Abstract:

This invention relates to perfluoropolyether silanes of Formula (1), a method for its preparation, and coating compositions made therefrom, wherein R₂ is R° (CF₂CF₂O)ₙCF (CF₂CF₂O)ₙCF₂- or R° (CF₂CF₂O)ₙCF₂-; or R° (CF₂CF₂O)ₙCF₂-; R¹, R², R₃, m, n, x, p, q and r are defined in the disclosure. Also disclosed are articles comprising a layer of the coating compositions cured thereon, and methods of making the same. Said coatings improve the abrasion resistance of the articles.
PERFLUOROPOLYETHER SILANES AND METHOD OF FORMING THE SAME

FIELD OF THE INVENTION

Novel perfluoropolyether silanes, methods for their preparations, and coating compositions made therefrom are provided. Also provided are articles being coated with the coating compositions, and methods of making the same.

BACKGROUND OF THE INVENTION

Many glass surfaces, such as surfaces of handheld electronics, display or optical devices, monitors, eyewear (e.g., glasses and goggles), windows and mirrors are susceptible to contaminations like fingerprints, soil, cosmetics, etc. Generally, surfaces with high surface energy are more liable to be stained and harder to clean than those with low surface energy. The use of perfluoropolyether silanes for rendering substrates such as glass and ceramics oil and water repellent are known.

For example, U.S. Pat. No. 3,646,085 discloses fluorinated polyether amidoalkylsilanes having the general formula of \( R_1O(CF_2F_60)_nCF(CF_3)C(0)N(R)R'\text{Si(OR"}_3 \) for rendering the surface of glass oil and water repellent and scratch resistant.

More recently, WO2009/008380 A1 discloses a surface treating agent containing a compound of formula (a): \( R^{F_1}0(CF_2CF_20)_nCF_2X \), wherein \( R^{F_1} \) is a perfluoro monovalent saturated hydrocarbon group having 1-20 carbon atoms or the like, a represents an integer of 1-200, X, \( \text{inter alia} \), is -C(0)N(CH\(_2\)CH\(_2\)CH\(_2\)Si\(_p\)R\(_{3-p}\)\(_2\)) (X7), L is a hydrolyzable group, R represents H or monovalent hydrocarbon group, and \( p \) represents an integer of 1-3.

WO2013/074299 A9 also discloses a curable fluorinated coating composition including both a perfluoropolyether silane of Formula (I): \( X(CF(CF_3)CFO)_mCF(CF_3)CH\(_2\)CH\(_2\)CH\(_2\)L-Si(R\(_1\))\(_3-x\)(R\(_2\))^x \) and a fluorinated polyether oil. In Formula (I), L is a single bond or -S-CH\(_2\)CH\(_2\)CH\(_2\). \( R^1 \) is hydroxy or a hydrolyzable group, \( R^2 \) is a non-hydrolyzable group, \( n \) is an integer of 4 to 100, \( x \) is 0, 1 or 2.

Although many perfluoropolyether silane compositions are known in the art for treating substrates to render them oil and water repellent, there continues to be a desire to provide further improved compositions for the treatment of substrates, in particular substrates having a hard surface such as glass and ceramics, in order to render them antisoiling, i.e. stain, dirt, oil and/or water resistant. Moreover, it would be desirable to improve the durability of the coatings, specifically, an improved abrasion resistance of the coatings. Furthermore, improving the ease of cleaning of such substrates while using less detergents, water or manual labor, is not only a desire by the end consumer, but has also a positive impact on the environment.
Therefore, there is a need for new perfluoropolyether silanes which can be coated on the glass and ceramic surface to impart low surface energy and high abrasion resistance characteristics.

**SUMMARY OF THE INVENTION**

The present invention provides novel perfluoropolyether silanes of Formula 1:

![Chemical structure](image)

wherein

- $R_f$ is $R^3\theta(CF(CF_3)CF_2\theta)_pCF(CF_3)-$, $R^3\theta(CF_2CF_2CF_2\theta)_qCF_2CF_2-$, or $R^3\theta(CF_2CF_2\theta)_rCF_2-$;
- $R^1$ is hydroxy or C1-C4 alkoxy;
- $R^2$ is H or C1-C4 alkyl;
- $R^3$ is C1-C6 perfluoroalkyl;
- $m$ and $n$ are each independently an integer ranging from 3 to 20;
- $x$ is 1, 2, or 3; and
- $p$, $q$, and $r$ are each independently an integer ranging from 5 to 60.

The present invention also provides a method for preparing the perfluoropolyether silane of Formula 1

![Chemical structure](image)

comprising:

- contacting a carbinol of Formula 2
The present invention further provides a method for preparing the carbinol of Formula 2 comprising:

contacting a compound of Formula 5 at a temperature below 10°C
with a mixture of a compound of Formula 6 and a compound of Formula 7

wherein

\[ R_i \text{ is } R^3 \text{0} (\text{CF(CF}_3\text{)CF}_2\text{O})_p \text{CF(CF}_3\text{)}^-, \text{ R}^3 \text{0} (\text{CF}_2\text{CF}_2\text{CF}_2\text{O})_q \text{CF}_2\text{CF}_2^-, \text{ or} \]

\[ R^3 \text{0} (\text{CF}_2\text{CF}_2\text{O})_q \text{CF}_2^-; \]

5 \[ R^3 \text{ is } \text{Ci-C}_6 \text{ perfluoroalkyl; and} \]

\[ R^4 \text{ is } \text{H, or Ci-C}_3 \text{ alkyl;} \]

\[ \text{Hal} \quad \text{M} \quad (\text{CH}_2)_m \quad = \quad 6 \]

\[ \text{Hal} \quad \text{M} \quad (\text{CH}_2)_n \quad = \quad 7 \]

\[ M \text{ is Mg, Li, or Sn; and} \]

Hal is Cl, Br, or I.

The present invention further provides a coating composition comprising:

(a) about 0.01-30 weight % of a perfluoropolyether silane of Formula 1, and

(b) about 70-99.99 weight % of at least one solvent,

wherein the at least one solvent is miscible with the perfluoropolyether silane of

Formula 1, and the weight % is based on the total weight of the coating

composition.

15 Additionally, the present invention provides an article comprising:

a siliceous substrate, and

a layer of a coating composition cured on at least one surface of the siliceous

substrate, wherein the coating composition comprises the perfluoropolyether silane of

Formula 1 described herein.

Furthermore, the present invention provides a method for making the above mentioned

article.

Various other features, aspects, and advantages of the present invention will become

more apparent with reference to the following description, examples, and appended claims.

25 DETAILS OF THE INVENTION

All publications, patent applications, patents and other references mentioned herein, if

not otherwise indicated, are explicitly incorporated by reference herein in their entirety for

all purposes as if fully set forth.

Unless otherwise defined, all technical and scientific terms used herein have the same

meaning as commonly understood by one of ordinary skill in the art to which this invention

belongs. In case of conflict, the present specification, including definitions, will control.

As used herein, the term "produced from" is synonymous to "comprising". As used

herein, the terms "comprises," "comprising," "includes," "including," "has," "having,"

"contains" or "containing," or any other variation thereof, are intended to cover a non-
exclusive inclusion. For example, a composition, process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such composition, process, method, article, or apparatus.

The transitional phrase "consisting of" excludes any element, step, or ingredient not specified. If in the claim, such a phrase would close the claim to the inclusion of materials other than those recited except for impurities ordinarily associated therewith. When the phrase "consisting of" appears in a clause of the body of a claim, rather than immediately following the preamble, it limits only the element set forth in that clause; other elements are not excluded from the claim as a whole.

The transitional phrase "consisting essentially of" is used to define a composition, method or apparatus that includes materials, steps, features, components, or elements, in addition to those literally discussed, provided that these additional materials, steps features, components, or elements do not materially affect the basic and novel characteristic(s) of the claimed invention. The term "consisting essentially of" occupies a middle ground between "comprising" and "consisting of.

The term "comprising" is intended to include embodiments encompassed by the terms "consisting essentially of" and "consisting of. Similarly, the term "consisting essentially of" is intended to include embodiments encompassed by the term "consisting of.

When an amount, concentration, or other value or parameter is given as either a range, preferred range or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. For example, when a range of "1 to 5" is recited, the recited range should be construed as including ranges "1 to 4", "1 to 3", "1-2", "1-2 & 4-5", "1-3 & 5", and the like. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range.

When the term "about" is used in describing a value or an end-point of a range, the disclosure should be understood to include the specific value or end-point referred to.

Further, unless expressly stated to the contrary, "or" refers to an inclusive "or" and not to an exclusive "or". For example, a condition A "or" B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

Also, the indefinite articles "a" and "an" preceding an element or component of the invention are intended to be nonrestrictive regarding the number of instances (i.e. occurrences) of the element or component. Therefore "a" or "an" should be read to include one or at least one, and the singular word form of the element or component also includes the plural unless the number is obviously meant to be singular.
The term 'fluorinated" refers to a group or compound contains at least one fluorine atom attached to a carbon atom. The term 'perfluorinated" refers to a group or compound having all C-H bonds replaced with C-F bonds. Examples include perfluoropolyether (PFPE) groups or compounds, or perfluoroether groups or compounds, and perfluoroalkane groups or compounds. Perfluorinated groups of compounds are a subset of fluorinated groups or compounds.

The term "ether" refers to a group or compound having an oxygen group between two carbon atoms.

The term "hydrofluorocarbon", as used herein, means a compound containing hydrogen, carbon, and fluorine, which is a "fluorinated" compound and has been partially fluorinated. A hydrofluorocarbon in this disclosure can be saturated or unsaturated. The term "hydrofluoroolefin" or "unsaturated hydrofluorocarbon" as used herein, means a compound containing hydrogen, carbon, fluorine, and at least one carbon-carbon double bond. The term "saturated hydrofluorocarbon ether", as used herein, means a compound containing hydrogen, carbon, fluorine, and at least one ether functional group. The term "unsaturated hydrofluorocarbon ether", as used herein, means a compound containing hydrogen, carbon, fluorine, at least one carbon-carbon double bond, and at least one ether functional group.

The term "fluorocarbon" or "perfluorocarbon", as used herein interchangeably, means a compound containing carbon and fluorine, which is a "perfluorinated" compound and has all C-H bonds replaced with C-F bonds completely. A (per)fluorocarbon in this disclosure can be saturated or unsaturated. The term "unsaturated fluorocarbon", as used herein, means a compound containing carbon, fluorine, and at least one carbon-carbon double bond. The term "unsaturated fluorocarbon ether", as used herein, means a compound containing carbon, fluorine, at least one carbon-carbon double bond, and at least one ether functional group.

Embodiments of the present invention as described in the Summary of the Invention include any other embodiments described herein, can be combined in any manner, and the descriptions of variables in the embodiments pertain not only to the perfluoropolyether silanes of the present invention, but also to the coating compositions made therefrom.

The materials, methods, and examples herein are illustrative only and, except as specifically stated, are not intended to be limiting. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described herein.

The invention is described in detail hereunder.

Perfluoropolyether Silanes of Formula 1
The present disclosure provides novel perfluoropolyether silanes of Formula 1:

\[
\text{(CH}_2\text{)}_m\text{-SiR}_1^x\text{R}_3^{3-x}\text{xOH}
\]

wherein

- \( R_f \) is \( R_0(CF(CF_3)CF_20)_{p}CF(CF_3)^- \), \( R_0(CF_2CF_2CF_20)^{q}CF_2CF_2^- \), or \( R_0(CF_2CF_2CF_20)^{r}CF_2^- \);
- \( R^1 \) is hydroxy or \( C_1-C_4 \) alkoxy;
- \( R^2 \) is \( H \) or \( C_1-C_4 \) alkyl;
- \( R^3 \) is \( C_6 \) perfluoroalkyl;
- \( m \) and \( n \) are each independently an integer ranging from 3 to 20;
- \( x \) is 1, 2, or 3; and
- \( p \), \( q \), and \( r \) are each independently an integer ranging from 5 to 60.

Embodiments of the present invention include:

- **Embodiment 1A.** A perfluoropolyether silane of Formula 1, wherein \( R_f \) is a monovalent perfluoropolyether group, and is \( R_0(CF(CF_3)CF_20)_{p}CF(CF_3)^- \), \( R_0(CF_2CF_2CF_20)^{q}CF_2CF_2^- \), or \( R_0(CF_2CF_2CF_20)^{r}CF_2^- \).

- **Embodiment 1B.** The compound of Embodiment 1A, wherein \( R_f \) is \( R_0(CF(CF_3)CF_20)_{p}CF(CF_3)^- \) or \( R_0(CF_2CF_2CF_20)^{q}CF_2CF_2^- \).

- **Embodiment 1C.** The compound of Embodiment 1B, wherein \( R_f \) is \( R_0(CF(CF_3)CF_20)_{p}CF(CF_3)^- \).

- **Embodiment 2A.** A perfluoropolyether silane of Formula 1, wherein \( R^1 \) is hydroxy or \( C_1-C_4 \) alkoxy.

- **Embodiment 2B.** A compound of Embodiment 2A, wherein \( R^1 \) is \( C_1-C_4 \) alkoxy.

- **Embodiment 2C.** The compound of Embodiment 2B, wherein \( R^1 \) is \( -OCH_3 \) or \( -OC_3H_5 \).

- **Embodiment 3A.** A perfluoropolyether silane of Formula 1, wherein \( R^2 \) is \( H \) or \( C_1-C_4 \) alkyl.

- **Embodiment 3B.** The compound of Embodiment 3A, wherein \( R^2 \) is \( C_1-C_4 \) alkyl.

- **Embodiment 4A.** A perfluoropolyether silane of Formula 1, wherein \( R^3 \) is \( C_6 \) perfluoroalkyl.

- **Embodiment 4B.** The compound of Embodiment 4A, wherein \( R^3 \) is \( C_3 \) perfluoroalkyl.
Embodiment 5A. A perfluoropolyether silane of Formula 1, wherein m and n are each independently an integer ranging from 3 to 20.

Embodiment 5B. The compound of Embodiment 5A, wherein m and n are each independently an integer ranging from 3 to 10.

Embodiment 5C. The compound of Embodiment 5B, wherein m and n are each independently an integer ranging from 3 to 7.

Embodiment 5D. The compound of Embodiment 5A, 5B or 5C, wherein m and n are the same.

Embodiment 6A. A perfluoropolyether silane of Formula 1, wherein x is 1, 2, or 3.

Embodiment 6B. The compound of Embodiment 6A, wherein x is 2 or 3.

Embodiment 6C. The compound of Embodiment 6B, wherein x is 3.

Embodiment 7A. A perfluoropolyether silane of Formula 1, wherein p, q and r are each independently an integer ranging from 5 to 60.

Embodiment 7B. The compound of Embodiment 7A, wherein p, q and r are each independently an integer ranging from 6 to 45.

Embodiment 7C. The compound of Embodiment 7B, wherein p, q and r are each independently an integer ranging from 7 to 30.

Combinations of Embodiments 1A-7C are illustrated by:

Embodiment A. A perfluoropolyether silane of Formula 1, wherein

\[ R_1 \text{ is } R^3 \theta (\text{CF(CF}_3)\text{CF}_2\theta)_p \text{CF(CF}_3)- \text{ or } R^3 \theta (\text{CF}_2\text{CF}_2\text{CF}_2\theta)_q \text{CF}_2\text{CF}_2-; \]

\[ R^1 \text{ is hydroxy or C1-C4 alkoxy; } \]

\[ R^2 \text{ is H or C1-C4 alkyl; } \]

\[ R^3 \text{ is C5-C6 perfluoroalkyl; } \]

\[ m \text{ and } n \text{ are each independently an integer ranging from 3 to 20; } \]

\[ x \text{ is 1, 2, or 3; and } \]

\[ p, q \text{ and } r \text{ are each independently an integer ranging from 6 to 45. } \]

Embodiment B. A perfluoropolyether silane of Formula 1, wherein

\[ R^1 \text{ is } -\text{OCH}_3 \text{ or } -\text{OC}_2\text{H}_5; \]

\[ m \text{ and } n \text{ are each independently an integer ranging from 3 to 10; and } \]

\[ p, q \text{ and } r \text{ are each independently an integer ranging from 6 to 45. } \]

Embodiment C. A perfluoropolyether silane of Formula 1, wherein

\[ m \text{ and } n \text{ are the same; and } \]

\[ p, q \text{ and } r \text{ are each independently an integer ranging from 7 to 30. } \]

Embodiment D. A perfluoropolyether silane of Formula 1, wherein

\[ R_1 \text{ is } R^3 \theta (\text{CF(CF}_3)\text{CF}_2\theta)_p \text{CF(CF}_3)-; \]

\[ R^1 \text{ is } \text{C1-C4 alkoxy; } \]

\[ R^3 \text{ is C5-C6 perfluoroalkyl; } \]
m and n are each independently an integer ranging from 3 to 10; 

x is 3; and 

p, q and r are each independently an integer ranging from 7 to 30.

Specific embodiments include perfluoropolyether silanes of Formula 1 selected from the group consisting of:

$$C_3 F_7 (CF(CF_3)CF_2 O)_p CF(CF_3)C(OH)(C_3 H_6 Si(OCH_3))_2,$$

$$C_3 F_7 (CF(CF_3)CF_2 O)_p CF(CF_3)C(OH)(C_3 H_{10} Si(OCH_3))_2,$$

$$C_3 F_7 (CF(CF_3)CF_2 O)_p CF(CF_3)C(OH)(C_3 H_{14} Si(OCH_3))_2,$$

$$C_3 F_7 (CF(CF_3)CF_2 O)_p CF(CF_3)C(OH)(C_7 H_{14} Si(OCH_3))_2,$$

$$C_3 F_7 (CF(CF_3)CF_2 O)_p CF(CF_3)C(OH)(C_3 H_{10} Si(OCH_3))_2,$$

$$C_3 F_7 (CF(CF_3)CF_2 O)_p CF(CF_3)C(OH)(C_3 H_{14} Si(OCH_3))_2,$$

$$C_3 F_7 (CF(CF_3)CF_2 O)_p CF(CF_3)C(OH)(C_7 H_{14} Si(OCH_3))_2,$$

$$C_3 F_7 (CF(CF_3)CF_2 O)_p CF(CF_3)C(OH)(C_3 H_{10} Si(OCH_3))_2,$$

$$C_3 F_7 (CF(CF_3)CF_2 O)_p CF(CF_3)C(OH)(C_3 H_{14} Si(OCH_3))_2,$$

$$C_3 F_7 (CF(CF_3)CF_2 O)_p CF(CF_3)C(OH)(C_7 H_{14} Si(OCH_3))_2;$$

wherein p, q and r are each independently an integer ranging from 5 to 60.

Further specific embodiments include any combination of the perfluoropolyether (hereunder is abbreviated as "PFPE") silanes of Formula 1 selected from the group immediately above.

PFPE silanes of Formula 1 suitable for compositions for treating substrates of the present invention have a molecular weight of at least about 1,000, and preferably, at least about 1,500. Preferably, their molecular weights are no greater than about 10,000.

The PFPE silane of Formula 1 can be synthesized by contacting a carbinol of Formula 2 with a hydrosilane of Formula 3 in the presence of a catalyst 4 as shown in Scheme 1.
wherein $R^1$, $R^2$, $R_f$, $m$, $n$ and $x$ are as previously defined for Formula 1.

The addition of the hydrosilane 3 to the carbinol of Formula 2 may be effected using a catalyst 4 suitable for hydrosilylation. Hydrosilylation of olefin was firstly reported by Sommer in 1947 using peroxide as catalyst. It has become an important synthetic route to organosilicon compounds since the discovery of Speier catalyst (hexachloroplatinic acid) in 1957 and Karstedt catalyst in 1973 (See references: Sommer, L. H.; Pietrusza, E. W.; Whitmore, F. C. J. Am. Chem. Soc. 1947, 69, 188; Speier, J. L.; Webster, J. A.; Barnes, G. H. J. Am. Chem. Soc. 1957, 79, 974-9; Karstedt, B. D. U.S. Pat. No. 3775452 A). Since then, a variety of effective catalytic systems have been developed, such as late transition metals (e.g., Ir, Ru, Rh, Pd or Fe), early transition metals (e.g., Y, Sm or Th) and Lewis acids (e.g., Al and B) (See references: (1) Muchnij, J. A.; Kwaramba, F. B.; Rahaim, R. J. Org. Lett., 2014, 7(5), 1330-1333; (2) Ge, S.; Meetsma A.; Hessen, B. Organometallics, 2008, 27(13), 3131-3135; and (3) Rubin, M.; Schwier, T.; Gevorgyan, V. J. Org. Chem., 2002, 67(6), 1936-1940).

Preferably, the catalyst 4 is a late transition metal catalyst based on Pt, Rh, Pd, Ru, Ir and Fe. More preferably, the catalyst 4 is a Pt based catalyst, also known as Karstedt catalyst, i.e. platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex. The above mentioned catalysts may be readily synthesized by known methods or are commercially available.

The carbinol of Formula 2 may be prepared by contacting a compound of Formula 5 at a temperature below 10°C with a mixture of a compound of Formula 6 and a compound of Formula 7 as shown in Scheme 2. In some embodiments, the compounds of Formula 6 and Formula 7 are the same.
wherein
\[ R_f, m, \text{ and } n \text{ are as previously defined for Formula 1;} \]
\[ R^4 \text{ is } \text{H or C}_1-\text{C}_3 \text{ alkyl;} \]
\[ M \text{ is } \text{Mg, Li, or Sn;} \text{ and} \]
\[ \text{Hal is } \text{Cl, Br, or I.} \]

PFPE esters or acids of Formula 5 are commercially available or may be readily synthesized by known methods. For example, the anionic polymerization of hexafluoropropylene epoxide (C\(_3\)F\(_6\)O, HFPO) as described by Moore in U.S. Pat. No. 3,322,826 can result in a PFPE carbonyl fluoride R\(_f\)C(0)F, wherein R\(_f\) is C\(_3\)F\(_7\)(CF\(_3\))\(_p\)CF(CF\(_3\))\(_q\). Alternatively, the methyl ester can also be prepared by the method described in WO2013/074299 A9, preparative example 2. For PFPE esters of Formula 5 where R\(_f\) is C\(_3\)F\(_7\)(CF\(_2\)CF\(_2\))\(_0\)CF\(_2\)CF\(_2\)-, can be produced by sequential oligomerization and fluorination of 2,2,3,3-tetrafluorooctane. For PFPE esters of Formula 5 where R\(_f\) is C\(_2\)F\(_2\)(CF\(_2\)CF\(_2\))\(_n\)CF\(_2\)-, can be produced similarly from polymerization of tetrafluoroethylene oxide (C\(_2\)F\(_4\)O). The carbonyl fluoride produced initially from polymerization may be converted into a corresponding acid or ester of Formula 5 by reactions well known to those skilled in the art.

Suitable fluorinated carboxylic acid are commercially available, for example, C\(_3\)F\(_7\)(CF\(_3\))\(_p\)CF(CF\(_3\))COOH under the trade name KYRTOX® 157FS with different number average molecular weight (M\(_n\)) are available from E. I. DuPont de Nemours Co., Wilmington, DE, USA, hereunder is referred as "DuPont."


It will be evident to one skilled in the art that a mixture of perfluoropolyether acid or ester of Formula 5 may be used to yield a mixture of the fluorinated polyether silanes of Formula 1, and coating composition made therefrom. Preferably, the perfluoropolyether silanes of Formula 1 having a PFPE moiety with a number average molecular weight of at least more than about 1,000 and less than about 10,000; or from about 1,500 to about 8,000.

Coating Composition

The present invention further provides a coating composition comprising:

(a) about 0.01-30 weight % of the PFPE silane of Formula 1, and
(b) about 70-99.99 weight % of at least one solvent,
wherein the at least one solvent is miscible with the PFPE silane of Formula 1 described herein and the weight % is based on the total weight of the coating composition.

Generally, at least one solvent is required to dissolve the PFPE silane of Formula 1 to make a coating solution for wet coating methods and some dry coating methods. Therefore, the coating composition comprises at least one solvent. A coating composition of the present invention for many siliceous substrates may include one or more solvents. Preferably, the at least one solvent is a fluorinated solvent, a non-fluorinated solvent, or a mixture thereof.

The solvent or mixture of solvents used must be capable of dissolving at least 0.01% by weight of the PFPE silane of Formula 1. If the solvent or mixture of solvents do not meet the criteria, it may not be possible to obtain a homogeneous composition having the PFPE silane of Formula 1, solvent(s), and optional additives. Although such non-homogeneous compositions could be used to treat a substrate, the coating obtained therefrom will generally not have the desired oil/water repellency and will not have sufficient durability properties.

Suitable solvents have normal boiling points of from about 50°C to about 150°C; and preferably, from about 60°C to about 120°C and can be a fluorinated solvent, a non-fluorinated solvent, or a mixture thereof.

In some embodiments of the present coating composition, the at least one solvent has normal boiling points of from about 50°C to about 150°C; or from about 60°C to about 120°C. In some embodiments of the present coating composition, the at least one solvent is a fluorinated solvent, a non-fluorinated solvent, or a mixture thereof.

Suitable fluorinated solvents include hydrofluorocarbons, hydrofluorocarbon ether, fluorocarbons, fluorocarbon ether, and mixtures thereof. These fluorinated solvents can be saturated or unsaturated. In some embodiments of this invention, the fluorinated solvent is selected from the group consisting of hydrofluorocarbons, hydrofluorocarbon ethers, fluorocarbons, fluorocarbon ethers, and mixtures thereof.

Examples of fluorinated solvents include hydrofluorocarbons such as pentafluorobutane, available from Solvay Solexis, or 2,3-dihydrodecafluoropentane (CF₃CFHCFHCF₂CF₃) available from DuPont as VERTREL™; hydrofluorocarbon ethers including alkyl perfluoroalkyl ether such as methyl perfluorobutyl ether or ethyl perfluorobutyl ether, available from 3M as NOVEC™ HFE 7100 and NOVEC™ HFE 7200, respectively; fluorocarbons such as perfluoroheptane, perfluoroheptane, or perfluoroocctane, available from 3M.

In some embodiments of this invention, the at least one solvent comprises, consists essentially of, or consists of a saturated hydrofluorocarbon. In some embodiments of this invention, the at least one solvent comprises, consists essentially of, or consists of CF₃CHFCHFCF₂CF₃.

Generally, unsaturated fluorocarbons have lower global warming potentials (GWPs) than their saturated counterparts. Examples of the unsaturated fluorocarbon include
hydrofluoroolefins, alkyl perfluoroalkene ethers, and mixtures thereof. Preferably, the alkyl perfluoroalkene ether is methyl perfluoroalkene ether, ethyl perfluoroalkene ether, or mixtures thereof. More preferably, the methyl perfluoroalkene ether is methyl perfluoroheptene ether, methyl perfluoropentene ether, or mixtures thereof.

Typically, methyl perfluoroheptene ether or methyl perfluoropentene ether is a mixture of its isomers respectively. For examples, methyl perfluoroheptene ether may be a mixture comprising \( \text{CF}_3\text{CF}_2\text{CF} = \text{CFCF(OCH}_3\text{)}\text{CF}_2\text{CF}_3 \), \( \text{CF}_3\text{CF}_2\text{C(OCH}_3\text{)}\text{CF}_2\text{CF}_3 \), and \( \text{CF}_3\text{CF} = \text{CFCF(OCH}_3\text{)}\text{CF}_2\text{CF}_3 \). Methyl perfluoropentene ether may be a mixture comprising \( \text{CF}_3\text{CF} = \text{C(OCH}_3\text{)}\text{CF}_2\text{CF}_3 \), \( \text{CF}_3\text{C(OCH}_3\text{)} = \text{CFCF}_2\text{CF}_3 \), and \( \text{CF}_3\text{CF} = \text{CF-OCH}_3\text{)}\text{CF}_3 \).

In some embodiments of this invention, the at least one solvent comprises, consists essentially of, or consists of an unsaturated fluorocarbon. In some embodiments of this invention, the at least one solvent comprises, consists essentially of, or consists of a hydrofluoroolefin. In some embodiments of this invention, the at least one solvent comprises, consists essentially of, or consists of an alkyl perfluoroalkene ether. In some embodiments of this invention, the alkyl perfluoroalkene ether is methyl perfluoroalkene ether, ethyl perfluoroalkene ether, or mixtures thereof. In some embodiments of this invention, the methyl perfluoroalkene ether is methyl perfluoroheptene ether, methyl perfluoropentene ether, or mixtures thereof.

Suitable non-fluorinated solvents include alcohols, ketones, nitriles, cyclic ethers, noncyclic ethers, and mixtures thereof. In some embodiments of this invention, the non-fluorinated solvent is selected from the group consisting of alcohols, ketones, nitriles, cyclic ethers, noncyclic ethers, and mixtures thereof.

Examples of the non-fluorinated solvents include alcohols such as methanol, ethanol, 1-propyl alcohol, 2-propanol; ketones such as acetone or methyl ethyl ketone; nitriles such as acetonitrile, cyclic ethers such as tetrahydrofuran, noncyclic ethers such as diethyl ether, diisopropyl ether, methyl \( \text{t-butyl} \), ether, and dipropylene glycol monomethyl ether, and mixtures thereof.

In some embodiments of this invention, the non-fluorinated solvent is selected from the group consisting of methanol, ethanol, 1-propanol, 2-propanol, acetone, methyl ethyl ketone, acetonitrile, tetrahydrofuran, and mixtures thereof. In some embodiments of this invention, the non-fluorinated solvent is selected from the group consisting of methanol, ethanol, 1-propanol, 2-propanol, tetrahydrofuran, and mixtures thereof.

The amount of the at least one solvent used in the coating composition can be selected to provide the desired viscosity for application of the coating composition to a siliceous substrate. Generally, the coating compositions, based on the total weight of the coating compositions, may contain at least 70 weight %, up to 80 weight %, up to 90 weight %, up to 95 weight %, up to 99.9 weight %, or up to 99.99 weight % of at least one solvent.
In some embodiments, the coating compositions can comprise 70 to 99.99 weight %, 80 to 99.9 weight %, or 90 to 95 weight % of at least one solvent. A coating composition of the present invention may further comprise additives such as curing catalysts, provided they do not react with the perfluoropoly ether silane of Formula 1. The curing catalysts can be any of the catalysts typically used to cure reactive organosilanes by hydrolysis and condensation. Suitable curing catalysts are those that are soluble in the coating composition (e.g., in the fluorinated solvent, non-fluorinated solvent, or mixtures thereof).

In some embodiments of this invention, the at least one curing catalyst comprises, consists essentially of, or consists of acids, bases, or water.

Examples of acids include inorganic acids, alkyl sulfonic acids, halogenated alkyl sulfonic acids, carboxylic acids, halogenated carboxylic acids, and mixtures thereof. Examples of inorganic acids include HC1, H2SO4, HNO3, and mixtures thereof. Examples of carboxylic acids include formic acid, acetic acid, trifluoroacetic acid, and mixtures thereof. Examples of bases include inorganic bases, substituted and unsubstituted trialkylamines, pyridine and its derivatives, and mixtures thereof. Examples of inorganic bases include NaOH, KOH, and mixtures thereof.

When used, the curing catalysts are used in amounts that are soluble in the coating compositions. In some embodiments, the moisture curing agents are present in an amount ranging from about 0.001-5 weight %, about 0.01-3 weight %, or in a range of about 0.1-2 weight %, based on a total weight of the coating composition.

Coated articles and Method of manufacturing the coated article.

The present invention provides a coated article comprising: a siliceous substrate, and a layer of a coating composition cured on at least one surface of the siliceous substrate, wherein the coating composition comprises a perfluoropolyether silane of Formula 1 described herein.

Siliceous substrates include those formed of various materials that contain silicon distributed throughout the substrate. Examples of siliceous substrates include, but are not limited to, glass, ceramic materials, glazed ceramic materials, concrete, mortar, grout, and natural or man-made stone. The siliceous substrate can be, for example, part of an electronic display (e.g., an outer surface of an electronic display such as a touch screen), mirror, window, windshield, ceramic tile, shower stall, toilet, sink, or the like. In many embodiments, the siliceous substrate is transparent, which means that it is possible to see through the siliceous substrate with an unaided human eye. The transparent substrate can be clear or colored.

The coating composition of the invention can be applied onto the siliceous substrate by either wet coating methods or dry coating methods. Examples of dry coating methods
include chemical vapor deposition (CVD) and physical vapor deposition (PVD). Examples of wet coating methods include spray coating, knife coating, dip coating, spin coating, meniscus coating, flow coating, roll coating, gravure coating, or the like.

In some embodiments, the coating composition is applied using a method selected from spray coating, knife coating, dip coating, spin coating, meniscus coating, flow coating, roll coating, and gravure coating.

Preferably, the surface of the siliceous substrate should be extremely clean prior to applying the coating composition for optimum coating characteristics, particularly durability, to be obtained. That is, the surface of the siliceous substrate to be coated should be substantially free of organic contamination prior to coating. Cleaning techniques depend on the type of siliceous substrate and include, for example, ultrasound cleaning in a solvent bath (e.g., ethanol/chloroform), gas-phase discharge techniques such as air corona treatment, plasma treatment, UV ozone treatment, washing with detergent and/or hot water, or combinations of these techniques. Specific examples of support surface preparation are described in the Example section.

In some embodiments, article of the present invention comprises a siliceous substrate and a layer of a coating composition cured on at least one surface of the siliceous substrate. The cured coating includes a reaction product of the PFPE silane of Formula 1 present in the coating composition with the siliceous substrate surface. Any coating composition comprising the PFPE silane of Formula 1 described herein can be used to form the cured coating composition.

As used herein, the term "curing" refers to the reaction of the silyl group of the PFPE silane of Formula 1 with the siliceous substrate. As used herein, the term "cured coating" refers to a layer of coating formed by a coating composition that has undergone curing. The curing reaction results in the formation of a -Si-O-Si- group (i.e. a siloxane group) and the covalent attachment of the PFPE silane to at least one surface of the siliceous substrate. In this siloxane group, one silicon atom is from the silyl group of the PFPE silane of Formula 1 and the other silicone atom is from the siliceous substrate. Therefore, the cured coating shall comprise a reaction product of the present coating composition with at least one surface of the siliceous substrate, said reaction product is covalently attached to the siliceous substrate surface.

Depending on how far the curing reaction goes, a cured coating prepared from the coating composition containing the PFPE silane of Formula 1 may also include unreacted or uncondensed silyl groups. It is believed that the curing reaction is formed as a result of hydrolysis of the silyl groups of the PFPE silane with residual water, which is either in the coating composition or adsorbed to the substrate surface, for example, and then condensation of the hydrolyzed silyl groups on and to the siliceous substrate surface.

 Typically, sufficient water is present for the preparation of a durable coating if the coating method is carried out at room temperature in the atmosphere, preferably, with a
relative humidity (RH) of at least about 30% and up to 90% at an elevated temperature, such as at least about 30°C or higher.

Following application using any method described above, the coating composition is dried to remove solvent and then cured at a temperature in a range of about 30°C to about 160°C for a time sufficient for curing to take place. The coated substrate is often held at the curing temperature for at least 5 minutes and up to 24 hours. The drying and curing steps can occur concurrently or separately by adjustment of the temperature.

In some embodiments, the article of the present invention is prepared by the method comprising:

i. applying a coating composition to a siliceous substrate;
ii. drying and curing at a temperature from about 30°C to about 160°C for about 5 min to about 24 hours; and
iii. cooling to ambient temperature;

wherein the coating composition of step i comprising:

(a) about 0.01-30 weight % of the perfluoropolyether silane of Formula 1, and
(b) about 70-99.99 weight % of at least one solvent,

wherein the at least one solvent is miscible with the perfluoropolyether silane, and the weight % is based on the total weight of the coating composition.

The layer of the cured coating of the present article can have any desired thickness.

The layer thickness of the cured coating is generally greater than a monolayer, which is typically greater than about 10 Angstroms thick. Generally, it is less than about 500 Angstroms thick, and preferably, less than about 400 Angstroms thick.

In some embodiments, the layer thickness of the cured coating corresponds to at least one monolayer. This thickness is often in a range of about 10 to 400 Angstroms. In some embodiments, the overall coating thickness of the cured coating composition can be in a range of about 10 to 400, about 50-300, about 100 to 250, or about 150 to 200 Angstroms.

The articles having a cured coating often have improved abrasion resistance compared to the uncoated siliceous substrate. The coated siliceous substrate can be abraded with steel wool (e.g., steel wool No. 0000 that is capable of scratching a glass surface) while retaining water repellent and/or oil repellant properties of the cured coating.

The articles having a cured coating provide a good tactile response. That is, a finger can slide over the surface of the articles easily. This is particularly desirable when the article is used in electronic displays such as in touch screens.

The articles also have an easy to clean surface. This easy to clean surface is provided by the PFPE silane of Formula 1 present in the coating composition. The surfaces of the articles with cured coatings tend to be hydrophobic. The initial water contact angle is often equal to at least 100°, at least 105°, or at least 110°.

Without further elaboration, it is believed that one skilled in the art using the preceding description can utilize the present invention to its fullest extent. The following Examples are,
therefore, to be construed as merely illustrative, and not limiting of the disclosure in any way whatsoever.

EXEMPLARY

The abbreviation "PE" stands for "Preparative Example", "E" stands for "Example" and "CE" stands for "Comparative Example" is followed by a number indicating in which example the PFPE silanes and their precursors is synthesized, or prepared. The examples and comparative examples were all prepared and tested in a similar manner. Percentages are based by mole unless otherwise indicated.

All solvents and reagents were purchased from commercial sources and were used without further purification unless specified otherwise.

NMR spectra were recorded on a Varian VXL-400 NMR using Wilmad® coaxial NMR tube and sample was dissolved in a fluorinated solvent using deuterated solvent sealed in a capillary tube as an external lock. The resonances are reported in ppm downfield from tetramethylsilane; s means singlet, d means doublet, m means multiplet, br s means broad singlet.

Materials

NOVECTM 7100: methyl perfluorobutyl ether, CAS number: 163702-07-6, purchased from 3M Company (Saint Paul, MN, USA), b.p. is 64.5°C.

VERTRELTM XF: 2,3-dihydrodecafluoropentane, CAS number: 138495-42-8, obtained from DuPont DC&F, b.p. is 55°C.

Perfluoropolyether methyl ester-A: C3F7O(CF(CF3)CF20)pCF(CF3)C(0)OCH3, p is about 9, Mn is approximately 1600, derived from KRYTOX® 157FSL, which available from DuPont.

Perfluoropolyether methyl ester-B: C3F7O(CF(CF3)CF20)pCF(CF3)C(0)OCH3, p is about 20, Mn is approximately 3860, derived from KRYTOX® 157FSM, which is available from DuPont.

Perfluoropolyether trimethoxysilylpropyl ether (Silyl ether-I): CAS number: 211931-77-0, C3F7O(CF(CF3)CF20)3bCF(CF3)CH20(CH2)3Si(OCH3)3, b is about 9, Mn is approximately 1800, obtained from DuPont, and was used in Comparative Example 1.

Karstedt catalyst: platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, CAS number 68478-92-2, 2 % Pt solution in xylene, purchased from Sigma-Aldrich.

Allylmagnesium chloride: CAS Number: 2622-05-1, 2 M solution in THF, purchased from Sigma-Aldrich.

4-Pentenylmagnesium bromide: CAS Number: 34164-50-6, 0.5 M solution in THF, purchased from Sigma-Aldrich.
1,3-Bis(trifluoromethyl)benzene: CAS Number: 402-31-3, purchased from Alfa Aesar.
Triethoxysilane: CAS Number: 998-30-1, purchased from TCI.
Trimethoxysilane: CAS Number: 2487-90-3, purchased from TCI.
Mighty ZS-18: a detergent for optical glass, obtained from Zhongsheng Rongtian (Beijing) International Technology and Trading Co., Ltd.

**Preparative Example 1: Preparation of Perfluoropolyether Silane 1a**

**STEP A. Preparation of Carbinol 2a**

To a 2-neck round-bottom flask (50 mL) was added perfluoropolyether methyl ester-A (5 g, 3 mmol, \( M_n = 1600 \)), NOVEC™ 7100 (10 mL) and tetrahydrofuran (THF, 5 mL) under nitrogen. The reaction mixture was cooled to 0-5 °C. Allyl magnesium chloride (5 mL, 2 M solution in THF, 10 mmol) was added dropwise at 0-5 °C. After addition, the reaction mixture was stirred for 15 minutes and then poured into IN aqueous HC1 solution (10 mL) at 0-5 °C. The mixture was extracted with NOVEC™ 7100 (10 mL) twice. The combined organic extracts were washed with 5% NaHC03 aqueous solution (20 mL), brine (20 mL) and then dried with anhydrous sodium sulfate. After filtration, the filtrate was concentrated under reduced pressure to yield the carbinol 2a (4.2 g, 82%).

\[ \text{H NMR (400 MHz, CDC13, ppm): } \delta 5.65-5.59 (m, 2H), 5.00 (t, 8 Hz, 2H), 4.94 (d, 8 Hz, 2H), 2.42-2.34 (m, 2H), 2.23-2.17 (m, 2H). \]

**STEP B. Preparation of Perfluoropolyether Silane 1a**

To a 2-neck round-bottom flask (50 mL) was added carbinol 2a (4 g, 2.5 mmol, \( M_n = 1650 \)) obtained from Step A, and 1,3-bis(trifluoromethyl)benzene (10 mL) under dry nitrogen. The mixture was heated to 60 °C and triethoxysilane (2 g, 12 mmol) was added. Karstedt catalyst (2 % Pt solution in xylene, 50 μL) was added. The solution was heated at 60°C for four hours. The homogeneous solution was cooled to room temperature. The excess triethoxysilane was removed under reduced pressure and then washed with anhydrous methanol. The resulting mixture was concentrated under reduced pressure to give the perfluoropolyether silane 1a, a compound of the present invention, as clear liquid (3.9 g, 80%).

**Preparative Example 2: Preparation of Perfluoropolyether Silane 1b**

**STEP A. Preparation of the Carbinol 2b**

To a 2-neck round-bottom flask (250 mL) was added perfluoropolyether methyl ester-B (25 g, 6.5 mmol, \( M_n = 3860 \)), followed by the addition of THF (35 mL) and NOVEC™ 7100 (50 mL) under nitrogen. The reaction was cooled to 0-5°C. Allyl magnesium chloride (13 mL, 2 M solution in THF, 26 mmol) was added dropwise at 0-5°C. After addition the
reaction mixture was stirred for 15 minutes and then poured into IN aqueous HCl solution at 0-5°C. The mixture extracted with NOVECTM 7100 (50 mL) twice. The combined organic extracts were washed with 5% NaHCO3 aqueous solution (100 mL), brine (100 mL) and dried with sodium sulfate. After filtration, the filtrate was concentrated under reduced pressure to yield 24 g (95 %) of 2b.

STEP B. Preparation of Perfluoropolyether Silane 1b

To a 2-neck round-bottom flask (50 mL) was added carbinol 2b (4 g, 1 mmol, Mn = 3,900) obtained from Step A, and 1,3-bis(trifluoromethyl)benzene (8 mL) under dry nitrogen. The mixture was heated to 60°C and triethoxysilane (1.5 g, 9 mmol) was added. Karstedt catalyst (2 % Pt solution in xylene, 30 µL) was added. The solution was heated at 60°C for four hours. The homogeneous solution was cooled to room temperature. The excess triethoxysilane was removed under reduced pressure and then washed with anhydrous methanol. The resulting mixture was concentrated by rotary evaporation at reduced pressure to give perfluoropolyether silane 1b, a compound of the present invention, as clear liquid (3.5 g, 81%).

Preparative Example 3: Preparation of Perfluoropolyether Silane 1c

To a 2-neck round-bottom flask (25 mL) was added carbinol 2a (4 g, 2.5 mmol, Mn = 1,650) (prepared according to the procedures described in the Prep. Example 1, Step A) and 1,3-bis(trifluoromethyl)benzene (8 mL) under dry nitrogen. The mixture was heated to 60°C and trimethoxysilane (1.2 g, 10 mmol) was added. Karstedt catalyst (2 % Pt solution in xylene, 20 µL) was added. The solution was heated at 60°C overnight. The homogeneous solution was cooled to room temperature. The excess trimethoxysilane was removed under reduced pressure and the residue was washed with anhydrous methanol. The resulting mixture was concentrated by rotary evaporation at reduced pressure to give perfluoropolyether silane 1c, a compound of the present invention, as clear liquid (3.1 g, 64%).

Preparative Example 4: Preparation of Perfluoropolyether silane 1d

To a 2-neck round-bottom flask (25 mL) was added carbinol 2b (4 g, 1 mmol, Mn = 3,900) (obtained from the Prep. Example 2, Step A) and 1,3-bis(trifluoromethyl)benzene (8 mL) under dry nitrogen. The mixture was heated to 60°C and trimethoxysilane (1 g, 8 mmol) was added. Karstedt catalyst (2 % Pt solution in xylene, 50 µL) was added. The solution was heated at 60°C overnight. The homogeneous solution was cooled to room temperature. The excess silane was removed under vacuum and the residue was washed with anhydrous methanol. The resulting mixture was concentrated by rotary evaporation at reduced pressure...
to give perfluoropoly ether silane 1d, a compound of the present invention, as clear liquid (3.5 g, 82%).

Preparative Example 5: Preparation of Perfluoropolyether Silane 1e

STEP A. Preparation of Carbinol 2c

To a 2-neck round-bottom flask (250 mL) was added perfluoropolyether methyl ester-A (5 g, 3 mmol, M_n = 1,600), followed by the addition of THF (5 mL) and NOVEC™ 7100 (20 mL) under nitrogen. The reaction was cooled to 0-5°C. 4-Pentenyl magnesium bromide (18.7 mL, 0.5 M solution in THF, 9.4 mmol) was added dropwise at 0-5°C. After addition the reaction was warm to room temperature and stirred for 4 hours. The mixture was poured into IN aqueous HCl solution at 0-5°C. The mixture extracted with NOVEC™ 7100 (20 mL) twice. The combined organic extracts were washed with 5% NaHCO_3 aqueous solution (50 mL), brine (50 mL) and dried with sodium sulfate. After filtration, the filtrate was concentrated under reduced pressure to give 4.8 g of the carbinol 2c (90%).

H NMR (600 MHz, CDC13, ppm): δ 5.59-5.51 (m, 2H), 4.74 (d, 18 Hz, 2H), 4.68 (d, 18 Hz, 2H), 2.00 (br s, 1H), 1.97-1.87 (m, 4H), 1.67-1.54 (m, 4H), 1.44-1.27 (m, 4H).

STEP B. Preparation of Perfluoropolyether Silane 1e

To a 2-neck round-bottom flask (50 mL) was added carbinol 2c (4 g, 2.2 mmol, M_n =1,700) obtained from Step A, and 1,3-bis(trifluoromethyl)benzene under nitrogen. The mixture was heated to 60°C and trimethoxysilane (1.5 g, 12 mmol) was added. Then Karstedt catalyst (2 % Pt solution in xylene, 50 µE) was added. The solution was heated at 60°C for additional four hours. The homogeneous solution was then cooled to room temperature. The excess trimethoxysilane was removed under vacuum and the residue was washed with anhydrous methanol. The resulting mixture was concentrated by rotary evaporation at reduced pressure to give perfluoropolyether silane 1e, a compound of the present invention, as clear liquid (3.2 g, 70%).

The perfluoropolyether silanes of Formula 1 and the respective carbinol of Formula 2 synthesized in the Preparative Examples 1-5 are summarized in Table 1.
Table 1

\[
\begin{align*}
\text{Preparation} & \quad \text{Example No.} & \quad \text{Compound} & \quad \text{ID} & \quad \text{P} & \quad \text{M}_n & \quad \text{m} & \quad \text{n} & \quad -\text{SiR}^3\text{R}^2_{3-x} \\
\text{PE1-Step A} & \quad 2a & \quad 9 & \quad 1650 & \quad 3 & \quad 3 & \quad - \\
\text{PE1-Step B} & \quad 1a & \quad 9 & \quad 2000 & \quad 3 & \quad 3 & \quad -\text{Si(OCH}_3\text{)}_3 \\
\text{PE2-Step A} & \quad 2b & \quad 20 & \quad 3900 & \quad 3 & \quad 3 & \quad - \\
\text{PE2-Step B} & \quad 1b & \quad 20 & \quad 4250 & \quad 3 & \quad 3 & \quad -\text{Si(OCH}_3\text{)}_3 \\
\text{PE3} & \quad 1c & \quad 9 & \quad 1900 & \quad 3 & \quad 3 & \quad -\text{Si(OCH}_3\text{)}_3 \\
\text{PE4} & \quad 1d & \quad 20 & \quad 4150 & \quad 3 & \quad 3 & \quad -\text{Si(OCH}_3\text{)}_3 \\
\text{PE5-Step A} & \quad 2c & \quad 9 & \quad 1700 & \quad 5 & \quad 5 & \quad - \\
\text{PE5-Step B} & \quad 1e & \quad 9 & \quad 1950 & \quad 5 & \quad 5 & \quad -\text{Si(OCH}_3\text{)}_3 \\
\end{align*}
\]

wherein \( R_f \) is \( C_3F_{70}(CF(CF_3)CF_20)_pCF(CF_3)^{-} \), and
\( p \) is an estimated number based on the \( M_n \).

General Procedures for the Preparation of Examples 1-5 and Comparative Example 1

The glass slides, VWR Micro Slides Superfrost® White, were placed in a glass vertical staining jar containing 100 mL of a detergent solution (5 weight% of Mighty ZS-1 18) and were sonicated in an ultrasonic bath (Shanghai Kudos Ultrasonic Instrument Co., Ltd. model: Kudos SK5210LHC) for 10 minutes, followed by deionized water rinsing for 4 times. Each rinsing step was consisted of placing the slides in 100 mL of fresh deionized water and sonicated for 3 minutes. The cleaned slides were dried in an oven at 80°C for 10 minutes, then treated with UV ozone in a UVO cleaner machine (Jelight Company Inc., Model No. 42-220) for 20 minutes. The slides were then contacted with a coating composition having 0.5 weight % of a perfluoropoly ether silane prepared in PE1-PE5 as specified in Table 2 in VERTREL™ XF within approximately 30 minutes.

The coating compositions were applied to the glass slides with a spray gun (Anest Iwata, part number of RG-3L-3S (Yokohama, Japan)). Each coating composition (5 mL) was applied to 8 slides, which were placed flat on bench top under a pressure of 0.1 MPa. The wet glass slides were then dried and cured in an oven set at 100°C with 50-60% relative humidity for 1 hour.
Method for Measuring Water Contact Angle

Contact angle measurements can be used to determine the surface energy of a substrate. Generally, a larger contact angle indicates a smaller surface energy.

The term "contact angle", as used herein, means the angle formed between the liquid/substrate surface interface and the liquid/air interface. The term "static contact angle", as used herein, means the contact angle measured on a static sessile drop of liquid on a substrate surface.

Static water contact angles (WCA) were measured on a Kruss DSA100, Tangent Method-1. Reported values are the averages of measurements on six drops of water. Each drop volume was 3 µL.

Method for Abrasion Testing

A linear abrader (Taber Industries of North Tonawanda, TABER 5900 (NY, USA)) was fitted with a square tool having a flat surface area of 1 cm². One piece of steel wool (No. 0000) was fixed on the square tool to be used for the abrasion test of the coated glass substrates.

The samples were abraded in increments of 100 cycles (or as specified otherwise) at a rate of 60 cycles/minute with a 1 Kg load and a stroke length of 50 millimeters. One cycle consisted of a forwarded scrub followed by a backward scrub.

<table>
<thead>
<tr>
<th>Table 2</th>
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<tbody>
<tr>
<td>Entry</td>
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<tr>
<td>CE1</td>
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<td>E5</td>
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From the resulted shown in Table 2, the following are evident.

The sample of CE1, coated with a composition containing silyl ether-I (i.e. C3F7,0(CF(CF3)CF2,0)bCF(CF3)CH,0(CH2,3Si(OCH3)3), had shown excellent water repellency initially as indicated by the measured water contact angle (WCA = 118°). However, after 100 cycles of scrubbing, the WCA of the sample of CE1 decreased down to
about 81°. Hence, the coating composition used for the sample of CE1 had less than desired durability.

In contrast, the samples of Examples 1-5 that were applied with coating compositions of the invention had shown excellent water repellency and high durability as evidenced by maintaining their WCA being above 90° after 200-1,000 cycles of scrubbing.

Treatment of the a siliceous substrate (i.e. glass slides) with the inventive coating compositions comprising the perfluoropolyether silanes of Formula 1 results in a layer of a cured coating on the siliceous substrate surface. Said cured coatings render the treated surfaces of the articles less retentive of soil and more readily cleanable due to the water and/or oil repellent nature. These desirable properties are maintained despite repeated abrasions because of the high durability of the cured coatings as can be obtained through the coating compositions of this invention.

While the invention has been illustrated and described in typical embodiments, it is not intended to be limited to the details shown, since various modifications and substitutions are possible without departing from the spirit of the present invention. As such, modifications and equivalents of the invention herein disclosed may occur to persons skilled in the art using no more than routine experimentation, and all such modifications and equivalents are believed to be within the spirit and scope of the invention as defined by the following claims.
What is claimed is:

1. A perfluoropolyether silane of Formula 1:

   \[
   \begin{align*}
   &\text{(CH}_2\text{)}_m\text{-SiR}_x^1\text{R}_3^3\text{x} \\
   &R_f\text{---}(\text{CH}_2\text{)}_n\text{-SiR}_x^1\text{R}_3^3\text{x} \\
   &\text{OH}
   \end{align*}
   \]

   wherein
   - \(R_f\) is \(R_0(CF(CF_3)CF_20)_pCF(CF_3)-\), \(R_3^0(CF_2CF_2CF_20)_qCF_2CF_2^2-\), or \(R_3^0(CF_2CF_20)_rCF_2^2-\);
   - \(R^1\) is hydroxy or C1-C4 alkoxy;
   - \(R^2\) is H or C1-C4 alkyl;
   - \(R^3\) is C1-C6 perfluoroalkyl;
   - \(m\) and \(n\) are each independently an integer ranging from 3 to 20;
   - \(x\) is 1, 2, or 3; and
   - \(p\), \(q\) and \(r\) are each independently an integer ranging from 5 to 60.

2. The perfluoropolyether silane of Claim 1, wherein
   - \(R^1\) is -OCH\(_3\) or -OC\(_2\)H\(_5\);
   - \(m\) and \(n\) are each independently an integer ranging from 3 to 10; and
   - \(p\), \(q\) and \(r\) are each independently an integer ranging from 6 to 45.

3. The perfluoropolyether silane of Claims 1 or 2, wherein
   - \(m\) and \(n\) are the same; and
   - \(p\), \(q\) and \(r\) are each independently an integer ranging from 7 to 30.

4. A method for preparing a perfluoropolyether silane of Formula 1:

   \[
   \begin{align*}
   &\text{(CH}_2\text{)}_m\text{-SiR}_x^1\text{R}_3^3\text{x} \\
   &R_f\text{---}(\text{CH}_2\text{)}_n\text{-SiR}_x^1\text{R}_3^3\text{x} \\
   &\text{OH}
   \end{align*}
   \]
comprising:

contacting a carbinol of Formula \(2\)

\[
\begin{align*}
\text{(CH}_2\text{)_{m-2}} \\
\text{R}_f \quad \text{C} \quad \text{(CH}_2\text{)_{n-2}} \\
\text{OH}
\end{align*}
\]

with a hydrosilane of Formula \(3\)

\[
\text{H-SiR}^{1}_{3} \text{R}^{2}_{3-x}
\]

in the presence of a catalyst \(4\),

wherein

\[\text{R}_f\text{ is } R^{30}(\text{CF(CF}_3\text{)CF}_2\text{)0}_p\text{CF(CF}_3\text{)}^- , R^{30}(\text{CF}_2\text{CF}_2\text{CF}_2\text{0})_q\text{CF}_2\text{CF}_2^- , \text{ or}\]

\[R^{30}(\text{CF}_2\text{CF}_2\text{0})_q\text{CF}_2^- ;\]

\[\text{R}^{1}\text{ is hydroxy or C1-C4 alkoxy;}\]

\[\text{R}^{2}\text{ is H or C1-C4 alkyl;}\]

\[\text{R}^{3}\text{ is C}_6\text{ perfluoroalkyl;}\]

\[m \text{ and } n \text{ are each independently an integer ranging from 3 to 20;}\]

\[x \text{ is } 1, 2, \text{ or } 3; \text{ and}\]

\[p, q \text{ and } r \text{ are each independently an integer ranging from 5 to 60.}\]

5. The method of claim 4, wherein the catalyst \(4\) is a transition metal catalyst based on Pt, Rh, Pd, Ru, Ir and Fe.

6. A method for preparing a carbinol of Formula \(2\)

\[
\begin{align*}
\text{(CH}_2\text{)_{m-2}} \\
\text{R}_f \quad \text{C} \quad \text{(CH}_2\text{)_{n-2}} \\
\text{OH}
\end{align*}
\]

comprising:
contacting a compound of Formula 5 at a temperature below 10°C

\[
\begin{align*}
R_t & \quad \text{C} \quad \text{OR}^4 \\
\text{5}
\end{align*}
\]

with a mixture of a compound of Formula 6 and a compound of Formula 7

\[
\begin{align*}
\text{Hal} & \quad \text{M} \quad \text{-(CH}_2)_m \text{-} \\
\text{6}
\end{align*}
\]

\[
\begin{align*}
\text{Hal} & \quad \text{M} \quad \text{-(CH}_2)_n \text{-} \\
\text{7}
\end{align*}
\]

wherein

- \( R_t \) is \( R^30(CF(CF_3)CF_20)_{p}CF(CF_3)^{-} \), \( R^30(CF_2CF_2CF_20)_{q}CF_2CF_2^{-} \), or \( R^30(CF_2CF_20)_{r}CF_2^{-} \);
- \( R^3 \) is \( \text{Ci-C}_6 \) perfluoroalkyl;
- \( R^4 \) is \( \text{H} \), or \( \text{Ci-C}_3 \) alkyl;
- \( m \) and \( n \) are each independently an integer ranging from 3 to 20;
- \( M \) is \( \text{Mg} \), \( \text{Li} \), or \( \text{Sn} \); and
- \( \text{Hal} \) is \( \text{Cl} \), \( \text{Br} \), or \( \text{I} \).

7. A coating composition comprising:
   (a) about 0.01-30 weight % of the perfluoropolyether silane of Formula 1 of Claim 1, and
   (b) about 70-99.99 weight % of at least one solvent,

wherein the at least one solvent is miscible with the perfluoropolyether silane of Formula 1, and the weight % is based on the total weight of the coating composition.

8. An article comprising:
   a siliceous substrate, and
   a layer of a coating composition cured on at least one surface of the siliceous substrate,

wherein the coating composition comprises the perfluoropolyether silane of Formula 1 of Claim 1.

9. A method for making the article of Claim 8, comprising:
i. applying the coating composition of Claim 7 to a siliceous substrate;
ii. drying and curing at a temperature from about 30°C to about 160°C for about 5 min to about 24 hours; and
iii. cooling to ambient temperature.

10. The method of Claim 9, wherein the coating composition of Claim 7 is applied to the siliceous substrate by spray coating, knife coating, dip coating, spin coating, meniscus coating, flow coating, roll coating, or gravure coating.
INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2014/094848

A. CLASSIFICATION OF SUBJECT MATTER
C08G 65/336(2006.01)i; C08G 77/46(2006.01)i; C09D 171/02(2006.01)i; C09D 183/12(2006.01)i

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)
C08G 65/-;C08G 77/-;C09D 171/-;C09D 183/-

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)
CNKI;CNABS;VEN;STN:DU C08G

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Relevant to claim No.</th>
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Further documents are listed in the continuation of Box C.

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<sup>`Y</sup>` document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
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Date of the actual completion of the international search 21 September 2015
Date of mailing of the international search report 08 October 2015

Name and mailing address of the ISA/CN
STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA
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WANG, Dongtao

Facsimile No. (86-10)62019451
Telephone No. (86-10)62084413

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