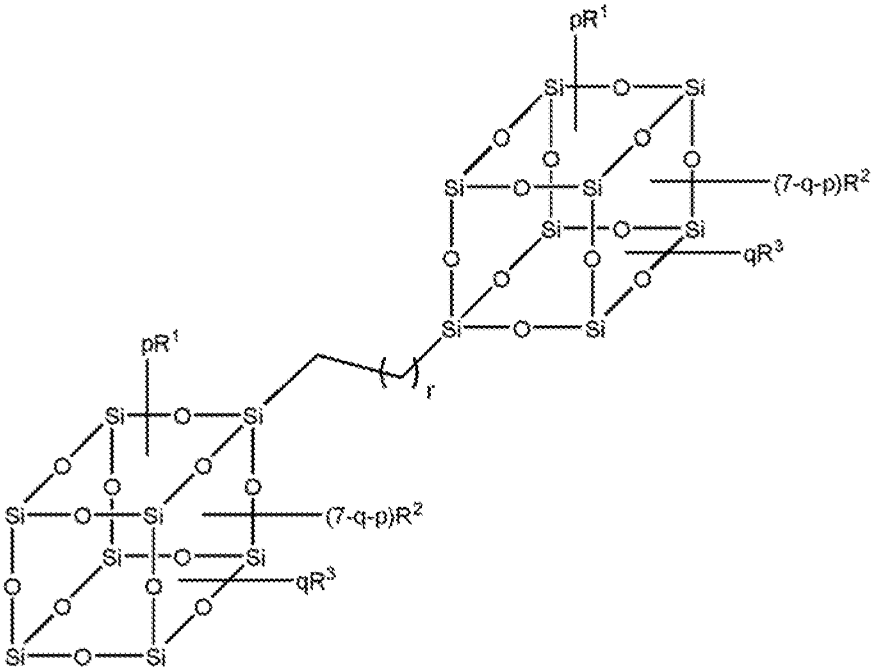
,

where each corner will bear a substituent, such as a fluorinated alkyl group, or a group bearing a reactive functionality such as an alkylsilane or an alkylisocyanate.

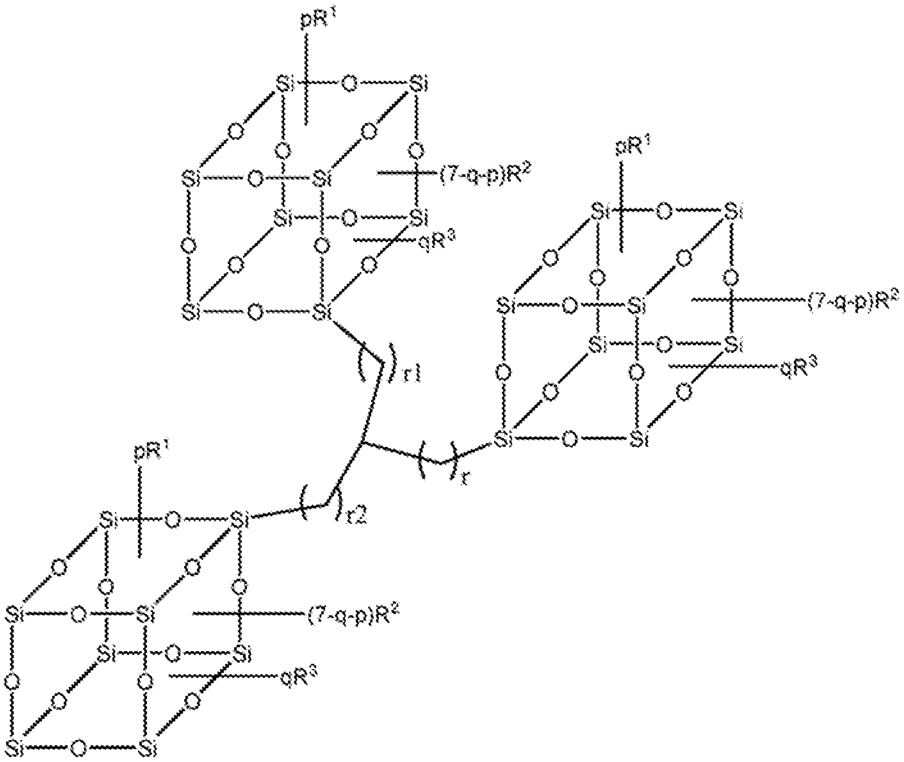
[0020] In certain embodiments, the polyhedral oligomeric silsesquioxane is of the formula (I), (II), or (III):



(I),



(II) or



(III)

wherein

R^1 is a long chain alkyl or long chain fluorinated alkyl;

R^2 and R^3 are each independently selected from the group consisting of C_1-C_{15} alkyl, C_2-C_{15} alkenyl, -NCO, -CH(0)CH_2, -NH_2, -NHC_1-C_6 alkyl, -OC(O)NHC_1-C_6 alkyl, -OC(O)NH_2, -P(O)(OC_1-C_6, alkyl)$_2$, -C_i-C_6 alkylSi(Ci-C_6 alkyl)$_3$, -C_1-C_6 alkylSi(C_1-C_6 alkyl)$_2$(OC_1-C_6 alkyl), -C_1-C_6 alkylSi(C_1-C_6 alkyl)(OC_1-C_6 alkyl)$_2$ –C_1-C_6 alkylSi(OC_1-C_6 alkyl)$_3$, -Si(CrC_6 alkyl)$_2$(OC_1-C_6 alkyl), -Si(C_1-C_6 alkyl)(OC_1-C_6 alkyl)$_2$ and -Si(OC_1-C_6 alkyl)$_3$, wherein one or more hydrogen atoms in C_1-C_{15} alkyl or C_1-C_6 alkyl is independently optionally substituted with a -OC(O)C_1-C_4 alkenyl, -NCO, -(OC_1-C_4 alkyl)-CH(O)CH_2, -CH(O)CH_2, -NH_2, -NHC_1-C_4 alkyl, -OC(O)NHC_1-C_4 alkyl, -OC(O)NH_2, -P(O)(OC_1-C_4 alkyl)$_2$, -Si(C_1-C_4 alkyl)$_2$(OC_1-C_4 alkyl), -Si(C_1-C_4 alkyl)(OC_1-C_4 alkyl)$_2$ or -Si(OC_1-C_4 alkyl)$_3$;

m is an integer from 0 to 7;

n is an integer from 0 to 7;

p is an integer from 0 to 6;

q is an integer from 0 to 6;

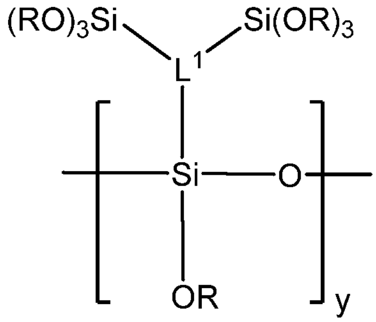
the sum of n and m is less than or equal to 7; and

the sum of p and q is less than or equal to 6.

[0021] In certain embodiments, the end functionalities employed on the R^2 and R^3 groups may incorporate one or more functional groups to allow the polyhedral oligomeric silsesquioxane to covalently bond to various topcoat compositions, including the topcoat compositions described below that form the topcoat layer. Such end functionalities include those described for R^2 and R^3 in formulas (I), (II), and (III) above.

[0022] In certain other preferred embodiments, the adhesion promoter composition comprises a linear organosilane polymer. The term “linear” as used herein may refer to a structure having non-branched or non-caged structure in polymeric backbone.

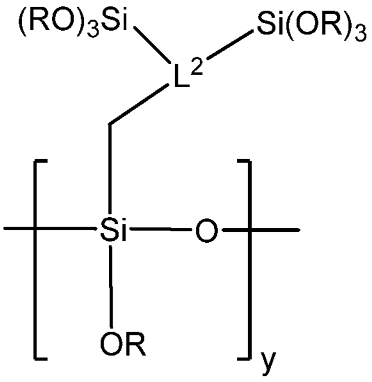
[0023] In certain embodiments, the linear organosilane polymer may include units having the following formula:



(IV), wherein each R is the same or different and may be a hydrogen or non-hydrogen substituent; L^1 is a linker group; and y is a positive integer.

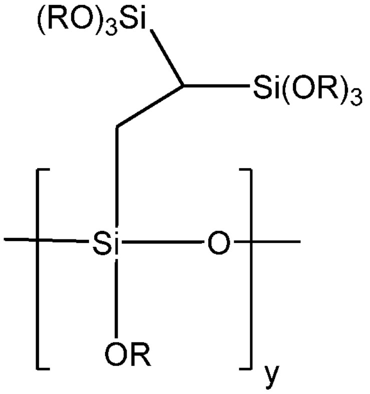
[0024] In some embodiments, each L^1 is a bond, alkylene, or heteroalkylene. In some embodiments, each L^1 is not a bond. In some embodiments, each L^1 is a C_1-C_{20} alkylene which may be substituted or unsubstituted. In some embodiments, each L^1 is a C_1-C_{10} alkylene which may be substituted or unsubstituted. In some embodiments, each L^1 is a C_1-C_8 alkylene which may be substituted or unsubstituted. In some embodiments, each L^1 is a C_1-C_6 alkylene which may be substituted or unsubstituted. In some embodiments, each L^1 is a C_1-C_4 alkylene which may be substituted or unsubstituted. In some embodiments, each L^1 is a C_1-C_2 alkylene which may be substituted or unsubstituted. In some embodiments, each L^1 is methylene or ethylene. In some embodiments, each L^1 is a heteroalkylene which may be substituted or unsubstituted. In some embodiments, each L^1 is a heteroalkylene including at least one selected from O, S, N, or P, which may be substituted or unsubstituted. In some embodiments, each L^1 is a 2 to 20 membered heteroalkylene including at least one selected from O, S, N, or P, which may be substituted or unsubstituted. In some embodiments, each L^1 is a 2 to 10 membered heteroalkylene including at least one selected from O, S, N, or P, which may be substituted or unsubstituted. In some embodiments, each L^1 is a 2 to 8 membered heteroalkylene including at least one selected from O, S, N, or P, which may be substituted or unsubstituted. In some embodiments, each L^1 is a 2 to 5 membered heteroalkylene including at least one selected from O, S, N, or P, which may be substituted or unsubstituted. In some embodiments, each L^1 is a 2 to 3 membered heteroalkylene including at least one selected from O, S, N, or P, which may be substituted or unsubstituted.

[0025] In certain embodiments, the linear organosilane polymer may include units of the following formula:

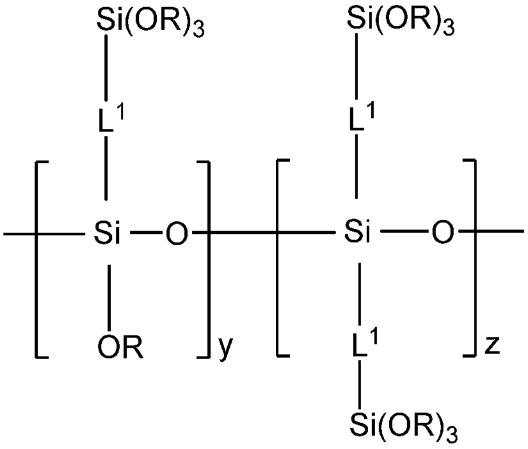


(V), wherein each R is the same or different and may be a hydrogen or non-hydrogen substituent; L^2 is a linker group; and y is a positive integer.

[0026] In some embodiments, each L^2 is a bond, alkylene, or heteroalkylene. In some embodiments, each L^2 is not a bond. In some embodiments, each L^2 is a C_1-C_{20} alkylene which may be substituted or unsubstituted. In some embodiments, each L^2 is a C_1-C_{10} alkylene which may be substituted or unsubstituted. In some embodiments, each L^2 is a C_1-C_8 alkylene which may be substituted or unsubstituted. In some embodiments, each L^2 is a C_1-C_6 alkylene which may be substituted or unsubstituted. In some embodiments, each L^2 is a C_1-C_4 alkylene which may be substituted or unsubstituted. In some embodiments, each L^2 is a C_1-C_2 alkylene which may be substituted or unsubstituted. In some embodiments, each L^2 is methylene or ethylene. In some embodiments, each L^2 is a heteroalkylene which may be substituted or unsubstituted. In some embodiments, each L^2 is a heteroalkylene including at least one selected from O, S, N, or P, which may be substituted or unsubstituted. In some embodiments, each L^2 is a 2 to 20 membered heteroalkylene including at least one selected from O, S, N, or P, which may be substituted or unsubstituted. In some embodiments, each L^2 is a 2 to 10 membered heteroalkylene including at least one selected from O, S, N, or P, which may be substituted or unsubstituted. In some embodiments, each L^2 is a 2 to 8 membered heteroalkylene including at least one selected from O, S, N, or P, which may be substituted or unsubstituted. In some embodiments, each L^2 is a 2 to 5 membered heteroalkylene including at least one selected from O, S, N, or P, which may be substituted or unsubstituted. In some embodiments, each L^2 is a 2 to 3 membered heteroalkylene including at least one selected from O, S, N, or P, which may be substituted or unsubstituted.

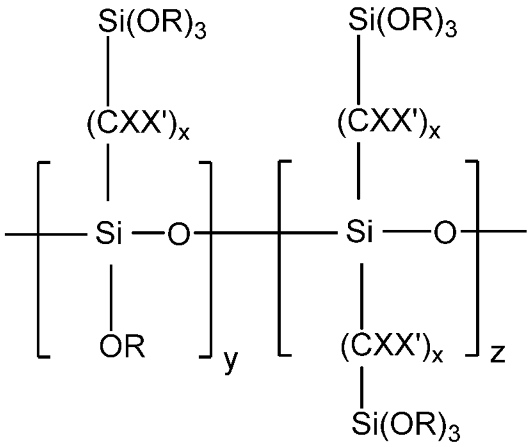
[0027] In certain embodiments, the linear organosilane polymer may include units of the following formula: 

(VI), wherein each R is the same or different and may be a hydrogen or non-hydrogen substituent; and y is a positive integer.

[0028] In certain embodiments, the linear organosilane polymer may include units of the following formula: 

(VII), wherein each R is the same or different and may be a hydrogen or non-hydrogen substituent; each L^1 is the same or different linker group; and z is a positive integer.

[0029] In some embodiments, the linear organosilane polymer may include units of the following formula:

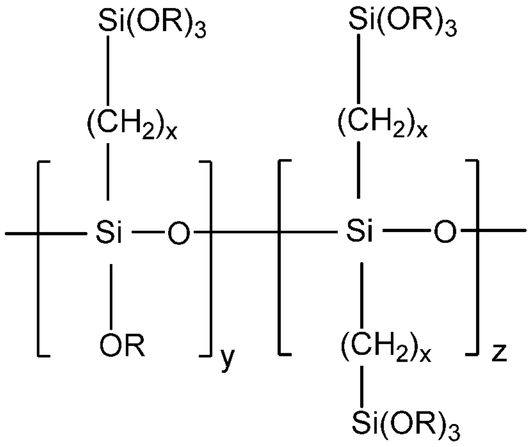


(VIII), wherein each R is the same or different and may be a hydrogen or non-hydrogen substituent; each X and X’ is the same or different and may be hydrogen or a non-hydrogen substituent; each x is the same or different positive integer; and y and z are each the same or different positive integer.

[0030] In some embodiments, each X and X’ is hydrogen. In some embodiments, each X and X’ is other than hydrogen.

[0031] In some embodiments, each X and X’ is alkyl, which may be substituted or unsubstituted. In some embodiments, X and X’ is unsubstituted alkyl. In some embodiments, X and X’ is unsubstituted C_1-C_3 alkyl. In some embodiments, each X and X’ is ethyl. In some embodiments, each X and X’ is methyl. In some embodiments, each X and X’ is halogen (e.g., F, Cl, Br, or I).

[0032] In some embodiments, the linear organosilane polymer may include units of the following formula:



(IX), wherein each R is the same or different and may be a hydrogen or non-hydrogen substituent; each x is the same or different positive integer; and y and z are each the same or different positive integer.

[0033] In some embodiments, each R is other than hydrogen. In some embodiments, each R is alkyl, which may be substituted or unsubstituted. In some embodiments, R is unsubstituted alkyl. In some embodiments, R is unsubstituted C_1-C_3 alkyl. In some embodiments, each R is ethyl. In some embodiments, each R is methyl.

[0034] In some embodiments, y is an integer from 1 to 1000. In some embodiments, y is an integer from 1 to 900. In some embodiments, y is an integer from 1 to 800. In some embodiments, y is an integer from 1 to 700. In some embodiments, y is an integer from 1 to 600. In some embodiments, y is an integer from 1 to 500. In some embodiments, y is an integer from 1 to 400. In some embodiments, y is an integer from 1 to 300. In some embodiments, y is an integer from 1 to 200. In some embodiments, y is an integer from 1 to 100. In some embodiments, y is an integer from 1 to 90. In some embodiments, y is an integer from 1 to 80. In some embodiments, y is an integer from 1 to 70. In some embodiments, y is an integer from 1 to 60. In some embodiments, y is an integer from 1 to 50. In some embodiments, y is an integer from 1 to 40. In some embodiments, y is an integer from 1 to 30. In some embodiments, y is an integer from 1 to 20. In some embodiments, y is an integer from 1 to 10. In some embodiments, z is an integer from 0 to 1000. In some embodiments, z is an integer from 0 to 900. In some embodiments, z is an integer from 0 to 800. In some embodiments, z is an integer from 0 to 700. In some embodiments, z is an integer from 0 to 600. In some embodiments, z is an integer from 0 to 500. In some embodiments, z is an integer from 0 to 400. In some embodiments, z is an integer from 0 to 300. In some embodiments, z is an integer from 0 to 200. In some embodiments, z is an integer from 0 to 100. In some embodiments, z is an integer from 0 to 90. In some embodiments, z is an integer from 0 to 80. In some embodiments, z is an integer from 0 to 70. In some embodiments, z is an integer from 0 to 60. In some embodiments, z is an integer from 0 to 50. In some embodiments, z is an integer from 0 to 40. In some embodiments, z is an integer from 0 to 30. In some embodiments, z is an integer from 0 to 20. In some embodiments, z is an integer from 0 to 10. In some embodiments, x is an integer from 1 to 30. In some embodiments, x is an integer from 1 to 20. In some embodiments, x is an integer from 1 to 10. In some embodiments, x is an integer from 1 to 9. In some embodiments, x is an integer from 1 to 8. In some embodiments, x is an integer from 1 to 7. In some embodiments, x is an integer from 1 to 6. In some embodiments, x is an integer from 1 to 5. In some embodiments, x is an integer from 1 to 4. In some embodiments, x is an integer from 1 to 9. In some embodiments, x is an integer from 1 to 3. In some embodiments, x is an integer from 1 to 9. In some embodiments, x is an integer from 1 to 2. In some embodiments, x is 1.

[0035] In certain embodiments, the adhesion promoter composition is of the formula: $C_mH_nO_pSi_q$, wherein the subscript m ranges from 64 to 170, the subscript n ranges from 150 to 402, the subscript p ranges from 36 to 99, and the subscript q ranges from 15 to 45. In certain embodiments, the adhesion promoter composition is a polyhedral oligomeric silsesquioxane of the formula: $C_{170}H_{402}O_{99}Si_{45}$. In certain other embodiments, the adhesion promoter composition is a linear organosilane polymer of the formula: $C_{64}H_{152}O_{36}Si_{16}$.

[0036] In certain embodiments, the adhesion promoter composition, in addition to the polyhedral oligomeric silsesquioxane or the linear organosilane polymer, also comprises additional components. Such additional components include, but are not limited to solvents and acids. Suitable solvents that can be included include organic solvents, including polar organic solvents such as ethanol or methanol. One exemplary polar organic solvent that can be used is ethanol. Suitable acids include any acids that are capable of adjusting the pH of the adhesion promoter composition to approximately 2 and include, but are aqueous acids and certain, but are not limited to, nitric acid, sulfuric acid, hydrochloric acid, and the like.

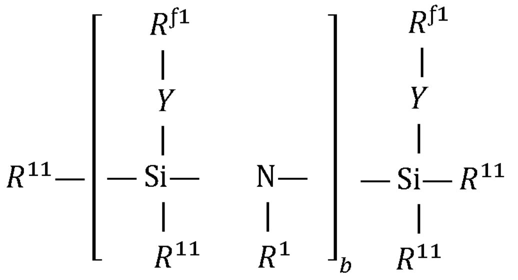
III. Topcoat Layer

[0037] As noted above, the treated substrate 10 also includes the topcoat layer 18 disposed on the adhesion promoter layer 16.

[0038] The topcoat layer 18 is formed from a topcoat composition that comprises at least one fluorinated organic silicon compound which contains no etheric oxygen atom (i.e., Compound (A)) and at least one fluorinated organic silicon compound which contains an etheric oxygen atom (i.e., Compound (B)).

[0039] In certain embodiments, the compound (A) is selected from the group consisting of a compound represented by the following formula (la), its partially hydrolyzed condensate, and a compound represented by the following formula (1b):

$$R^{f1} - Y - Si(R^{11})_r(X^1)_{3-r} \qquad (1a)$$

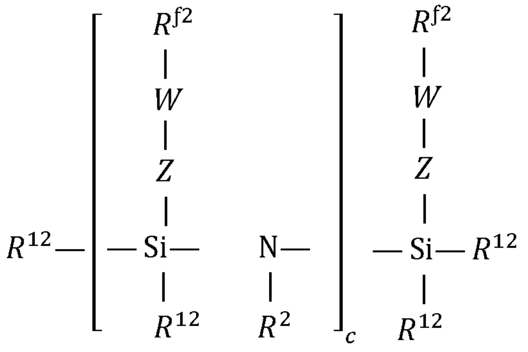


$$R^{11}-\left[\begin{array}{cc} R^{f1} & \\ | & \\ Y & \\ | & \\ -\mathrm{Si}- & \mathrm{N}- \\ | & | \\ R^{11} & R^{1} \end{array}\right]_b \begin{array}{c} R^{f1} \\ | \\ Y \\ | \\ -\mathrm{Si}-R^{11} \\ | \\ R^{11} \end{array} \qquad (1b)$$

[0040] In the formulae (la) and (lb), R^{f1} is a C_{1-20} perfluoroalkyl group which contains no etheric oxygen atom between carbon-carbon atoms and which may have a ring structure, Y is a C_{1-6} bivalent organic group which contains no fluorine atom, R^{11} each independently is a hydrogen atom or a C_{1-6} hydrocarbon group which contains no fluorine atom, X^1 each independently is a halogen atom, an alkoxy group or an isocyanate group, r is an integer of from 0 to 2, R^1 is a hydrogen atom or a C_{1-3} hydrocarbon group which contains no fluorine atom, and b is an integer of from 1 to 100).

[0041] In certain embodiments, the compound (B) is selected from the group consisting of a compound represented by the following formula (2a), its partially hydrolyzed condensate, and a compound represented by the following formula (2b):

$$R^{f2} - W - Z - Si(R^{12})_p(X^2)_{3-p} \qquad (2a),$$

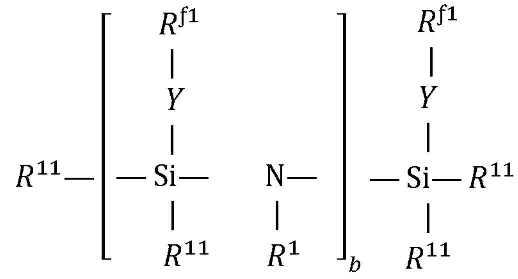


$$R^{12}-\left[\begin{array}{cc} R^{f2} & \\ | & \\ W & \\ | & \\ Z & \\ | & \\ -\mathrm{Si}- & \mathrm{N}- \\ | & | \\ R^{12} & R^{2} \end{array}\right]_c \begin{array}{c} R^{f2} \\ | \\ W \\ | \\ Z \\ | \\ -\mathrm{Si}-R^{12} \\ | \\ R^{12} \end{array} \qquad (2b)$$

[0042] In the formulae (2a) and (2b), R^{f2} is a C_{1-20} perfluoroalkyl group which may have an etheric oxygen atom inserted between carbon-carbon atoms and which may have a ring structure, W is —O—$(CF_2CF_2O)_a$—CF_2— (wherein a is an integer of from 1 to 200), Z is a bivalent organic group, R^{12} each independently is a hydrogen atom or a C_{1-16} hydrocarbon group which contains no fluorine atom, X^2 each independently is a halogen atom, an alkoxy group or an isocyanate group, p is an integer of from 0 to 2, R^2 is a hydrogen atom or a C_{1-3} hydrocarbon group which contains no fluorine atom, and c is an integer of from 1 to 100).

[0043] The compound (A) which is contained in the topcoat composition for forming a topcoat layer of the exemplary embodiment, is at least one fluorinated organic silicon compound which contains no etheric oxygen atom and which is selected from the group consisting of a compound represented by the following formula (la), its partially hydrolyzed condensate, and a compound represented by the following formula (lb). A partially hydrolyzed condensate of the compound represented by the following formula (la) will be described later. Firstly, the compound (A) which is not a partially hydrolyzed condensate, will be described.

$$R^{f1}-Y-Si(R^{11})_r(X^1)_{3-r} \qquad \text{(1a)},$$



$$R^{11}-\left[-\underset{\substack{|\\R^{11}}}{\overset{\substack{R^{f1}\\|\\Y\\|}}{Si}}-\quad\underset{\substack{|\\R^{1}}}{N}-\right]_b-\underset{\substack{|\\R^{11}}}{\overset{\substack{R^{f1}\\|\\Y\\|}}{Si}}-R^{11} \qquad \text{(1b)}$$

[0044] The compound (A) may be composed solely of the compound represented by the above formula (la), may be composed solely of the compound represented by the above formula (lb), or may be composed of their mixture.

[0045] In each of the above formulae (la) and (lb), R^{f1} is a C_{1-20} perfluoroalkyl group which contains no etheric oxygen atom between carbon-carbon atoms and which may have a ring structure. So long as the above conditions are satisfied, R^{f1} may be of a linear structure, a branched structure or a cyclic structure, or of a structure which partially has a branched structure and a cyclic structure. As such R^{f1}, the following groups may specifically be mentioned:

$$CF_3(CF_2)_i—,$$

$$C\frac{F}{Y}—(CF_2)_m—,$$

$$A\frac{F}{d}—(CF_2)_n—.$$

[0046] Here, 1 is an integer of from 0 to 19, preferably an integer of from 0 to 15, particularly preferably an integer of from 0 to 6. $C\frac{F}{Y}$ is a perfluorocyclohexyl group. $A\frac{F}{d}$ is a perfluoroadamantyl group. Each of m and n is an integer of from 0 to 15.

[0047] Among them, as R^{f1} in the subject invention, $CF_3(CF_2)_l$— is preferred, and one having a linear structure is further preferred. Further, a preferred number of carbon atoms in R^{f1} may be from 3 to 8.

[0048] In each of the formulae (la) and (lb), Y being a group which links R^{f1} and a silicon atom, is a C_{1-6} bivalent organic group which contains no fluorine atom and is not particularly limited other than such a condition. Y is preferably a bivalent organic group selected from —$(CH_2)_i$— (wherein i is an integer of from 1 to 6), —$CONH(CH_2)_j$— (wherein j is an integer of from 1 to 5) and —$CONH(CH_2)_{5-k}$— (wherein k is an integer of from 1 to 4), more preferably —$(CH_2)_2$—, —$CONH(CH_2)_3$—, —$CONH(CH_2)_2NH(CH_2)_3$— or the like.

[0049] In each of the formulae (la) and (lb), R^{11} each independently is a hydrogen atom or a C_{1-6} hydrocarbon group which contains no fluorine atom. Among them, in the formula (la), R^{11} is preferably a C_{1-4} hydrocarbon group, particularly preferably a methyl group or an ethyl group. Further, in the formula (lb), R^{11} is preferably a hydrogen atom.

[0050] In the formula (1a), X^1 is a halogen atom, an alkoxy group or an isocyanate group. Each of them is a hydrolyzable group. When r is 0 or 1, a plurality of X^1 may be the same or different. Further, X^1 is preferably a chlorine atom, a C_{1-4} alkoxy group or an isocyanate group, particularly preferably a chlorine atom. Still further, r is an integer of from 0 to 2, preferably 0 or 1, since the adhesion, the durability, etc. of the formed layer will be thereby excellent.

[0051] In the formula (lb), R^1 each independently is a hydrogen atom or a C_{1-3} hydrocarbon group which contains no fluorine atom. R^1 is preferably a hydrogen atom with a view to improvement of the reactivity.

[0052] In the formula (lb), b is an integer of from 1 to 100. Here, b represents the number of units of the silicon-nitrogen bond in the compound represented by the formula (lb), and in the subject invention, b is preferably from 1 to 50 from the viewpoint of the coating property.

[0053] In the composition for forming a topcoat layer of the exemplary embodiment, one type of the compound (A) may be used alone, or two or more types of the compound (A) may be used in combination.

[0054] Specific examples of the compound (A) will be shown below with respect to each of the compound represented by the formula (la) and the compound represented by the formula (lb). However, X^1 and R^{11} in the following formulae have the same meanings as mentioned above, and their preferred embodiments are also the same, e is an integer of from 1 to 20, f is an integer of from 1 to 6, g is an integer of from 1 to 5, and h is an integer of from 1 to 4.

(Compounds represented by the formula (la))

$F(CF_2)_e(CH_2)_fSiX^1_3$,

$F(CF_2)_e(CH_2)_fSi(R^{11})X^1_2$,

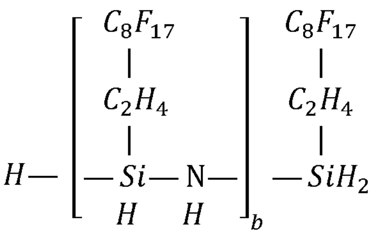
$F(CF_2)_eCONH(CH_2)_9SiX^1_3$,

$F(CF_2)_eCONH(CH_2)_gSi(R^{11})\ X^1_2$,

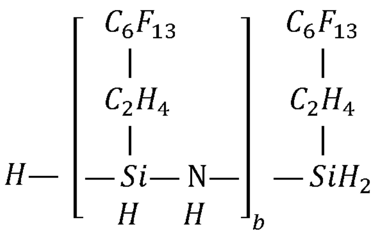
$F(CF_2)_eCONH(CH_2)_hNH(CH_2)_{5\text{-}h}SiX^1_3$,

$F(CF_2)_eCONH(CH_2)_hNH(CH_2)_{5\text{-}h}Si(R^{11})X^1_2$

(Compounds represented by the formula (lb))



$$H-\left[\begin{array}{c} C_8F_{17} \\ | \\ C_2H_4 \\ | \\ -\underset{H}{Si}-\underset{H}{N}- \end{array}\right]_b \begin{array}{c} C_8F_{17} \\ | \\ C_2H_4 \\ | \\ -SiH_2 \end{array}$$

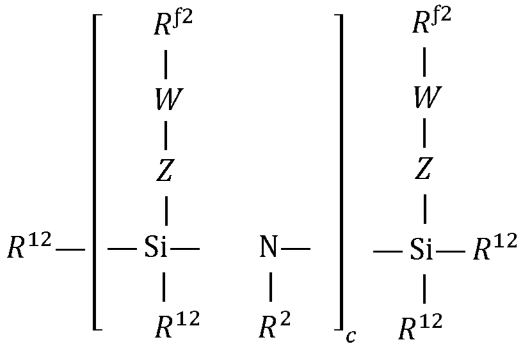


$$H-\left[\begin{array}{c} C_6F_{13} \\ | \\ C_2H_4 \\ | \\ -\underset{H}{Si}-\underset{H}{N}- \end{array}\right]_b \begin{array}{c} C_6F_{13} \\ | \\ C_2H_4 \\ | \\ -SiH_2 \end{array}$$

[0055] The above compound (A) to be used in the subject invention can be produced by a common method. Further, as the compound (A), a commercial product is available, and therefore, in the subject invention, it is possible to employ such a commercial product.

[0056] The compound (B) contained in the composition of the exemplary embodiment is at least one fluorinated organic silicon compound which contains an etheric oxygen atom and which is selected from the group consisting of a compound represented by the following formula (2a), its partially hydrolyzed condensate, and a compound represented by the following formula (2b). The partially hydrolyzed condensate of the compound represented by the following formula (2a) will be described later. Firstly, the compound (B) which is not a partially hydrolyzed condensate, will be described. Compounds represented by formulae (2a) and (2b) may be as follows:

$$R^{f2} - W - Z - Si(R^{12})_p(X^2)_{3-p} \qquad (2a),$$



$$R^{12}- \left[\begin{array}{cc} R^{f2} & \\ | & \\ W & \\ | & \\ Z & \\ | & \\ -Si- & N- \\ | & | \\ R^{12} & R^{2} \end{array} \right]_c \begin{array}{c} R^{f2} \\ | \\ W \\ | \\ Z \\ | \\ -Si-R^{12} \\ | \\ R^{12} \end{array} \qquad (2b)$$

[0057] The compound (B) may be composed solely of the compound represented by the above formula (2a), may be composed solely of the compound represented by the above formula (2b), or may be composed of their mixture.

[0058] In each of the above formulae (2a) and (2b), R^{f2} is a C_{1-20} perfluoroalkyl group, (which may have a ring structure or may have an etheric oxygen atom inserted between carbon-carbon atoms). The C_{1-20} perfluoroalkyl group represented by R^{f2} may be of a linear structure, a branched structure, a cyclic structure, or a structure which partially has a branched structure and a cyclic structure. As such R^{f2}, the following groups may specifically be mentioned:

$$CF_3(CF_2)_l—,$$

$$C\frac{F}{Y}—(CF_2)_m—,$$

$$A\frac{F}{d}—(CF_2)_n—.$$

[0059] Here, 1 is an integer of from 0 to 19, preferably an integer of from 0 to 15, particularly preferably an integer of from 0 to 6. $C\frac{F}{Y}$ is a perfluorocyclohexyl group. $A\frac{F}{d}$ is a perfluoroadamantyl group. Each of m and n is an integer of from 0 to 15.

[0060] Among them, as R^{f2} in the subject invention, $CF_3(CF_2)_m$— is preferred, and one having a linear structure is more preferred. Further, the number of carbon atoms in R^{f2} is preferably from 1 to 16, particularly preferably from 1 to 8.

[0061] The perfluoroalkyl group having an etheric oxygen atom inserted between carbon-carbon atoms is a group having an etheric oxygen atom inserted between carbon-carbon atoms of the above-mentioned perfluoroalkyl group. Depending upon the inserted etheric oxygen atom, in a case where a perfluoro(oxyethylene) group i.e. —OCF_2CF_2— is formed on the bond terminal side in the perfluoroalkyl group, such a perfluoro(oxyethylene) group is regarded as a perfluoro(oxyethylene) group in W in the above formula. In a case where such a perfluoro(oxyethylene) group is not linked to the perfluoro(oxyethylene) group in W, it is a perfluoro(oxyethylene) group in R^{12}. The etheric oxygen atom in R^{12} may form a perfluoro(oxypropylene) group, but a perfluoro(oxypropylene) group may not be able to sufficiently exhibit the desired effect due to the presence of a trifluoromethyl) group as its side chain. Therefore, in a case where there are two or more etheric oxygen atoms inserted in R^{f2}, they preferably form a structure wherein two or more units of perfluoro(oxyethylene) groups are repeated.

[0062] It is preferred that a perfluoroalkyl group having an etheric oxygen atom inserted does not have a —OCF_2O— structure. This means that the — OCF_2O— structure is a structure, on which the presence of a nuclear structure cannot be detected by a usual analytical method (such as ^{19}F-NMR (nuclear magnetic resonance)). In a case where R^{f2} has a structure wherein two or more units of perfluoro(oxyethylene) groups are repeated, — OCF_2O— is likely to be formed at one end of such a structure in many cases. However, the — OCF_2O— structure in R^{f2} is unstable and is likely to bring about deterioration of the heat resistance.

[0063] When etheric oxygen atoms are inserted between carbon-carbon atoms, the number of oxygen atoms to be inserted is preferably from 1 to 7, more preferably from 1 to 4. The positions of such oxygen atoms to be inserted are between carbon atom-carbon atom single bonds, and the number of carbon atoms present between oxygen atoms is at least 2.

[0064] In each of the above formulae (2a) and (2b), W is a bivalent organic group represented by —O—$(CF_2CF_2O)_a$— CF_2—, wherein a is an integer of from 1 to 200. Here, a is preferably an integer of from 3 to 50, more preferably from 4 to 25, further preferably from 5 to 10. By adjusting the number for a within this range, it becomes possible to impart a sufficient water droplets-removing property to the topcoat layer which is formed from the composition for forming a topcoat layer of the exemplary embodiment.

[0065] In each of the above formulae (2a) and (2b), Z is a bivalent organic group. This bivalent organic group preferably has at most 10 carbon atoms and may have a hetero atom such as an oxygen atom or a nitrogen atom. Usually, the compound (B) is produced by reacting a compound having R^{f2}—W— with a compound having a silicon atom (i.e. by reacting a functional group at the silicon atom side terminal of W with a functional group of the compound having a silicon atom). Z is preferably a bivalent organic group to be formed by a reaction of a reactive group-containing organic group bonded to such a silicon atom with the above-mentioned reactive group bonded to the terminal of W. Further, a compound having an alkenyl group at the silicon atom side terminal of W and a silicon atom having hydrogen atoms bonded to the silicon atom may be bonded by a hydrosilylation reaction to obtain a compound wherein Z is an alkylene group.

[0066] Preferably, Z is a bivalent organic group to be formed by a reaction of a functional group at the silicon atom side terminal of W with a functional group of the compound having a silicon atom. The reactive group bonded to a difluoromethylene group at the terminal of W may, for example, be a reactive group having a carbonyl group such as a carboxyl group, a halocarbonyl group or an alkoxycarbonyl group, or a hydroxymethyl group. On the other hand, the reactive group in the compound having a silicon atom may be a reactive group having an organic group bonded to the silicon atom. For example, an amino group in e.g. a 3-aminopropyl group or an N-(2-aminoethyl)-3-aminopropyl group, an isocyanate group such as a 3-isocyanate propyl group, a chlorine atom group bonded to a carbon atom such as a 3-chloropropyl group, an epoxy group such as a 3-glycidyl oxypropyl group, a hydroxy group such as a 3-hydroxypropyl group, or a mercapto group such as a 3-mercaptooxypropyl group, may be mentioned. For example, by a reaction of a reactive group having a carbonyl group with a 3-aminopropyl group, Z represented by $—CONHC_3H_6—$ will be formed.

[0067] Z is preferably a bivalent organic group selected from $—CONHC_3H_6—$, $—CONHC_2H_4—$, $—CH_2OCONHC_3H_6—$, $—COCH_2CH(OH)CH_2OC_3H_6—$, —

$CH_2OCH_2CH(OH)CH_2OC_3H_6$—,—$CH_2OC_3H_6$—, —$CF_2OC_3H_6$—, —$C_2H_4$— and —$C_3H_6$—. Among them, —$CONHC_3H_6$—, —$CONHC_2H_4$— or —$C_2H_4$— is particularly preferred.

[0068] In each of the above formulae (2a) and (2b), R^{12} may be the same groups as R^{11} in the above-mentioned formulae (la) and (lb). Its preferred examples are also the same as mentioned above.

[0069] In the formula (2a), X^2 may be the same group as X^1 in the above formula (la). Its preferred examples are also the same as mentioned above.

[0070] In the formula (2a), p is an integer of from 0 to 2, but is preferably 0 or 1, since the adhesion, the durability, etc. of the formed layer will thereby be excellent.

[0071] In the formula (2b), R^2 may be the same group as R^1 in the above formula (lb). Its preferred examples are also the same as mentioned above, c is one representing the number of units of silicon-nitrogen bonds in the compound represented by the formula (2b), and in the subject invention, c is preferably from 1 to 50 from the viewpoint of the coating property.

[0072] In the topcoat composition for forming a topcoat layer of the exemplary embodiment, one type of the compound (B) may be used alone, or two or more types may be used in combination.

[0073] Specific examples of the compound (B) will be shown below with respect to each of the compound represented by the formula (2a) and the compound represented by the formula (2b):

(Compounds represented by the formula (2a))

R^{f2}—O—$(CF_2CF_2O)_a$—CF_2—$CONHC_3H_6Si(R^{12})_p$ (B1)

R^{f2}—O—$(CF_2CF_2O)_a$—CF_2—$CH_2OCONHC_3H_6Si(R^{12})_p(X^2)_{3-p}$ (B2)

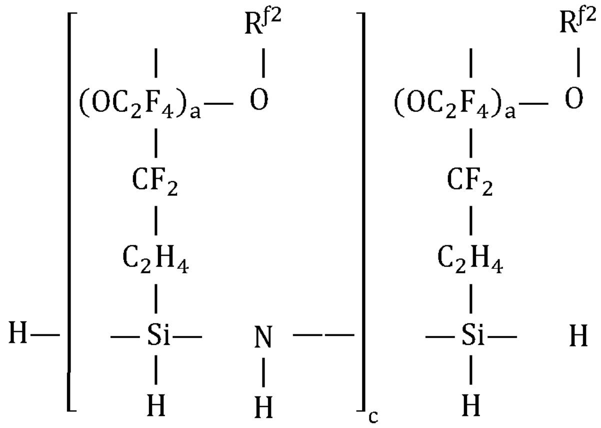
R^{f2}—O—$(CF_2CF_2O)_a$—CF_2—$CH_2OC_3H_6Si(R^{12})_p$ (B3)

R^{f2}—O—$(CF_2CF_2O)_a$—CF_2—$CF_2OC_3H_6Si(R^{12})_p$ (B4)

R^{f2}—O—$(CF_2CF_2O)_a$—CF_2—$C_2H_4Si(R^{12})_p(X^2)_{3-p}$ (B5)

R^{f2}—O—$(CF_2CF_2O)_a$—CF_2—$C_3H_6Si(R^{12})_p(X^2)_{3-p}$ (B6)

(Compounds represented by the formula (2b))



$$H-\left[\begin{array}{cc} & R^{f2}\\ | & |\\ (OC_2F_4)_a- & O\\ | & \\ CF_2 & \\ | & \\ C_2H_4 & \\ | & \\ -Si- & N-\\ | & |\\ H & H\end{array}\right]_c \begin{array}{cc} & R^{f2}\\ | & |\\ (OC_2F_4)_a- & O\\ | & \\ CF_2 & \\ | & \\ C_2H_4 & \\ | & \\ -Si- & H\\ | & \\ H & \end{array}$$

[0074] Among them, preferred specific examples as the compound (B) in the subject invention, are as follows:

$CF_3—O—(CF_2CF_2O)_a—CF_2—CONHC_3H_6Si(OCH_3)_3$

$CF_3—O—(CF_2CF_2O)_a—CF_2—CONHC_3H_6Si(OC_2H_5)_3$

$CF_3—O—(CF_2CF_2O)_a—CF_2—CONHC_2H_4Si(OCH_3)_3$

$CF_3—O—(CF_2CF_2O)_a—CF_2—CONHC_2H_4Si(OC_2H_5)_3$

$CF_3—O—(CF_2CF_2O)_a—CF_2—C_2H_4Si(OCH_3)_3$

$CF_3—O—(CF_2CF_2O)_a—CF_2—C_2H_4Si(OC_2H_5)_3$

[0075] In all of the above compounds (B), a=7 to 8, and the average value of a is 7.3 (hereinafter referred to as “a=7 to 8, average value: 7.3”.)

[0076] The above compound (B) to be used in the subject invention can be produced by a known method. For example, the above compound (B) can be produced specifically by the method disclosed in WO2009-008380, which is herein incorporated by reference.

[0077] The compound represented by the formula (la) and the compound represented by the formula (2a) may be their respective partially hydrolyzed condensates. A partially hydrolyzed condensate is meant for an oligomer to be formed by hydrolysis of all or some of hydrolyzable silyl groups in a solvent in the presence of a catalyst such as an acid catalyst or an alkali catalyst, followed by dehydration condensation. However, the condensation degree (oligomerization degree) of such a partially hydrolyzed condensate is required to be such a degree that the product is soluble in a solvent. Therefore, the compound (A) to be contained in the composition for forming a topcoat layer of the exemplary embodiment may be a partially hydrolyzed condensate of the compound represented by the formula (la), and likewise, the compound (B) may be a partially hydrolyzed condensate of the compound represented by the formula (2a). Further, they may contain the respective unreacted compounds represented by the formulae (la) and (2a).

[0078] The topcoat composition for forming a topcoat layer of the exemplary embodiment comprises the above compounds (A) and (B).

[0079] Here, the compounds (A) and (B) may be contained in the form of the above-described compounds themselves in the topcoat composition for forming a topcoat layer of the exemplary embodiment. The topcoat composition for forming a topcoat layer of the exemplary embodiment preferably contains the compound (A) in the form of the compound represented by the formula (la) and/or its partially hydrolyzed condensate, and the compound (B) preferably is in the form of the compound represented by the formula (2a) and/or its partially hydrolyzed condensate. In such a case, it is more preferred that they are contained in the form of a partially hydrolyzed co-condensate of the compounds (A) and (B).

[0080] As mentioned above, the partially hydrolyzed co-condensate of the compounds (A) and (B) is also meant for an oligomer to be formed by hydrolysis of all or some of hydrolyzable silyl groups in a solvent in the presence of a catalyst such as an acid catalyst or an alkali catalyst, followed by dehydration condensation, but here, the oligomer is one obtainable by hydrolytic condensation of a mixture of two types of hydrolyzable silyl group-containing compounds (i.e. the compound (A): a compound represented by the formula (la) and/or its partially hydrolyzed condensate, and the compound (B): a compound represented by the formula (2a) and/ or its partially hydrolyzed condensate), and therefore is called as a partially hydrolyzed “co-” condensate. The condensation degree (oligomerization degree) of such a partially hydrolyzed co-condensate is required to be such that the product is soluble in a solvent.

[0081] Further, the partially hydrolyzed co-condensate is one to be formed by reacting, as the compound (A), a compound represented by the formula (la) and/or its partially hydrolyzed condensate, and, as the compound (B), a compound represented by the formula (2a) and/or its partially hydrolyzed condensate in a solvent containing them, and may contain unreacted compounds (A) and (B). In the case of producing the partially hydrolyzed co-condensate, it is preferred that as the compound (A), a compound represented by the formula (la) (not its partially hydrolyzed condensate) is used, and as the compound (B), a compound represented by the formula (2a) (not its partially hydrolyzed condensate) is used.

[0082] The partially hydrolyzed co-condensate of the compounds (A) and (B) can be produced by dissolving in a solvent a prescribed amount of a compound represented by the formula (la) and/or its partially hydrolyzed condensate, and a prescribed amount of a compound represented by the formula (2a) and/or its partially hydrolyzed condensate, followed by stirring for a prescribed time in the presence of a catalyst such as an acid catalyst or an alkali catalyst, and water. As the acid catalyst, hydrochloric acid, nitric acid, acetic acid, sulfuric acid, phosphoric acid, sulfonic acid, methane sulfonic acid or p-toluene sulfonic acid may, for example, be used. As the alkali catalyst, sodium hydroxide, potassium hydroxide or aqueous ammonia may, for example, be used. By using an aqueous solution of such a catalyst, water required for the hydrolysis may be present in the reaction system. By heating in the presence of the catalyst and water, the reaction may be accelerated, but if the reaction proceeds too much, the condensation degree becomes too high, and the product is likely to be insoluble in a solvent. So long as a proper amount of the catalyst is present, it is preferred to carry out the reaction at normal temperature. The obtained solution of the partially hydrolyzed co-condensate may be used as it is, as the composition for forming a topcoat layer of the exemplary embodiment.

[0083] By using the above partially hydrolyzed co-condensate, it is possible to form a topcoat layer having a higher performance. For example, in the case of a topcoat layer which is formed from the compound represented by the formula (la) and the compound represented by the formula (2a), the topcoat layer is made of a hydrolyzed co-condensate of the two compounds and becomes a film wherein units derived from the two compounds are uniformly dispersed. The hydrolyzed co-condensate of the two compounds can be formed in a relatively short time, and in a film directly formed from the compound represented by the formula (la) and the compound represented by the formula (2a), it is likely that the uniformity in the distribution of the units derived from the two compounds tends to deteriorate. By preliminarily preparing the partially hydrolyzed co-condensate containing units derived from the two compounds, such uniformity is considered to be improved.

[0084] The compositional proportions of effective components in the topcoat composition for forming a topcoat layer of the exemplary embodiment can be determined from the amounts of the compounds (A) and (B) to be used. In a case where the composition comprises the compounds (A) and (B), the compositional proportions can be determined by the proportions of the two compounds used for producing the composition. However, in a case where the composition for forming a topcoat layer of the exemplary embodiment contains the above-mentioned partially hydrolyzed co-condensate, it is difficult to measure the compositional proportions of the effective components in such a partially hydrolyzed co-condensate. In such a case, in the subject invention, the compositional pro-portions of the effective components are determined by the starting material composition before producing the partially hydrolyzed co-condensate. That is, the compositional proportions of the effective components are determined from the amounts of the compounds (A) and (B) used as starting materials for the partially hydrolyzed co-condensate. For example, in a case where the composition for forming a topcoat layer is formed by producing a partially hydrolyzed co-condensate from the compound represented by the formula (la) and the compound represented by the formula (2a), the compositional proportions of units of the compound represented by the formula (la) and units of the compound represented by the formula (2a) in the partially hydrolyzed co-condensate are regarded to be the same as the compositional proportions of the two starting material compounds used.

[0085] The proportion of the compound (B) in the topcoat composition for forming a topcoat layer of the exemplary embodiment is preferably from 10 to 90 mass %, more preferably from 10 to 60 mass %, particularly preferably from 10 to 30 mass %, as the mass percentage of the compound (B) to the total mass of the compounds (A) and (B) represented by [compound (B)]/[compounds (A) and (B)]x100.

[0086] Further, in such a case, the proportion of the compound (A) in the topcoat composition for forming a topcoat layer of the exemplary embodiment is preferably from 90 to 10 wt %, more preferably from 90 to 40 mass %, particularly preferably from 90 to 70 mass %, as mass percentage of the compound (A) to the total mass of the compounds (A) and (B). As mentioned above, in the case of the partially hydrolyzed co-condensate, the mass percentage here is a compositional proportion calculated from the amounts of the compounds (A) and (B) before the reaction.

IV. Method of Application

[0087] The subject invention is also directed to a method for producing a treated substrate utilizing the afore-mentioned adhesion promoter composition and topcoat composition, each in accordance with the subject invention.

[0088] The method begins by providing the substrate (i.e., the untreated substrate) as described above. Preferably, the substrate has been cleaned using a solvent or an appropriate cleaning treatment known to those of ordinary skill. By way of example, the substrate may be cleaned first with a 2% CeO_2 solution, then rinsed with deionized water and dried using compressed air.

[0089] The process continues by applying the adhesion promoter composition onto at least a part of a surface of a substrate. The adhesion promoter composition, in certain embodiments, comprises the polyhedral oligomeric silsesquioxane as described above, such as the polyhedral oligomeric silsesquioxane of formula (I), (II), or (III). In other embodiments, the adhesion promoter composition comprises the linear organosilane polymer described above, such as the linear organosilane polymers comprising units of the formula (IV), (V), (VI), (VII), (VIII) or (IX) described above. The method of application of the adhesion promoter composition is not limited, and may include applying the composition by a spray application, a dipping application, a wiping application, or the like. In certain embodiments, a wiping application is used, wherein the adhesion promoter composition is wiped onto the cleaned and dried substrate using a soaked sponge in one or more application processes. Preferably, if multiple layers are applied, such application of the subsequent layers is within approximately thirty seconds such that the total wet thickness of the applied adhesion promoter composition is in the range of 100 nanometers or less, such as from 20 to 50 nanometers, corresponding to an applied monolayer of the adhesion promoter composition.

[0090] Next, the applied adhesion promoter composition is cured to form the adhesion promoter layer disposed on the substrate. In certain embodiments, the curing process includes wherein the applied adhesion promoter composition is allowed to air dry at room temperature for at least 5 seconds, such as 20 to 40 seconds, such as 25 seconds. While there is no upper limit to the time for allowing the applied adhesion promoter composition to cure, it is preferred that the curing process extends no more than about a minute prior to the application of the topcoat composition. The resultant cured layer of the adhesion promoter composition has a dry layer thickness in the range of 100 nanometers or less, such as from 20 to 50 nanometers, and the lower limit is the dry thickness of a monomolecular layer of the adhesion promoter composition and is preferred.

[0091] Next, the method continues by applying the topcoat composition onto the formed adhesion promoter layer and/or onto portions of the cleaned substrate not including the applied adhesion promoter composition layer. The method of application may be the same or different as the application of the adhesion promoter composition, and may include applying the topcoat composition by a spray application, a dipping application, a wiping application, or the like. In certain embodiments, a wiping application is used, wherein the topcoat composition is applied using a soaked sponge in one or more application processes.

[0092] Next, the applied topcoat composition is cured to form a topcoat layer disposed on the formed adhesion promoter layer and/or onto portions of the cleaned substrate. Preferably, the curing process is cured at ambient temperatures or higher and relatively high relative humidity for a sufficient period of time to ensure that the topcoat layer is dry and adhered to the cured adhesion promoter layer and/or substrate. In certain embodiments, the topcoat composition is cured for about 30 to 120 minutes, such as about 45 minutes, at a temperature between 60 and 80 degrees Fahrenheit (i.e., about 15-30 degrees Celsius) at a relative humidity of at least 50%, such as from 50 to 90%, such as from 60 to 80%. The thickness of the cured topcoat composition forming the topcoat layer is not particularly limited. However, if the formed topcoat layer is too thick, a damage may distinctly be observed. In certain embodiments, a dry thickness of the formed topcoat layer is at most 100 nanometers, such as at most 50 nanometers, such as from 20 to 50 nanometers, and the lower limit is the dry thickness of a monomolecular topcoat layer and is preferred.

[0093] Finally, and optionally, the produced treated substrate may be cleaned using a solvent such as isopropyl alcohol or acetone. More specifically, an outer surface of the formed topcoat layer may be wiped with the solvent.

[0094] The treated substrates, produced in accordance with the method described above, provide excellent initial hydrophobic properties, and corresponding water repellent properties, and such treated substrates retain such hydrophobic and water repellent properties under a wide variety of test conditions intended to simulate environmental conditions, thereby confirming the durability properties of the treated substrate, which is surprising and unexpected.

[0095] In certain embodiments, the treated substrate has an initial water contact angle of 95 degrees or more, and preferably above 100 degrees, such as from 100 to 115 degrees, with the water contact angle being measured in accordance with ASTM D7334-08 (2013). In particular, an outer surface of the treated substrate has the initial water contact angles as described above. Such water contact angle properties are an indication that the treated substrate has the desired hydrophobic properties, and also has water repellent properties.

[0096] In certain embodiments, the treated substrate has a sliding angle of less than or equal to 30 degrees, such as from 10 to 20 degrees, as also measured by ASTM D7334-08 (2013). In particular, an outer surface of the treated substrate has the initial sliding angle as described above. Such slide angle properties are another indication that the treated substrate has the desired hydrophobic properties, and also has water repellent properties.

[0097] In certain embodiments, the treated substrate, and in particular the outer surface of the treated substrate, substantially retains its water contact angle properties after various environmental tests, including mechanical durability (Flannel 1500 or 3000 testing), Xenon weatherometer testing, hot water testing, chemical strength testing, high temperature high humidity testing (HTHH), and salt spray (a description of each of these tests is described below). In particular, the treated substrate, maintains its water contact angles at above 80 degrees after each of such various environmental tests. When the water contact angle, as measured in accordance with ASTM D7334-08 (2013) is below 80 degrees, the treated substrate loses its hydrophobic and water repellent properties.

[0098] The treated substrate of the subject invention may be used as an article for a transport equipment in the transportation industry. The article for a transport equipment may, for example, be a body of e.g. an electric train, an automobile, a ship or an aircraft, window glass (front glass, side glass or rear glass), a mirror or a bumper. Due to its hydrophobic properties, the treated substrate has an excellent water droplet removal property (i.e., water repellent properties), whereby deposition of water droplets on the surface of the topcoat layer is scarce, and deposited water droplets will be quickly repelled. In addition, by the interaction with wind pressure resulting from the movement of the transport equipment, deposited water droplets swiftly move on the surface and will not stay as water droplets. Thus, adverse effects caused by water droplets can be eliminated.

[0099] In particular, the treated substrate of the subject invention may be utilized as window glass for a vehicle such as an automobile or truck. In particular, the treated substrate of the subject invention may be utilized as side window glass for a vehicle such as an automobile or truck. Accordingly, in these embodiments, the treated substrates also are also substantially transparent, with the term “substantially transparent” used in the same manner as described above with respect to the substrate 14 prior to the application of the layers as described above. In these transparent window applications, it becomes very easy to secure a visual field through the treated substrate by easy removal of water droplets, whereby the safety can be improved in the operation of the vehicles. Further, even in a freezing environment, water droplets tend to be hardly frozen to the treated substrate, and even if frozen, thawing is very fast. Further, deposition of water droplets on the treated substrate is scarce, whereby the number of cleaning operations of the treated substrate can be reduced, and yet, cleaning operations of the treated substrates can easily be carried out.

[00100] Now, the subject invention will be described with reference to Examples. However, the subject invention is by no means restricted to such specific Examples.

Examples

[00101] In the Examples provided herein, various combinations of adhesion promoter compositions and topcoat compositions were applied to a glass substrate material, including adhesion promoter compositions and topcoat compositions (WRC) of the subject invention, with the resultant treated substrates evaluated for initial water contact angle and for water contact angle after the performance of various environmental and/or physical tests.

Process of making WRC Topcoat Composition

[00102] The water resistant topcoat (WRC) coating composition for use in forming the topcoat layer is formed, with the components as shown in Table 1, by introducing 80 parts by weight of a 7.5/92.5 weight percent mixture of a fluorine-containing chlorosilane compound (i.e., a fluorinated organic silicon compound having no etheric oxygen atom corresponding to compound (A) above) and hydrofluoroether (AE3000, manufactured by Asahi Glass Company, Limited) to a container. The mixture is stirred using a magnetic stirrer. 1.25 parts by weight of a 94/6 weight percent mixture of CF3—O—$(CF_2CF_2O)_a$—CF2—$CONHC_3H_6Si(OCH_3)_3$ (with the subscript a = 7 to 8) (i.e., a fluorinated organic silicon compound having an etheric oxygen atom corresponding to compound (B) above) and methanol was added dropwise to the container. Finally, 18.5 parts by weight of butyl acetate was added to the container. A lid is placed on the container and the resultant mixture is mixed for 60 minutes to form the WRC coating composition in accordance with one embodiment of the subject invention.

Table 1. WRC Composition

Component	Parts By Weight
Fluorine-containing chlorosilane compound	6
AES 3000	74
CF_3—O—$(CF_2CF_2O)_a$—CF_2—$CONHC_3H_6Si(OCH_3)_3$	1.175
Methanol	0.075
Butyl Acetate	18.75
TOTAL	100

Process of making Adhesion Promoter Composition 1 or 2

[00103] The adhesion promotor composition is formed according to the process illustrated and described in Table 2. The adhesion promoter composition listed in Sequence 1 refers to the polyhedral oligomeric silsesquioxane according to the formula: $C_{170}H_{402}O_{99}Si_{45}$, which is used to form the Adhesion Promoter Composition 1.

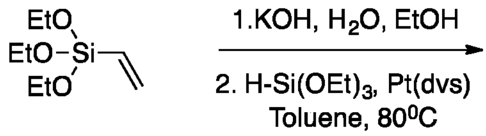
Table 2. Process for Making Adhesion Promoter Composition 1

Sequence	Process Step
1	Add 1 gram of concentrated polyhedral oligomeric silsesquioxane into a vial.
2	Add 10 mL (milliliters) of Ethanol (EtOH) to the vial and shake for 2 minutes. Transfer to a container.
3	Rinse the vial with 10 mL of EtOH and pour into a jar. Repeat this step until all of the solids are transferred to the jar.
4	Fill the jar with EtOH to a volume of 500 mL. Shake or agitate the jar until all solids are dissolved.
5	Add 3.75 mL of Nitric Acid to the 500 mL jar.
6	Tighten the cap on the jar and shake the jar vigorously for 3 minutes to form the Adhesion Promoter Composition 1. Use within 2 hours.

[00104] The same process can also be used to form Adhesion Promoter Composition 2, wherein Sequence 1 substitutes the linear organosilane polymer according to the formula: $C_{64}H_{152}O_{36}Si_{16}$ for the polyhedral oligomeric silsesquioxane according to the formula: $C_{170}H_{402}O_{99}Si_{45}$.

Synthesis of compounds for Adhesion Promoter Composition

Example 1 – Octa(triethoxysilyl)-T8-silsesquioxane: (A)

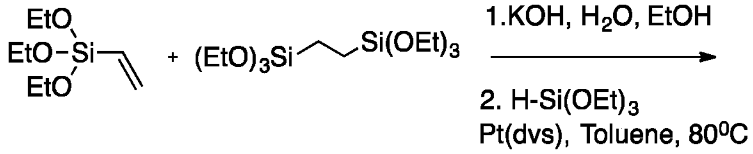


(reaction product to be discussed).

[00105] Triethoxyvinylsilane (11g, 0.058 mol) was dissolved in 30 mL of EtOH at room temperature followed by the addition of 2.0 ml of aqueous KOH solution (10mg/ml). The reaction mixture was stirred for overnight at RT. The next day a white precipitate was filtered off and dried *in-vacuo* to provide 2.3g of white solid. (51%). Obtained white solid/ or commercially available octavinyl-T8-silsesquioxane (5.0 g, 7.9 mmol, 1 eq) and triethoxysilane (10.4 g, 0.063 mol, 8 eq) were dissolved in anhydrous toluene (40 mL) and purged under Argon for 30 minutes. Then, catalytic amount of Pt(dvs) (25μL) was added to the reaction mixture and heated up to 80 °C for overnight. The solution was filtered through silica to remove excess starting material. The organic filtrate is dried *in-vacuo*. Obtained pale yellow oil. Yield: 11.8 g (79%).

[00106] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.63-0.66 (t, 32H), 1.20-1.23 (t, 72H), 3.78-3.81 (d, 48H), ^{13}C NMR ($CDCl_3$, 120 MHz): 1.61 (8C), 3.35 (8C), 18.27 (24C), 58.32 (24C).

Example 2 – 1,2-bis-octa(triethoxysilyl)-T8-silsesquioxane: (B)



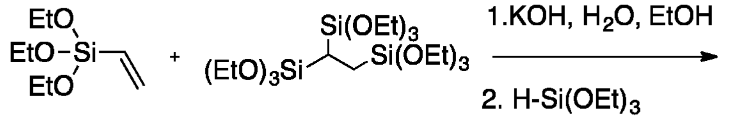
(reaction product to be discussed).

[00107] 7.50g of vinyl triethoxysilane (39.5mmol, 14 eq) and 1.0g of 1,2-bis(triethoxysilyl)ethane (2.82 mmol, 1 eq) with a catalytic amount of aqueous KOH solution were dissolved in ethanol at room temperature, and stirred for five hours. During the reaction, a white precipitate formed in the reaction vessel. The solid portion was filtered off, and dried *in-vacuo*. Obtained 2.60g of white powder (2.10 mmol, Yield 74%).

[00108] 1.0g of the white powder (0.95 mmol, 1 eq) and 2.35g of triethoxysilane (14.3 mmol, 15 eq) were dissolved in toluene at 40 °C for 30 minutes under Ar gas purging. A catalytic amount of Pt(0) was added to the reaction mixture, and heated to 80 °C for 8 hours. The solution was filtered through silica to remove by-product. The organic filtrate was dried *in-vacuo* to provide 0.34g of pale yellow oil (0.09 mmol, Yield 10%).

[00109] ^{1}H NMR (CDCl$_3$, 500 MHz): δ 0.12 (t, 4H), 0.63-0.66 (t, 56H), 1.20-1.23 (t, 126H), 3.78-3.81 (d, 84H), ^{13}C NMR (CDCl$_3$, 120 MHz): 1.37 (14C), 2.1 (2C), 2.52 (14C), 18.27 (42C), 58.32 (42C).

Example 3 – 1,1,2-tris-octa(triethoxysilyl)-T8-silsesquioxane: (C)



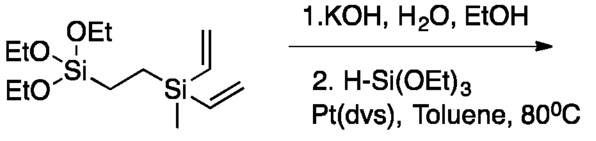
(reaction product to be discussed).

[00110] 27.2g of vinyl triethoxysilane (143.0 mmol, 21 eq) and 3.51g of 1,1,2-tris(triethoxysilyl)ethane (6.79 mmol, 1 eq) with catalytic amount of aqueous KOH solution were dissolved in ethanol at room temperature, and stirred for five hours. During the reaction, a white precipitate formed in the reaction vessel. The solid portion was filtered off, and dried *in-vacuo* to provide 12g of white solid (6.50 mmol, Yield 96%)

[00111] 7.56 g of white solid prepared by the method described in the preceding paragraph (5.18 mmol, 1 eq) and 17.88 g of triethoxysilane (108.82 mmol, 21 eq) were dissolved in toluene at 40 °C for 30 minutes under Ar gas purging. A catalytic amount, 0.2mL, of Pt(0) was added to the reaction mixture, and heated up to 80 °C for 8 hours. The solution was filtered through silica to remove by-product. The organic filtrate was dried *in-vacuo* to provide 18.85 g of pale yellow oil (3.56 mmol, Yield 69%).

[00112] ^{1}H NMR (CDCl$_3$, 500 MHz): δ -0.98 (1H), 0.11 (2H), 0.56-0.69 (t, 84H), 1.10-1.13 (t, 189H), 3.72-3.74 (d, 126H), ^{13}C NMR (CDCl$_3$, 120 MHz): -2.17(1C), 1.35 (1C), 1.38 (21C), 2.52 (21C), 17.88 (63C), 58.07 (63C).

Example 4 – Bis-octa(triethoxysilyl)-T8-silsesquioxane-ethylmethylsilane: (F)

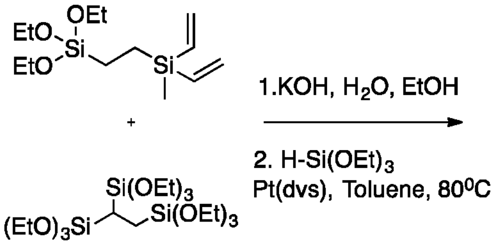


(reaction product to be discussed).

[00113] 5.0g of 2-(divinylmethylsilyl)ethyltriethoxysilane (17.32 mmol, 1 eq) with a catalytic amount of aqueous KOH solution were dissolved in ethanol at room temperature, and stirred for five hours. During the reaction, the solution became turbid. The product was dried *in-vacuo* to provide 3.2g of liquid (2.29mmol, Yield 64%)

[00114] 1.58g of the liquid from the first step (1.11 mmol, 1 eq) and 3.10g of triethoxysilane (18.88 mmol, 16 eq) were dissolved in toluene at 40 °C for 30 minutes under Ar gas purging. A catalytic amount of Pt(0) was added to the reaction mixture, and heated up to 80 °C for 8 hours. The solution was filtered through silica to remove by-product. The organic filtrate was dried *in-vacuo* to provide 2.3g of pale yellow oil (0.57 mmol, Yield 51%).

Example 5 – 1,1,2-tris-octa(triethoxysilyl)-T8-silsesquioxane-ethylmethylsilane

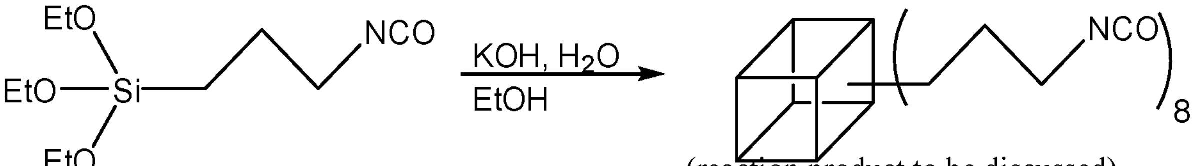


(reaction product to be discussed).

[00115] 2-(divinylmethylsilyl)ethyltriethoxysilane and 1,1,2-tris(triethoxysilyl)ethane with catalytic amount of aqueous KOH solution were dissolved in ethanol at room temperature, and stirred for five hours. During the reaction, a white precipitate formed in the reaction vessel. The solid portion was filtered off and dried *in-vacuo*.

[00116] 2.41g of the solid obtained in the first step (0.58 mmol, 1 eq) and 4.17g of triethoxysilane (25.38 mmol, 45 eq) were dissolved in toluene at 40 °C for 30 minutes under Ar gas purging. A catalytic amount of Pt(0) was added to the reaction mixture and heated up to 80 °C for 8 hours. The solution was filtered through silica to remove by-product. The organic filtrate was dried *in-vacuo*. Obtained 1.89g of pale yellow oil (0.17 mmol, Yield 30%).

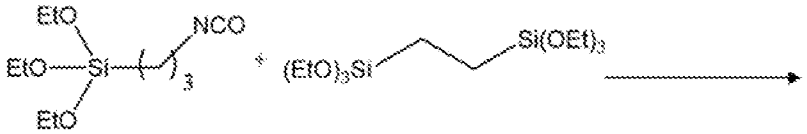
Example 6 - Octa(3-propylisocyanate)-T8-silsesquioxane:



(reaction product to be discussed).

[00117] 5g of 3-isocyanatopropyl triethoxysilane (20.21 mmol,1 eq) with catalytic amount of aqueous KOH solution were dissolved in ethanol at room temperature and stirred for five hours. Added ethyl acetate to the reaction mixture and washed out with distilled water couple of times. Organic filtrate was dried over $MgSO_4$ and evaporated the solvent *in-vacuo*. Obtained 3.0g of pale yellow oil (2.75 mmol, yield 95%).

Example 7 - 1,2-bis-octa(3-propylisocyanate)-T8-silsesquioxane:

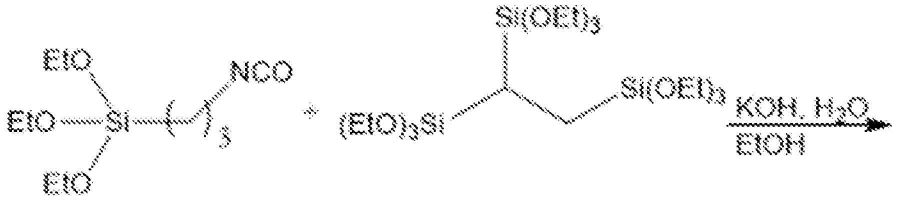


(reaction product to be discussed).

Example 8 - Tris(3-propylisocyanate)-T8-silsesquioxane:

[00118] 4.48g of 3-isocyanatopropyl triethoxysilane (18.11 mmol, 14 eq) and 0.45g of 1, 2-bis(triethoxysilyl)ethane (1.26 mmol, 1 eq) with catalytic amount of aqueous KOH solution were dissolved in ethanol at room temperature, and stirred for five hours. Added ethyl acetate to the reaction mixture, and washed out with distilled water couple of times. The organic filtrate was dried over $MgSO_4$ and evaporated the solvent *in-vacuo* to provide 2.32g of pale yellow oil (1.26mmol, yield quantitative).

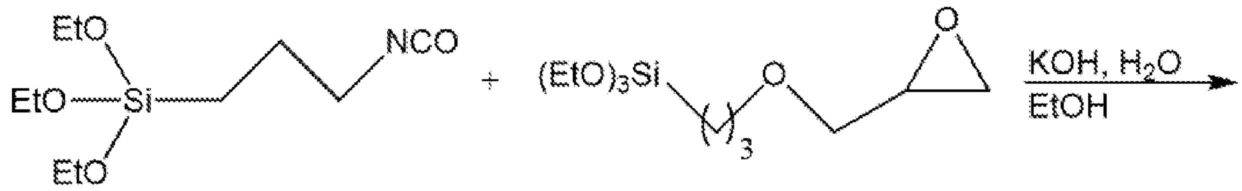
Example 9



(reaction product to be discussed).

[00119] 2.51g of 3-isocyanatopropyl triethoxysilane (20.31 mmol, 21 eq) and 0.25g of 1,1,2-tris(triethoxysilyl)ethane (0.97 mmol, 1 eq) with catalytic amount of aqueous KOH solution were dissolved in ethanol at room temperature and stirred for five hours. Added ethyl acetate to the reaction mixture and washed out with distilled water couple of times. The organic filtrate was dried over $MgSO_4$, and evaporated the solvent *in-vacuo* to provide 2.2g of pale yellow oil (0.83 mmol, yield 86%)

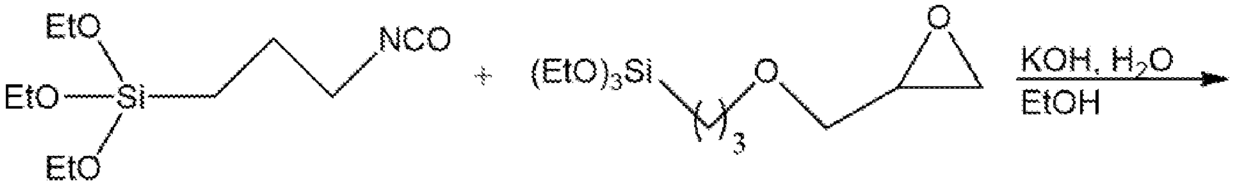
Example 10



(reaction product to be discussed).

[00120] 5.0g of 3-Isocyanatopropyl triethoxysilane (21.21 mmol, 6 eq) and 1.59g of 3-glycidoxypropyl triethoxysilane (6.73 mmol, 2 eq) with catalytic amount of aqueous KOH solution are dissolved in ethanol at room temperature and stirred for five hours. Added ethyl acetate to the reaction mixture and washed out distilled water couple of times. Organic filtrate was dried over $MgSO_4$ and evaporated the solvent *in-vacuo*. Obtained 4.10g of white solid (3.56 mmol, yield 99%).

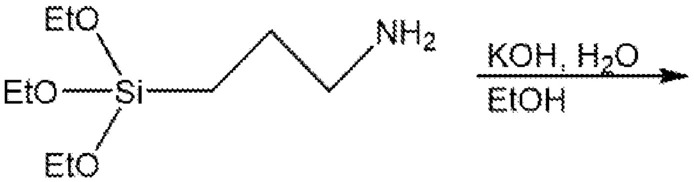
Example 11



(reaction product to be discussed).

[00121] 4.0g of 3-isocyanatopropyl triethoxysilane (16.17 mmol, 4 eq) and 3.82g of 3-glycidoxypropyl triethoxysilane (16.17 mmol, 4 eq) with catalytic amount of aqueous KOH solution were dissolved in ethanol at room temperature, and stirred for five hours. Added ethyl acetate to the reaction mixture and washed out with distilled water couple of times. The organic filtrate was dried over $MgSO_4$, and evaporated the solvent *in-vacuo* to provide 4.95g of white solid (4.0 mmol, yield 99%).

Example 12

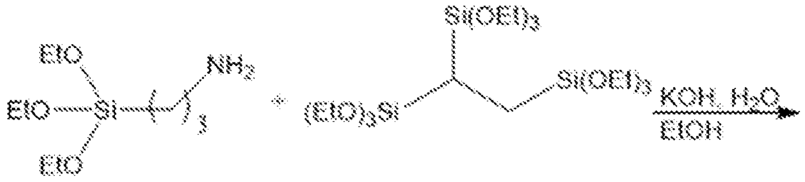


(reaction product to be discussed).

[00122] 20.32g of 3-propylamine triethoxysilane (91.99 mmol,1 eq) with catalytic amount of aqueous KOH solution were dissolved in ethanol at room temperature and stirred for five hours. Added ethyl acetate to the reaction mixture and washed out with distilled water couple of times. Organic filtrate was dried over $MgSO_4$ and evaporated the solvent *in-vacuo*. Obtained 9.71g of pale yellow oil (11.01 mmol, yield 96%).

[00123] ^{1}H NMR ((EtOH-D, 500 MHz): δ 0.56-0.61 (t, 16H), 1.25-1.34 (m, 16H), 2.65-2.87 (t, 16H), 3.16-3.19 (b, 16H), ^{13}C NMR ((EtOH-D, 500 MHz): δ 1.93 (8C), 24.8 (8C), 64.5 (8C)

Example 13



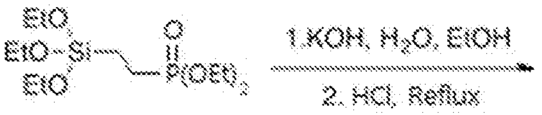
(reaction product to be discussed).

[00124] 5.00 g of 3-propylamine triethoxysilane (22.58 mmol,1 eq) and 0.55g of 1,1,2-tris(triethoxysilyl)ethane (1.07 mmol, 1 eq) with catalytic amount of aqueous KOH solution were dissolved in ethanol at room temperature and stirred for five hours. Added ethyl acetate to the reaction mixture and washed out with distilled water couple of times. Organic filtrate was dried over $MgSO_4$ and evaporated the solvent *in-vacuo*. Obtained 2.34g of pale yellow oil (1.01 mmol, yield 95%).

[00125] ^{1}H NMR ((EtOH-D, 500 MHz): δ 0.58-0.65 (t, 16H), 1.28-1.37 (m, 16H), 2.64-2.87 (t, 16H), ^{13}C NMR ((EtOH-D, 120 MHz): δ 1.93 (8C), 2.1 (1C), 25.8 (8C), 64.5 (8C),

Certain exemplary embodiments and aspects thereof are described below in greater detail.

Example 14. - Ethylphosphonicacid-T8-silsesquioxane:



(reaction product to be discussed).

[00126] Phosphonatoethyltriethoxysilane (5.12g, 15.59 mmol) was dissolved in 10 mL of EtOH at room temperature followed by the addition of 2.0 ml of aqueous KOH solution (10mg/ml). The reaction mixture was stirred for overnight at RT. The next day, the solution was extracted with ethylacetate. Organic layer was dried over Na_2SO_4 and dried *in-vacuo* to provide 2.39g of liquid (1.54 mmol, Yield 79%). Obtained liquid were dissolved in a mixture of 10ml of ethanol and water. Then, 3ml of HCl was added to the reaction mixture and refluxed for overnight. The solution was filtered through silica to remove excess starting material. The organic filtrate is dried *in-vacuo*. Obtained liquid. Yield: 1.09g (8.47 mmol, 55%).

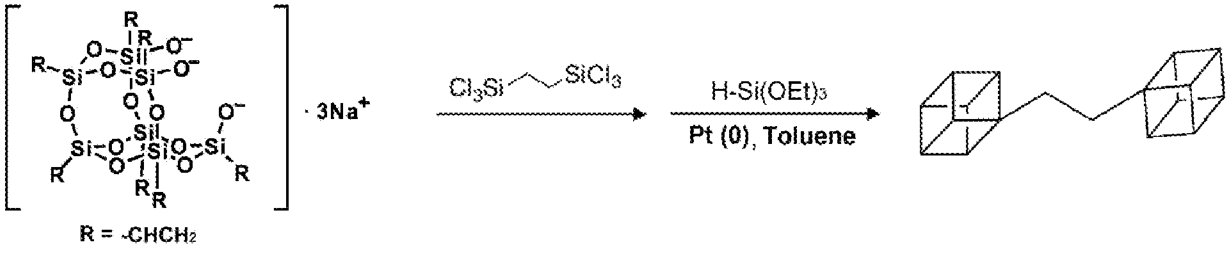
[00127] ^{1}H NMR (Acetone-D, 500 MHz): δ 0.75-0.80 (t, 16H), 1.21-1.29 (t, 48H), 1.62-1.69 (t, 16H), 3.99-4.08 (q, 32H), ^{13}C NMR (Acetone-D, 120 MHz): 15.97 (8C), 28.81 (8C).

Example 15

[00128] Vinyltriethoxysilane (10g, 52.5 mmol), THF (50ml), distilled water (1g), and sodium hydroxide (0.79g, 19.8 mmol) are charged into a four-necked flask equipped with a reflux condenser and a thermometer at 70 °C for 5h with magnetically stirring. The system is allowed to get cool to room temperature and left for 15 h. The volatile components are removed by heating at 95 °C under atmospheric pressure to obtain a white precipitate, which is collected by a membrane filter having a pore diameter of 0.5 µm, washed with THF, and dried at 80 °C for 3 h in a vacuum oven to yield hepta(vinyl)-tricycloheptasiloxane trisodium silanolate.

[00129] Hepta(vinyl)-tricycloheptasiloxane trisodium silanolate (2.2g, 3.40 mmol), triethylamine (0.35g, 3.45 mmol) and dry THF (50 ml) are charged into a round-bottomed flask, to which 1,2-bis(trichlorosilyl)ethane (0.50g, 1.1 mmol) is quickly added at room temperature. The mixture is magnetically stirred for 4h at room temperature. The resultant precipitate is removed by filtration, and the filtrate is concentrated by a rotary evaporator to obtain a crude product. The resultant solid is dispersed in methanol, collected with a membrane filter, and dried at 75 °C for 5h to yield 1,2-bis(heptavinyladhesion promoters)ethane as a white solid.

[00130] 1,2-bis(heptavinyladhesion promoters) (2g, 1.61 mmol) and triethoxysilane (3.7g, 22.58 mol) in toluene (50 ml) are charged into a round-bottomed flask. The reaction mixture is stirred at 40 °C for 30 minutes under Ar(g) purging. Then, the catalytic amount of Pt (0) is added to the reaction mixture and heated up to 80 °C for 8 hours. The solution is filtered through Celite to remove unreacted reactant. The organic filtrate is dried in-vacuo to yield 1,2-bis(hepta(triethoxysilyl)adhesion promoters)ethane as pale yellow oil.

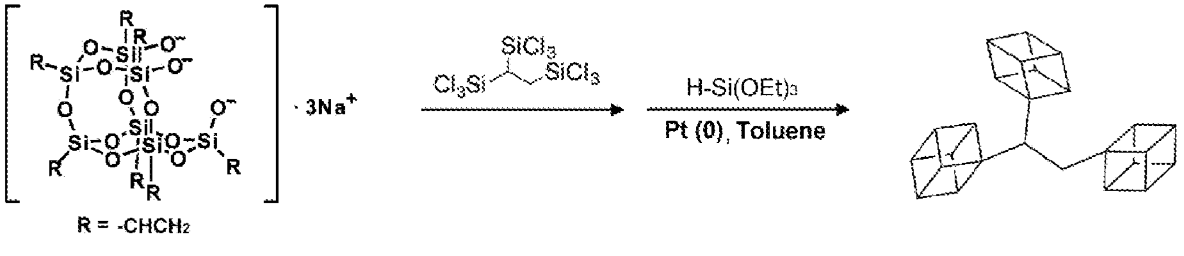


Example 16

[00131] Vinyltriethoxysilane (10g, 52.5 mmol), THF (50ml), distilled water (1g), and sodium hydroxide (0.79g, 19.8 mmol) are charged into a four-necked flask equipped with a reflux condenser and a thermometer at 70 °C for 5h with magnetically stirring. The system is allowed to get cool to room temperature and left for 15 h. The volatile components are removed by heating at 95 °C under atmospheric pressure to obtain a white precipitate, which is collected by a membrane filter having a pore diameter of 0.5 μm, washed with THF, and dried at 80 °C for 3 h in a vacuum oven to yield hepta(vinyl)-tricycloheptasiloxane trisodium silanolate.

[00132] Hepta(vinyl)-tricycloheptasiloxane trisodium silanolate (2.2g, 3.40 mmol), triethylamine (0.35g, 3.45 mmol) and dry THF (50 ml) are charged into a round-bottomed flask, to which 1,1,2-tris(trichlorosilyl)ethane (0.47g, 1.1 mmol) is quickly added at room temperature. The mixture is magnetically stirred for 4h at room temperature. The resultant precipitate is removed by filtration, and the filtrate is concentrated by a rotary evaporator to obtain a crude product. The resultant solid is dispersed in methanol, collected with a membrane filter, and dried at 75 °C for 5h to yield 1,1,2-tris(heptavinyladhesion promoters)ethane as a white solid.

[00133] 1,1,2-tris(heptavinyladhesion promoters) (1g, 1.54 mmol) and triethoxysilane (5.33g, 32.46 mol) in toluene (50 ml) are charged into a round-bottomed flask. The reaction mixture is stirred at 40 °C for 30 minutes under Ar(g) purging. Then, the catalytic amount of Pt (0) is added to the reaction mixture and heated up to 80 °C for 8 hours. The solution is filtered through Celite to remove unreacted reactant. The organic filtrate is dried in-vacuo to yield 1,1,2-tris(hepta(triethoxysilyl)adhesion promoters)ethane as pale yellow oil.

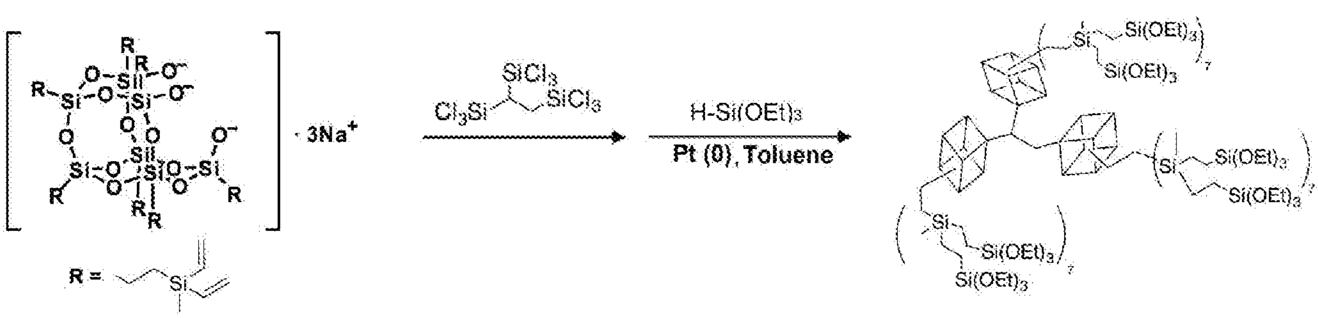


Example 17

[00134] 2-(divinylmethylsilyl)ethyltriethoxysilane (10g, 34.65 mmol), THF (50ml), distilled water (1g), and sodium hydroxide (0.79g, 19.8 mmol) are charged into a four-necked flask equipped with a reflux condenser and a thermometer at 70 °C for 5h with magnetically stirring. The system is allowed to get cool to room temperature and left for 15 h. The volatile components are removed by heating at 95 °C under atmospheric pressure to obtain a white precipitate, which is collected by a membrane filter having a pore diameter of 0.5 μm, washed with THF, and dried at 80 °C for 3 h in a vacuum oven to yield hepta(2-(divinylmethylsilyl)ethyl)-tricycloheptasiloxane trisodium silanolate.

[00135] Hepta(2-(divinylmethylsilyl)ethyl)-tricycloheptasiloxane trisodium silanolate (5g, 3.74 mmol), triethylamine (0.38g, 3.75 mmol) and dry THF (60 ml) are charged into a round-bottomed flask, to which 1,1,2-tris(trichlorosilyl)ethane (0.51g, 1.18 mmol) is quickly added at room temperature. The mixture is magnetically stirred for 4h at room temperature. The resultant precipitate is removed by filtration, and the filtrate is concentrated by a rotary evaporator to obtain a crude product. The resultant solid is dispersed in methanol, collected with a membrane filter, and dried at 75 °C for 5h to yield 1,1,2-tris(hepta((divinylmethylsilyl)ethyl)adhesion promoters)ethane as a white solid.

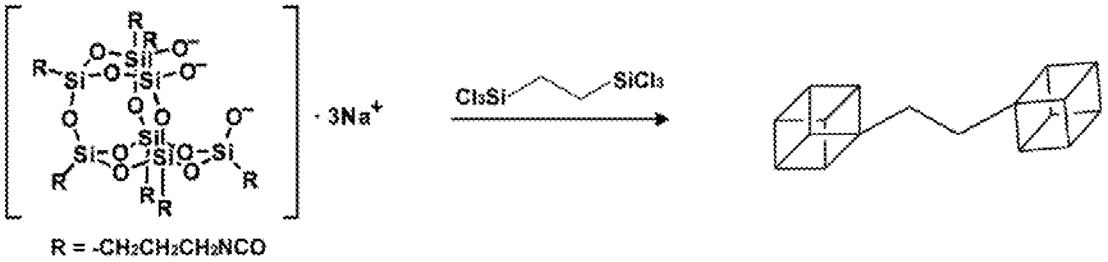
[00136] 1,1,2-tris(hepta((divinylmethylsilyl)ethyl)adhesion promoters)ethane (1g, 0.75 mmol) and triethoxysilane (5.17g, 31.5 mol) in toluene (50 ml) are charged into a round-bottomed flask. The reaction mixture is stirred at 40 °C for 30 minutes under Ar(g) purging. Then, the catalytic amount of Pt (0) is added to the reaction mixture and heated up to 80 °C for 8 hours. The solution is filtered through Celite to remove unreacted reactant. The organic filtrate is dried in-vacuo to yield 1,1,2-tris(hepta((di(triethoxysilyl)methylsilyl)ethyl)adhesion promoters)ethane as pale yellow oil.



Example 18

[00137] 3-Isocyanatoppropyltriethoxysilane (10g, 40.42 mmol), THF (50ml), distilled water (1g), and sodium hydroxide (0.8g, 20 mmol) are charged into a four-necked flask equipped with a reflux condenser and a thermometer at 70 °C for 5h with magnetically stirring. The system is allowed to get cool to room temperature and left for 15 h. The volatile components are removed by heating at 95 °C under atmospheric pressure to obtain a white precipitate, which is collected by a membrane filter having a pore diameter of 0.5 µm, washed with THF, and dried at 80 °C for 3 h in a vacuum oven to yield hepta(3-isocayanatopropyl)-tricycloheptasiloxane trisodium silanolate.

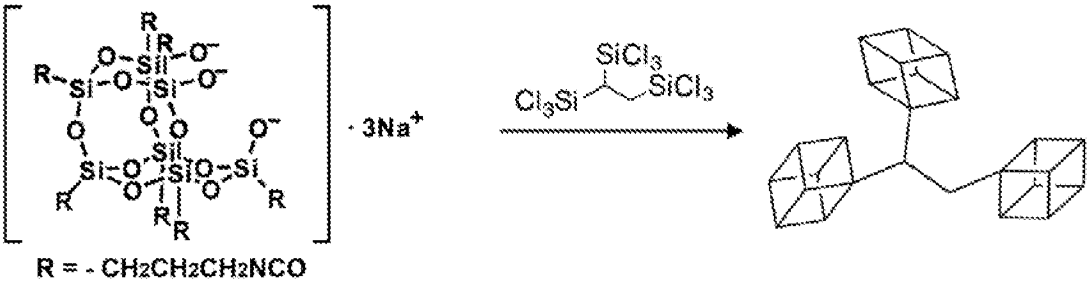
[00138] Hepta(3-isocyanatopropyl)-tricycloheptasiloxane trisodium silanolate (3g, 2.87 mmol), triethylamine (0.29g, 2.87 mmol) and dry THF (50 ml) are charged into a round-bottomed flask, to which 1,2-bis(trichlorosilyl)ethane (0.42g, 1.43 mmol) is quickly added at room temperature. The mixture is magnetically stirred for 4h at room temperature. The resultant precipitate is removed by filtration, and the filtrate is concentrated by a rotary evaporator to obtain a crude product. The resultant solid is dispersed in methanol, collected with a membrane filter, and dried at 75 °C for 5h to yield 1,2-bis(hepta(isocyanatopropyl)adhesion promoters).



Example 19

[00139] 3-Isocyanatoppropyltriethoxysilane (10g, 40.42 mmol), THF (50ml), distilled water (1g), and sodium hydroxide (0.8g, 20 mmol) are charged into a four-necked flask equipped with a reflux condenser and a thermometer at 70 °C for 5h with magnetically stirring. The system is allowed to get cool to room temperature and left for 15 h. The volatile components are removed by heating at 95 °C under atmospheric pressure to obtain a white precipitate, which is collected by a membrane filter having a pore diameter of 0.5 µm, washed with THF, and dried at 80 °C for 3 h in a vacuum oven to yield hepta(3-isocayanatopropyl)-tricycloheptasiloxane trisodium silanolate.

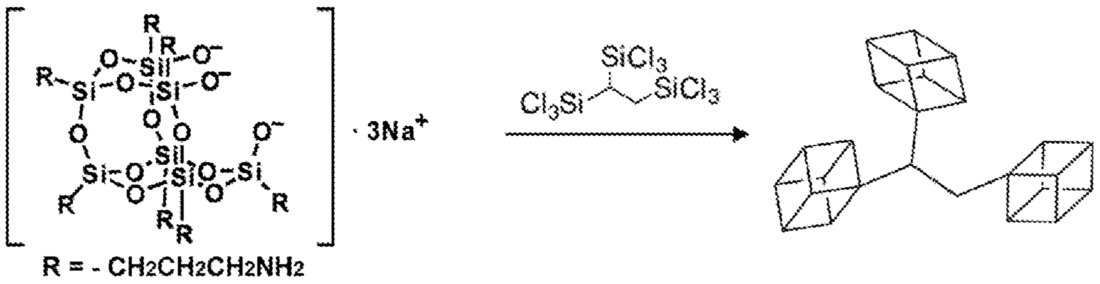
[00140] Hepta(2-(divinylmethylsilyl)ethyl)-tricycloheptasiloxane trisodium silanolate (3g, 2.87 mmol), triethylamine (0.29g, 2.87 mmol) and dry THF (50 ml) are charged into a round-bottomed flask, to which 1,1,2-tris(trichlorosilyl)ethane (0.41g, 0.95 mmol) is quickly added at room temperature. The mixture is magnetically stirred for 4h at room temperature. The resultant precipitate is removed by filtration, and the filtrate is concentrated by a rotary evaporator to obtain a crude product. The resultant solid is dispersed in methanol, collected with a membrane filter, and dried at 75 °C for 5h to yield 1,1,2-tris(hepta(isocyanatopropyl)adhesion promoters)ethane as a white solid.



Example 20

[00141] 3-Propylaminotriethoxysilane (10g, 45.17 mmol), THF (50ml), distilled water (1g), and sodium hydroxide (0.8g, 20 mmol) are charged into a four-necked flask equipped with a reflux condenser and a thermometer at 70 °C for 5h with magnetically stirring. The system is allowed to get cool to room temperature and left for 15 h. The volatile components are removed by heating at 95 °C under atmospheric pressure to obtain a white precipitate, which is collected by a membrane filter having a pore diameter of 0.5 μm, washed with THF, and dried at 80 °C for 3 h in a vacuum oven to yield hepta(3-aminopropyl)-tricycloheptasiloxane trisodium silanolate.

[00142] Hepta(3-aminopropyl)-tricycloheptasiloxane trisodium silanolate (3g, 3.47 mmol), triethylamine (0.35g, 3.47 mmol) and dry THF (50 ml) are charged into a round-bottomed flask, to which 1,1,2-tris(trichlorosilyl)ethane (0.47g, 1.1 mmol) is quickly added at room temperature. The mixture is magnetically stirred for 4h at room temperature. The resultant precipitate is removed by filtration, and the filtrate is concentrated by a rotary evaporator to obtain a crude product. The resultant solid is dispersed in methanol, collected with a membrane filter, and dried at 75 °C for 5h to yield 1,1,2-tris(hepta(aminopropyl)adhesion promoters)ethane as a pale yellow solid.



Comparative Topcoat Compositions

[00143] Comparative topcoat compositions that include a 5:1 blend of fluorosilane and a fluorine-containing polyhedral oligomeric silsesquioxane (F-POSS) were included for evaluation with respect to Treated Samples 2 and 3, respectively, as described below. The product EnduroShield Home, commercially available from PCT Global LLC of Santa Barbara, California and sold at home improvement stores throughout the United States (such as Lowe's) was purchased at a local retailer and applied to the substrates as a topcoat in accordance with the instructions provided on its packaging and was included in Treated Sample 6 below.

Process of making the Treated Substrates

[00144] The process for forming the treated substrates evaluated in the subject invention were as follows.

[00145] First, a glass substrate was obtained and cleaned with a 2% CeO_2 solution. The glass substrate was then rinsed with deionized water, and dried using compressed air.

[00146] Next, a first layer of an adhesion promoter composition (when utilized) was wiped onto the cleaned glass substrate using a soaked sponge. After thirty seconds, a second layer of the adhesion promoter composition was wiped onto the first layer using a soaked sponge. The resultant total thickness was between 20 and 50 nanometers.

[00147] Next, a topcoat composition was applied onto the layers of adhesion promoter composition, or directly onto the cleaned glass substrate in samples not including the adhesion promoter composition, using a soaked sponge. The topcoat composition was then cured for 45 minutes at a temperature of between about 60 and 80 degrees Fahrenheit (about 15 to 27 degrees Celsius) at 70% relative humidity for about 45 minutes.

[00148] Finally, the formed treated substrates were cleaned using a solvent such as isopropyl alcohol or acetone.

Process of Evaluating the Treated Substrates

[00149] The treated substrates, formed in accordance with the procedures described above, were first evaluated for initial water contact angle using ASTM standard D7334 – 08 (2013). Next the treated substrates were subjected to the following further environmental testing conditions (see Table 3 below), and then the conditioned substrates were reevaluated for water contact angle in the manner described above for the initial water contact angle.

Table 3 Tests, Testing Standards, Testing Conditions

Test	Testing Standard	Conditions
Mechanical durability (Flannel 1500 or Flannel 3000)	---	Traverse the surface of the treated substrate with a cloth at a force of 9.81N/4cm^2 (Cloth Abrasion) 1500 times (cycles) (Flannel 1500) or 3000 times (cycles) (Flannel 3000)
Weatherability	JIS 1960	Xenon Weatherometer: Boiling point 63 degrees Celsius for 2500 hours
Hot water	---	50°C 1000hr immersion
Chemical strength	---	Alkali base soak (immerse) the treated substrate in a 0.1N (pH=11 or 13) solution of sodium hydroxide (NaOH) for 24 hours
High Temperature Humidity Test (HTHH	---	80 degrees Celsius/95% Relative Humidity for 1000 1000 or 2000 hours
Salt Spray	ASTM B117	500 or 2000 hours

[00150] The testing results for the treated substrates, formed and evaluated according to the procedures above, are summarized in Tables 4 and 5 below:

Table 4 – Treated Samples

Treated Sample	Adhesion Promoter	Topcoat
1	Silane-based Adhesion Promoter Composition	WRC
2	Adhesion Promoter Composition 1	Fluorosilane and F-POSS (5:1) topcoat composition
3	Adhesion Promoter Composition 2	Fluorosilane and F-POSS (5:1) topcoat composition
4	Adhesion Promoter Composition 1	WRC

5	Adhesion Promoter Composition 2	WRC
6	None	EnduroShield

Table 5 – Test Results

Water Contact Angle Test	**Treated Sample 1**	**Treated Sample 2**	**Treated Sample 3**	**Treated Sample 4**	**Treated Sample 5**	**Treated Sample 6**
Initial	107	107	110	106	102	103
UV - 500 hrs.	108	113	112	112	112	103
UV – 2000 hrs.	108	104	99	103	98	99
Flannel – 1500 cycles	99	82	30	97	96	100
Flannel - 3000 cycles	92	72	25	82	91	100
Base Soak - pH 11	108	107	107	100	106	103
Base Soak - pH 13	100	NA	NA	102	95	NA
Water Soak - 500 hrs.	90	109	108	93	104	67
Water Soak - 1000 hrs.	78	NA	NA	92	98	65
HTHH – 500 hrs.	109	110	112	107	111	97
HTHH – 2000 hrs.	98	88	106	89	107	75
Salt Spray – 500 hrs.	72	97	64	105	109	60
Salt Spray – 1000 hrs.	40	90	24	62	107	10

[00151] As confirmed in Table 5, treated substrates formed that includes layers of Adhesion promoter composition (1 or 2) and topcoat composition in accordance with the embodiments of the subject invention (WRC) provided initial water contact angles indicative of the treated substrate having the desired hydrophobic properties, and most closely retained their initial water contact angle measurements over the variety of testing conditions than the other combinations of adhesion promoter compositions and/or topcoat compositions which confirms the durability of the applied layers to maintain such hydrophobic properties.

[00152] The invention has been described in an illustrative manner, and it is to be understood that the terminology which has been used is intended to be in the nature of words of description rather than of limitation. As is now apparent to those skilled in the art, many modifications and variations of the subject invention are possible in light of the above teachings. It is, therefore, to be understood that within the scope of the appended claims, wherein reference numerals are merely for convenience and are not to be in any way limiting, the invention may be practiced otherwise than as specifically described.

CLAIMS

What is claimed is:

1. A treated substrate comprising:

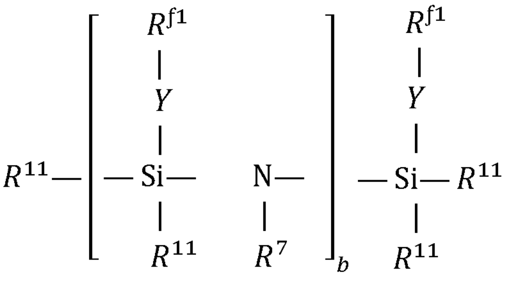
a substrate;

an adhesion promoter layer disposed on said substrate, said adhesion promoter layer formed from an adhesion promoter composition, said adhesion promoter composition comprising a polyhedral oligomeric silsesquioxane or a linear organosilane polymer; and

a topcoat layer disposed on said adhesion layer such that said adhesion layer is between said topcoat layer and said substrate, said topcoat layer formed from a topcoat composition, said topcoat composition comprising at least one fluorinated organic silicon compound which contains no etheric oxygen atom and at least one fluorinated organic silicon compound which contains an etheric oxygen atom.

2. The treated substrate according to claim 1, wherein said at least one fluorinated organic silicon compound which contains no etheric oxygen atom is selected from the group consisting of a compound represented by the following formula (1a), its partially hydrolyzed condensate, and a compound represented by the following formula (1b):

$$R^{f1} - Y - Si(R^{11})_g(X^1)_{3-g} \qquad (1a),$$



$$R^{11}-\left[\begin{array}{cc} R^{f1} & \\ | & \\ Y & \\ | & \\ -\mathrm{Si}- & \mathrm{N}- \\ | & | \\ R^{11} & R^{7}\end{array}\right]_b \begin{array}{c} R^{f1}\\ |\\ Y\\ |\\ -\mathrm{Si}-R^{11}\\ |\\ R^{11}\end{array}$$

(1b); and

wherein:

R^{f1} is a $C_{1\text{-}20}$ perfluoroalkyl group which contains no etheric oxygen atom between carbon-carbon atoms and which may have a ring structure,

Y is a $C_{1\text{-}6}$ bivalent organic group which contains no fluorine atom,

R^{11} each independently is a hydrogen atom or a $C_{1\text{-}6}$ hydrocarbon group which contains no fluorine atom,

X^1 each independently is a halogen atom, an alkoxy group or an isocyanate group,

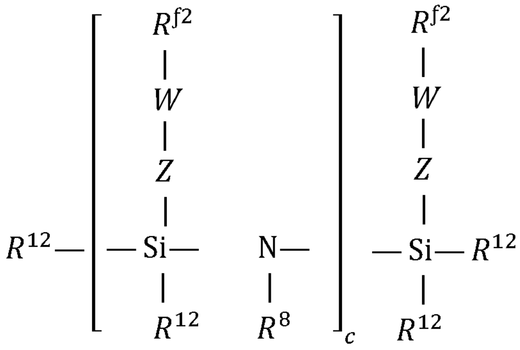
g is an integer of from 0 to 2,

R^7 is a hydrogen atom or a $C_{1\text{-}3}$ hydrocarbon group which contains no fluorine atom, and

b is an integer of from 1 to 100.

3. The treated substrate according to claim 1 or claim 2, wherein said at least one fluorinated organic silicon compound which contains an etheric oxygen atom is selected from the group consisting of a compound represented by the following formula (2a), its partially hydrolyzed condensate, and a compound represented by the following formula (2b):

$$R^{f2}-W-Z-Si(R^{12})_g(X^2)_{3-g} \qquad \text{(2a),}$$



$$R^{12}-\left[\begin{array}{cc} R^{f2} & \\ | & \\ W & \\ | & \\ Z & \\ | & \\ -\mathrm{Si}- & \mathrm{N}- \\ | & | \\ R^{12} & R^{8}\end{array}\right]_c \begin{array}{c} R^{f2}\\ |\\ W\\ |\\ Z\\ |\\ -\mathrm{Si}-R^{12}\\ |\\ R^{12}\end{array}$$

(2b),

wherein:

R^{f2} is a C_{1-20} perfluoroalkyl group which may have an etheric oxygen atom inserted between carbon-carbon atoms and which may have a ring structure,

-W-Z- is $—O—(CF_2CF_2O)_a—CF_2—CONHC_3H_6$- or $—O—(CF_2CF_2O)_a—CF_2—CH_2OCONHC_3H_6$-, wherein a is an integer of from 1 to 200,

R^{12} each independently is a hydrogen atom or a C_{1-8} hydrocarbon group which contains no fluorine atom,

X^2 each independently is a halogen atom, an alkoxy group or an isocyanate group,

g is an integer of from 0 to 2,

R^8 is a hydrogen atom or a C_{1-3} hydrocarbon group which contains no fluorine atom, and

c is an integer of from 1 to 100.

4. The treated substrate of any one of claims 1 to 3, wherein said topcoat composition further comprises a compound according to the formula SiX^3_4, wherein X^3 is a halogen atom or a hydrolysable group.

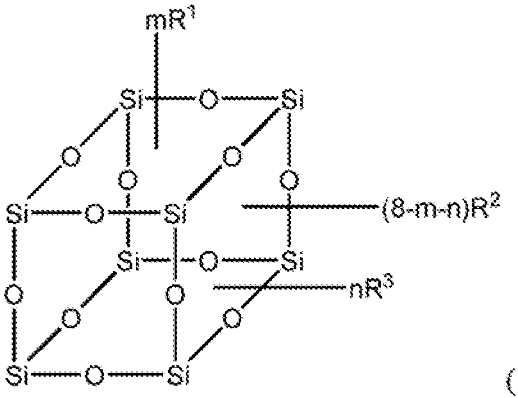
5. The treated substrate of claim 4, wherein X^3 is chlorine.

6. The treated substrate of claim 4, wherein X^3 is an alkoxy group or an isocyanate group.

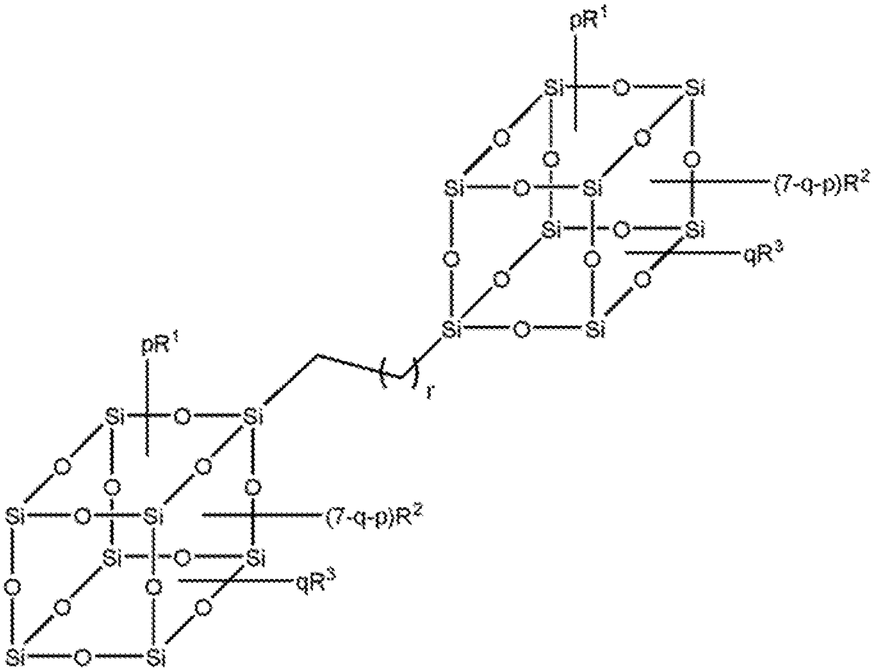
7. The treated substrate of any one of claims 1 to 6, wherein the mass percentage of said at least one fluorinated organic silicon compound which contains an etheric oxygen atom to a total

mass of said at least one fluorinated organic silicon compound which contains an etheric oxygen atom and said at least one fluorinated organic silicon compound which contains no etheric oxygen atom is from 10 to 90 mass %, wherein the amounts of said at least one fluorinated organic silicon compound which contains an etheric oxygen atom and said at least one fluorinated organic silicon compound which contains no etheric oxygen atom are the amounts before the hydrolytic condensation reaction.

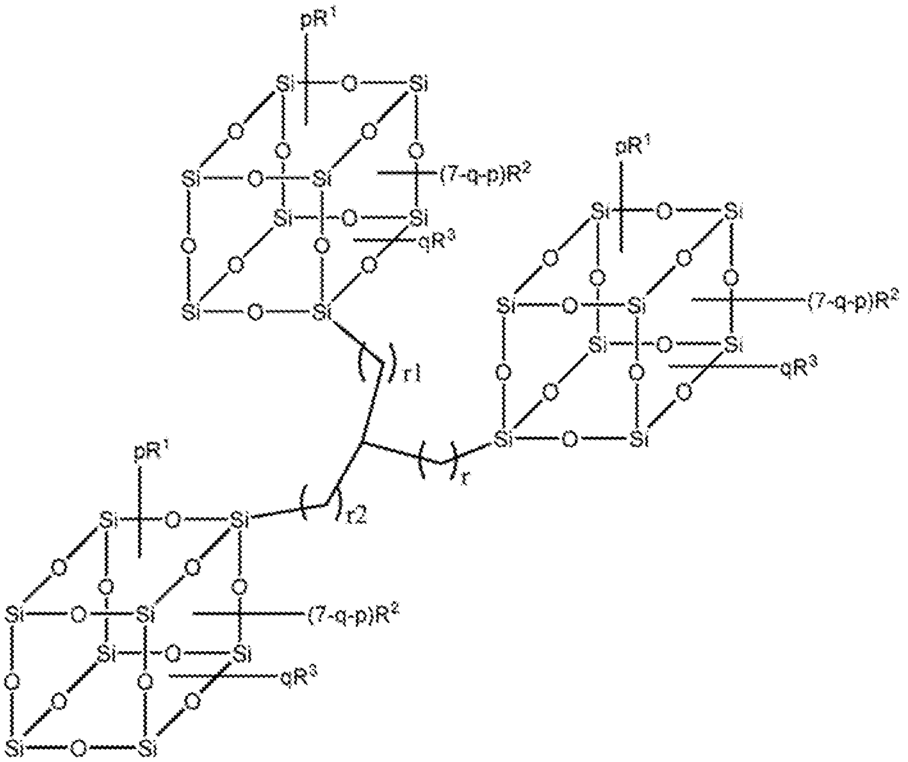
8. The treated substrate of any one of claims 1 to 7, wherein said adhesion promoter composition comprises a polyhedral oligomeric silsesquioxane of the formula (I), (II), or (III):



(I),



(II) or



(III)

wherein:

R^1 is a long chain alkyl or long chain fluorinated alkyl;

R^2 and R^3 are each independently selected from the group consisting of C_1-C_{15} alkyl, C_2-C_{15} alkenyl, -NCO, -CH(0)CH_2, -NH_2, -NHC_1-C_6 alkyl, -OC(O)NHC_1-C_6 alkyl, -OC(O)NH_2, -P(O)(OC_1-C_6, alkyl)$_2$, -C_1-C_6 alkylSi(C_1-C_6 alkyl)$_3$, -C_1-C_6 alkylSi(C_1-C_6 alkyl)$_2$(OC_1-C_6 alkyl), -C_1-C_6 alkylSi(C_1-C_6 alkyl)(OC_1-C_6 alkyl)$_2$ –C_1-C_6 alkylSi(OC_1-C_6 alkyl)$_3$, -Si(C_1-C_6 alkyl)$_2$(OC_1-C_6 alkyl), -Si(C_1-C_6 alkyl)(OC_1-C_6 alkyl)$_2$ and -Si(OC_1-C_6 alkyl)$_3$, wherein one or more hydrogen atoms in C_1-C_{15} alkyl or C_1-C_6 alkyl is independently optionally substituted with a -OC(O)C_1-C_4 alkenyl, -NCO, -(OC_1-C_4 alkyl)-CH(O)CH_2, -CH(O)CH_2, -NH_2, -NHC_1-C_4 alkyl, -OC(O)NHC_1-C_4 alkyl, - OC(O)NH_2, -P(O)(OC_1-C_4 alkyl)$_2$, -Si(C_1-C_4 alkyl)$_2$(OC_1-C_4 alkyl), -Si(C_1-C_4 alkyl)(OC_1-C_4 alkyl)$_2$ or -Si(OC_1-C_4 alkyl)$_3$;

m is an integer from 0 to 7;

n is an integer from 0 to 7;

p is an integer from 0 to 6;

q is an integer from 0 to 6; and

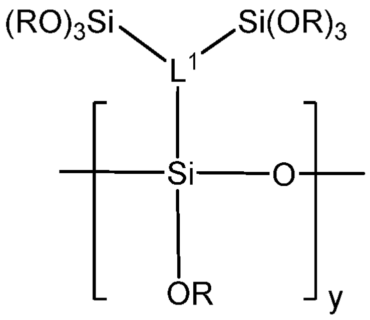
the sum of n and m is less than or equal to 7; and the sum of p and q is less than or equal to 6.

9. The treated substrate of claim 8, wherein said polyhedral oligomeric silsesquioxane is of the formula: $C_mH_nO_pSi_q$, wherein the subscript m ranges from 64 to 170, the subscript n ranges from 150 to 402, the subscript p ranges from 36 to 99, and the subscript q ranges from 15 to 45.

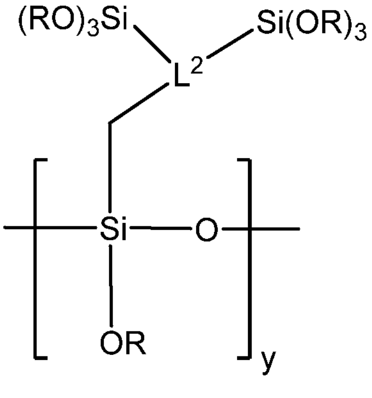
10. The treated substrate of any one of claims 8 to 9, wherein said polyhedral oligomeric silsesquioxane is of the formula: $C_{170}H_{402}O_{99}Si_{45}$.

11. The treated substrate of any one of claims 8 to 9, wherein said polyhedral oligomeric silsesquioxane is of the formula: $C_{64}H_{152}O_{36}Si_{16}$.

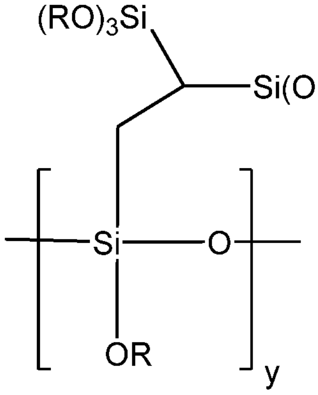
12. The treated substrate of any one of claims 1 to 7, wherein said adhesion promoter composition comprises a linear organosilane polymer comprising units having the following formula: (IV), (V), (VI), (VII), (VIII), or (IX):



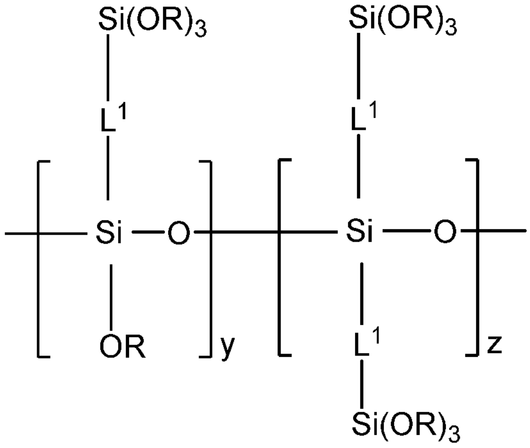
(IV),



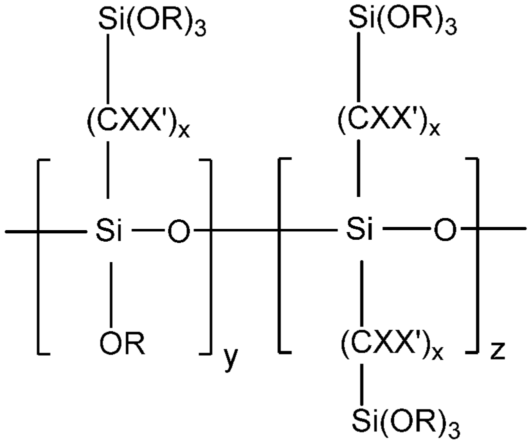
(V),



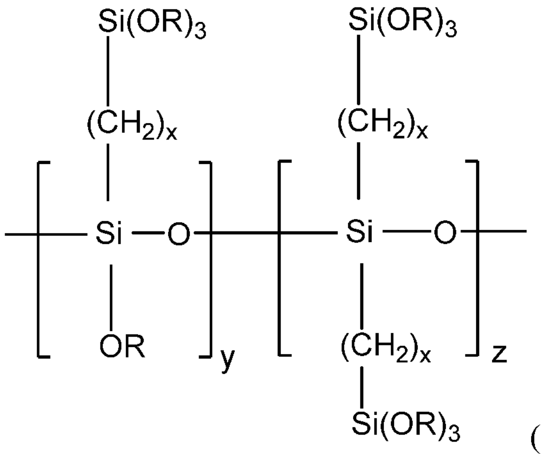
(VI),



(VII),



(VIII), or



(IX),

wherein:

each R is the same or different and may be a hydrogen or non-hydrogen substituent;

L^1 and L2 are independently a linker group;

each x is the same or different positive integer; and

each y is the same or different positive integer; and

each z is the same or different positive integer.

13. The treated substrate of claim 12, wherein each R is alkyl.

14. The treated substrate of claim 12, wherein each R is ethyl.

15. The treated substrate of any one of claims 1 to 14, wherein said substrate comprises a glass panel.

16. The treated substrate of any one of claims 1 to 15, wherein an outer surface of the topcoat layer opposite said adhesion promoter layer has a water contact angle of from 100 to 110 degrees as measured by ASTM D7334-08 (2013).

17. The treated substrate of any one of claims 1 to 16, wherein an outer surface of the topcoat layer opposite said adhesion promoter layer has a sliding angle of from 10 to 20 degrees as measured by ASTM D7334-08 (2013).

18. A method for producing a treated substrate comprising:

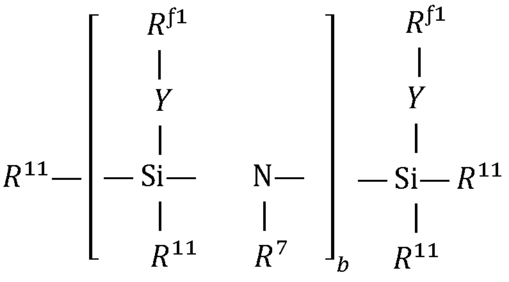
applying an adhesion promoter composition onto at least a part of a surface of a substrate, the adhesion promoter composition comprising a polyhedral oligomeric silsesquioxane or a linear organosilane polymer;

curing said applied adhesion promoter composition to form an adhesion promoter layer disposed on the substrate;

applying a topcoat composition onto said formed adhesion promoter layer, the topcoat composition comprising:

at least one fluorinated organic silicon compound which contains no etheric oxygen atom and which is selected from the group consisting of a compound represented by the following formula (la), its partially hydrolyzed condensate, and a compound represented by the following formula (lb):

$$R^{f1}-Y-Si(R^{11})_g(X^1)_{3-g} \qquad (1a),$$

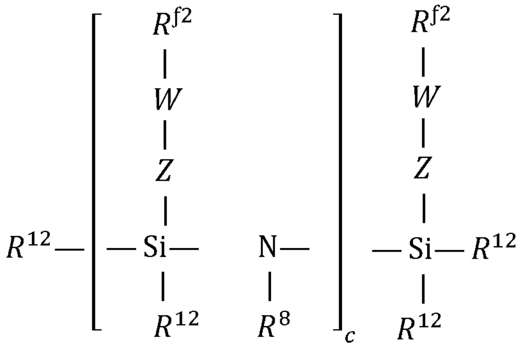


$$R^{11}-\left[\begin{array}{cc} R^{f1} & \\ | & \\ Y & \\ | & \\ -\mathrm{Si}- & \mathrm{N}- \\ | & | \\ R^{11} & R^{7} \end{array}\right]_b \begin{array}{c} R^{f1} \\ | \\ Y \\ | \\ -\mathrm{Si}-R^{11} \\ | \\ R^{11} \end{array}$$

(1b); and

at least one fluorinated organic silicon compound which contains an etheric oxygen atom and which is selected from the group consisting of a compound represented by the following formula (2a), its partially hydrolyzed condensate, and a compound represented by the following formula (2b):

$$R^{f2} - W - Z - Si(R^{12})_g(X^2)_{3-g} \qquad (2a),$$



$$R^{12}-\left[\begin{array}{cc} R^{f2} & \\ | & \\ W & \\ | & \\ Z & \\ | & \\ -\mathrm{Si}- & \mathrm{N}- \\ | & | \\ R^{12} & R^{8}\end{array}\right]_c \begin{array}{c} R^{f2}\\ | \\ W \\ | \\ Z \\ | \\ -\mathrm{Si}-R^{12} \\ | \\ R^{12}\end{array} \qquad (2b),$$

wherein:

R^{f1} is a C_{1-20} perfluoroalkyl group which contains no etheric oxygen atom between carbon-carbon atoms and which may have a ring structure,

Y is a C_{1-6} bivalent organic group which contains no fluorine atom,

R^{11} each independently is a hydrogen atom or a C_{1-6} hydrocarbon group which contains no fluorine atom,

X^1 each independently is a halogen atom, an alkoxy group or an isocyanate group,

g is an integer of from 0 to 2,

R^7 is a hydrogen atom or a C_{1-3} hydrocarbon group which contains no fluorine atom,

b is an integer of from 1 to 100:

R^{f2} is a C_{1-20} perfluoroalkyl group which may have an etheric oxygen atom inserted between carbon-carbon atoms and which may have a ring structure,

-W-Z- is $—O—(CF_2CF_2O)_a—CF_2—CONHC_3H_6$- or $—O—(CF_2CF_2O)_a—CF_2—CH_2OCONHC_3H_6$-, wherein a is an integer of from 1 to 200,

R^{12} each independently is a hydrogen atom or a C_{1-8} hydrocarbon group which contains no fluorine atom,

X^2 each independently is a halogen atom, an alkoxy group or an isocyanate group,

R^8 is a hydrogen atom or a C_{1-3} hydrocarbon group which contains no fluorine atom, and

c is an integer of from 1 to 100; and

curing said applied topcoat composition to form a topcoat layer disposed on said formed adhesion promoter layer.

19. The method of claim 18, wherein said step of curing said applied adhesion promoter composition to form an adhesion promoter layer disposed on the substrate comprises curing said applied adhesion promoter composition at ambient temperature for at least 15 seconds and less than 60 seconds to form an adhesion promoter layer.

20. The method of claim 18 or claim 19, wherein said step of curing said applied topcoat composition to form a topcoat layer disposed on the substrate comprises curing said applied topcoat composition at a temperature ranging from 15 to 30 degree Celsius at a relative humidity of at least 50% relative humidity for a sufficient period of time to form a topcoat layer disposed on said formed adhesion promoter layer.

21. The method of any one of claims 18 to 20, wherein said step of applying an adhesion promoter composition onto at least a part of a surface of a substrate comprises applying a monolayer of an adhesion promoter composition onto at least a part of a surface of a substrate.

22. A treated substrate formed according to the method of any one of claims 18 to 21.

23. A vehicle having a window comprising the treated substrate of claim 22, wherein said substrate comprises a glass panel.

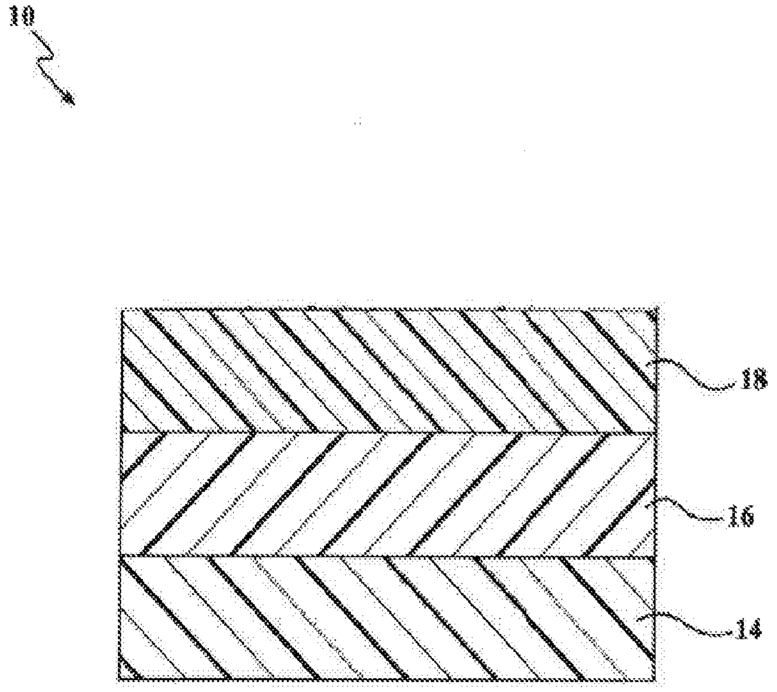


FIG. 1

Box No. II **Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-17, 21-23
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III **Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2018/047919

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C08G 77/22; B32B 7/12; B32B 27/26; C07F 7/21; C08L 83/04; C09D 183/08 (2018.01)

CPC - B32B 7/12; B32B 27/26; C07F 7/21; C08G 77/22; C08L 83/04; C09D 183/08 (2018.08)

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)

See Search History document

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

USPC - 428/448; 556/458 (keyword delimited)

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

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/0135252 A1 (KISHIKAWA et al) 31 May 2012 (31.05.2012) entire document	1-3, 18-20
A	US 2016/0288450 A1 (3M INNOVATIVE PROPERTIES COMPANY) 06 October 2016 (06.10.2016) entire document	1-3, 18-20
A	US 2004/0034143 A1 (HUBERT et al) 19 February 2004 (19.02.2004) entire document	1-3, 18-20
A	US 2016/0083612 A1 (NBD NANOTECHNOLOGIES INC) 24 March 2016 (24.03.2016) entire document	1-3, 18-20

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

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 05 October 2018	Date of mailing of the international search report 18 OCT 2018
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450 Facsimile No. 571-273-8300	Authorized officer Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774