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(54) **Title:** COMPOSITION FOR SURFACE TREATMENT, A METHOD OF PREPARING A SURFACE-TREATED ARTICLE AND SURFACE-TREATED ARTICLE

(57) **Abstract:** A composition for surface treatment comprises a siloxane polymer and a polyfluoropolyether silane. The composition forms layers that are easy to clean and which have excellent physical properties, including smudge and stain resistance. In addition, durability and coefficient of friction of the layers may be selectively controlled based on the composition. A surface-treated article and a method of preparing the surface-treated article with the composition are also disclosed.



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**COMPOSITION FOR SURFACE TREATMENT, A METHOD  
OF PREPARING A SURFACE-TREATED ARTICLE  
AND SURFACE-TREATED ARTICLE**

**FIELD OF THE INVENTION**

**[0001]** The present invention generally relates to a composition for surface treatment and, more specifically, to a composition comprising a siloxane polymer and a polyfluoropolyether silane. The present invention also relates to a method of preparing a surface-treated article with the composition, and to the surface-treated article formed therewith.

**DESCRIPTION OF THE RELATED ART**

**[0002]** Surfaces of electronic and optical devices/components are susceptible to staining and smudging, oftentimes due to oils from hands and fingers. For example, electronic devices including an interactive touch-screen display, e.g. smart phones, are generally smudged with fingerprints, skin oil, sweat, cosmetics, etc., when used. Once these stains and/or smudges adhere to the surfaces of these devices, the stains and/or smudges are not easily removed. Moreover, such stains and/or smudges decrease the usability of these devices.

**[0003]** In an attempt to minimize the appearance and prevalence of such stains and smudges, conventional surface treatment compositions have been applied on the surfaces of various devices/components to form conventional layers. Such conventional surface treatment compositions typically consist of a fluorinated polymer and a solvent. However, such fluorinated polymers are typically expensive to manufacture or obtain. Further, it is generally difficult to modify, e.g. decrease, the coefficient of friction of conventional layers formed from such conventional surface treatment compositions.

**SUMMARY OF THE INVENTION AND ADVANTAGES**

**[0004]** The present invention provides a composition for surface treatment of a substrate. The composition comprises a siloxane polymer comprising repeating  $R_2SiO_{2/2}$  units, where R is an independently selected substituted or unsubstituted hydrocarbyl group. The composition further comprises a polyfluoropolyether silane.

[0005] The present invention also provides a method of preparing a surface-treated article. The method comprises applying the composition for surface treatment on a surface of an article to form a layer on the surface of the article.

[0006] Finally, the present invention provides a surface-treated article formed in accordance with the method.

[0007] The composition forms layers that are easy to clean and which have excellent physical properties, including stain and smudge resistance. Further, the layers formed from the composition may have a selectively controlled coefficient of friction contingent on the relative amounts of the siloxane polymer and the polyfluoropolyether silane in the composition. Additionally, the layers and composition may be prepared at a significantly lower cost than conventional layers formed from conventional compositions while still maintaining such excellent physical properties and while providing additional benefits.

#### DETAILED DESCRIPTION OF THE INVENTION

[0008] The present invention provides a composition for surface treatment, a method of preparing a surface-treated article with the composition, and the surface-treated article formed in accordance with the method. The composition forms layers that are easy to clean and which have excellent physical properties, including smudge and stain resistance. Further, the layers formed from the composition have a desirable coefficient of friction and a significantly reduced cost relative to conventional layers formed from conventional compositions including fluorinated polymers.

[0009] The composition comprises a siloxane polymer. The siloxane polymer comprises repeating  $R_2SiO_{2/2}$  units, where R is an independently selected substituted or unsubstituted hydrocarbyl group. For example, R may be aliphatic, aromatic, cyclic, alicyclic, etc. Further, R may include ethylenic unsaturation. By “substituted,” it is meant that one or more hydrogen atoms of the hydrocarbon may be replaced with atoms other than hydrogen (e.g. a halogen atom, such as chlorine, fluorine, bromine, etc.), or a carbon atom within the chain of R may be replaced with an atom other than carbon, i.e., R may include one or more heteroatoms within the chain, such as oxygen, sulfur, nitrogen, etc. R typically has from 1 to 10 carbon atoms, alternatively from 1 to 6 carbon atoms. Substituted or unsubstituted hydrocarbyl groups containing at least 3 carbon atoms can have a branched or unbranched structure. Examples of hydrocarbyl groups represented by R include, but are not limited to, alkyl, such as

methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, pentyl, 1-methylbutyl, 1-ethylpropyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl, hexyl, heptyl, octyl, nonyl, and decyl; alkenyl, such as vinyl; cycloalkyl, such as cyclopentyl, cyclohexyl, and methylcyclohexyl; aryl, such as phenyl and naphthyl; alkaryl, such as tolyl and xylyl; and aralkyl, such as benzyl and phenethyl. Examples of halogen-substituted hydrocarbyl groups represented by R include, but are not limited to, 3,3,3-trifluoropropyl, 3-chloropropyl, chlorophenyl, dichlorophenyl, 2,2,2-trifluoroethyl, 2,2,3,3-tetrafluoropropyl, and 2,2,3,3,4,4,5,5-octafluoropentyl.

**[0010]** In addition to groups represented by R, the siloxane polymer may include additional substituents or functional groups at any terminal or pendent position. For example, the siloxane polymer may include silicon-bonded hydroxyl groups, hydrogen atoms, amine groups, silazane groups, (meth)acrylate groups, epoxy groups, etc. Such groups or atoms may be present in the repeating D units (described below) or in terminal M units (which generally have the formula  $R_3SiO_{1/3}$ , unless one or more of R is replaced by one of these additional substituents or functional groups). Most typically, if present, such groups are terminal in the siloxane polymer.

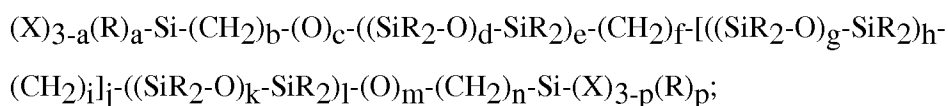
**[0011]** Because the siloxane polymer comprises repeating  $R_2SiO_{2/2}$  units, the siloxane polymer has a linear portion. However, the siloxane polymer may optionally be branched, partially branched, and/or may include a resinous portion having a three-dimensional networked structure. In such embodiments, the siloxane polymer further comprises includes  $RSiO_{3/2}$  units and/or  $SiO_{4/2}$  units.  $R_2SiO_{2/2}$  units are generally referred to as D units,  $RSiO_{3/2}$  units are generally referred to as T units, and  $SiO_{4/2}$  units are generally referred to as Q units. Branching of the siloxane polymer itself, or the resinous portion of the siloxane polymer, if present, is attributable to the presence of T and/or Q units.

**[0012]** The siloxane polymer may consist of siloxane bonds (Si-O-Si) within the backbone of the siloxane polymer. Alternatively, the siloxane polymer may include siloxane bonds separated by one or more bivalent groups, e.g. a  $CH_2$  linking group, where  $CH_2$  may be repeated up to, for example, 10 times. The presence of absence of such bivalent groups is generally attributable to the reaction mechanism by which the siloxane polymer is formed, with siloxane polymers consisting of siloxane bonds

being formed from condensation and siloxane polymers including one or more bivalent groups being formed from hydrosilylation.

**[0013]** The siloxane polymer may optionally have functional groups, such as silicon-bonded alkenyl groups, silicon-bonded hydroxyl groups, silicon-bonded alkoxy groups, etc. In various embodiments including such functional groups, the functional groups may be terminal, pendent, or both. Typically, the functional groups are terminal. For example, the siloxane polymer may be dimethylvinyl endblocked, divinylmethyl endblocked, dimethylhydroxyl endblocked, dihydroxylmethyl endblocked, etc. In certain embodiments, the siloxane polymer includes a terminal group selected from a hydrolysable group, an alkenyl group, or combinations thereof. Generally, physical properties of the layers formed from the compositions are improved when the siloxane polymer includes such a terminal group.

**[0014]** In various embodiments in which the siloxane polymer is linear, the siloxane polymer has the following general formula (A):

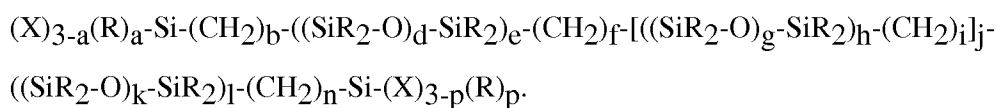


wherein X is an independently selected hydrolysable group; R is defined above; a and p are each integers independently selected from 0 to 3; b, f, i, and n are each integers independently selected from 0 to 10; c and m are each independently 0 or 1; d, g, and k are each integers independently selected from 0 or from 1 to 200 with the proviso that d, g, and k are not simultaneously 0; e, h, and l are each integers independently selected from 0 and 1 with the proviso that e, h, and l are not simultaneously 0; and j is an integer selected from 0 to 5; provided that when subscript d is 0, subscript e is also 0; when subscript d is greater than 0, subscript e is 1; when subscript g is 0, subscripts h, i, and j are also 0; when subscript g is greater than 1, subscript h is 1 and subscript j is at least 1; when subscript k is 0, subscript l is also 0; and when subscript k is greater than 0, subscript l is 1.

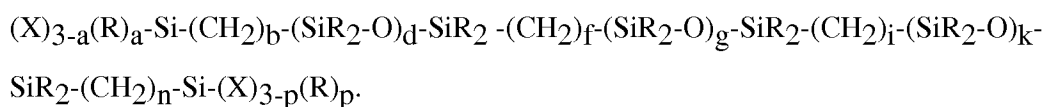
**[0015]** The hydrolysable groups represented by X in general formula (A) are independently selected from H, a halide group,  $-OR^3$ ,  $-NHR^3$ ,  $-NR^3R^4$ ,  $-OOC-R^3$ ,  $O-N=CR^3R^4$ ,  $O-C(=CR^3R^4)R^5$ , and  $-NR^3COR^4$ , wherein  $R^3$ ,  $R^4$  and  $R^5$  are each independently selected from H and a  $C_1$ - $C_{22}$  hydrocarbon group, and wherein  $R^3$  and  $R^4$  optionally can form a cyclic amine in the alkylamino group.

**[0016]** In general formula (A) above, subscripts d, g, and k represent the repeating  $R_2SiO_{2/2}$  units of the siloxane polymer.

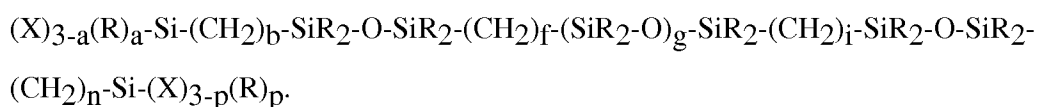
**[0017]** In various embodiments, subscripts c and m are 0 and subscripts b, d, e, f, g, h, i, j, k, l, and n are each integers of 1 or more. When subscript j is 1, the resulting siloxane polymer includes three segments of repeating siloxane bonds each separated by a bivalent linking group, which such bivalent linking groups being represented by subscripts b, f, i, and n, respectively. In these embodiments, the siloxane polymer is typically formed from hydrosilylation and may be represented by the following general formula:



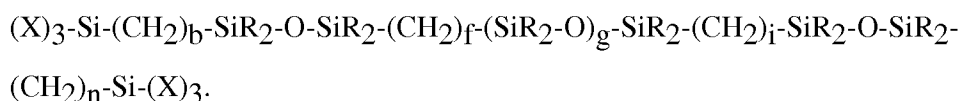
Typically, when subscripts d, g, and k are 1 or more, subscript j is 1 (and as defined above, because subscripts d is greater than 0, subscript e is 1, and because subscript g is greater than 0, subscript h is 1. In these embodiments, the siloxane polymer has the following general formula:



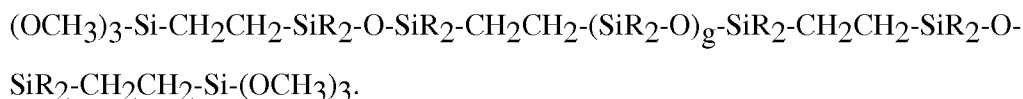
Most typically, subscripts d and k are each 1 and subscript g is an integer greater than 1 such that the block represented by subscript g provides the repeating  $R_2SiO_{2/2}$  units in the siloxane polymer. In these embodiments, the siloxane polymer has the following general formula:



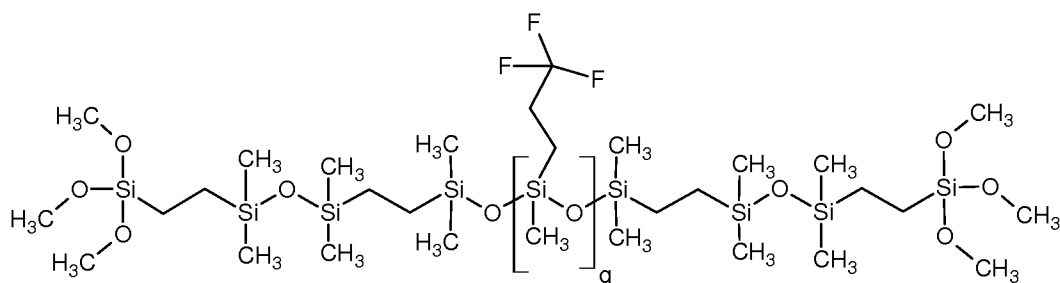
**[0018]** In certain embodiments introduced above, subscripts a and p are each 0 such that the siloxane polymer is endblocked with three silicon-bonded hydrolysable groups (represented by X) at each end. However, as noted above, the siloxane polymer need not have any silicon-bonded hydrolysable groups as subscripts a and p may each be 3. In embodiments in which subscripts a and p are each 0, the siloxane polymer has the following general formula:



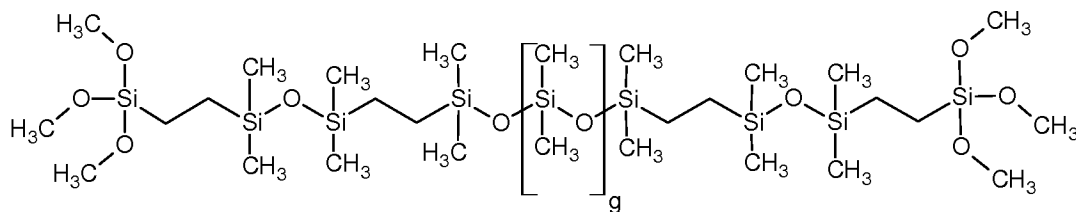
In these embodiments, subscripts b, f, i, and n are each 2. Accordingly, when the hydrolysable groups represented by X are each alkoxy groups, e.g. methoxy groups, the siloxane polymer has the following general formula:



Specific species of the siloxane polymer within the general formula immediately above are set forth below for illustrative purposes only, where each R is independently methyl or  $\text{CH}_2\text{CH}_2\text{CF}_3$ :

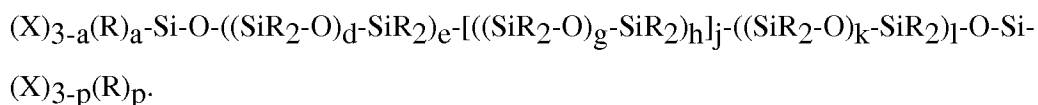


, and



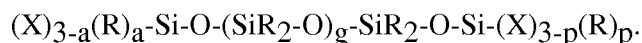
As noted above, R is independently selected such that even within the repeating block represented by subscript g there may be different substituents represented by R in different blocks. For example, in the first structure above, R may independently vary between methyl and  $\text{CH}_2\text{CH}_2\text{CF}_3$ .

**[0019]** In other embodiments, subscripts c and m are 1 and subscripts b, f, i, and n are each 0. In these embodiments, the siloxane polymer is typically formed from condensation and may be represented by the following general formula:

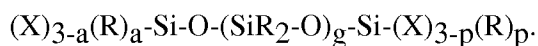


Because R is independently selected and may vary in different  $\text{R}_2\text{SiO}_{2/2}$  units, the general formula above may be rewritten to exclude any of the blocks represented by subscripts e, h, j, and l, so long as not all of these subscripts are simultaneously 0. For

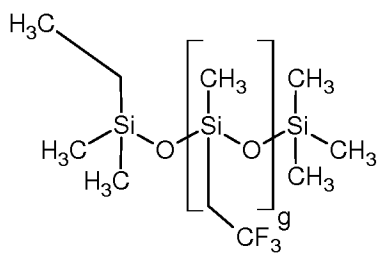
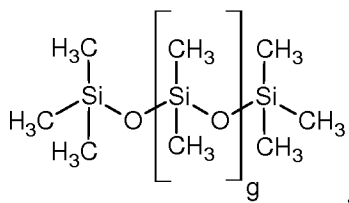
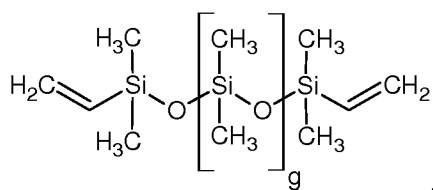
example, the general formula above may be rewritten while only including the  $R_2SiO_{2/2}$  units within the block represented by subscript d, subscript h, subscript j, and/or subscript l, as each of these formulas would be duplicative with one another, save for potential differences in molecular weight in embodiments in which the siloxane polymer includes greater than 200 repeating  $R_2SiO_{2/2}$  units. As but one example, the general formula introduced above is rewritten below where subscripts d, e, k, and l are 0, subscript g is an integer greater than 1, and subscripts h and j are 1:

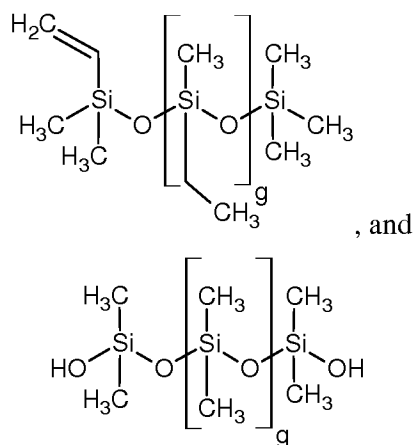


Further, because R is independently selected, the general formula introduced immediately above may be further condensed as follows:



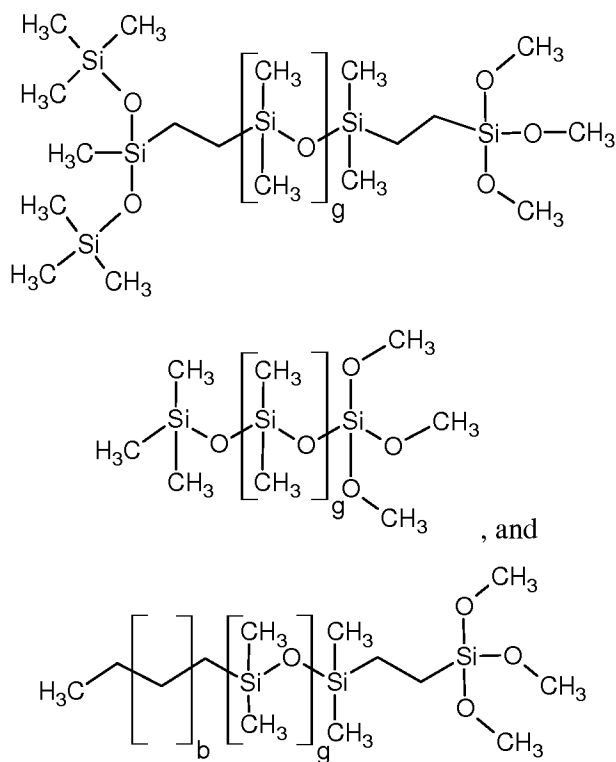
Subscripts a and p may each independently be from 0 to 3 such that the siloxane polymer of these embodiments need not have any silicon-bonded hydrolysable groups. Specific species of the siloxane polymer within the general formula immediately above are set forth below for illustrative purposes only:





In each of these examples, subscript  $g$  represents the repeating  $\text{R}_2\text{SiO}_{2/2}$  units, and  $g$  is selected based on the desired molecular weight and viscosity of the siloxane polymer.

**[0020]** Further examples of the siloxane polymer when the siloxane polymer includes hydrolysable groups are set forth below for illustrative purposes only:



In each of these examples, subscript  $g$  represents the repeating  $\text{R}_2\text{SiO}_{2/2}$  units, and  $g$  is selected based on the desired molecular weight and viscosity of the siloxane

polymer. Subscript b represents an optionally repeating  $\text{CH}_2$  group and is defined above.

**[0021]** A single species of the siloxane polymer may be utilized or various combinations of different species of the siloxane polymer may be utilized in concert with one another in the composition. For example, two different types of siloxane polymers may be utilized in combination with one another, or a siloxane polymer may be utilized in combination with a silicone resin, e.g. an MQ resin. The siloxane polymer may be obtained or formed and included in the composition as a discrete component, or the siloxane polymer may be disposed in a carrier solvent or vehicle prior to incorporating the siloxane polymer and the carrier solvent or vehicle in the composition. When the carrier solvent or vehicle is utilized, the carrier solvent or vehicle may be any of those disclosed below, although the carrier solvent or vehicle is not so limited.

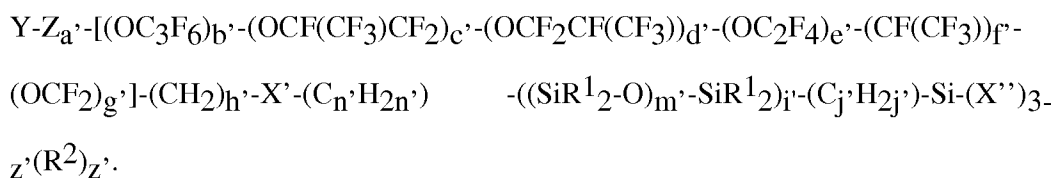
**[0022]** The carrier vehicle of the siloxane polymer composition may be any vehicle capable of solubilizing, partially solubilizing, or otherwise dispersing the siloxane polymer. The carrier vehicle may, in certain embodiments, be referred to as a solvent when capable of solubilizing the siloxane polymer. The vehicle is generally referred to as a vehicle as opposed to a solvent because the vehicle need only disperse the siloxane polymer, but not solubilize the siloxane polymer, although solubilization is typical. For example, in certain embodiments, the carrier vehicle comprises a siloxane fluid. Specific examples of siloxane fluids suitable for the purposes of the carrier vehicle of the composition include volatile methylsiloxane fluids, such as hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, and combinations thereof. Volatile methylsiloxane fluids are commercially available, such as OS-10, OS-20, or OS-30, from Dow Corning® Corporation of Midland, MI. In other embodiments, the carrier vehicle of the siloxane polymer is a non-polar hydrocarbon carrier, which may be aromatic, aliphatic, cyclic, alicyclic, etc. Specific examples of aliphatic hydrocarbon vehicles suitable for the carrier vehicle include hexane, heptane, octane, etc. Specific examples of aromatic hydrocarbon vehicles suitable for the carrier vehicle include toluene, xylene, trimethylbenzene, etc. Generally, however, the carrier vehicle is the siloxane fluid, which has improved miscibility with the vehicle generally utilized to solubilize the polyfluoropolyether silane, as described below.

**[0023]** The molecular weight or viscosity of the siloxane polymer is generally not limited when the composition is utilized in wet coating methods. In these embodiments, the viscosity of the siloxane polymer is typically such that the composition including the siloxane polymer is flowable. However, when the composition is utilized in other methods, e.g. physical vapor deposition, the molecular weight or viscosity of the siloxane polymer is typically selected such that the siloxane polymer volatilizes. In these embodiments, the siloxane polymer typically has a viscosity of from 50 to 500,000, alternatively from 100 to 300,000, alternatively from 300 to 100,000, cSt at 25 °C.

**[0024]** The relative amount of the siloxane polymer utilized in the composition may vary dependent upon the desired physical properties of the layer formed from the composition as well as the method by which the layer is formed. For example, when the composition is utilized in wet coating applications and the composition further comprises a vehicle, the siloxane polymer is typically present in the composition in an amount of from 0.01 to 0.5, alternatively from 0.05 to 0.35, alternatively from 0.10 to 0.30, percent by weight based on the total weight of the composition. When the composition does not include the vehicle, the siloxane polymer is typically present in the composition in an amount of from greater than 1 to less than 99, alternatively from 5 to 95, alternatively from 25 to 75, percent by weight based on the total weight of the composition. The amount of the siloxane polymer present in the composition may vary from the ranges set forth immediately above contingent on the absence or presence of various optional components employed in the composition, as described in greater detail below.

**[0025]** The composition further comprises a polyfluoropolyether silane. The polyfluoropolyether silane may be any known perfluoropolyether silane, which are often utilized in conventional surface treatment compositions.

**[0026]** In various embodiments, the polyfluoropolyether silane has the following general formula (B):



**[0027]** While the polyfluoropolyether silane of the composition is not limited to that of general formula (B), specific aspects of general formula (B) are described in greater detail below. The groups represented by subscripts b'-g', i.e., the groups within the square brackets in formula (B), may be present in any order within the polyfluoropolyether silane, including a different order as that which is represented in general formula (B) above and throughout this disclosure. Moreover, these groups may be present in randomized or block form. In addition, the group represented by subscript b' is typically linear, i.e., the group represented by subscript b' may alternatively be written as (O-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>)<sub>b'</sub>. In the description below, C<sub>p'</sub> - C<sub>q'</sub> (with p' and q' each being integers) regarding a hydrocarbon or alkyl group means such group has from p' to q' carbon atoms.

**[0028]** In general formula (B) above, Z is independently selected from -(CF<sub>2</sub>)-, -(CF(CF<sub>3</sub>)CF<sub>2</sub>O)-, -(CF<sub>2</sub>CF(CF<sub>3</sub>)O)-, -(CF(CF<sub>3</sub>)O)-, -(CF(CF<sub>3</sub>)-CF<sub>2</sub>)-, -(CF<sub>2</sub>-CF(CF<sub>3</sub>))-, and -(CF(CF<sub>3</sub>))- . Z is typically selected such that the polyfluoropolyether silane does not include an oxygen-oxygen (O-O) bond within the backbone. In addition, in this general formula, a' is an integer from 1 to 200; b', c', d', e', f', and g' are integers each independently selected from 0 or from 1 to 200; h', n' and j' are integers each independently selected from 0 or from 1 to 20; i' and m' are integers each independently selected from 0 or from 1 to 5; X' is a divalent organic group or an oxygen atom; R<sup>1</sup> is an independently selected C<sub>1</sub>-C<sub>22</sub> hydrocarbon group; z' is an integer independently selected from 0 to 2; X'' is an independently selected hydrolysable group; R<sup>2</sup> is an independently selected C<sub>1</sub>-C<sub>22</sub> hydrocarbon group which is free of aliphatic unsaturation; and Y is selected from F and Si-(X'')<sub>3</sub>. z'(R<sup>2</sup>)<sub>z'</sub>(C<sub>j'</sub>H<sub>2j'</sub>)<sub>j'</sub>-((SiR<sup>1</sup><sub>2</sub>-O)<sub>m'</sub>-SiR<sup>1</sup><sub>2</sub>)<sub>i'</sub>-(C<sub>n'</sub>H<sub>2n'</sub>)-X'-(CH<sub>2</sub>)<sub>h'</sub>-; wherein X'', X', z', R<sup>1</sup>, R<sup>2</sup>, j', m', i', n' and h' are as defined above.

**[0029]** R<sup>1</sup>, which is an independently selected C<sub>1</sub>-C<sub>22</sub> hydrocarbon group, may be linear, branched, or cyclic. In addition, R<sup>1</sup> may include heteroatoms within the hydrocarbon group, such as oxygen, nitrogen, sulfur, etc., and may be substituted or unsubstituted. Typically, R<sup>1</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl group. In addition, the groups represented by subscripts n' and j', i.e., groups (C<sub>n'</sub>H<sub>2n'</sub>) and (C<sub>j'</sub>H<sub>2j'</sub>), may also be

independently linear or branched. For example, when  $n'$  is 3, these groups may independently have the structure  $-\text{CH}_2-\text{CH}_2-\text{CH}_2$ ,  $-\text{CH}(\text{CH}_3)-\text{CH}_2$ , or  $-\text{CH}_2-\text{CH}(\text{CH}_3)$ , wherein the latter two structures have pendent alkyl groups, i.e., these structures are branched and not linear.

**[0030]** With respect to the moieties represented by subscripts  $m'$ ,  $i'$  and  $j'$ : when subscript  $i'$  is 0, subscript  $j'$  is also 0; when subscript  $i'$  is an integer greater than 0, subscript  $j'$  is also an integer greater than 0; and when subscript  $i'$  is an integer greater than 0,  $m'$  is also an integer greater than 0. Said differently, when the group represented by subscript  $i'$  is present, the group represented by subscript  $j'$  is also present. The inverse is also true, i.e., when the group represented by subscript  $i'$  is not present, the group represented by subscript  $j'$  is also not present. In addition, when  $i'$  is an integer greater than 0, the group represented by subscript  $m'$  is present, and  $m'$  is also an integer greater than 0. In certain embodiments, subscripts  $m'$  and  $i'$  are each 1. Typically, the subscript  $i'$  does not exceed 1, although the subscript  $m'$  may be an integer greater than 1 such that siloxane bonds (i.e., Si-O bonds) are present within the group represented by subscript  $i'$ .

**[0031]** In certain embodiments, the polyfluoropolyether silane of the composition is subject to the proviso that when Y is F; Z is  $-(\text{CF}_2)-$ ;  $a'$  is an integer from 1 to 3; and subscripts  $c'$ ,  $d'$ ,  $f'$ ,  $i'$ ,  $m'$ , and  $j'$  are each 0.

**[0032]** The hydrolysable group represented by  $X''$  in general formula (B) is independently selected from H, a halide group, an alkoxy ( $-\text{OR}^3$ ) group, an alkylamino ( $-\text{NHR}^3$  or  $-\text{NR}^3\text{R}^4$ ) group, a carboxy ( $-\text{OOC}-\text{R}^3$ ) group, an alkyliminoxy ( $-\text{O}-\text{N}=\text{CR}^3\text{R}^4$ ) group, an alkenyloxy ( $\text{O}-\text{C}(\text{=CR}^3\text{R}^4)\text{R}^5$ ) group, or an N-alkylamido ( $-\text{NR}^3\text{COR}^4$ ) group, wherein  $\text{R}^3$ ,  $\text{R}^4$  and  $\text{R}^5$  are each independently selected from H and a  $\text{C}_1\text{-C}_{22}$  hydrocarbon group. When  $\text{R}^3$ ,  $\text{R}^4$  and  $\text{R}^5$  are independently  $\text{C}_1\text{-C}_{22}$  hydrocarbon groups,  $\text{R}^3$ ,  $\text{R}^4$  and  $\text{R}^5$  may be linear, branched, or cyclic. In addition,  $\text{R}^3$ ,  $\text{R}^4$  and  $\text{R}^5$  may independently include heteroatoms within the hydrocarbon group, and may be substituted or unsubstituted. Typically,  $\text{R}^3$ ,  $\text{R}^4$  and  $\text{R}^5$  are each independently selected  $\text{C}_1\text{-C}_4$  alkyl groups. In certain embodiments, the hydrolysable group represented by  $X''$  in general formula (B) is independently selected from an alkoxy ( $-\text{OR}^3$ ) group and an alkylamino ( $-\text{NHR}^3$  or  $-\text{NR}^3\text{R}^4$ ) group.

When the hydrolysable group represented by X'' in general formula (B) is an alkylamino group, R<sup>3</sup> and R<sup>4</sup> optionally can form a cyclic amine in the alkylamino group.

**[0033]** Non-limiting, exemplary embodiments of particular species of the polyfluoropolyether silane of the composition are described in detail below. Typically in these embodiments, z' is 0 such that polyfluoropolyether silane includes three hydrolysable groups represented by X''. However, as described above, z' can be an integer other than 0 (e.g. 1 or 2) such that these particular polyfluoropolyether silanes include fewer than three hydrolysable groups.

**[0034]** In certain embodiments, Y in general formula (B) is F. Typically, when Y in general formula (B) is F, subscripts c', d' and g' in general formula (B) are 0. As such, in these embodiments, when the groups represented by subscripts c', d' and g' are absent, the polyfluoropolyether silane has the general formula F-Z<sub>a'</sub>-(OC<sub>3</sub>F<sub>6</sub>)<sub>b'</sub>-(OC<sub>2</sub>F<sub>4</sub>)<sub>e'</sub>-(CF(CF<sub>3</sub>))<sub>f'</sub>-(CH<sub>2</sub>)<sub>h'</sub>-X'-(C<sub>n'</sub>H<sub>2n'</sub>)-((SiR<sup>1</sup><sub>2</sub>-O)<sub>m'</sub>-SiR<sup>1</sup><sub>2</sub>)<sub>i'</sub>-(C<sub>j'</sub>H<sub>2j'</sub>)-Si-(X'')<sub>3-z'</sub>(R<sup>2</sup>)<sub>z'</sub>.

**[0035]** In one embodiment of the composition in which Y in general formula (B) is F, as introduced above, Z in general formula (B) is -(CF<sub>2</sub>)-, subscripts c', d', f' and g' in general formula (B) are 0 and subscripts b', e', h' and n' in general formula (B) are each independently an integer greater than 0. As but one example of this embodiment, subscript a' is 3, subscript b' is at least 1, subscript e' is 1, subscript h' is 1, X' is an oxygen atom, subscript n' is 3, and subscripts m', i' and j' are each 0. In this one example, the polyfluoropolyether silane has the following general formula: CF<sub>3</sub>-CF<sub>2</sub>-CF<sub>2</sub>-(O-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>)<sub>b'</sub>-O-CF<sub>2</sub>-CF<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si-(X'')<sub>3-z'</sub>(R<sup>2</sup>)<sub>z'</sub>. Thus, when the hydrolysable groups represented by X'' are all alkoxy groups, e.g. methoxy groups, this particular polyfluoropolyether silane has the following general formula: CF<sub>3</sub>-CF<sub>2</sub>-CF<sub>2</sub>-(O-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>)<sub>b'</sub>-O-CF<sub>2</sub>-CF<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si-(OCH<sub>3</sub>)<sub>3</sub>. Alternatively, when the hydrolysable groups represented by X'' are all alkylamino groups, e.g. N(CH<sub>3</sub>)<sub>2</sub> groups, this particular polyfluoropolyether silane has the following general formula: CF<sub>3</sub>-CF<sub>2</sub>-CF<sub>2</sub>-(O-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>)<sub>b'</sub>-O-CF<sub>2</sub>-CF<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si-(N(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>. In these embodiments, subscript b' is typically an integer from 17 to 25.

**[0036]** In another embodiment of the surface treatment composition in which Y in general formula (B) is F and Z in general formula (B) is  $-(CF_2)-$ , as described above, subscripts  $c'$ ,  $d'$ ,  $f'$  and  $g'$  in general formula (B) are 0 and subscripts  $b'$ ,  $e'$ ,  $h'$ ,  $n'$ ,  $m'$ ,  $i'$  and  $j'$  in general formula (B) are each independently an integer greater than 0. As but one example of this embodiment, subscript  $a'$  is 3, subscript  $b$  is at least 1, subscript  $e'$  is 1, subscript  $h'$  is 1,  $X'$  is an oxygen atom, subscript  $n'$  is 3, subscript  $m'$  and  $i'$  are each 1, and subscript  $j'$  is 2. In this one example, the polyfluoropolyether silane has the following general formula:  $CF_3-CF_2-CF_2-(O-CF_2-CF_2-CF_2)_{b'}-O-CF_2-CF_2-CH_2-O-CH_2-CH_2-CH_2-Si(CH_3)_2-O-Si(CH_3)_2-CH_2-CH_2-Si(X'')_3-$

$z'(R^2)_z$ . Thus, when the hydrolysable groups represented by  $X''$  are all alkoxy groups, e.g. methoxy groups, and  $z$  is 0, this particular polyfluoropolyether silane has the following general formula:  $CF_3-CF_2-CF_2-(O-CF_2-CF_2-CF_2)_{b'}-O-CF_2-CF_2-CH_2-O-CH_2-CH_2-CH_2-Si(CH_3)_2-O-Si(CH_3)_2-CH_2-CH_2-Si(OCH_3)_3$ . In these embodiments, subscript  $b'$  is typically an integer from 17 to 25.

**[0037]** In another embodiment of the surface treatment composition in which Y in general formula (B) is F, as introduced above, Z in general formula (B) is  $-(CF(CF_3)CF_2O)-$ . In this embodiment, subscripts  $b'$ ,  $c'$ ,  $d'$ ,  $e'$  and  $g'$  in general formula (B) are 0, and subscripts  $f'$ ,  $h'$  and  $n'$  in general formula (B) are each independently an integer greater than 0. As but one example of this embodiment, subscripts  $b'$ ,  $c'$ ,  $d'$ ,  $e'$  and  $g'$  in general formula (B) are 0, subscript  $a'$  is at least 1, subscript  $f'$  is 1, subscript  $h'$  is 1,  $X'$  is an oxygen atom, subscript  $n'$  is 3, and subscripts  $i'$ ,  $m'$  and  $j'$  are each 0. In this one example, the polyfluoropolyether silane has the following general formula:  $F-(CF(CF_3)-CF_2-O)_{a'}-CF(CF_3)-CH_2-O-CH_2-CH_2-CH_2-Si(X'')_3-z'(R^2)_z$ . Thus, when the hydrolysable groups represented by  $X''$  are all alkoxy groups, e.g. methoxy groups, and  $z'$  is 0, this particular polyfluoropolyether silane has the following general formula:  $F-(CF(CF_3)-CF_2-O)_{a'}-CF(CF_3)-CH_2-O-CH_2-CH_2-CH_2-Si(OCH_3)_3$ . Alternatively, when the hydrolysable groups represented by  $X''$  are all alkylamino groups, e.g.  $N(CH_3)_2$  groups, this particular polyfluoropolyether silane has the following general formula:  $F-(CF(CF_3)-CF_2-O)_{a'}-CF(CF_3)-CH_2-O-CH_2-CH_2-CH_2-Si(N(CH_3)_2)_3$ . In these embodiments, subscript  $a'$  is typically an integer from 14 to 20.

**[0038]** In another embodiment of the surface treatment composition in which Y in general formula (B) is F and Z in general formula (B) is  $-(CF(CF_3)CF_2O)-$ , as introduced immediately above, subscripts  $b'$ ,  $c'$ ,  $d'$ ,  $e'$  and  $g'$  in general formula (B) are 0, subscript  $a'$  is at least 1, subscript  $f'$  is 1, subscript  $h'$  is 1,  $X'$  is an oxygen atom, subscript  $n'$  is 3, subscript  $m'$  and  $i'$  are each 1, and subscript  $j'$  is 2. In this one example, the polyfluoropolyether silane has the following general formula:  $F-(CF(CF_3)CF_2O)_{a'}-CF(CF_3)-CH_2-O-CH_2-CH_2-CH_2-Si(CH_3)_2-O-Si(CH_3)_2-CH_2-CH_2-Si-(X'')_{3-z'}(R^2)_{z'}$ . Thus, when the hydrolysable groups represented by  $X''$  are all alkoxy groups, e.g. methoxy groups, and  $z'$  is 0, this particular polyfluoropolyether silane has the following general formula:  $F-(CF(CF_3)CF_2O)_{a'}-CF(CF_3)-CH_2-O-CH_2-CH_2-CH_2-Si(CH_3)_2-O-Si(CH_3)_2-CH_2-CH_2-Si(OCH_3)_3$ . In these embodiments, subscript  $a'$  is typically an integer from 14 to 20.

**[0039]** In other embodiments, Y in general formula (B) is  $Si-(X'')_{3-z'}(R^2)_{z'}(C_jH_{2j'})-((SiR^{12}_2-O)_m'-SiR^{12}_2)_{i'}-(C_nH_{2n'})-X'-(CH_2)_{h'}$ . Typically, when Y in general formula (B) is  $Si-(X'')_{3-z'}(R^2)_{z'}(C_jH_{2j'})-((SiR^{12}_2-O)_m'-SiR^{12}_2)_{i'}-(C_nH_{2n'})-X'-(CH_2)_{h'}$ , subscripts  $b'$ ,  $c'$ , and  $f'$  in general formula (B) are 0. As such, in these embodiments, when the groups represented by subscripts  $b'$ ,  $c'$ , and  $f'$  are absent, the polyfluoropolyether silane has the following general formula:  $Y-Z_{a'}-[OCF_2CF(CF_3)]_{d'}-(OC_2F_4)_{e'}-(OCF_2)_{g'}-(CH_2)_{h'}-X'-(C_nH_{2n'})-((SiR^{12}_2-O)_m'-SiR^{12}_2)_{i'}-(C_jH_{2j'})-Si-(X'')_{3-z'}(R^2)_{z'}$ .

**[0040]** In one embodiment in which Y in general formula (B) is  $Si-(X'')_{3-z'}(R^2)_{z'}(C_jH_{2j'})-((SiR^{12}_2-O)_m'-SiR^{12}_2)_{i'}-(C_nH_{2n'})-X'-(CH_2)_{h'}$ , as introduced immediately above, Z is  $-(CF_2)-$ ,  $X'$  is an oxygen atom, subscripts  $b'$ ,  $c'$ ,  $d'$ , and  $f'$  in general formula (B) are 0, and subscripts  $e'$  and  $g'$  in general formula (B) are each independently an integer greater than 0. As but one example of this embodiment, Z is  $-(CF_2)-$ ,  $X'$  is an oxygen atom, subscripts  $b'$ ,  $c'$ ,  $d'$ ,  $f'$ ,  $m'$ ,  $i'$ , and  $j'$  in general formula (B) are 0, subscript  $e'$  is at least 1, subscript  $g'$  is at least 1, subscript  $h'$  is 1,  $X'$  is an oxygen atom, and subscript  $n'$  is 3. In this one example, the polyfluoropolyether silane has the following general formula:  $(R^2)_{z'}(X'')_{3-z'}Si-CH_2-$

CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CF<sub>2</sub>-(OCF<sub>2</sub>CF<sub>2</sub>)<sub>e</sub>'-(OCF<sub>2</sub>)<sub>g</sub>'-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si-(X'')<sub>3-z'</sub>(R<sup>2</sup>)<sub>z'</sub>. Thus, when the hydrolysable groups represented by X'' are all alkoxy groups, e.g. methoxy groups, and z' is 0, this particular polyfluoropolyether silane has the following general formula: (CH<sub>3</sub>O)<sub>3</sub>Si-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CF<sub>2</sub>-(OCF<sub>2</sub>CF<sub>2</sub>)<sub>e</sub>'-(OCF<sub>2</sub>)<sub>g</sub>'-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si-(OCH<sub>3</sub>)<sub>3</sub>. Alternatively, when the hydrolysable groups represented by X'' are all alkylamino groups, e.g. N(CH<sub>3</sub>)<sub>2</sub> groups, and z' is 0, this particular polyfluoropolyether silane has the following general formula: ((CH<sub>3</sub>)<sub>2</sub>N)<sub>3</sub>Si-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CF<sub>2</sub>-(OCF<sub>2</sub>CF<sub>2</sub>)<sub>e</sub>'-(OCF<sub>2</sub>)<sub>g</sub>'-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si-(N(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>.

**[0041]** Alternatively, in another embodiment in which Y in general formula (B) is Si-(X'')<sub>3-z'</sub>(R<sup>2</sup>)<sub>z'</sub>(C<sub>j</sub>H<sub>2j</sub>)'-((SiR<sup>1</sup><sub>2</sub>-O)<sub>m</sub>'-SiR<sup>1</sup><sub>2</sub>)<sub>i</sub>'-(C<sub>n</sub>H<sub>2n</sub>)'-X'-(CH<sub>2</sub>)<sub>h</sub>'-, as introduced above, Z is -(CF<sub>2</sub>)-, X' is an oxygen atom, subscripts b', c', e' and f' in general formula (B) are 0, and subscripts d' and g' in general formula (B) are each independently an integer greater than 0.

**[0042]** The polyfluoropolyether silane may be obtained or formed and included in the composition as a discrete component, or the polyfluoropolyether silane may be disposed in a carrier vehicle prior to incorporating the polyfluoropolyether silane and the carrier vehicle in the composition. When the carrier vehicle is utilized, the carrier vehicle is typically selected from vehicles disclosed below, although other vehicles may alternatively be utilized.

**[0043]** The relative amount of the polyfluoropolyether silane utilized in the composition may vary dependent upon the desired physical properties of the layer formed from the composition as well as the method by which the layer is formed. For example, when the composition is utilized in wet coating applications and the composition further comprises a vehicle, the polyfluoropolyether silane is typically present in the composition in an amount of from 0.01 to 0.5, alternatively from 0.05 to 0.35, alternatively from 0.10 to 0.30, percent by weight based on the total weight of the composition. When the composition does not include the vehicle, the polyfluoropolyether silane is typically present in the composition in an amount of from greater than 1 to less than 99, alternatively from 5 to 95, alternatively from 25 to 75, percent by weight based on the total weight of the composition, with the balance

of the composition being the siloxane polymer. The amount of the polyfluoropolyether silane present in the composition may vary from the ranges set forth immediately above contingent on the absence or presence of various optional components employed in the composition, as described in greater detail below.

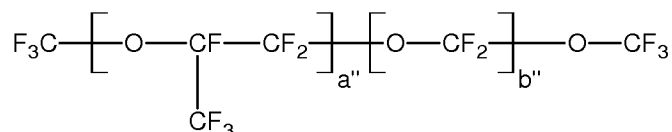
**[0044]** The siloxane polymer and the polyfluoropolyether silane may be present in the composition in various ratios from 0.1/99.9 to 99.9/0.1. As described in detail below, the relative amounts of the siloxane polymer and the polyfluoropolyether silane are typically selected based on the desired physical properties of the layer formed from the composition. For example, as the amount of the siloxane polymer increases in the composition relative to the amount of the polyfluoropolyether silane in the composition, the layer formed from the composition generally has a lesser coefficient of friction (kinetic), which is desirable in certain applications. Conversely, as the amount of the siloxane polymer decreases in the composition relative to the amount of the polyfluoropolyether silane in the composition, the layer formed from the composition generally has a greater durability (as determined based on a water contact angle after abrasion, as described below), which is also desirable in certain applications. Accordingly, the ratio of the siloxane polymer and the polyfluoropolyether silane in the composition may be selectively chosen based on whether a lesser coefficient of friction or a greater durability of the layer is more desirable based on the particular application in which the layer is utilized.

**[0045]** In various embodiments, the composition further comprises a vehicle. The vehicle of the composition may be any vehicle capable of solubilizing the polyfluoropolyether silane and/or the siloxane polymer. The vehicle is typically selected such that the vehicle is non-reactive relative to the polyfluoropolyether silane. The vehicle is generally a fluorinated vehicle, though the vehicle need not be perfluorinated, e.g. the vehicle may be polyfluorinated. Specific examples of vehicles suitable for the composition include perfluoroaliphatic C<sub>5</sub>-C<sub>12</sub> hydrocarbons, such as decafluoropentane, perfluorohexane, perfluoromethylcyclohexane, and perfluoro-1,3-dimethylcyclohexane; polyfluorinated aromatic hydrocarbons, such as bis(trifluoromethyl)benzene; polyfluorinated aliphatic hydrocarbons; hydrofluoroethers (HFEs), such as perfluorobutyl methyl ether (C<sub>4</sub>F<sub>9</sub>OCH<sub>3</sub>), ethyl nonafluorobutyl ether (C<sub>4</sub>F<sub>9</sub>OC<sub>2</sub>H<sub>5</sub>), ethyl nonafluoroisobutyl ether (C<sub>4</sub>F<sub>9</sub>OC<sub>2</sub>H<sub>5</sub>), and like HFEs; perfluoropolyethers; perfluoroethers; nitrogen-containing

perfluorinated or polyfluorinated vehicles; etc. The composition may employ a single vehicle or a combination of two or more vehicles. Such vehicles may be linear, branched, cyclic, alicyclic, aromatic, or may contain combinations thereof. In certain embodiments, the vehicle is not perfluorinated for improved miscibility with siloxane fluids that may be present in the composition, for example as the carrier vehicle for the siloxane polymer. In these embodiments, the vehicle is typically polyfluorinated and may be selected from polyfluorinated aromatic hydrocarbons, such as bis(trifluoromethyl)benzene; polyfluorinated aliphatic hydrocarbons; (HFEs), such as perfluorobutyl methyl ether, ethoxy-nonafluorobutane, and like HFEs, and combinations thereof. Typically, the vehicle comprises an HFE.

**[0046]** In various embodiments including the vehicle, the vehicle comprises a perfluoropolyether vehicle. In these embodiments, the perfluoropolyether vehicle typically has a boiling point temperature of at least 40, alternatively at least 60, alternatively at least 80, alternatively at least 100, °C at atmospheric pressure. In one specific embodiment, the perfluoropolyether vehicle has a boiling point temperature of from 125 to 145, alternatively from 130 to 140, °C at atmospheric pressure. In another specific embodiment, the perfluoropolyether vehicle has a boiling point temperature of from 160 to 180, alternatively from 165 to 175, °C at atmospheric pressure. Typically, the boiling point temperature of the perfluoropolyether vehicle is from greater than 120 to 180, alternatively from greater than 125 to 180, alternatively from greater than 160 to 180, °C at atmospheric pressure. However, the depending on the molecular weight of the perfluoropolyether vehicle, the boiling point temperature of the perfluoropolyether vehicle may be greater than the upper range of 180 °C, e.g. to 200, 230, or 270 °C.

**[0047]** In embodiments in which the vehicle comprises the perfluoropolyether vehicle, the vehicle of the composition typically has the following general formula;

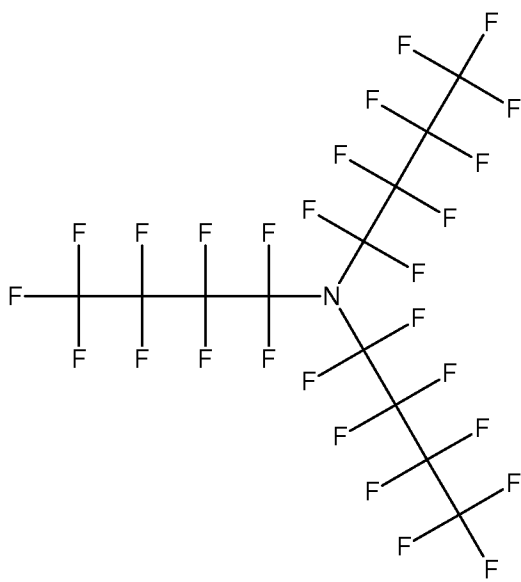


wherein  $a''$  is an integer greater than 1 and  $b''$  is 0 or an integer of at least 1. Specifically, subscripts  $a''$  and  $b''$  of the general formula above are chosen so as to provide the desired boiling point temperature of the perfluoropolyether vehicle. In particular, the relationship between subscripts  $a''$  and  $b''$ , the boiling point

temperature, and the molecular weight of the perfluoropolyether vehicle is set forth below:

| Boiling Point (°C) | Typical a'' | Typical b'' | Average MW (Da) |
|--------------------|-------------|-------------|-----------------|
| 125-145            | 1-3         | 1-7         | 600-620         |
| 160-180            | 1-4         | 1-10        | 750-770         |
| 190-210            | ≥1          | ≥1          | 860-880         |
| 220-240            | ≥1          | ≥1          | 1010-1030       |
| 260-280            | ≥1          | ≥1          | 1540-1560       |

**[0048]** Alternatively, the vehicle may comprise a nitrogen-containing perfluorinated or polyfluorinated vehicle. In these embodiments, the nitrogen-containing perfluorinated or polyfluorinated vehicle is typically a tertiary amine in which the nitrogen atom is a center atom having three polyfluorinated or perfluorinated substituents, optionally including heteroatoms, such as oxygen. Typically, each of the substituents bonded to the nitrogen atom are identical, although these substituents may differ in terms of the number of carbon atoms present, the presence or absence of heteroatoms, and/or fluorine content. These substituents generally independently include from 2 to 10 carbon atoms, and are typically perfluorinated. As but one example of such a nitrogen-containing perfluorinated vehicle, a structure representative of  $C_{12}F_{27}N$  is set forth below for illustrative purposes only:



Typically, when the vehicle comprises the nitrogen-containing perfluorinated or polyfluorinated vehicle, the vehicle comprises a combination of different nitrogen-containing perfluorinated or polyfluorinated vehicles.

**[0049]** The vehicle may comprise any combination of vehicles, although such a combination typically includes the perfluoropolyether vehicle and/or the nitrogen-containing perfluorinated vehicle. For example, the perfluoropolyether vehicle may be utilized in concert with the nitrogen-containing perfluorinated vehicle. Alternatively, the perfluoropolyether vehicle and/or the nitrogen-containing perfluorinated vehicle may be utilized in combination with one another and/or with other vehicles.

**[0050]** When the composition utilizes the vehicle, the vehicle is typically present in the composition in an amount of from 90 to 99.99, alternatively from 95 to 99.99 alternatively from 97 to 99.99, alternatively from 99 to 99.9, percent by weight based on the total weight of the composition, independent of the particular vehicle utilized. The amount of the vehicle may vary from the ranges set forth immediately above contingent on the absence or presence of various optional components employed in the composition, as described in greater detail below. Further, the ranges set forth above not include any of the vehicles described above for solubilizing the polyfluoropolyether silane, but also any carrier vehicles utilized to solubilize the siloxane polymer. The relative amounts of the vehicle and the carrier vehicle will be contingent on the relative amounts of the polyfluoropolyether silane and the siloxane polymer in the composition.

**[0051]** The composition may additionally include any other suitable component(s), such as a coupling agent, an antistatic agent, an ultraviolet absorber, a plasticizer, a leveling agent, a pigment, a catalyst, and so on.

**[0052]** Catalysts may optionally be utilized to promote surface modification by the composition. These catalysts promote the reaction between the hydrolysable groups of the polyfluoropolyether silane and the surface of the article. These catalysts can be used individually or as a combination of two or more in the composition. Examples of suitable catalytic compounds include acids, such as carboxylic acid, e.g. formic acid, acetic acid, propionic acid, butyric acid, and/or valeric acid; bases; metal salts of organic acids, such as dibutyl tin dioctoate, iron stearate, and/or lead octoate; titanate esters, such as tetraisopropyl titanate and/or tetrabutyl titanate; chelate compounds, such as acetylacetonato titanium; aminopropyltriethoxysilane, and the

like. If utilized, the catalysts are typically utilized in an amount of from greater than 0 to 5, alternatively 0.01 to 2, percent by weight, based on 100 parts by weight of the composition.

**[0053]** Alternatively or in addition to the above, the composition may further comprise various additive compounds for improving adhesion and/or durability of the layer formed from the composition. Examples of additive compounds are silanes, such as tetrakis(dimethylamine)silane, methyltrimethoxysilane, tetraethylorthosilicate, glycidoxypyltrimethoxysilane, triethylsilane, isobutyltrimethoxysilane; and siloxanes, such as heptamethyltrisiloxane, tetramethyldisiloxane etc.

**[0054]** As set forth above, the present invention further provides a surface-treated article and a method of preparing the surface-treated article, which are described collectively in greater detail below.

**[0055]** The surface-treated article comprises an article presenting a surface. A layer is deposited on the surface of the article. The layer is formed from the composition, which is applied on the surface of the article to prepare the surface-treated article. For example, when the composition further comprises the vehicle, the method of preparing the surface-treated article comprises applying the composition on the surface of the article to form a wet layer thereof on the surface of the article. The method further comprises removing the vehicle from the wet layer to form a layer on the surface of the article and give the surface-treated article. Although the article may be any article, because of the excellent physical properties obtained from the composition of the present invention, the article is typically an electronic article, an optical article, consumer appliances and components, automotive bodies and components, etc. Most typically, the article is an article for which it is desirable to reduce stains and/or smudges resulting from fingerprints or skin oils.

**[0056]** Examples of electronic articles typically include those having electronic displays, such as LCD displays, LED displays, OLED displays, plasma displays, etc. These electronic displays are often utilized in various electronic devices, such as computer monitors, televisions, smart phones, GPS units, music players, remote controls, portable readers, etc. Exemplary electronic articles include those having interactive touch-screen displays or other components which are often in contact with the skin and which oftentimes display stains and/or smudges.

**[0057]** As introduced above, the article may also be a metal article, such as consumer appliances and components. Exemplary articles include a dishwasher, a stove, a microwave, a refrigerator, a freezer, etc, typically having a glossy metal appearance, such as stainless steel, brushed nickel, etc.

**[0058]** Alternatively, the article may be an automotive body or component. For example, the composition may be applied directly on a top coat of an automobile body to form the layer, which imparts the automobile body with a glossy appearance, which is aesthetically pleasing and resists stains, such as dirt, etc., as well as smudges from fingerprints.

**[0059]** Examples of suitable optical articles include inorganic materials, such as glass plates, glass plates comprising an inorganic layer, ceramics, and the like. Additional examples of suitable optical articles include organic materials, such as transparent plastic materials and transparent plastic materials comprising an inorganic layer, etc. Specific examples of optical articles include antireflective films, optical filters, optical lenses, eyeglass lenses, beam splitters, prisms, mirrors, etc.

**[0060]** Among organic materials, examples of transparent plastic materials include materials comprising various organic polymers. From the view point of transparency, refractive index, dispersibility and like optical properties, and various other properties such as shock resistance, heat resistance and durability, materials used as optical members usually comprise polyolefins (polyethylene, polypropylene, etc.), polyesters (polyethylene terephthalate, polyethylene naphthalate, etc.), polyamides (nylon 6, nylon 66, etc.), polystyrene, polyvinyl chloride, polyimides, polyvinyl alcohol, ethylene vinyl alcohol, acrylics, celluloses (triacylcellulose, diacylcellulose, cellophane, etc.), or copolymers of such organic polymers. It is to be appreciated that these materials may be utilized in ophthalmic elements. Non-limiting examples of ophthalmic elements include corrective and non-corrective lenses, including single vision or multi-vision lenses like bifocal, trifocal and progressive lenses, which may be either segmented or non-segmented, as well as other elements used to correct, protect, or enhance vision, including without limitation contact lenses, intra-ocular lenses, magnifying lenses and protective lenses or visors. Preferred material for ophthalmic elements comprises one or more polymers selected from polycarbonates, polyamides, polyimides, polysulfones, polyethylene terephthalate and polycarbonate copolymers, polyolefins, especially polynorbornenes,

diethylene glycol-bis(allyl carbonate) polymers - known as CR39 - and copolymers, (meth)acrylic polymers and copolymers, especially (meth)acrylic polymers and copolymers derived from bisphenol A, thio(meth)acrylic polymers and copolymers, urethane and thiourethane polymers and copolymers, epoxy polymers and copolymers, and episulfide polymers and copolymers.

**[0061]** In addition to the articles described above, the composition of the invention can be applied to form the layer on other articles, such as window members for automobiles or airplanes, thus providing advanced functionality. To further improve surface hardness, it is also possible to perform surface modification by a so-called sol-gel process using a combination of the composition and TEOS (tetraethoxysilane).

**[0062]** One particular substrate of interest on which the composition may be applied to form the layer is any generation of Gorilla<sup>®</sup> Glass, commercially available from Corning Incorporated of Corning, New York. Another particular substrate of interest is Dragontrail<sup>®</sup> glass, commercially available from Asahi Glass Company of Tokyo, Japan.

**[0063]** In certain embodiments, e.g. those in which the composition comprises the vehicle, the step of applying the composition on the surface of the article to form the layer comprises a wet coating method.

**[0064]** Specific examples of wet coating application methods suitable for the method include dip coating, spin coating, flow coating, spray coating, roll coating, gravure coating, sputtering, slot coating, inkjet printing, and combinations thereof. The vehicle may be removed from the wet layer via heating or other known methods.

**[0065]** In other embodiments, the step of applying the composition on the surface of the article may comprise forming the layer on the surface of the article with a deposition apparatus. For example, when the deposition apparatus is utilized, the deposition apparatus typically comprises a physical vapor deposition apparatus. In these embodiments, the deposition apparatus is typically selected from a sputtering apparatus, an atomic layer deposition apparatus, a vacuum apparatus, and a DC magnetron sputtering apparatus. The optimum operating parameters of each of these physical deposition vapor apparatuses are based upon the composition utilized, the article on which the layer is to be formed, etc., as readily understood in the art. In certain embodiments, the deposition apparatus comprises a vacuum apparatus.

**[0066]** For example, when the layer is formed via physical vapor deposition (PVD), the method comprises combining the composition and a pellet to form an impregnated pellet. The pellet typically comprises a metal, alloy, or other robust material, such as iron, stainless steel, aluminum, carbon, copper, ceramic, etc. Typically, the pellet has a very high surface area to volume ratio for contacting the siloxane polymer and the polyfluoropolyether silane of the composition. The surface area to volume ratio of the pellet may be attributable to porosity of the pellet, i.e., the pellet may be porous. Alternatively, pellet may comprise woven, unwoven, and/or randomized fibers, such as nanofibers, so as to provide the desired surface area to volume ratio. The pellet may comprise a material selected from, for example, SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>, CaSO<sub>4</sub>, Cu, Fe, Al, stainless steel, carbon, or combinations thereof. The material may be a plug within a casing, which comprises the metal, alloy, or other robust material. The composition may be introduced in or to the pellet in any manner so long as the porous material, the polyfluoropolyether silane, and the siloxane polymer are combined. For example, the pellet may be submerged in the composition, or the composition may be disposed within the casing such that the porous material is impregnated with the composition. When the composition includes the vehicle, the method further comprises removing the vehicle from the impregnated pellet to form a neat pellet prior to deposition. For example, the vehicle may be flashed from the pellet via the application of heat. Alternatively, the vehicle may be removed from the pellet by drying at room temperature or a slightly elevated temperature, optionally in the presence of a vacuum or purging air.

**[0067]** The neat pellet may be stored until utilized in the deposition apparatus. In various embodiments, the neat pellet is stored in a vacuum-sealed aluminum bag.

**[0068]** One specific example of a vacuum apparatus suitable for forming the layer from the composition is an HVC-900DA vacuum apparatus, commercially available from Hanil Vacuum Machine Co., Ltd. of Incheon, South Korea. Another example of a deposition apparatus is an Edwards AUTO 306, commercially available from Edwards of Sanborn, NY.

**[0069]** The neat pellet is generally placed on a substrate in a chamber of the deposition apparatus along with the article to be coated and the siloxane polymer and the polyfluoropolyether silane are volatilized via resistive heat evaporation, thereby forming the layer on the surface of the article.

**[0070]** Independent of the method by which the layer is formed, once the layer is formed on the surface of the article from the composition, the layer may further undergo heating, humidification, catalytic post treatment, photoirradiation, electron beam irradiation, etc. For example, when the composition is applied via the deposition apparatus, the layer formed therefrom is generally heated at an elevated temperature, e.g. 80-150 °C, for a period of time, e.g. 45-75 minutes. Alternatively, the layer formed from the composition may be allowed to stand at room temperature and ambient conditions for a period of time, e.g. 24 hours.

**[0071]** Typically, the thickness of the layer formed from the composition is from 1-1,000, alternatively 1-200, alternatively 1-100, alternatively 5-75, alternatively 10-50, nm.

**[0072]** As noted above, layers formed from the composition may have a selectively controlled coefficient of friction and/or durability based on the relative amounts of the siloxane polymer and the polyfluoropolyether silane within the composition. This is true regardless of whether the composition is applied via a wet coating method or via the deposition apparatus. For example, sliding (kinetic) coefficient of friction may be measured by disposing an object having a determined surface area and mass onto a surface-treated article including a layer formed from the composition with a select material (e.g. a standard piece of legal paper) between the object and the layer. A force is then applied perpendicular to gravitational force to slide the object across the layer for a predetermined distance, which allows for a calculation of the sliding coefficient of friction of the layer. The sliding coefficient of friction may vary depending not only on the relative amounts of the siloxane polymer and the polyfluoropolyether silane in the composition, but also on the particular siloxane polymer and polyfluoropolyether silane utilized in the composition. To this end, in certain embodiments, the sliding coefficient may be significantly reduced (e.g. up to or greater than 50%) by incorporating the siloxane polymer in the composition as compared to a composition that is otherwise identical but does not include the siloxane polymer. Conversely, however, the durability of the layer may be reduced by up to 50% by including a significant amount of the siloxane polymer in the composition relative to the polyfluoropolyether silane utilized in the composition. Durability of the layers formed from the composition is generally measured via the water contact angles of the layers after subjecting the layers to an abrasion test. For

example, for layers having a lesser durability, the water contact angle decreases after abrasion, which generally indicates that the layer has at least partially deteriorated. As such, as introduced above, the relative amounts are typically determined based on the application in which the layer is utilized, where optimization between a minimal coefficient of friction and a maximum durability may be calculated.

**[0073]** In certain embodiments, the layers formed from the composition have a water contact angle of from 75 to 125, alternatively from 80-120, alternatively from 90-110, before and after subjecting the layers to the abrasion test. In these embodiments, the layers also typically have a sliding (kinetic) coefficient of friction of less than 0.1  $\mu$ .

**[0074]** It is to be understood that the appended claims are not limited to express and particular compounds, compositions, or methods described in the detailed description, which may vary between particular embodiments which fall within the scope of the appended claims. With respect to any Markush groups relied upon herein for describing particular features or aspects of various embodiments, different, special, and/or unexpected results may be obtained from each member of the respective Markush group independent from all other Markush members. Each member of a Markush group may be relied upon individually and or in combination and provides adequate support for specific embodiments within the scope of the appended claims.

**[0075]** Further, any ranges and subranges relied upon in describing various embodiments of the present invention independently and collectively fall within the scope of the appended claims, and are understood to describe and contemplate all ranges including whole and/or fractional values therein, even if such values are not expressly written herein. One of skill in the art readily recognizes that the enumerated ranges and subranges sufficiently describe and enable various embodiments of the present invention, and such ranges and subranges may be further delineated into relevant halves, thirds, quarters, fifths, and so on. As just one example, a range “of from 0.1 to 0.9” may be further delineated into a lower third, i.e., from 0.1 to 0.3, a middle third, i.e., from 0.4 to 0.6, and an upper third, i.e., from 0.7 to 0.9, which individually and collectively are within the scope of the appended claims, and may be relied upon individually and/or collectively and provide adequate support for specific embodiments within the scope of the appended claims. In addition, with respect to the

language which defines or modifies a range, such as “at least,” “greater than,” “less than,” “no more than,” and the like, it is to be understood that such language includes subranges and/or an upper or lower limit. As another example, a range of “at least 10” inherently includes a subrange of from at least 10 to 35, a subrange of from at least 10 to 25, a subrange of from 25 to 35, and so on, and each subrange may be relied upon individually and/or collectively and provides adequate support for specific embodiments within the scope of the appended claims. Finally, an individual number within a disclosed range may be relied upon and provides adequate support for specific embodiments within the scope of the appended claims. For example, a range “of from 1 to 9” includes various individual integers, such as 3, as well as individual numbers including a decimal point (or fraction), such as 4.1, which may be relied upon and provide adequate support for specific embodiments within the scope of the appended claims.

**[0076]** The following examples are intended to illustrate the invention and are not to be viewed in any way as limiting to the scope of the invention.

#### EXAMPLES

**[0077]** Compositions for surface treatment are prepared in accordance with the subject disclosure. In particular, each of the compositions described below comprises a siloxane polymer and a polyfluoropolyether silane. Because the vehicles utilized in the Examples solubilize the siloxane polymers and the polyfluoropolyether silanes, respectively, the vehicles are referred to herein as solvents. Unless otherwise indicated, any percentages set forth below relate to weight percentages.

**[0078]** Table 1 below illustrates 5 different compositions (corresponding to Comparative Examples 1 and 2 and Practical Examples 1-3). In particular, Comparative Example 1 comprises a polyfluoropolyether silane but does not comprise a siloxane polymer, and Comparative Example 2 comprises a siloxane polymer but does not comprise a polyfluoropolyether silane. In contrast, Practical Examples 1-3 vary the relative amounts of the polyfluoropolyether silane and the siloxane polymer. For example, in Practical Example 1, the polyfluoropolyether silane and the siloxane polymer are utilized in a ratio of about 2:1 (by volume). In practical Example 2, the polyfluoropolyether silane and the siloxane polymer are utilized in an inverted ratio relative to Practical Example 1, i.e., in Practical Example 2, the polyfluoropolyether

silane and the siloxane polymer are utilized in a ratio of about 1:2 (by volume). In practical Example 3, the polyfluoropolyether silane and the siloxane polymer are utilized in a ratio of about 5.5:1 (by volume). All values in Table 1 below relate to parts by volume as opposed to parts by weight.

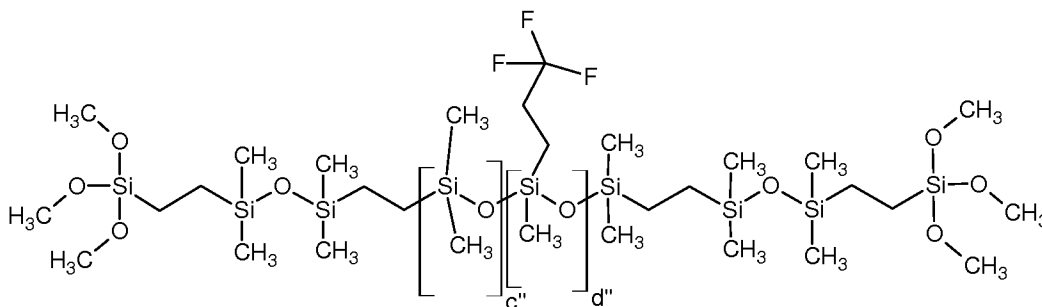
**[0079]** Table 1:

| Component                    | Comparative Example 1 | Practical Example 1 | Practical Example 2 | Practical Example 3 | Comparative Example 2 |
|------------------------------|-----------------------|---------------------|---------------------|---------------------|-----------------------|
| Polyfluoropolyether Silane 1 | 0.15                  | 0.09                | 0.05                | 0.02                | 0                     |
| Solvent 1                    | 99.85                 | 61.37               | 34.65               | 15.03               | 0                     |
| Siloxane Polymer 1           | 0                     | 0.05                | 0.09                | 0.11                | 0.13                  |
| Carrier Solvent 1            | 0                     | 38.49               | 65.2                | 84.83               | 99.87                 |

**[0080]** Polyfluoropolyether Silane 1 has the general formula  $F(CF(CF_3)CF_2O)_c'CF(CF_3)CH_2O(CH_2)_3-Si(CH_3)_2-O-Si(CH_3)_2-(CH_2)_2-Si(OCH_3)_3$ , where  $c'$  is an integer of from about 14 to about 20.

**[0081]** Solvent 1 is ethoxy-nonafluorobutane ( $C_4F_9OC_2H_5$ ).

**[0082]** Siloxane Polymer 1 has the general formula:



, where  $c''$  and  $d''$  are selected such that the Siloxane Polymer 1 has a viscosity of about 38,000 centistokes at 25 °C.

**[0083]** Carrier Solvent 1 is hexamethyldisiloxane.

**[0084]** The Carrier Solvent 1 is generally utilized as a carrier solvent for the siloxane polymer, which is why the Carrier Solvent 1 is absent in Comparative Example 1 (which does not include a siloxane polymer). In contrast, the Solvent 1 is generally utilized for solubilizing the polyfluoropolyether silane, which is why the Solvent 1 is absent in Comparative Example 2 (which does not include a polyfluoropolyether silane).

**[0085]** The respective compositions of Practical Examples 1-3 and Comparative Examples 1-2 are each applied to a surface of a substrate via spray coating. In particular, these compositions are applied to a glass substrate via a PVA-1000

dispensing machine (commercially available from PVA of Cohoes, NY) having an atomization pressure of 8 psi, a liquid pressure of 5 psi, a stroke of from 2 to 2.5 mil, a nozzle height of 5.3 cm, and a speed of about 100 mm/sec. Once the respective compositions are applied to the substrates, the compositions are cured at room temperature for about 24 hours to form layers on the substrates.

**[0086]** Physical properties of the layers formed from the compositions are measured. In particular, physical properties of the respective layers are measured before and after subjecting the layers to an abrasion resistance test, as described below.

**[0087]** More specifically, sliding coefficient of friction (COF) is measured for each of the layers. The sliding coefficient of friction is measured by placing a sled having a load of about 156 grams onto each of the layers with a piece of standard paper disposed between each of the layers and the sled. The sled has an area of about 25 x 25 millimeters. A force is applied in a direction perpendicular to gravity to move the sled along each of the layers at a speed of about 2.5 millimeters/sec for a distance of about 42 millimeters to measure the sliding coefficient of friction.

**[0088]** Each of the layers is then subjected to an abrasion test, after which the water contact angle (WCA) for each of the layers is measured, for determining durability of the layers.

**[0089]** The abrasion resistance test utilizes a reciprocating abraser – Model 5900, which is commercially available from Taber Industries of North Tonawanda, NY. The abrading material utilized is a rubbing eraser having dimensions of 6.0 x 12.2 mm. The reciprocating abraser is operated for 1,500 cycles at a speed of 40 cycles per minute with a stroke length of 1 inch and a load of 5 N.

**[0090]** The water contact angle (WCA) of each of the layers is measured via a VCA Optima XE goniometer, which is commercially available from AST Products, Inc., Billerica, MA. The water contact angle measured is a static contact angle based on a 2  $\mu$ L droplet on each of the layers. The water contact angle is measured after the abrasion resistance test. Generally, the greater the WCA, the greater the durability of the layer.

**[0091]** Table 2 below illustrates the physical properties of each of the layers formed from Practical Examples 1-3 and Comparative Examples 1-2.

**[0092]** Table 2:

| Property:                         | Comparative Example 1 | Practical Example 1 | Practical Example 2 | Practical Example 3 | Comparative Example 2 |
|-----------------------------------|-----------------------|---------------------|---------------------|---------------------|-----------------------|
| Coefficient of Friction ( $\mu$ ) | 0.176                 | 0.171               | 0.160               | 0.144               | 0.07                  |
| WCA After Abrasion                | 110.1                 | 109.6               | 107.2               | 78.5                | 67.8                  |

**[0093]** As is readily apparent from Table 2 above, the sliding coefficient of friction for the layers formed from Practical Examples 1-3 and Comparative Examples 1-2 decreases as the amount of the siloxane polymer in the respective compositions increases. For example, from left to right in Table 2 above, the amount of the siloxane polymer utilized increases, and the sliding coefficient of friction decrease. However, the durability of the layers generally decreases with an increased amount of the siloxane polymer utilized in the compositions. In certain applications, it is more desirable to maintain a lower coefficient of friction than maintaining a higher durability, and vice versa. As such, for a particular application, the relative amounts of the siloxane polymer and the perfluoropolyether silane of a composition may be selectively modified to balance the desired sliding coefficient of friction and durability.

**[0094]** Table 3 below illustrates 5 different compositions (corresponding to Comparative Examples 3 and 4 and Practical Examples 4-6). In particular, Comparative Example 3 comprises a polyfluoropolyether silane but does not comprise a siloxane polymer, and Comparative Example 4 comprises a siloxane polymer but does not comprise a polyfluoropolyether silane. In contrast, Practical Examples 4-6 vary the relative amounts of the polyfluoropolyether silane and the siloxane polymer. For example, in Practical Example 4, the polyfluoropolyether silane and the siloxane polymer are utilized in a ratio of about 2:1 (by volume). In practical Example 5, the polyfluoropolyether silane and the siloxane polymer are utilized in an inverted ratio relative to Practical Example 4, i.e., in Practical Example 5, the polyfluoropolyether silane and the siloxane polymer are utilized in a ratio of about 1:2 (by volume). In practical Example 6, the polyfluoropolyether silane and the siloxane polymer are utilized in a ratio of about 5.5:1 (by volume). All values in Table 3 below relate to parts by volume as opposed to parts by weight.

**[0095]** Table 3:

| Component                    | Comparative Example 3 | Practical Example 4 | Practical Example 5 | Practical Example 6 | Comparative Example 4 |
|------------------------------|-----------------------|---------------------|---------------------|---------------------|-----------------------|
| Polyfluoropolyether Silane 2 | 0.15                  | 0.09                | 0.05                | 0.02                | 0                     |
| Solvent 1                    | 99.85                 | 61.37               | 34.65               | 15.03               | 0                     |
| Siloxane Polymer 1           | 0                     | 0.05                | 0.09                | 0.11                | 0.13                  |
| Carrier Solvent 1            | 0                     | 38.49               | 65.2                | 84.83               | 99.87                 |

**[0096]** Polyfluoropolyether Silane 2 has the general formula:  $F((CF_2)_3O)_c \cdot CF_2CF_2CH_2O(CH_2)_3Si(OMe)_3$ , where c' is from 17-25.

**[0097]** The Carrier Solvent 1 is generally utilized as a carrier solvent for the siloxane polymer, which is why the Carrier Solvent 1 is absent in Comparative Example 3 (which does not include a siloxane polymer). In contrast, the Solvent 1 is generally utilized for solubilizing the polyfluoropolyether silane, which is why the Solvent 1 is absent in Comparative Example 4 (which does not include a polyfluoropolyether silane).

**[0098]** The respective compositions of Practical Examples 4-6 and Comparative Examples 3-4 are each applied to a surface of a substrate via spray coating. In particular, these compositions are applied to a glass substrate via a PVA-1000 dispensing machine having an atomization pressure of 8 psi, a liquid pressure of 5 psi, a stroke of from 2 to 2.5 mil, a nozzle height of 5.3 cm, and a speed of about 100 mm/sec. Once the respective compositions are applied to the substrates, the compositions are cured at room temperature for about 24 hours to form layers on the substrates.

**[0099]** Physical properties of the layers formed from the compositions are measured. In particular, physical properties of the respective layers are measured before and after subjecting the layers to an abrasion resistance test in accordance with the procedure described above with respect to Practical Examples 1-3 and Comparative Examples 1-2.

**[00100]** Table 4 below illustrates the physical properties of each of the layers formed from the compositions of Practical Examples 4-6 and Comparative Examples 3-4.

**[00101]** Table 4:

| Property:                         | Comparative<br>Example 3 | Practical<br>Example 4 | Practical<br>Example 5 | Practical<br>Example 6 | Comparative<br>Example 4 |
|-----------------------------------|--------------------------|------------------------|------------------------|------------------------|--------------------------|
| Coefficient of Friction ( $\mu$ ) | 0.097                    | 0.089                  | 0.076                  | 0.070                  | 0.070                    |
| WCA After Abrasion                | 114.1                    | 113.2                  | 111.7                  | 110.3                  | 67.8                     |

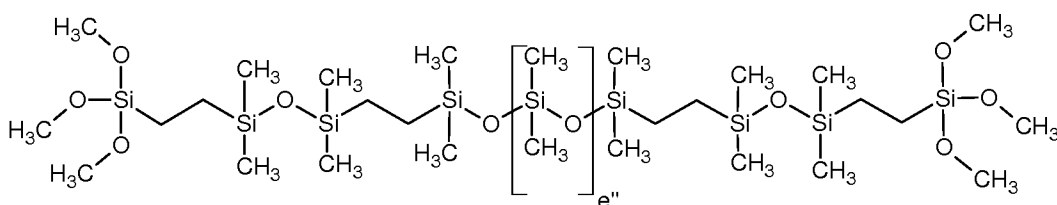
**[00102]** As is readily apparent from Table 4 above, the sliding coefficient of friction for the layers formed from Practical Examples 4-6 and Comparative Examples 3-4 decreases as the amount of the siloxane polymer in the respective compositions increases. For example, from left to right in Table 4 above, the amount of the siloxane polymer utilized increases, and the sliding coefficient of friction decrease. However, the durability of the layers generally decreases with an increased amount of the siloxane polymer utilized in the compositions, although the decrease in durability from increasing the relative amount of the siloxane polymer was fairly insignificant in Practical Examples 4-6 and Comparative Examples 3-4 until the polyfluoropolyether silane was absent from the composition altogether (in Comparative Example 4). In certain applications, it is more desirable to maintain a lower coefficient of friction than maintaining a higher durability, and vice versa. As such, for a particular application, the relative amounts of the siloxane polymer and the perfluoropolyether silane of a composition may be selectively modified to balance the desired sliding coefficient of friction and durability.

**[00103]** Table 5 below illustrates 5 different compositions (corresponding to Comparative Examples 5 and 6 and Practical Examples 7-9). In particular, Comparative Example 5 comprises a polyfluoropolyether silane but does not comprise a siloxane polymer, and Comparative Example 6 comprises a siloxane polymer but does not comprise a polyfluoropolyether silane. In contrast, Practical Examples 7-9 vary the relative amounts of the polyfluoropolyether silane and the siloxane polymer. For example, in Practical Example 7, the polyfluoropolyether silane and the siloxane polymer are utilized in a ratio of about 3:2 (by volume). In practical Example 8, the polyfluoropolyether silane and the siloxane polymer are utilized in a ratio of about 1:2 (by volume). In practical Example 9, the polyfluoropolyether silane and the siloxane polymer are utilized in a ratio of about 1:6.5 (by volume). All values in Table 5 below relate to parts by volume as opposed to parts by weight.

**[00104]** Table 5:

| Component                    | Comparative Example 5 | Practical Example 7 | Practical Example 8 | Practical Example 9 | Comparative Example 6 |
|------------------------------|-----------------------|---------------------|---------------------|---------------------|-----------------------|
| Polyfluoropolyether Silane 2 | 0.15                  | 0.09                | 0.05                | 0.02                | 0                     |
| Solvent 1                    | 99.85                 | 61.36               | 34.65               | 15.03               | 0                     |
| Siloxane Polymer 2           | 0                     | 0.06                | 0.1                 | 0.13                | 0.16                  |
| Carrier Solvent 1            | 0                     | 38.48               | 65.2                | 84.82               | 99.84                 |

**[00105]** Siloxane Polymer 2 has the general formula:



where  $e''$  is selected such that the Siloxane Polymer 2 has a viscosity of about 650 centistokes at 25 °C.

**[00106]** The Carrier Solvent 1 is generally utilized as a carrier solvent for the siloxane polymer, which is why the Carrier Solvent 1 is absent in Comparative Example 5 (which does not include a siloxane polymer). In contrast, the Solvent 1 is generally utilized for solubilizing the polyfluoropolyether silane, which is why the Solvent 1 is absent in Comparative Example 6 (which does not include a polyfluoropolyether silane).

**[00107]** The respective compositions of Practical Examples 7-9 and Comparative Examples 5-6 are each applied to a surface of a substrate via spray coating. In particular, these compositions are applied to a glass substrate via a PVA-1000 dispensing machine having an atomization pressure of 8 psi, a liquid pressure of 5 psi, a stroke of from 2 to 2.5 mil, a nozzle height of 5.3 cm, and a speed of about 100 mm/sec. Once the respective compositions are applied to the substrates, the compositions are cured at room temperature for about 24 hours to form layers on the substrates.

**[00108]** Physical properties of the layers formed from the compositions are measured. In particular, physical properties of the respective layers are measured before and after subjecting the layers to an abrasion resistance test in accordance with the procedure described above with respect to Practical Examples 1-3 and Comparative Examples 1-2.

**[00109]** Table 6 below illustrates the physical properties of each of the layers formed from the compositions of Practical Examples 7-9 and Comparative Examples 5-6.

**[00110]** Table 6:

| Property:                         | Comparative Example 5 | Practical Example 7 | Practical Example 8 | Practical Example 9 | Comparative Example 6 |
|-----------------------------------|-----------------------|---------------------|---------------------|---------------------|-----------------------|
| Coefficient of Friction ( $\mu$ ) | 0.097                 | 0.083               | 0.081               | 0.072               | 0.067                 |
| WCA After Abrasion                | 114.1                 | 111.6               | 108                 | 90.4                | 57.1                  |

**[00111]** As is readily apparent from Table 6 above, the sliding coefficient of friction for the layers formed from Practical Examples 7-9 and Comparative Examples 5-6 decreases as the amount of the siloxane polymer in the respective compositions increases. For example, from left to right in Table 6 above, the amount of the siloxane polymer utilized increases, and the sliding coefficient of friction decreases. However, the durability of the layers generally decreases with an increased amount of the siloxane polymer utilized in the compositions (albeit gradually between Practical Examples 7-9). In certain applications, it is more desirable to maintain a lower coefficient of friction than maintaining a higher durability, and vice versa. As such, for a particular application, the relative amounts of the siloxane polymer and the perfluoropolyether silane of a composition may be selectively modified to balance the desired sliding coefficient of friction and durability.

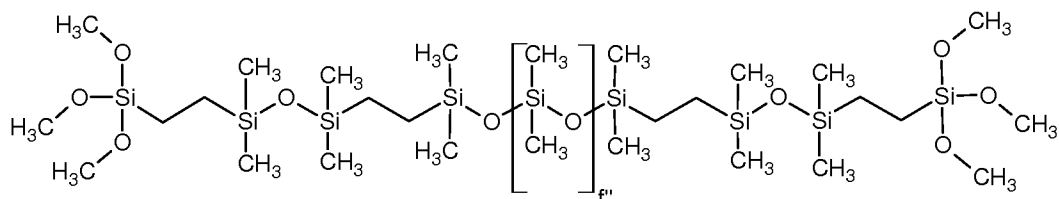
**[00112]** Table 7 below illustrates 3 different compositions (corresponding to Practical Examples 10-11 and Comparative Example 7). In particular, Practical Examples 10-11 vary the relative amounts of the polyfluoropolyether silane and the siloxane polymer. In contrast, Comparative Example 7 comprises a polyfluoropolyether silane but does not comprise a siloxane polymer. All values in Table 7 below relate to parts by weight.

**[00113]** Table 7:

| Component                    | Practical Example 10 | Practical Example 11 | Comparative Example 7 |
|------------------------------|----------------------|----------------------|-----------------------|
| Polyfluoropolyether Silane 3 | 70                   | 75                   | 100                   |
| Siloxane Polymer 3           | 30                   | 0                    | 0                     |
| Siloxane Polymer 4           | 0                    | 25                   | 0                     |

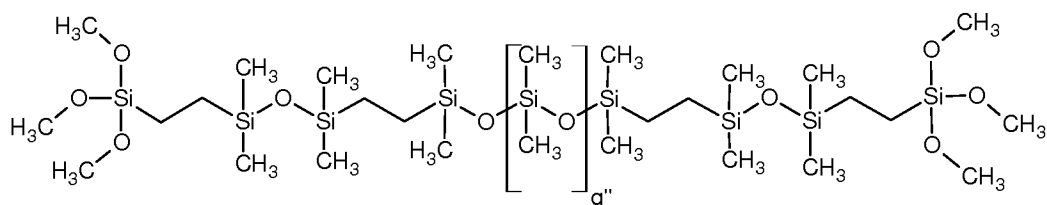
**[00114]** Polyfluoropolyether Silane 3 has the following general formula:  $\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-(O-CF}_2\text{-CF}_2\text{-CF}_2\text{)}_{b'}\text{-O-CF}_2\text{-CF}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-CH}_2\text{-Si-(OCH}_3\text{)}_3$ , where  $b'$  is an integer from 17 to 25.

**[00115]** Siloxane Polymer 3 has the general formula:



where  $f''$  is selected such that the Siloxane Polymer 3 has a viscosity of about 125 centistokes at 25 °C.

**[00116]** Siloxane Polymer 4 has the general formula:



where  $g''$  is selected such that the Siloxane Polymer 4 has a viscosity of about 380 centistokes at 25 °C.

**[00117]** The compositions of Practical Examples 10-11 and Comparative Example 7 along with a solvent are impregnated into a pellet comprising steel wool and a copper casing. Solvent is driven from the pellet at room temperature under vacuum purge. The compositions of Practical Examples 10-11 and Comparative Example 7 are each deposited via a vacuum apparatus (HVC-900DA from Hanil Vacuum Machine Co., LTD). The vacuum apparatus operates at a vacuum of  $2.0\text{E-}5$  torr to deposit layers on a surface of glass. Each of the layers had a thickness of from 20-30 nm.

**[00118]** Once the respective compositions are applied to the substrates via the vacuum apparatus, the compositions are cured at 125 °C for about 1 hour to form layers on the substrates.

**[00119]** Physical properties of the layers formed from the compositions are measured. In particular, physical properties of the respective layers are measured

before and after subjecting the layers to an abrasion resistance test, in accordance with the methods described above.

**[00120]** Table 8 below illustrates the physical properties of each of the layers formed from the compositions of Practical Examples 10-11 and Comparative Example 7.

**[00121]** Table 8:

| Property:                         | Practical<br>Example 10 | Practical<br>Example 11 | Comparative<br>Example 7 |
|-----------------------------------|-------------------------|-------------------------|--------------------------|
| Coefficient of Friction ( $\mu$ ) | 0.065                   | 0.069                   | 0.078                    |
| WCA After Abrasion                | 101.7                   | 109.1                   | 109.1                    |
| WCA Initial                       | 112.8                   | 113.5                   | 113.0                    |

**[00122]** As is readily apparent from Table 8 above, the sliding coefficient of friction for the layers formed from Practical Examples 10-11 and Comparative Example 7 decreases as the amount of the siloxane polymer in the respective compositions increases. For example, from left to right in Table 8 above, the amount of the siloxane polymer utilized decreases, and the sliding coefficient of friction increases. However, the durability of the layers generally decreases with an increased amount of the siloxane polymer utilized in the compositions. For example, Practical Example 11, which utilized a greater amount of the polyfluoropolyether silane than Practical Example 10, maintained a greater WCA after abrasion than did Practical Example 10, which is generally attributable to the decreased amount of the siloxane polymer and the increased amount of the polyfluoropolyether silane. In certain applications, it is more desirable to maintain a lower coefficient of friction than maintaining a higher durability, and vice versa. As such, for a particular application, the relative amounts of the siloxane polymer and the perfluoropolyether silane of a composition may be selectively modified to balance the desired sliding coefficient of friction and durability.

**[00123]** 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. Obviously, many modifications and variations of the present invention are possible in light of the above teachings. The invention may be practiced otherwise than as specifically described.

## CLAIMS

What is claimed is:

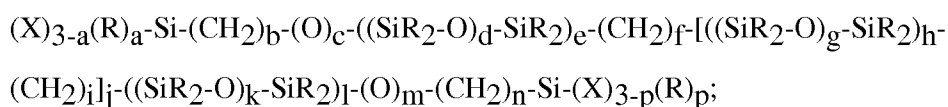
1. A composition for surface treatment of a substrate, said composition comprising:

a siloxane polymer comprising repeating  $R_2SiO_{2/2}$  units, where R is an independently selected substituted or unsubstituted hydrocarbyl group; and  
a polyfluoropolyether silane.

2. The composition of claim 1 further comprising a solvent.

3. The composition of claims 1 or 2 wherein said siloxane polymer further comprises  $RSiO_{3/2}$  units and/or  $SiO_{4/2}$  units.

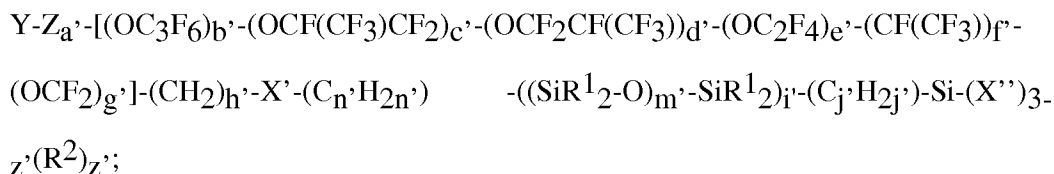
4. The composition of claims 1 or 2 wherein said siloxane polymer has the following general formula (A):



wherein X is an independently selected hydrolysable group; R is defined above; a and p are each integers independently selected from 0 to 3; b, f, i, and n are each integers independently selected from 0 to 10; c and m are each independently 0 or 1; d, g, and k are each integers independently selected from 0 to 200 with the proviso that d, g, and k are not simultaneously 0; e, h, and l are each integers independently selected from 0 and 1 with the proviso that e, h, and l are not simultaneously 0; and j is an integer selected from 0 to 5;

provided that when subscript d is 0, subscript e is also 0; when subscript d is greater than 0, subscript e is 1; when subscript g is 0, subscripts h, i, and j are also 0; when subscript g is greater than 1, subscript h is 1 and subscript j is at least 1; when subscript k is 0, subscript l is also 0; and when subscript k is greater than 0, subscript l is 1.

5. The composition of any one preceding claim wherein said polyfluoropolyether silane has the following general formula (B):



wherein Z is independently selected from  $-(CF_2)-$ ,  $-(CF(CF_3)CF_2O)-$ ,  $-(CF_2CF(CF_3)O)-$ ,  $-(CF(CF_3)O)-$ ,  $-(CF(CF_3)CF_2)-$ ,  $-(CF_2CF(CF_3))-$ , and  $-(CF(CF_3))-$ ; a' is an integer from 1 to 200; b', c', d', e', f', and g' are integers each independently selected from 0 to 200; h', n' and j' are integers each independently selected from 0 to 200; i' and m' are integers each independently selected from 0 to 5; X' is a bivalent organic group or an oxygen atom; R<sup>1</sup> is an independently selected C<sub>1</sub>-C<sub>22</sub> hydrocarbon group; z' is an integer independently selected from 0 to 2; X'' is an independently selected hydrolysable group; R<sup>2</sup> is an independently selected C<sub>1</sub>-C<sub>22</sub> hydrocarbon group which is free of aliphatic unsaturation; and Y is selected from F and  $Si-(X'')_3-Z'(R^2)_Z'(C_j'H_{2j'})-((SiR^1_2-O)_m'-SiR^1_2)_i'-(C_n'H_{2n'})-X'-(CH_2)_h'-$ ; wherein X'', X', z', R<sup>1</sup>, R<sup>2</sup>, j', m', i', n' and h' are as defined above;

provided that when subscript i' is 0, subscript j' is also 0; when subscript i' is an integer greater than 0, subscript j' is also an integer greater than 0; and when subscript i' is an integer greater than 0, m' is also an integer greater than 0.

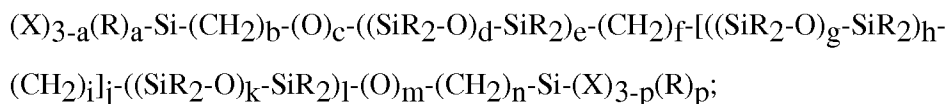
6. The composition of claim 4 wherein said hydrolysable groups represented by X in general formula (A) of said siloxane polymer are independently selected from H, a halide group,  $-OR^3$ ,  $-NHR^3$ ,  $-NR^3R^4$ ,  $-OOC-R^3$ ,  $O-N=CR^3R^4$ ,  $O-C(=CR^3R^4)R^5$ , and  $-NR^3COR^4$ , wherein R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> are each independently selected from H and a C<sub>1</sub>-C<sub>22</sub> hydrocarbon group, and wherein R<sup>3</sup> and R<sup>4</sup> optionally can form a cyclic amine in the alkylamino group.

7. The composition of claim 5 wherein said hydrolysable groups represented by X'' in general formula (B) of said polyfluoropolyether silane are independently selected from H, a halide group,  $-OR^3$ ,  $-NHR^3$ ,  $-NR^3R^4$ ,  $-OOC-R^3$ ,  $O-N=CR^3R^4$ ,  $O-C(=CR^3R^4)R^5$ , and  $-NR^3COR^4$ , wherein R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> are each independently selected from H and a C<sub>1</sub>-C<sub>22</sub> hydrocarbon group, and wherein R<sup>3</sup> and R<sup>4</sup> optionally can form a cyclic amine in the alkylamino group.

8. A method of preparing a surface-treated article, said method comprising:  
applying the composition of claim 1 on a surface of an article to form a layer  
on the surface of the article.

9. The method of claim 8 wherein the siloxane polymer further comprises  
RSiO<sub>3/2</sub> units and/or SiO<sub>4/2</sub> units.

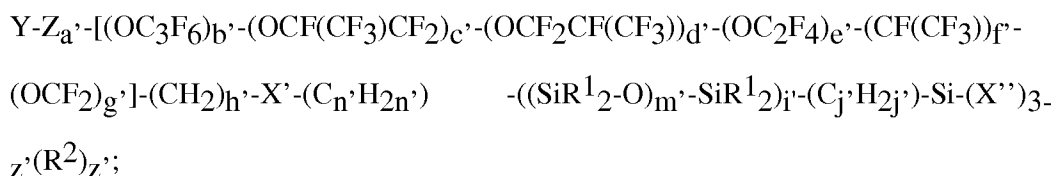
10. The method of claim 8 wherein the siloxane polymer has the following  
general formula (A):



wherein X is an independently selected hydrolysable group; R is defined  
above; a and p are each integers independently selected from 0 to 3; b, f, i, and n are  
each integers independently selected from 0 to 10; c and m are each independently 0  
or 1; d, g, and k are each integers independently selected from 0 to 200 with the  
proviso that d, g, and k are not simultaneously 0; e, h, and l are each integers  
independently selected from 0 and 1 with the proviso that e, h, and l are not  
simultaneously 0; and j is an integer selected from 0 to 5;

provided that when subscript d is 0, subscript e is also 0; when subscript d is  
greater than 0, subscript e is 1; when subscript g is 0, subscripts h, i, and j are also 0;  
when subscript g is greater than 1, subscript h is 1 and subscript j is at least 1; when  
subscript k is 0, subscript l is also 0; and when subscript k is greater than 0, subscript l  
is 1.

11. The method of any one of claims 8-10 wherein the polyfluoropolyether  
silane has the following general formula (B):



wherein Z is independently selected from -(CF<sub>2</sub>)-, -(CF(CF<sub>3</sub>)CF<sub>2</sub>O)-, -  
(CF<sub>2</sub>CF(CF<sub>3</sub>)O)-, -(CF(CF<sub>3</sub>)O)-, -(CF(CF<sub>3</sub>)CF<sub>2</sub>)-, -(CF<sub>2</sub>CF(CF<sub>3</sub>))-, and -  
(CF(CF<sub>3</sub>))-; a' is an integer from 1 to 200; b', c', d', e', f', and g' are integers each  
independently selected from 0 to 200; h', n' and j' are integers each independently  
selected from 0 to 20; i' and m' are integers each independently selected from 0 to 5;

X' is a bivalent organic group or an oxygen atom; R<sup>1</sup> is an independently selected C<sub>1</sub>-C<sub>22</sub> hydrocarbon group; z' is an integer independently selected from 0 to 2; X'' is an independently selected hydrolysable group; R<sup>2</sup> is an independently selected C<sub>1</sub>-C<sub>22</sub> hydrocarbon group which is free of aliphatic unsaturation; and Y is selected from F and Si-(X'')<sub>3-z'</sub>(R<sup>2</sup>)<sub>z'</sub>(C<sub>j'</sub>H<sub>2j'</sub>)<sub>j'</sub>((SiR<sup>1</sup><sub>2</sub>-O)<sub>m'</sub>-SiR<sup>1</sup><sub>2</sub>)<sub>i'</sub>-(C<sub>n'</sub>H<sub>2n'</sub>)-X'-(CH<sub>2</sub>)<sub>h'</sub>; wherein X'', X', z', R<sup>1</sup>, R<sup>2</sup>, j', m', i', n' and h' are as defined above;

provided that when subscript i' is 0, subscript j' is also 0; when subscript i' is an integer greater than 0, subscript j' is also an integer greater than 0; and when subscript i' is an integer greater than 0, m' is also an integer greater than 0.

12. The method of any one of claims 8-11 wherein the composition further comprises a solvent and wherein the step of applying the composition is selected from dip coating, spin coating, flow coating, spray coating, roll coating, gravure coating, sputtering, slot coating, inkjet printing, and combinations thereof.

13. The method of any one of claims 8-11 wherein the step of applying the composition comprises depositing the composition with a deposition apparatus.

14. A surface treated article formed in accordance with the method of any one of claims 8-13.

15. The surface treated article of claim 14 wherein said layer has a water contact angle of from 75 to 125 and a sliding (kinetic) coefficient of friction of less than 0.1 μ.

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/013169

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C09D183/12 C08L83/12  
ADD.

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09D C08G C08L

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

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

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                             | Relevant to claim No.   |
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| X         | EP 0 527 008 A1 (SHINETSU CHEMICAL CO [JP]) 10 February 1993 (1993-02-10)<br><br>example 1<br>page 14, line 21<br>-----        | 1-3,5,<br>7-9,<br>11-15 |
| X         | EP 1 321 480 A2 (SHINETSU CHEMICAL CO [JP]) 25 June 2003 (2003-06-25)<br><br>example 1<br>paragraph [0046]<br>-----<br><br>-/- | 1-3,5,<br>7-9,<br>11-15 |



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

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"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

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"&amp;" document member of the same patent family

Date of the actual completion of the international search

20 May 2014

Date of mailing of the international search report

28/05/2014

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## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/013169

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages               | Relevant to claim No. |
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Information on patent family members

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