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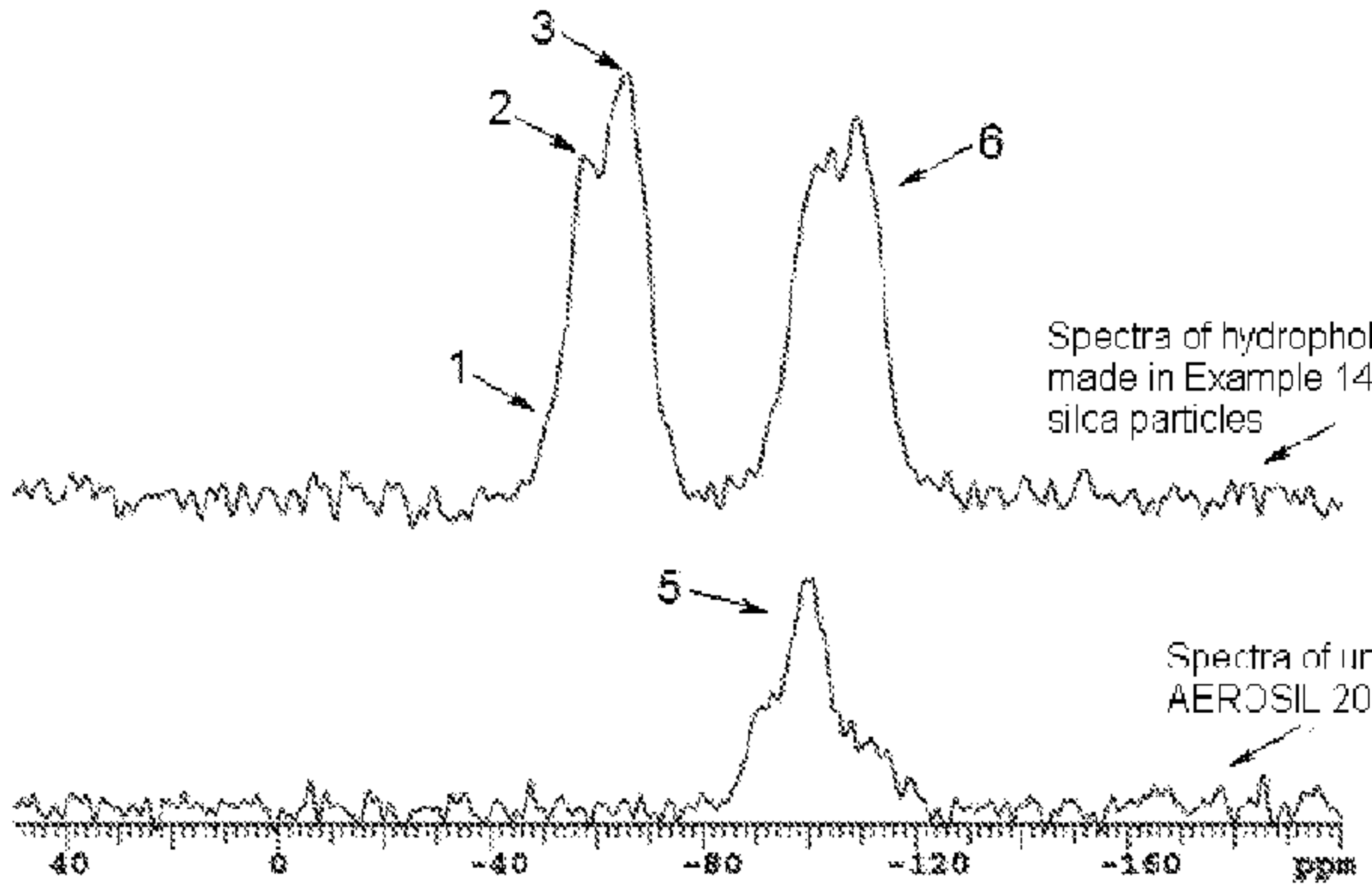
(54) Titre : PARTICULES INORGANIQUES HYDROPHOBISEES AVEC DES FLUOROALKYLSILANES
(54) Title: INORGANIC PARTICLES HYDROPHOBIZED WITH FLUOROALKYL SILANES



^{29}Si CPMAS NMR spectra

(57) Abrégé/Abstract:
The present invention relates to particles, i.e., oxides of Si, Ti, Zn, Zr, Mn, Al and combinations thereof, where at least one particle has a surface covalently bonded to at least one fluorosilane group. The particle is first bonded to a divalent organic linking group which in turn is bonded to a perfluoroalkyl group. It has been discovered that incorporation of the aforementioned divalent organic linking group can improve the ability of the resulting hydrophobized inorganic particles to impart hydrophobic and oleophobic properties.

ABSTRACT

The present invention relates to particles, i.e., oxides of Si, Ti, Zn, Zr, Mn, Al and combinations thereof, where at least one particle has a surface covalently bonded to at least one fluorosilane group. The particle is first bonded to a divalent organic linking group which in turn is bonded to a perfluoroalkyl group. It has been discovered that incorporation of the aforementioned divalent organic linking group can improve the ability of the resulting hydrophobized inorganic particles to impart hydrophobic and oleophobic properties.

TITLE OF INVENTION

INORGANIC PARTICLES HYDROPHOBIZED WITH FLUOROALKYL SILANES

BACKGROUND OF THE INVENTION

Inorganic particles hydrophobized with fluorosilanes have been used to impart hydrophobic as well as oleophobic properties as exemplified by U.S. Patent Application, US2006/0222815, filed by Oles et al. which teaches making such hydrophobized particles by the covalent bonding (i.e. grafting) of fluorosilanes upon the surface of inorganic particles (e.g. silica). The fluorosilanes employed by Oles et al. consist of a silicon atom having four bonds, three of which are direct bonds to hydrolysable groups which can react with the surface of an inorganic particle thereby covalently bonding the fluorosilane to particle. The remaining bond is a direct bond from the silicon atom to a perfluoroalkyl group.

Despite the advances of Oles et al., it would be desirable to discover hydrophobized inorganic particles having improved ability to impart hydrophobic as well as oleophobic properties.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a simplified depiction of a hydrophobized particle made from silica particles (AEROSIL™200) obtained in accordance with the invention.

Figure 2 are spectra obtained by solid-state ^{29}Si NMR cross-polarization magic angle spinning analysis (CPMAS) of: 1) hydrophobized particle made from silica particles (AEROSIL™200) obtained in accordance with the invention; and 2) untreated silica particles (AEROSIL™200).

BRIEF SUMMARY OF THE INVENTION

Whereas previously known hydrophobized inorganic particles comprise residues from fluorosilanes wherein the silicon atom is directly bonded to a perfluoroalkyl group, the hydrophobized inorganic particles of the present invention comprise residues from fluorosilanes wherein the silicon atom is first bonded to a divalent organic linking group which in turn is bonded to a perfluoroalkyl group. It has been discovered that incorporation of the aforementioned divalent organic linking group can improve the ability of resulting hydrophobized inorganic particles to impart hydrophobic as well as oleophobic properties.

The present invention relates to surface modified inorganic particles (also known as hydrophobized inorganic particles) made by the method of covalently grafting fluorosilanes to their surface thereby imparting to the particles hydrophobic and/or oleophobic properties. The fluorosilanes used in the present invention have a divalent organic linking group which bonds the silicon atom thereof to a fluorine rich group such as a perfluoroalkyl group. The fluorosilanes useful in the aforementioned method of covalent grafting are described in U.S. Patent No. 8,058,463.

Specifically, the surface modified inorganic oxide particles comprise an oxide of M wherein M is independently selected from the group consisting of Si, Ti, Zn, Zr, Mn, Al, and combinations thereof; at least one of said particles having a surface covalently bonded to at least one fluorosilane group represented by Formula (1):

$$(L^1)_d(L^2)_cSi–(CH_2)_n–(Z^1)_a–[C(X^1)]_x–(Z^2)_l–Q^1–R_f$$

wherein:

L^1 represents an oxygen covalently bonded to an M; and each L^2 independently selected from the group consisting of H, a C_1-C_2 alkyl, and OH; d and c are integers such that: $d \geq 1$, $c \geq 0$, $d+c = 3$;

each n is independently an integer from 1 to 12;

a, x, and l are integers chosen such that the moiety of Formula 1 represented by $–(Z^1)_a–[C(X^1)]_x–(Z^2)_l–$ further represents at least one of the following moieties:

i) a first moiety wherein a=1, x=1, and l=1; and

ii) a second moiety wherein a=1, x=0, and l=0;

R_f is chosen from a C_2–C_{12} perfluoroalkyl provided that: i) one fluorine atom of the perfluoroalkyl can be optionally replaced by hydrogen, and/or ii) the perfluoroalkyl can be optionally interrupted by at least one oxygen, methylene, or ethylene;

Q^1 is chosen from the group consisting of a C_2-C_{12} hydrocarbylene optionally interrupted by at least one divalent organic group;

X^1 is chosen from O or S;

the first moiety further defined wherein Z^1 and Z^2 are chosen such that:

a) Z^1 is –NH– and Z^2 is from the group consisting of –NH–, –O–, –S–, $-NH-S(O)_2-$, –N[C(O)H]–, $-[HC(COOH)(R^1)]CH-S-$, and $-(R^1)CH-[HC(COOH)]-S-$;

b) alternatively, Z^2 is –NH– and Z^1 is from the group consisting of –O–, and –S–;

c) each R^1 is independently chosen from hydrogen, phenyl, or a monovalent C_1-C_8 alkyl optionally terminated by $-C_6H_5$, preferably H or CH_3;

the second moiety further defined wherein:

a) Z^1 is $-N[-Q^3-(R_f)]-$; and

b) Q^1 and Q^3 are independently chosen from the group consisting of a C_2-C_{12} hydrocarbylene interrupted by at least one of –C(O)–O– or –O–C(O)–, and optionally further interrupted by at least one divalent organic group.

Unless otherwise stated herein the definitions used herein for L^1, L^2, d, c, n, Z^1, X^1, Z^2, Q^1, Q^3, R^1, and R_f are identical to the definitions set forth above for Formula 1.

In one preferable embodiment, the surface modified inorganic oxide particles comprise at least one particle having a surface covalently bonded to a urea or thiourea fluorosilane group such that in Formula (1):

$a=1$, $x=1$, and $l=1$;

Z^1 is –NH– and Z^2 is –NH–;

said urea or thiourea fluorosilane group represented by the formula:

$(L^1)_d(L^2)_cSi–(CH_2)_n–NH–C(X^1)–NH–Q^1–R_f$

wherein:

X^1 is O to form a urea fluorosilane group, or X^1 is S to form a thiourea fluorosilane group; and

Q^1 is independently chosen from the group consisting of a C_2-C_{12} hydrocarbylene optionally interrupted by at least one divalent moiety chosen from the group consisting of –S–, –S(O)–, $–S(O)_2–$, and –O–C(O)–NH –.

In another preferable embodiment, the surface modified inorganic oxide particles comprise at least one particle having a surface covalently bonded to a urea or thiourea fluorosilane group such that R_f is chosen from a C_2–C_{12} perfluoroalkyl and Q^1 is independently chosen from the group consisting of a C_2-C_{12} hydrocarbylene interrupted by at least one divalent moiety chosen from the group consisting of –S–, –S(O)–, $–S(O)_2–$, and –O–C(O)–NH –.

In another preferable embodiment, the surface modified inorganic oxide particles comprise at least one particle having a surface covalently bonded to a urea or thiourea fluorosilane group such that R_f is chosen from a C_2–C_{12} perfluoroalkyl provided that: i) one fluorine atom of the perfluoroalkyl is replaced by hydrogen, and/or ii) the perfluoroalkyl is interrupted by at least one oxygen, methylene, or ethylene; Q is chosen from the group consisting of a C_2–C_{12} hydrocarbylene optionally interrupted by at least one divalent organic group.

In another preferable embodiment, the surface modified inorganic oxide particles comprise at least one particle having a surface covalently bonded to a carbamate fluorosilane such that in Formula (1):

Z^1 is –NH– and Z^2 is –O–, or Z^1 is –O– and Z^2 is –NH–; and

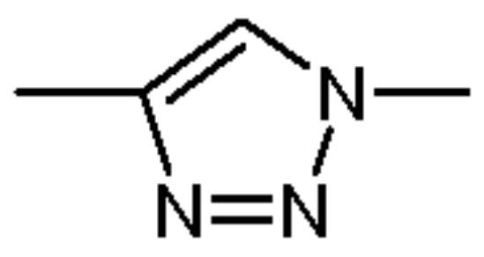
X^1 is O;

said particle having a surface covalently bonded to an isocyanate derived a carbamate fluorosilane group represented by the formulae:

$(L^1)_d(L^2)_cSi–(CH_2)_n–NH–C(O)–O–Q^1–R_f$, or

$(L^1)_d(L^2)_cSi–(CH_2)_n–O–C(O)–NH–Q^1–R_f$

wherein:

Q^1 is a $C_2–C_{12}$ hydrocarbylene interrupted by at least one divalent moiety chosen from the group consisting of –NH–C(O)–NH–, –NH–C(S)–NH–, –S–, –S(O)–, –S(O)$_2$–, –(R^1)N–S(O)$_2$–,  .

In another preferable embodiment, the surface modified inorganic oxide particles comprise at least one particle having a surface covalently bonded to a carbamate fluorosilane group such that R_f is chosen from a $C_2–C_{12}$ perfluoroalkyl and Q^1 is independently chosen from the group consisting of a C_2-C_{12} hydrocarbylene interrupted by at least one divalent moiety chosen from the group consisting of –S–, –S(O)–, –S(O)$_2$–, and –O–C(O)–NH –.

In another preferable embodiment, the surface modified inorganic oxide particles comprise at least one particle having a surface covalently bonded to a carbamate fluorosilane group such that R_f is chosen from a $C_2–C_{12}$ perfluoroalkyl provided that: i) one fluorine atom of the perfluoroalkyl is replaced by hydrogen, and/or ii) the perfluoroalkyl is interrupted by at least one oxygen, methylene, or ethylene; Q is chosen from the group consisting of a $C_2–C_{12}$ hydrocarbylene optionally interrupted by at least one divalent organic group.

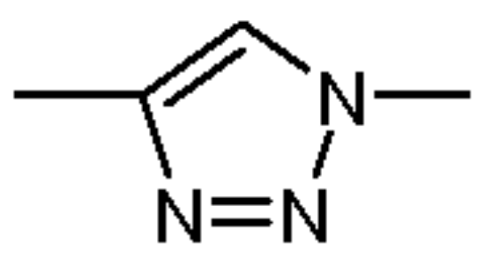
In another preferable embodiment, the surface modified inorganic oxide particles comprise at least one particle having a surface covalently bonded to a thiolcarbamate fluorosilane group such that in Formula (1):

Z^1 is –NH– and Z^2 is –S–, or Z^1 is –S– and Z^2 is–NH–; and
X^1 is O;

said thiolcarbamate fluorosilane group represented by the formulae:

$(L^1)_d(L^2)_cSi–(CH_2)_n–NH–C(O)–S–Q^1–R_f$ or
$(L^1)_d(L^2)_cSi–(CH_2)_n–S–C(O)–NH–Q^1–R_f$

wherein:

Q^1 is independently chosen from the group consisting of a C_2-C_{12} hydrocarbylene optionally interrupted by at least one divalent moiety chosen from the group consisting of –S–, –S(O)–, $–S(O)_2–$, $–N(R^1)–C(O)–$, $–C(O)–N(R^1)–$, $–(R^1)N–S(O)_2–$, and  .

In another preferable embodiment, the surface modified inorganic oxide particles comprise at least one particle having a surface covalently bonded to a thiolcarbamate fluorosilane group such that R_f is chosen from a C_2–C_{12} perfluoroalkyl and Q^1 is independently chosen from the group consisting of a C_2-C_{12} hydrocarbylene interrupted by at least one divalent moiety chosen from the group consisting of –S–, –S(O)–, $–S(O)_2–$, and –O–C(O)–NH –.

In another preferable embodiment, the surface modified inorganic oxide particles comprise at least one particle having a surface covalently bonded to a thiolcarbamate fluorosilane group such that R_f is chosen from a C_2–C_{12} perfluoroalkyl provided that: i) one fluorine atom of the perfluoroalkyl is replaced by hydrogen, and/or ii) the perfluoroalkyl is interrupted by at least one oxygen, methylene, or ethylene; Q is chosen from the group consisting of a C_2–C_{12} hydrocarbylene optionally interrupted by at least one divalent organic group.

In another preferable embodiment, the surface modified inorganic oxide particles comprise at least one particle having a surface covalently bonded to a N-sulfone urea fluorosilane group such that in Formula (1):

Z^1 is –NH–, and Z^2 is $–NH–S(O)_2–$; and

X^1 is O;

said N-sulfone urea fluorosilane group represented by the formula:

$(L^1)_d(L^2)_cSi–(CH_2)_n–NH–C(O)–NH–S(O)_2–Q^1–R_f$

wherein:

Q^1 is independently chosen from the group consisting of an uninterrupted C_2-C_{12} hydrocarbylene.

In another preferable embodiment, the surface modified inorganic oxide particles comprise at least one particle having a surface covalently bonded to a N-formyl urea fluorosilane group such that in Formula (1):

a=1, x=1, and l=1; and

Z^1 is –NH–, and Z^2 is –N[C(O)H]–;

said N-formyl urea group represented by the formula:

$(L^1)_d(L^2)_cSi–(CH_2)_n–NH–C(X^1)–N[C(O)H]–Q^1–R_f$

wherein:

Q^1 is independently chosen from the group consisting of a C_2-C_{12} hydrocarbylene interrupted by at least one divalent moiety chosen from the group consisting of –S– and –NH–.

In another preferable embodiment, the surface modified inorganic oxide particles comprise at least one particle having a surface covalently bonded to a thioether succinamic acid fluorosilane group such that in Formula (1):

a=1, x=1, and l=1;

Z^1 is –NH– and Z^2 is $–[HC(COOH)(R^1)]CH–S–$ or $–(R^1)CH–[HC(COOH)]–S–$;

X^1 is O; and Q^1 is $–(CH_2)_2–$

said thioether succinamic acid group represented by the formulae:

$(L)_3Si–(CH_2)_n–NH–C(O)–[HC(COOH)(R^1)]CR^1–(CH_2)_m–S–(CH_2)_2–R_f$, or

$(L)_3Si–(CH_2)_n–NH–C(O)–(R^1)CH–[CR^1(COOH)]–(CH_2)_m–S–(CH_2)_2–R_f$

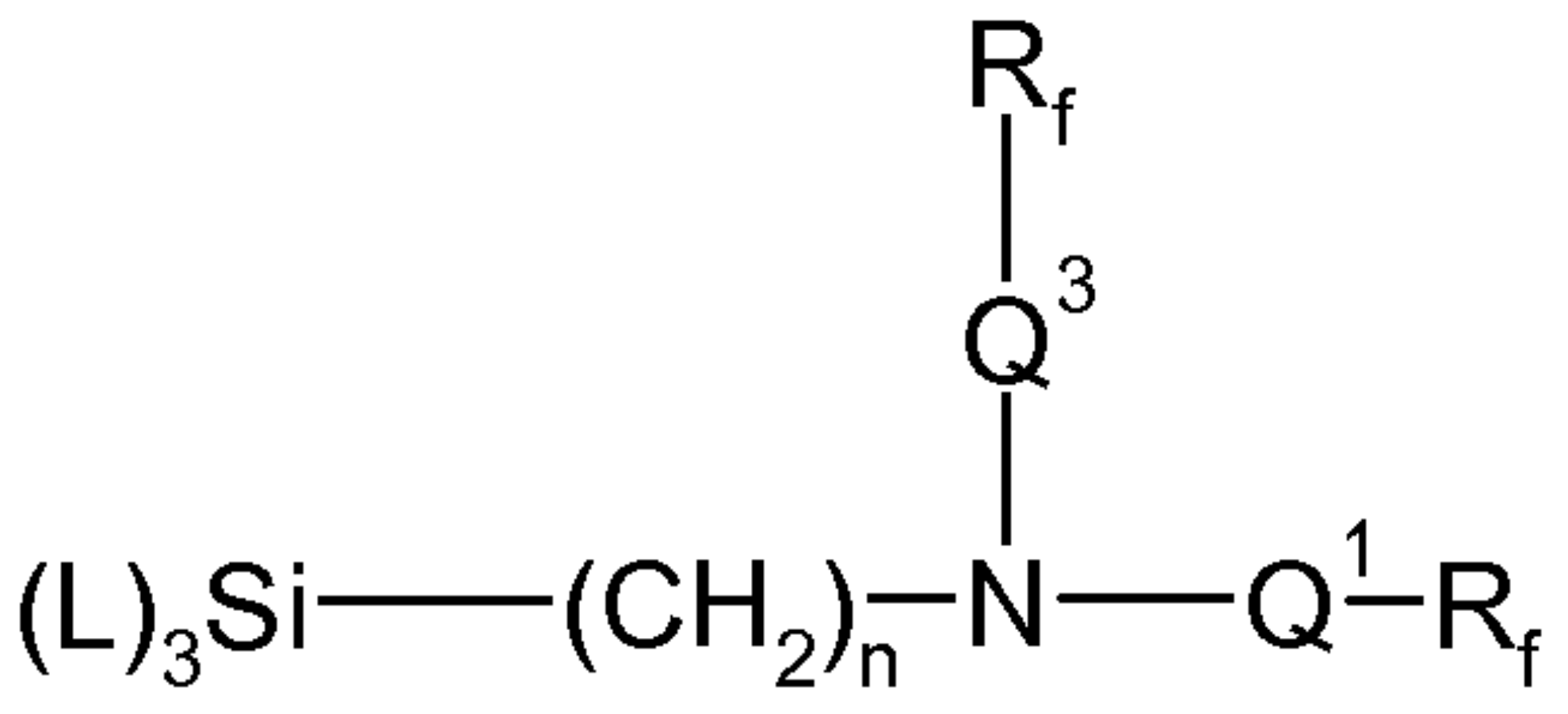
wherein m is 1 or 0; wherein each R^1 is independently chosen from methyl or hydrogen preferably H.

In another preferable embodiment, the surface modified inorganic oxide particles comprise at least one particle having a surface covalently bonded to a tertiary amine fluorosilane group such that in Formula (1):

a=1, x=0, and l=0; and

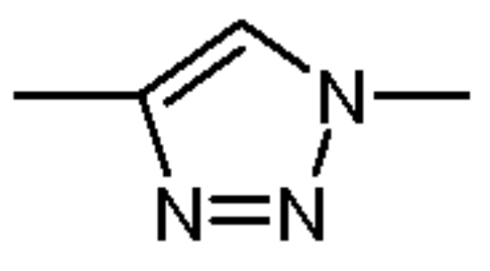
Z^1 is $–N[–Q^3–(R_f)]–$;

said tertiary amine fluorosilane group represented by the formula:



$$(L)_3Si—(CH_2)_n—N(—Q^3—R_f)—Q^1—R_f$$

wherein

Q^1 and Q^3 is independently chosen from the group consisting of a C_2-C_{12} hydrocarbylene interrupted by at least one –C(O)–O– and optionally further interrupted by at least one divalent moiety chosen from the group consisting of –S–, –S(O)–, $–S(O)_2–$, $–N(R^1)–C(O)–$, $–C(O)–N(R^1)–$, $–(R^1)N–S(O)_2–$, and  .

DETAILED DESCRIPTION OF THE INVENTION

The hydrophobized inorganic particles of the present invention can be made by covalently grafting fluorosilanes to their surface in order to impart to them both hydrophobic and oleophobic properties. The fluorosilanes used in the present invention have a divalent organic linking group which connects the silicon atom to a fluorine rich group such as a perfluoroalkyl group. Fluorosilanes useful for the invention have at least one hydrolysable group which reacts with the surface of an inorganic particle thereby creating a covalent bond between the fluorosilane and the inorganic particle. Fluorosilanes that are useful in the present invention are also known as fluoroalkyl silanes which are further described in U.S. Patent No. 8,058,463.

The hydrophobized inorganic particles of the present invention can be made by dispersing inorganic particles in a non-polar solvent (e.g. toluene) and adding to this dispersion the desired fluorosilane. The dispersion is then heated to an elevated temperature (e.g. 80-100 °C) for about 8-10 hours. The dispersion is then allowed to cool to ambient temperature (about 20 °C). The dispersion is then placed in a centrifuge, the solvent is decanted, and the resulting inorganic particles are washed with fresh solvent. Washing is preferably done at least twice. The washed inorganic particles are then dried in an oven at elevated temperature (about 100-110 °C). The resulting dried inorganic particles are the final product of the invention. However, the resulting dried inorganic particles can be re-dispersed in a non-polar solvent (e.g. toluene) and additional fluorosilane can be added to this dispersion by repeating the entire procedure described in this paragraph.

The procedure for making hydrophobized inorganic particles in the preceding paragraph is preferable and is known as the “convergent” approach. Alternatively, some of the hydrophobized inorganic particles of the present invention can also be made via a “divergent” approach wherein “functionalized inorganic particles” are made by reacting untreated inorganic particles with a first precursor wherein the first precursor comprises a silicon atom bonded to at least one terminal hydrolysable group which reacts with the surface of the inorganic particle thereby creating a covalent bond between the first precursor and the inorganic particle. The first precursor further comprises a terminal reactive group (e.g. an amine or an isocyante derived from an amine or an isothiocyanate derived an amine) thereby creating functionalized inorganic particles having “anchors” which comprise the terminal reactive group. These functionalized inorganic particles are then reacted with a second precursor wherein the second precursor comprises a corresponding reactive group (e.g. a terminal amine, an isocyante, an isothiocyanate, vinyl, sulfonyl chloride, or sulfonamide) capable of reacting with the terminal reactive group of the "anchors." The second precursor is also known herein by the term "capping agent." An example of a useful first precursor and second precursor combination is wherein the first precursor comprises a terminal amine group and the second precursor comprises a terminal isocyante, isothiocyanate, vinyl, sulfonyl chloride, or sulfonamide.

Inorganic particles useful to the invention include any inorganic particles that have reactive groups on the surface thereof wherein such groups are capable of reacting with the hydrolysable groups of the fluorosilanes (or precursors thereof) of the invention thereby creating a covalent bond between the inorganic particle and the fluorosilane (or precursor thereof). Particularly useful inorganic particles are oxides, such as oxides of silicon, titanium, zinc, zirconium, manganese, and aluminum.

As stated earlier, the "convergent" approach is preferable for making the hydrophobized inorganic particles of the invention. Fluorosilanes useful in the convergent approach are represented by

$$(L)_3\text{–Si–}(CH_2)_n\text{–}(Z^1)_a\text{–}[C(X^1)]_x\text{–}(Z^2)_l\text{–}Q^1\text{–}R_f \qquad \text{Formula 2}$$

wherein:

each n is independently an integer from 1 to 12;

a, x, and l are integers chosen such that the moiety of Formula 2 represented by $–(Z^1)_a–[C(X^1)]_x–(Z^2)_l–$ further represents at least one of the following moieties:

i) a first moiety wherein a=1, x=1, and l=1; and

ii) a second moiety wherein a=1, x=0, and l=0;

L is independently chosen from a hydrolysable or non-hydrolysable monovalent group

R_f is chosen from a C_2–C_{12} perfluoroalkyl provided that: i) one fluorine atom of the perfluoroalkyl can be optionally replaced by hydrogen, and/or ii) the perfluoroalk can be optionally interrupted by at least one oxygen, methylene, or ethylene; Q is chosen from the group consisting of a C_2–C_{12} hydrocarbylene optionally interrupted by at least one divalent organic group;

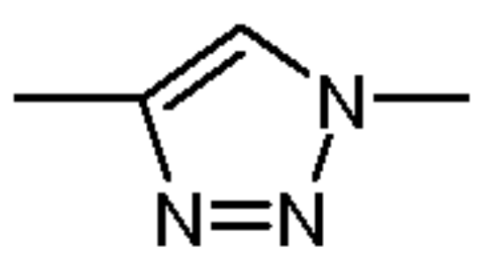
Q^1 is chosen from the group consisting of a C_2-C_{12} hydrocarbylene optionally interrupted by at least one divalent organic group;

X^1 is chosen from O or S;

the first moiety further defined wherein Z^1 and Z^2 are chosen such that:

a) Z^1 is –NH– and Z^2 is from the group consisting of –NH–, –O–, –S–, –NH–S(O)$_2$–, –N[C(O)H]–, –[HC(COOH)(R^1)]CH–S–, and –(R^1)CH–[HC(COOH)]–S–;

b) alternatively, Z^2 is –NH– and Z^1 is from the group consisting of –O–, and –S–;

c) when Z^1 or Z^2 is O, Q^1 is interrupted by at least one divalent moiety chosen from the group consisting of –S–, –S(O)–, –S(O)$_2$–, –NR^1–S(O)$_2$–, –N(CH)$_3$S(O)$_2$–, and  ;

d) each R^1 is independently chosen from hydrogen, phenyl, or a monovalent C_1-C_8 alkyl optionally terminated by –C_6H_5, preferably H or CH_3;

the second moiety further defined wherein:

a) Z^1 is–N(–Q^3–R_f; and

b) Q^1 and Q^3 are independently chosen from the group consisting of a C_2-C_{12} hydrocarbylene interrupted by at least one of –C(O)–O– or –O–C(O)–, and optionally further interrupted by at least one divalent organic group.

A preferred fluorosilane of Formula 2 is an isocyanate derived fluorosilane being a urea or thiourea fluorosilane wherein:

Z^1 and Z^2 are both –NH–;

said urea or thiourea represented by the formula:

$(L)_3Si–(CH_2)_n–NH–C(X^1)–NH–Q^1–R_f$

wherein:

X^1 is O to form a urea fluorosilane, or X^1 is S to form a thiourea fluorosilane; and

Q^1 is independently chosen from the group consisting of a C_2-C_{12} hydrocarbylene optionally interrupted by at least one divalent moiety chosen from the group consisting of –S–, –S(O)–, $–S(O)_2–$, and –O–C(O)–NH –.

A preferred urea or thiourea fluorosilane is one wherein R_f is chosen from a C_2–C_{12} perfluoroalkyl and Q^1 is independently chosen from the group consisting of a C_2-C_{12} hydrocarbylene interrupted by at least one divalent moiety chosen from the group consisting of –S–, –S(O)–, $–S(O)_2–$, and –O–C(O)–NH –.

A preferred urea or thiourea fluorosilane is one wherein R_f is chosen from a C_2–C_{12} perfluoroalkyl provided that: i) one fluorine atom of the perfluoroalkyl is replaced by hydrogen, and/or ii) the perfluoroalkyl is interrupted by at least one oxygen, methylene, or ethylene; Q is chosen from the group consisting of a C_2–C_{12} hydrocarbylene optionally interrupted by at least one divalent organic group.

Another preferred isocyanate derived fluorosilane of Formula 2 is a carbamate fluorosilane wherein:

Z^1 is –NH– and Z^2 is –O–, or Z^1 is –O– and Z^2 is –NH–; and

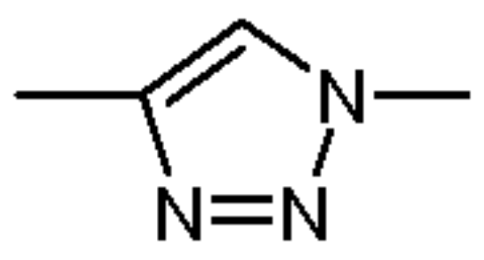
X^1 is O;

said carbamate represented by the formulae:

$(L)_3Si–(CH_2)_n–NH–C(O)–O–Q^1–R_f$, or

$(L)_3Si–(CH_2)_n–O–C(O)–NH–Q^1–R_f$

wherein:

Q^1 is a C_2–C_{12} hydrocarbylene interrupted by at least one divalent moiety chosen from the group consisting of –NH–C(O)–NH–, –NH–C(S)–NH–, –S–, –S(O)–, –S(O)$_2$–, –(R^1)N–S(O)$_2$–,  .

A preferred carbamate fluorosilane is one wherein R_f is chosen from a C_2–C_{12} perfluoroalkyl and Q^1 is independently chosen from the group consisting of a C_2-C_{12} hydrocarbylene interrupted by at least one divalent moiety chosen from the group consisting of –S–, –S(O)–, –S(O)$_2$–, and –O–C(O)–NH –.

A preferred carbamate fluorosilane is one wherein R_f is chosen from a C_2–C_{12} perfluoroalkyl provided that: i) one fluorine atom of the perfluoroalkyl is replaced by hydrogen, and/or ii) the perfluoroalkyl is interrupted by at least one oxygen, methylene, or ethylene; Q is chosen from the group consisting of a C_2–C_{12} hydrocarbylene optionally interrupted by at least one divalent organic group.

Another preferred isocyanate derived fluorosilane of Formula 2 is a thiolcarbamate fluorosilane wherein:

Z^1 is –NH– and Z^2 is –S–, or Z^1 is –S– and Z^2 is–NH–; and

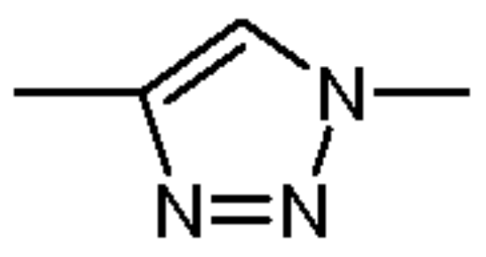
X^1 is O;

said carbamate represented by the formulae:

$(L)_3Si–(CH_2)_n–NH–C(O)–S–Q^1–R_f$ or

$(L)_3Si–(CH_2)_n–S–C(O)–NH–Q^1–R_f$

wherein:

Q^1 is independently chosen from the group consisting of a C_2-C_{12} hydrocarbylene optionally interrupted by at least one divalent moiety chosen from the group consisting of –S–, –S(O)–, –S(O)$_2$–, –N(R^1)–C(O)–, –C(O)–N(R^1)–, –(R^1)N–S(O)$_2$–, and  .

A preferred thiolcarbamate fluorosilane is one wherein R_f is chosen from a C_2–C_{12} perfluoroalkyl and Q^1 is independently chosen from the group consisting of a C_2-C_{12} hydrocarbylene interrupted by at least one divalent moiety chosen from the group consisting of –S–, –S(O)–, $–S(O)_2–$, and –O–C(O)–NH –.

A preferred thiolcarbamate fluorosilane is one wherein R_f is chosen from a C_2–C_{12} perfluoroalkyl provided that: i) one fluorine atom of the perfluoroalkyl is replaced by hydrogen, and/or ii) the perfluoroalkyl is interrupted by at least one oxygen, methylene, or ethylene; Q is chosen from the group consisting of a C_2–C_{12} hydrocarbylene optionally interrupted by at least one divalent organic group.

Another preferred isocyanate derived fluorosilane of Formula 2 is a N-sulfone urea fluorosilane wherein:

Z^1 is –NH–, and Z^2 is $–NH–S(O)_2–$; and

X^1 is O;

said N-sulfone urea represented by the formula:

$$(L)_3Si–(CH_2)_n–NH–C(O)–NH–S(O)_2–Q^1–R_f$$

wherein:

Q^1 is independently chosen from the group consisting of an uninterrupted C_2-C_{12} hydrocarbylene.

Another preferred isocyanate derived fluorosilane of Formula 2 is a N-formyl urea fluorosilane wherein:

a=1, x=1, and l=1; and

Z^1 is –NH–, and Z^2 is –N[C(O)H]–;

said N-formyl urea represented by the formula:

$$(L)_3Si–(CH_2)_n–NH–C(X^1)–N[C(O)H]–Q^1–R_f$$

wherein:

Q^1 is independently chosen from the group consisting of a C_2-C_{12} hydrocarbylene interrupted by at least one divalent moiety chosen from the group consisting of –S– and –NH–.

Another preferred fluorosilane of Formula 2 is a thioether succinamic acid fluorosilane wherein:

a=1, x=1, and l=1;

Z^1 is –NH– and Z^2 is $–[HC(COOH)(R^1)]CH–S–$ or

$–(R^1)CH–[HC(COOH)]–S–$;

X^1 is O; and Q^1 is $–(CH_2)_2–$

said thioether succinamic acid represented by the formulae:

$(L)_3Si–(CH_2)_n–NH–C(O)–[HC(COOH)(R^1)]CR^1–(CH_2)_m–S–(CH_2)_2–R_f$, or

$(L)_3Si–(CH_2)_n–NH–C(O)–(R^1)CH–[CR^1(COOH)]–(CH_2)_m–S–(CH_2)_2–R_f$

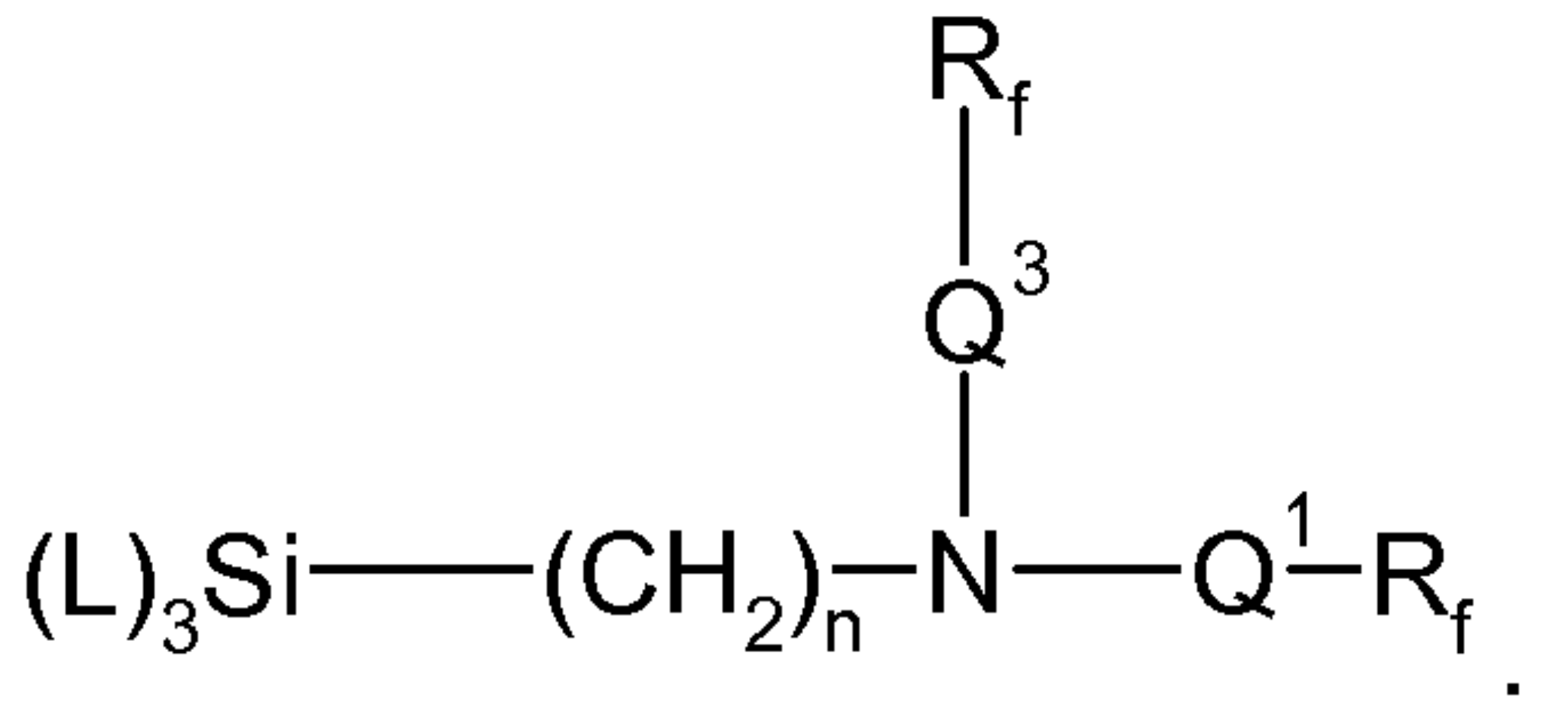
wherein m is 1 or 0, preferably 0, wherein each R^1 is independently chosen from methyl or hydrogen preferably H.

Another preferred fluorosilane of Formula 2 is a tertiary amine fluorosilane wherein:

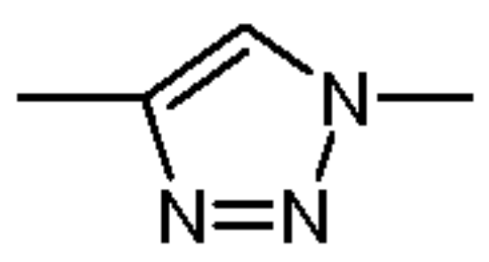
a=1, x=0, and l=0; and

Z^1 is $–N[–Q^3–(R_f)]–$;

said tertiary amine represented by the formula:



$$(L)_3Si–(CH_2)_n–N(–Q^3–R_f)–Q^1–R_f\ .$$

Q^1 and Q^3 is independently chosen from the group consisting of a C_2-C_{12} hydrocarbylene interrupted by at least one –C(O)–O– and optionally further interrupted by at least one divalent moiety chosen from the group consisting of –S–, –S(O)–, $–S(O)_2–$, $–N(R^1)–C(O)–$, $–C(O)–N(R^1)–$, $–(R^1)N–S(O)_2–$, and  .

EXAMPLES

The following inorganic particles were used as indicated in the examples below.

Table 1

Name of Inorganic Oxide	Description of Inorganic Oxide
SiO_2 #1	Silica having a primary particle size of about 12 nm obtained as AEROSIL™200 from Degussa AG now Evonik Degussa Industries AG.
ZnO #1	Zinc oxide nanopowder having a primary particle size of about 50-70 nm obtained from Sigma-Aldrich Corporation
$TiSiO_4$ #1	Silica coated titanium oxide nanopowder having a primary particle size of about 100 nm from Sigma-Aldrich Corporation.
SiO_2 #2	Silica having a primary particle size of about 7 nm obtained as AEROSIL™300 from Degussa AG now Evonik Degussa Industries AG.
SiO_2 #3	Silica having a primary particle size of about 20 nm obtained as AEROSIL™90 from Degussa AG now Evonik Degussa Industries AG.
SiO_2 #4	Silica having a primary particle size of about 40 nm obtained as OX50™from Degussa AG now Evonik Degussa Industries AG.
SiO_2 #5	Silica having an average particle size of about 11000 nm obtained as SPHERICEL 110P8™from Potters Industries Inc.
SiO_2 #6	Silica having an average particle size of about 7000 nm obtained as SPHERIGLASS 5000™from Potters Industries Inc.

The following fluorosilanes were used as indicated in the examples below.

Table 2

Name of Fluoro-silane	Description of Fluorosilane
FS #A	$(CH_3O)_3Si–(CH_2)_2–(CF_2)_5–CF_3$
FS #B	$(CH_3O)_3Si–(CH_2)_2–(CF_2)_7–CF_3$
FS #C	$(CH_3O)_3Si–(CH_2)_3–C_6F_5$
FS #1	$(CH_3O)_3Si–(CH_2)_3–NH–C(O)–NH–(CH_2)_2–S–(CH_2)_2–(CF_2)_5–CF_3$

Convergent Fluorosilane Single Grafting

The term “convergent fluorosilane single grafting” as used throughout the examples refers to the following procedure. About 125 g of a chosen inorganic oxide was placed in a 3 liter round bottom flask equipped with a mechanical stirrer and under nitrogen atmosphere. The stirred mixture was heated to about 50 °C for about 2 hours in order to achieve a homogeneous dispersion. 25 g of a chosen fluorinated silane was then quickly added to the stirred mixture followed by nitrogen sparging for 30 minutes. The reaction mixture temperature was then raised to 75 °C and stirred for about 15 hours under a nitrogen atmosphere. After this allotted reaction time period, the reaction mixture was cooled and centrifuged in portions at 3000 rpm for about 2 minutes. Excess hydrocarbon solvent was decanted and the remaining fluorine grafted fumed inorganic oxide product were washed 3 times with ethanol and centrifuged followed by drying in a vacuum oven at 110 °C for about 12 hours.

Convergent Fluorosilane Double Grafting

The term “convergent fluorosilane double grafting” as used throughout the examples refers to a procedure identical to “convergent fluorosilane single grafting” with the following additional steps. About 125 g the inorganic oxide product obtained after a convergent fluorosilane double grafting was placed in a 3 liter round bottom flask equipped with a mechanical stirrer and under nitrogen atmosphere. The stirred mixture was heated to about 50 °C for about 2 hours in order to achieve a homogeneous dispersion. 25 g of the same fluorinated silane used in the convergent fluorosilane single grafting was then quickly added to the stirred mixture followed by nitrogen sparging for 30 minutes. The reaction mixture temperature was then raised to 75 °C and stirred for about 15 hours under a nitrogen atmosphere. After the allotted reaction time period, the reaction mixture was cooled and centrifuged in portions at 3000 rpm for about 2 minutes. Excess hydrocarbon solvent was decanted and the remaining fluorine double grafted fumed inorganic oxide product were washed 3 times with ethanol and centrifuged followed by drying in a vacuum oven at 110 °C for about 12 hours.

Thin Film Casting

The term “thin film casting” as used throughout the examples refers to the following procedure. About 5 wt. % of chosen hydrophobized inorganic particles or untreated inorganic particles were dispersed in isopropanol. A thin film was made by casting three layers of this solution onto a clean glass slides wherein the slide were allowed to dry for about 10 minutes at 60 ºC after each casting thereby creating a homogenous coating of particles on the glass slides.

Advancing Water Contact Angle Measurement (“H_2O Adv.”)

The terms “advancing water contact angle” or “H_2O Adv.” refer to the results of a measurement conducted using a Ramé-Hart Standard Automated Goniometer Model 200 employing DROP image standard software and equipped with an automated dispensing system with 250 µl syringe, having an illuminated specimen stage assembly. A sample was glued to a glass slide using double-sided tape. The goniometer, which is connected through an interface to a computer with computer screen, had an integral eye piece connected to a camera having both horizontal axis line indicator and an adjustable rotating cross line and angle scale, both independently adjustable by separate verniers. The syringe used were carefully cleaned with alcohol and allowed to dry completely before use.

Prior to contact angle measurement, the sample on the glass slide was clamped into place and the vertical vernier adjusted to align the horizontal line (axis) of the eye piece coincident to the horizontal plane of the sample, and the horizontal position of the stage relative to the eye piece positioned so as to view one side of the test fluid droplet interface region at the sample interface.

To determine the contact angle of the test fluid on the sample, approximately one drop of test fluid was dispensed onto the sample using a small syringe fitted with a stainless steel needle and a micrometer drive screw to displace a calibrated amount of the test fluid, which was deionized water.

Horizontal and cross lines were adjusted via the software in the Model 200 after leveling the sample via stage adjustment, and the computer calculated the contact angle based upon modeling the drop appearance. Alternatively, immediately upon dispensing the test fluid, the rotatable vernier was adjusted to align the cross line and cross position, that is the intersection of the rotatable cross line and the fixed horizontal line, coincident with the edge of the test fluid droplet and the sample, and the cross line angle (rotation) then positioned coincident with the tangent to the edge of the test droplet surface, as imaged by the eye piece. The contact angle was then read from the angle scale, which was equivalent to the tangent angle.

Contact angle was measured after the droplet has been added to a surface.

Receding Water Contact Angle Measurement (“H_2O Rec.”)

The terms “receding water contact angle” or “H_2O Rec.” refer to the results of a measurement identical to the advancing water contact angle measurement described above except contact angle was measured after the droplet was partially withdrawn from a surface.

Advancing Oil Contact Angle Measurement (“$C_{16}H_{12}$ Adv.”)

The terms “advancing oil contact angle” or “$C_{16}H_{12}$ Adv.” refer to the results of a measurement identical to the advancing water contact angle measurement described above except hexadecane was used as the test liquid instead of water.

Receding Oil Contact Angle Measurement (“$C_{16}H_{12}$ Rec.”)

The terms “receding oil contact angle” or “$C_{16}H_{12}$ Rec.” refer to the results of a measurement identical to the advancing oil contact angle measurement described above except contact angle was measured after the droplet was partially withdrawn from a surface.

Evaluation of Contact Angle

Higher advancing and/or receding water contact angle measurements indicated higher water repellency while lower water contact angles measurements indicated lower water repellency. Cases where no water contact angle could be measured indicate wetting and very poor water repellency. Higher advancing and/or receding oil contact angle measurements indicated higher oil repellency while lower oil contact angles measurements indicated lower oil repellency. Cases where no oil contact angle could be measured indicate wetting and very poor oil repellency. A surface is said to be “super hydrophobic” in cases where the advancing water contact angle and receding water contact angle was greater than about 150 degrees and the hysteresis (difference between advancing and receding water contact angle) is less than about 10 degrees. A surface is said to be “super oleophobic” in cases where the advancing oil contact angle and receding oil contact angle was greater than about 150 degrees and the hysteresis (difference between advancing and receding oil contact angle) is less than about 10 degrees. A surface that is both super hydrophobic and super oleophobic is said to be “super amphiophobic.”

Weight Percent Fluorine Measurement

The percent fluorine in any given hydrophobized particle was determined by the Wickbold Torch method and are shown in the tables below under a column labeled “%F.”

Untreated Control Example

Using thin film casting, eight films were made respectively from SiO_2 #1, ZnO #1, $TiSiO_4$ #1, SiO_2 #2, SiO_2 #3, SiO_2 #4, SiO_2 #5, SiO_2 #6. The water and oil contact angles (advancing and receding) were measured for each of these eight films. In all eight cases, no water or oil contact angles could be measured which indicated wetting and very poor water and oil repellency.

Comparative Example A

Convergent fluorosilane single grafting was conducted wherein the chosen inorganic oxide was SiO_2 #1 and the chosen fluorosilane was FS #A resulting in hydrophobized particles. A film sample was made by thin film casting using these hydrophobized particles. Contact angle measurements were conducted on this film sample and are shown in Table 3.

Comparative Example B

Convergent fluorosilane single grafting was conducted wherein the chosen inorganic oxide was SiO_2 #1 and the chosen fluorosilane was FS #B. A film sample was made by thin film casting using these hydrophobized particles. Contact angle measurements were conducted on this film sample and are shown in Table 3.

Comparative Example C

Convergent fluorosilane single grafting was conducted wherein the chosen inorganic oxide was SiO_2 #1 and the chosen fluorosilane was FS

#C. A film sample was made by thin film casting using these hydrophobized particles. Contact angle measurements were conducted on this film sample and are shown in Table 3.

Example 1

Convergent fluorosilane single grafting was conducted wherein the chosen inorganic oxide was SiO_2 #1 and the chosen fluorosilane was FS #1. A film sample was made by thin film casting using these hydrophobized particles. Contact angle measurements were conducted on this film sample and are shown in Table 3.

Example 2

Convergent fluorosilane single grafting was conducted wherein the chosen inorganic oxide was ZnO #1 and the chosen fluorosilane was FS #1. A film sample was made by thin film casting using these hydrophobized particles. Contact angle measurements were conducted on this film sample and are shown in Table 3.

Example 3

Convergent fluorosilane single grafting was conducted wherein the chosen inorganic oxide was $TiSiO_4$ #1and the chosen fluorosilane was FS #1. A film sample was made by thin film casting using these hydrophobized particles. Contact angle measurements were conducted on this film sample and are shown in Table 3.

Comparative Example D

Convergent fluorosilane double grafting was conducted wherein the chosen inorganic oxide was SiO_2 #1 and the chosen fluorosilane was FS #A resulting in hydrophobized particles. A film sample was made by thin film casting using these hydrophobized particles. Contact angle measurements were conducted on this film sample and are shown in Table 3.

Comparative Example E

Convergent fluorosilane double grafting was conducted wherein the chosen inorganic oxide was SiO_2 #1 and the chosen fluorosilane was FS #B. A film sample was made by thin film casting using these hydrophobized particles. Contact angle measurements were conducted on this film sample and are shown in Table 3.

Comparative Example F

Convergent fluorosilane double grafting was conducted wherein the chosen inorganic oxide was SiO_2 #1 and the chosen fluorosilane was FS #C. A film sample was made by thin film casting using these hydrophobized particles. Contact angle measurements were conducted on this film sample and are shown in Table 3.

Example 4

Convergent fluorosilane double grafting was conducted wherein the chosen inorganic oxide was SiO_2 #1 and the chosen fluorosilane was FS #1. A film sample was made by thin film casting using these hydrophobized particles. Contact angle measurements were conducted on this film sample and are shown in Table 3.

Example 5

Convergent fluorosilane double grafting was conducted wherein the chosen inorganic oxide was ZnO #1 and the chosen fluorosilane was FS #1. A film sample was made by thin film casting using these hydrophobized particles. Contact angle measurements were conducted on this film sample and are shown in Table 3.

Example 6

Convergent fluorosilane double grafting was conducted wherein the chosen inorganic oxide was $TiSiO_4$ #1and the chosen fluorosilane was FS

#1. A film sample was made by thin film casting using these hydrophobized particles. Contact angle measurements were conducted on this film sample and are shown in Table 3.

Table 3

Example		Inorganic Oxide Particle	%F	Fluorosilane	Contact Angle Measurements (°)			
					H_2O Adv.	H_2O Rec.	$C_{16}H_{12}$ Adv.	$C_{16}H_{12}$ Rec.
single grafting	A	SiO_2 #1	4.49	FS #A	145	126	*	*
	B	SiO_2 #1	6.71	FS #B	159	156	*	*
	C	SiO_2 #1	2.87	FS #C	149	129	*	*
	1	SiO_2 #1	13.6	FS #1	81	80	105	92
	2	ZnO #1	3.09	FS #1	124	107	80	62
	3	$TiSiO_4$ #1	18.0	FS #1	160	157	*	*
double grafting	D	SiO_2 #1	5.51	FS #A	153	149	*	*
	E	SiO_2 #1	12.8	FS #B	158	155	*	*
	4	SiO_2 #1	22.1	FS #1	160	158	155	150
	5	ZnO #1	5.75	FS #1	161	161	98	72
	6	$TiSiO_4$ #1	11.2	FS #1	161	161	154	149

* indicates contact angle could not be measure because of wetting

In reference to Table 3 above, the fluorosilane used in Comparative Examples A-E is a fluorosilane wherein the silicon atom is directly bonded to a perfluoroalkyl group. In contrast, that the fluorosilane used in Examples 1-6 is a fluorosilane wherein the silicon atom is first bonded to a divalent organic linking group, represented by –NH–C(O)–NH–$(CH_2)_2$–S–$(CH_2)_2$–, which in turn is bonded to a perfluoroalkyl group. As shown by comparing the contact angle measurements of Example 1 to Comparative Examples A-C, without the incorporation of a divalent organic linking group it was only possible to achieve adequate water repellency but impossible to also achieve adequate oil repellency. The incorporation of a divalent organic linking group in Example 1 results in adequate water repellency as well as adequate oil repellency. Even when double grafting is performed such as in Comparative Examples D-E, without the incorporation of a divalent organic linking group it was only possible to achieve adequate water repellency but impossible to also achieve adequate oil repellency. Table 3 also shows that double grafting improves oil repellency over single grafting as evidenced by comparing: Example 1 to Example 4; Example 2 to Example 5; and Example 3 to Example 6.

Divergent Synthesis – Single Functionalization

The term "single functionalization" as used throughout the examples refers to the following procedure. About 125 g of a chosen inorganic oxide was placed in a 3 liter round bottom flask equipped with a mechanical stirrer and under nitrogen atmosphere. The stirred mixture was heated to about 50 °C for about 2 hours in order to achieve a homogeneous dispersion. 25 g of a first precursor, $(CH_3O)_3Si–(CH_2)_3–NH_2$ (commercially available as AMMO™ from Degussa AG), was then quickly added to the stirred mixture followed by nitrogen sparging for 30 minutes. The reaction mixture temperature was then raised to 75 °C and stirred for about 15 hours. After the allotted reaction time period, the reaction mixture was cooled and centrifuged in portions at 3000 rpm for about 2 minutes. Excess hydrocarbon solvent was decanted and the remaining fluorine grafted fumed inorganic oxide product were washed 3 times with ethanol and centrifuged followed by drying in a vacuum oven at 110 °C for about 12 hours. All of the above steps were preformed in a nitrogen atmosphere.

Divergent Synthesis – Double Functionalization

The term "double functionalization" as used throughout the examples refers to a procedure identical to "single functionalization" with the following additional steps. About 125 g of the inorganic oxide product obtained after single functionalization was placed in a 3 liter round bottom flask equipped with a mechanical stirrer and under nitrogen atmosphere. The stirred mixture was heated to about 50 °C for about 2 hours in order to achieve a homogeneous dispersion. 25 g of the first precursor,

$(CH_3O)_3Si-(CH_2)_3-NH_2$ (commercially available as AMMO™ from Degussa AG), was then quickly added to the stirred mixture followed by nitrogen sparging for 30 minutes. The reaction mixture temperature was then raised to 75 °C and stirred for about 15 hours. After the allotted reaction time period, the reaction mixture was cooled and centrifuged in portions at 3000 rpm for about 2 minutes. Excess hydrocarbon solvent was decanted and the remaining fluorine double grafted fumed inorganic oxide product were washed 3 times with ethanol and centrifuged followed by drying in a vacuum oven at 110 °C for about 12 hours. All of the above steps were preformed in a nitrogen atmosphere.

Comparative Example F

Single functionalization was conducted wherein the chosen inorganic oxide was SiO_2 #2 resulting in treated particles. A film sample was made by thin film casting using these treated particles. Contact angle measurements were conducted on this film sample and are shown in Table 4.

Comparative Example G

Single functionalization was conducted wherein the chosen inorganic oxide was SiO_2 #1 resulting in treated particles. A film sample was made by thin film casting using these treated particles. Contact angle measurements were conducted on this film sample and are shown in Table 4.

Comparative Example H

Single functionalization was conducted wherein the chosen inorganic oxide was SiO_2 #3 resulting in treated particles. A film sample was made by thin film casting using these treated particles. Contact angle measurements were conducted on this film sample and are shown in Table 4.

Comparative Example I

Single functionalization was conducted wherein the chosen inorganic oxide was SiO_2 #4 resulting in treated particles. A film sample was made by thin film casting using these treated particles. Contact angle measurements were conducted on this film sample and are shown in Table 4.

Comparative Example J

Single functionalization was conducted wherein the chosen inorganic oxide was SiO_2 #5 resulting in treated particles. A film sample was made by thin film casting using these treated particles. Contact angle measurements were conducted on this film sample and are shown in Table 4.

Comparative Example K

Double functionalization was conducted wherein the chosen inorganic oxide was SiO_2 #6 resulting in treated particles. A film sample was made by thin film casting using these treated particles. Contact angle measurements were conducted on this film sample and are shown in Table 4.

Comparative Example L

Double functionalization was conducted wherein the chosen inorganic oxide was SiO_2 #1 resulting in treated particles. A film sample was made by thin film casting using these treated particles. Contact angle measurements were conducted on this film sample and are shown in Table 4.

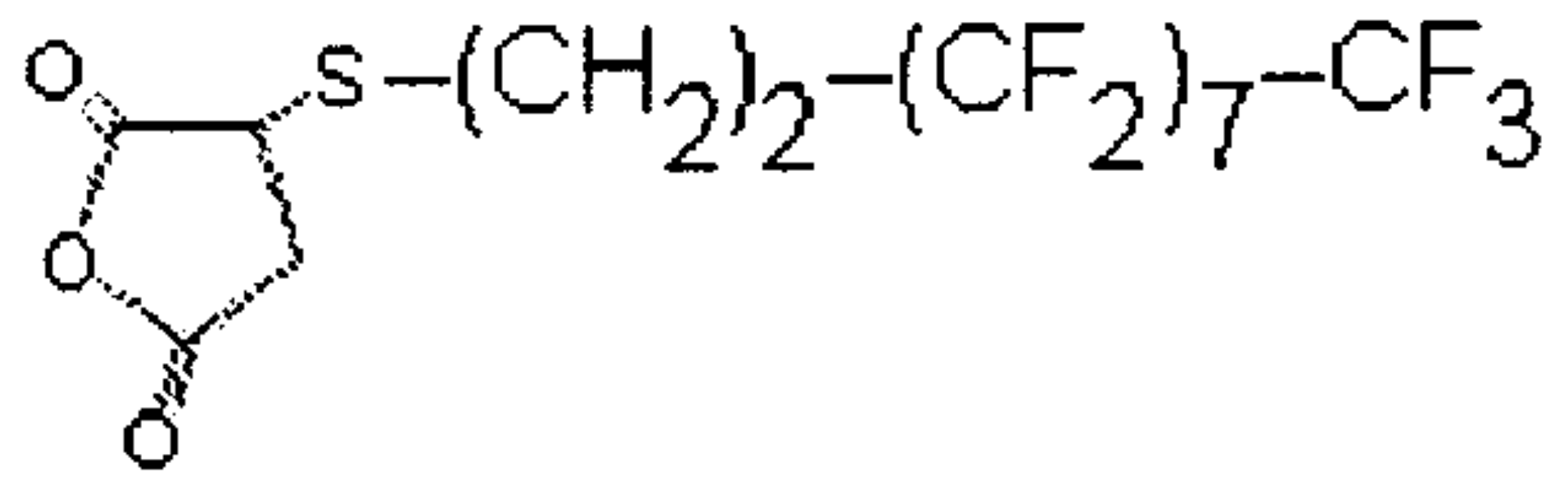
Table 4

Example	Inorganic Oxide Particle	%F	Contact Angle Measurements (°)			
			H_2O Adv.	H_2O Rec.	$C_{16}H_{12}$ Adv.	$C_{16}H_{12}$ Rec.
F	SiO_2#2	0	26	25	*	*
G	SiO_2#1	0	27	23	17	11
H	SiO_2#3	0	*	*	*	*
I	SiO_2#4	0	*	*	*	*
J	SiO_2#5	0	40	14	36	21
K	SiO_2#6	0	*	*	*	*
L	SiO_2#1	0	4	*	*	*

* indicates contact angle could not be measure because of wetting

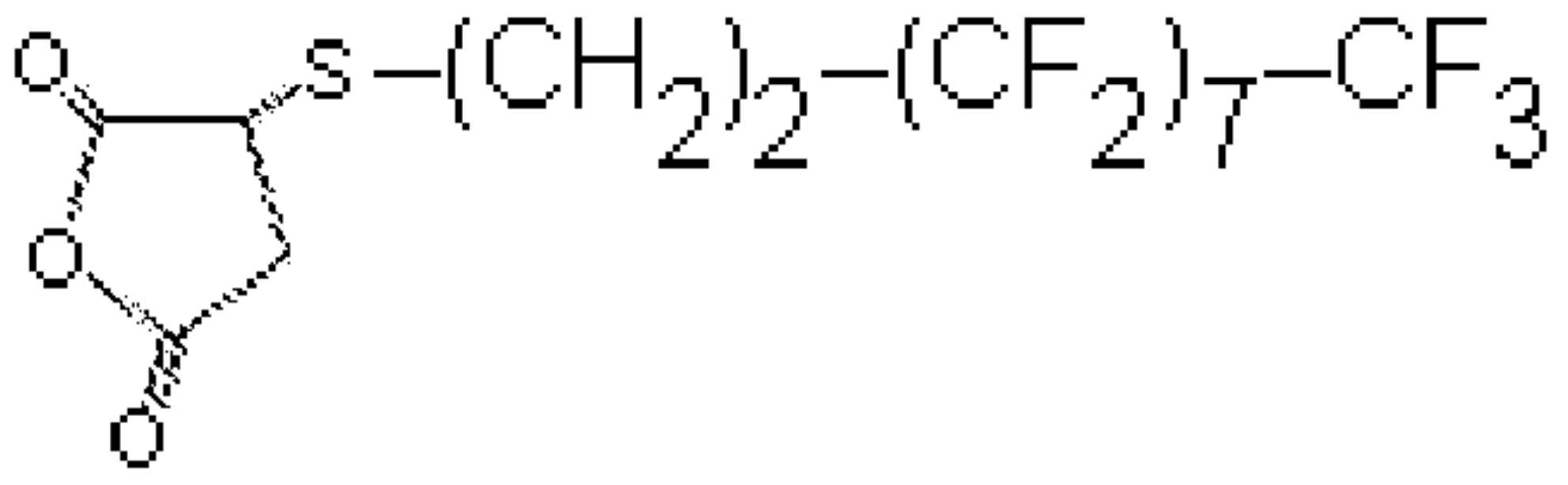
In reference to Table 4 above, it was shown that single functionalization or double functionalization does not result in adequate water or oil repellency.

Capping Step

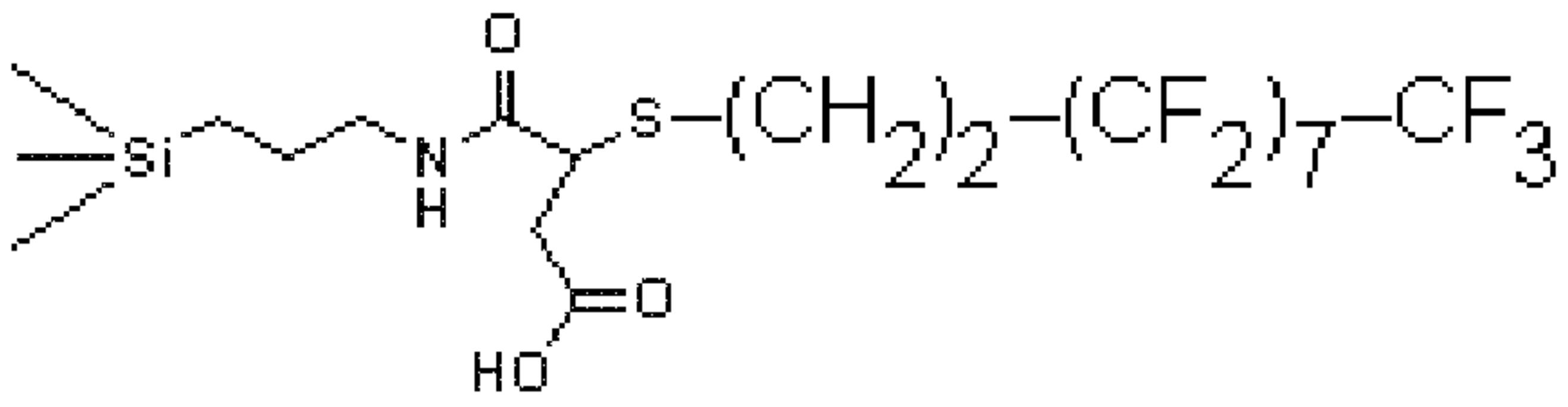
The term “capping step” as used throughout the examples refers to the following procedure. Inorganic particles obtained after single functionalization or after double functionalization are reacted with a chosen “capping agent” in an inert environment in toluene solvent. When the capping agent was a succinic anhydride, , the capping agent was synthesized in toluene and immediately reacted with the inorganic particles obtained after single functionalization or after double functionalization. Synthesis of the succinic anhydride was conducted as taught in US4171282.

Example 7

Single functionalization was conducted wherein the chosen inorganic oxide was SiO_2#2 resulting in treated particles. These treated particles wherein subjected to the capping step wherein the chosen



capping agent was thereby making hydrophobized particles. A film sample was made by thin film casting using these hydrophobized particles. Contact angle measurements were conducted on this film sample and are shown in Table 5. The resulting fluorosilane residue on these hydrophobized particles was



.

The symbol “  ” represents three covalent bonds from silicon, at least one of which is bonded to the particle surface.

Example 8

Example 7 was repeated except the chosen inorganic oxide was SiO_2 #1.

Example 9

Example 7 was repeated except the chosen inorganic oxide was SiO_2 #3.

Example 10

Example 7 was repeated except the chosen inorganic oxide was SiO_2 #4.

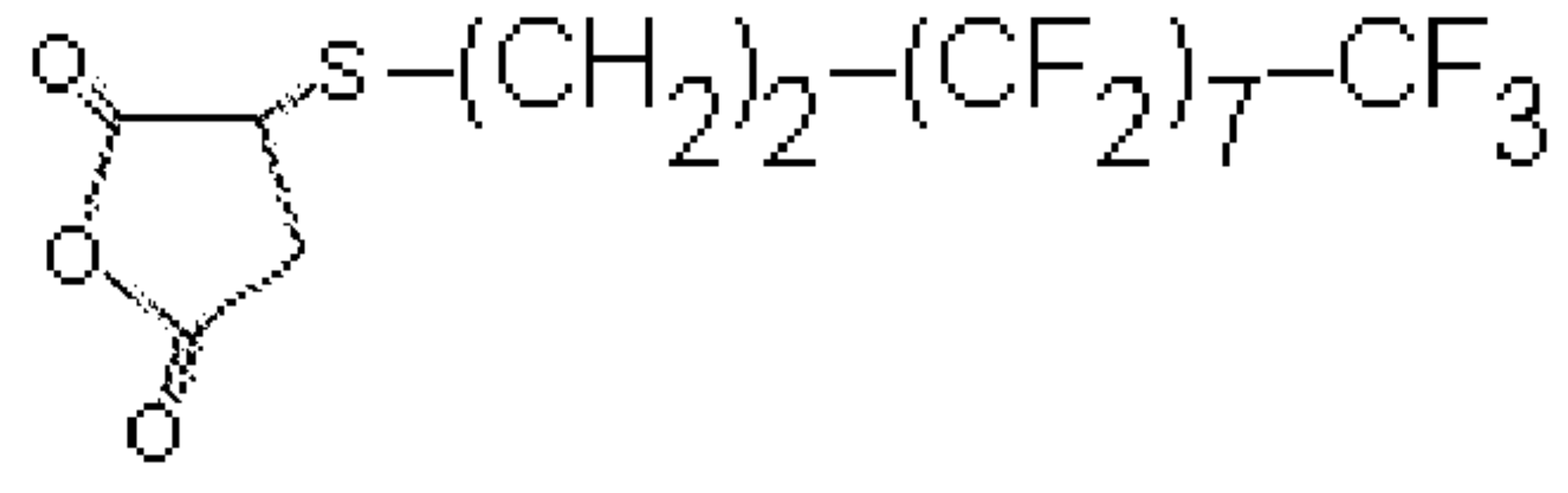
Example 11

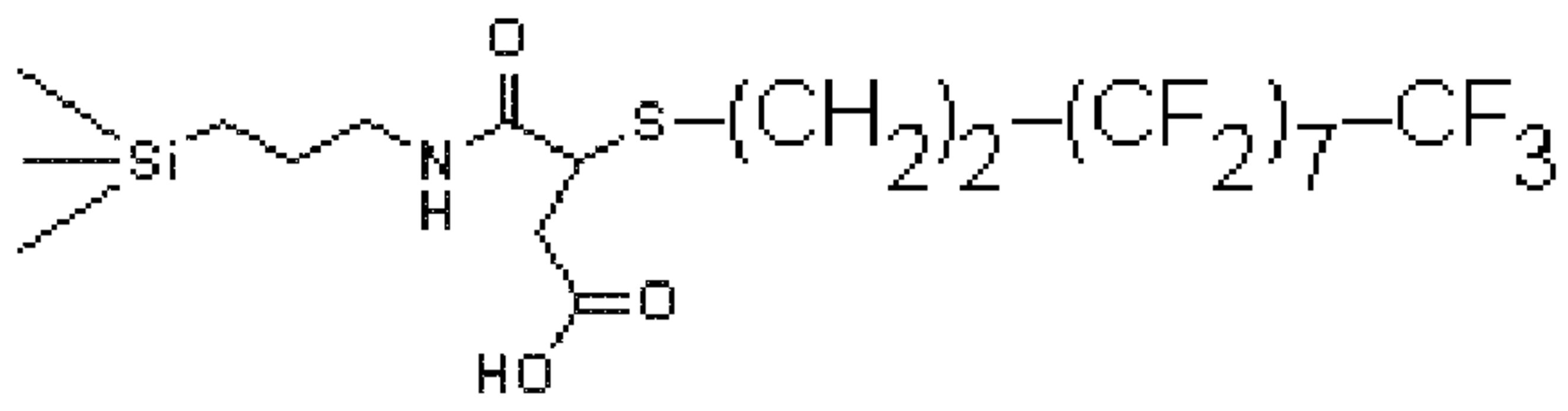
Example 7 was repeated except the chosen inorganic oxide was SiO_2 #5.

Example 12

Example 7 was repeated except the chosen inorganic oxide was SiO_2 #6.

Example 13

Double functionalization was conducted wherein the chosen inorganic oxide was SiO_2 #2 resulting in treated particles. These treated particles wherein subjected to the capping step wherein the chosen capping agent was  thereby making hydrophobized particles. A film sample was made by thin film casting using these hydrophobized particles. Contact angle measurements were conducted on this film sample and are shown in Table 5. The resulting fluorosilane residue on these hydrophobized particles was



The symbol "  " represents three covalent bonds from silicon, at least one of which is bonded to the particle surface.

Example 14

Example 13 was repeated except the chosen inorganic oxide was SiO_2 #1.

Table 5

Example	Inorganic Oxide Particle	%F	Contact Angle Measurements (°)			
			H_2O Adv.	H_2O Rec.	$C_{16}H_{12}$ Adv.	$C_{16}H_{12}$ Rec.
7	SiO_2 #2	10.7	158	155	*	*
8	SiO_2 #1	13.5	159	159	140	126
9	SiO_2 #3	6.23	159	157	34	16
10	SiO_2 #4	1.66	148	122	*	*
11	SiO_2 #5	0.72	*	*	47	35
12	SiO_2 #6	0.15	58	52	74	55
13	SiO_2 #2	13.2	160	160	*	*
14	SiO_2 #1	16.6	156	148	139	121

* indicates contact angle could not be measure because of wetting

Example 15

Single functionalization was conducted wherein the chosen inorganic oxide was SiO_2 #2 resulting in treated particles. These treated particles wherein subjected to the capping step wherein the chosen capping agent was $Cl–S(O)_2–(CH_2)_2–(CF_2)_5–CF_3$ thereby making hydrophobized particles having a fluorosilane residue of $\Xi Si–(CH_2)_3–NH–S(O)_2–(CH_2)_2–(CF_2)_5–CF_3$. The symbol "Ξ" represents three covalent bonds from silicon, at least one of which is bonded to the particle surface. A film sample was made by thin film casting using these hydrophobized particles. Contact angle measurements were conducted on this film sample and are shown in Table 6.

Example 16

Example 15 was repeated except the chosen inorganic oxide was SiO_2 #1.

Example 17

Double functionalization was conducted wherein the chosen inorganic oxide was SiO_2 #2 resulting in treated particles. These treated particles wherein subjected to the capping step wherein the chosen capping agent was $Cl–S(O)_2–(CH_2)_2–(CF_2)_5–CF_3$ thereby making hydrophobized particles having a fluorosilane residue of $\Xi Si–(CH_2)_3–NH–S(O)_2–(CH_2)_2–(CF_2)_5–CF_3$. The symbol "Ξ" represents three covalent bonds from silicon, at least one of which is bonded to the particle surface. A film sample was made by thin film casting using these hydrophobized particles. Contact angle measurements were conducted on this film sample and are shown in Table 6.

Example 18

Example 17 was repeated except the chosen inorganic oxide was SiO_2 #1.

Table 6

Example	Inorganic Oxide Particle	%F	Contact Angle Measurements (°)			
			H_2O Adv.	H_2O Rec.	$C_{16}H_{12}$ Adv.	$C_{16}H_{12}$ Rec.
15	SiO_2 #2	11.3	149	140	*	*
16	SiO_2 #1	12.9	150	148	132	126
17	SiO_2 #2	12.4	145	139	*	*
18	SiO_2 #1	10.6	147	146	147	144

* indicates contact angle could not be measure because of wetting

Example 19

Double functionalization was conducted wherein the chosen inorganic oxide was SiO_2 #1 resulting in treated particles. These treated particles wherein subjected to the capping step wherein the chosen capping agent was $CH_2{=}CH_2{-}C(O){-}O{-}(CH_2)_2{-}(CF_2)_5{-}CF_3$ thereby making hydrophobized particles having a fluorosilane residue of $\Xi Si{-}(CH_2)_3{-}N[(CH_2)_2{-}C(O){-}O{-}(CH_2)_2{-}(CF_2)_5{-}CF_3]_2$. The symbol "Ξ" represents three covalent bonds from silicon, at least one of which is bonded to the particle surface. A film sample was made by thin film casting using the hydrophobized particles obtained after second precursor double grafting. Contact angle measurements were conducted on this film sample and are shown in Table 7.

Table 7

Example	Inorganic Oxide Particle	%F	Contact Angle Measurements (°)			
			H_2O Adv.	H_2O Rec.	$C_{16}H_{12}$ Adv.	$C_{16}H_{12}$ Rec.
15	SiO_2 #1	18.9	154	151	129	116

* indicates contact angle could not be measure because of wetting

NMR Analysis of Example 14

The hydrophobized particles made from SiO_2 #1 (AEROSIL 200) silica particles obtained in Example 14 were subjected to solid-state ^{29}Si NMR cross-polarization magic angle spinning analysis (CPMAS) resulting in the spectra shown in Figure 2. Also shown in Figure 2 is the spectra using the same ^{29}Si NMR CPMAS analysis of untreated SiO_2#1 (AEROSIL™200) silica particles.

Figure 1 is a simplified depiction of a hydrophobized particle made from SiO_2#1 (AEROSIL™200) silica particles obtained in Example 14. Referring to Figure 1, the silicon atom of fluorosilane residues is depicted by **A1**, **A2**, **B1**, **B2**, **C1**, and **C2**. In the formula of the fluorosilane residue depicted in Figure 1, L^2 represents $-OCH_3$ or $-OH$. **A1** and **A2** show the silicon atom of fluorosilane residues bonded to the surface of the silica particle through one oxygen atom. **B1** and **B2** show the silicon atom of fluorosilane residues bonded to the surface of the silica particle through two oxygen atoms. **C1** and **C2** show the silicon atom of fluorosilane residues bonded to the surface of the silica particle through three oxygen atoms. **D1**, **D2**, **D3**, and **D4** depict silicon atoms at the surface of the silica particle which are not bonded to a fluorosilane residue.

Referring to Figure 2 and the spectra of hydrophobized particles, **1** depicts a signal consistent with the silicon atom of fluorosilane residues depicted as **C1** and **C2** in Figure 1. Referring to Figure 2 and the spectra of hydrophobized particles, **2** depicts a signal consistent with the silicon atom of fluorosilane residues depicted as **B1** and **B2** in Figure 1. Referring to Figure 2 and the spectra of hydrophobized particles, **3** depicts a signal consistent with the silicon atom of fluorosilane residues depicted as **A1** and **A2** in Figure 1. Referring to Figure 2 and the spectra of hydrophobized particles, **6** depicts a signal consistent silicon atoms at the surface of the silica particle which are not bonded to a fluorosilane residue depicted as **D1**, **D2**, **D3**, and **D4** in Figure 1.

Referring to Figure 2 and the spectra of untreated particles, **5** depicts a signal consistent with silicon atoms at the surface of the silica particle which are not bonded to a fluorosilane residue depicted as **D1**, **D2**, **D3**, and **D4** in Figure 1. Referring to Figure 2 and the spectra of untreated particles, notably absent are any signals corresponding to those depicted by **1**, **2**, and **3** in the spectra of hydrophobized particles.

CLAIMS

What is claimed is:

1. Surface modified inorganic oxide particles comprising an oxide of M wherein M is independently selected from the group consisting of Si, Ti, Zn, Zr, Mn, Al, and combinations thereof; at least one of said particles having a surface covalently bonded to at least one fluorosilane group represented by Formula (1)

$$(L^1)_d(L^2)_cSi–(CH_2)_n–(Z^1)_a–[C(X^1)]_x–(Z^2)_l–Q^1–R_f$$

wherein

L^1 represents an oxygen covalently bonded to an M; and each L^2 independently selected from the group consisting of H, a C_1-C_2 alkyl, and OH; d and c are integers such that: $d \geq 1$, $c \geq 0$, $d+c=3$;

each n is independently an integer from 1 to 12;

a, x, and l are integers chosen such that the moiety of Formula 1 represented by $–(Z^1)_a–[C(X^1)]_x–(Z^2)_l–$ represents a moiety wherein a=1, x=1, and l=1;

R_f is chosen from a $C_2–C_{12}$ perfluoroalkyl, a $C_2–C_{12}$ perfluoroalkyl having one fluorine atom of the perfluoroalkyl replaced by hydrogen, a $C_2–C_{12}$ perfluoroalkyl interrupted by at least one oxygen, methylene, or ethylene, or a $C_2–C_{12}$ perfluoroalkyl having one fluorine atom of the perfluoroalkyl replaced by hydrogen which is interrupted by at least one oxygen, methylene, or ethylene;

Q^1 is chosen from the group consisting of a C_2-C_{12} hydrocarbylene and a C_2-C_{12} hydrocarbylene interrupted by at least one divalent organic group;

X^1 is chosen from O or S;

wherein Z^1 and Z^2 are chosen from a) or b) such that:

a) Z^1 is –NH– and Z^2 is from the group consisting of –NH–, –O–, –S–, $–NH–S(O)_2–$, –N[C(O)H]–, $–[HC(COOH)(R^1)]CH–S–$, and $–(R^1)CH–[HC(COOH)]–S–$; where each R^1 is independently chosen from hydrogen, phenyl, a monovalent C_1-C_8 alkyl, or a monovalent C_1-C_8 alkyl terminated by $–C_6H_5$, or

b) Z^2 is –NH– and Z^1 is from the group consisting of –O–, and –S–.

2. The particles of claim 1 wherein the fluorosilane group represented by Formula (1) is a urea or thiourea fluorosilane group such that in Formula (1):

a=1, x=1, and l=1;

Z^1 is –NH– and Z^2 is –NH–;

said urea or thiourea fluorosilane group further represented by the formula:

$(L^1)_d(L^2)_cSi–(CH_2)_n–NH–C(X^1)–NH–Q^1–R_f$

wherein:

X^1 is O to form a urea fluorosilane group, or X^1 is S to form a thiourea fluorosilane group; and

Q^1 is independently chosen from the group consisting of a C_2-C_{12} hydrocarbylene and a C_2-C_{12} hydrocarbylene interrupted by at least one divalent moiety chosen from the group consisting of –S–, –S(O)–, $–S(O)_2–$, and –O–C(O)–NH–.

3. The particles of claim 2 wherein R_f is chosen from a C_2–C_{12} perfluoroalkyl and Q^1 is independently chosen from the group consisting of a C_2-C_{12} hydrocarbylene interrupted by at least one divalent moiety chosen from the group consisting of –S–, –S(O)–, $–S(O)_2–$, and –O–C(O)–NH –.

4. The particles of claim 2 wherein R_f is chosen from a C_2–C_{12} perfluoroalkyl having one fluorine atom of the perfluoroalkyl replaced by hydrogen, a C_2–C_{12} perfluoroalkyl interrupted by at least one oxygen, methylene, or ethylene, or a C_2–C_{12} perfluoroalkyl having one fluorine atom of the perfluoroalkyl replaced by hydrogen which is interrupted by at least one oxygen, methylene, or ethylene.

5. The particles of claim 1 wherein the fluorosilane group represented by Formula (1) is a carbamate fluorosilane group such that in Formula (1):

Z^1 is –NH– and Z^2 is –O–, or Z^1 is –O– and Z^2 is –NH–; and

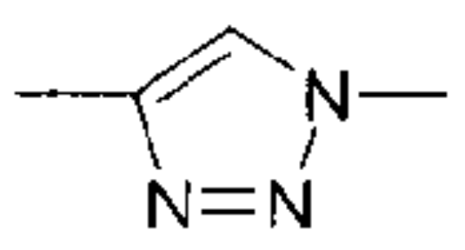
X^1 is O;

said carbamate fluorosilane group further represented by the formulae:

$(L^1)_d(L^2)_cSi–CH_2)_n–NH–C(O)–O–Q^1–R_f$, or

$(L^1)_d(L^2)_cSi–(CH_2)_n–O–C(O)–NH–Q^1–R_f$

wherein:

Q^1 is a $C_2–C_{12}$ hydrocarbylene or a $C_2–C_{12}$ hydrocarbylene interrupted by at least one divalent moiety chosen from the group consisting of –NH–C(O)–NH–, –NH–C(S)–NH–, –S–, –S(O)–, $–S(O)_2–$, $–(R^1)N–S(O)_2–$,  .

6. The particles of claim 5 wherein R_f is chosen from a $C_2–C_{12}$ perfluoroalkyl and Q^1 is independently chosen from the group consisting of a $C_2–C_{12}$ hydrocarbylene interrupted by at least one divalent moiety chosen from the group consisting of –S–, –S(O)–, $–S(O)_2–$, and –O–C(O)–NH –.

7. The particles of claim 5 wherein R_f is chosen from a $C_2–C_{12}$ perfluoroalkyl having one fluorine atom of the perfluoroalkyl replaced by hydrogen, a $C_2–C_{12}$ perfluoroalkyl interrupted by at least one oxygen, methylene, or ethylene, or a $C_2–C_{12}$ perfluoroalkyl having one fluorine atom of the perfluoroalkyl replaced by hydrogen which is interrupted by at least one oxygen, methylene, or ethylene.

8. The particles of claim 1 wherein the fluorosilane group represented by Formula (1) is a thiolcarbamate fluorosilane group such that in Formula (1):

Z^1 is –NH– and Z^2 is –S–, or Z^1 is –S– and Z^2 is–NH–; and

X^1 is O;

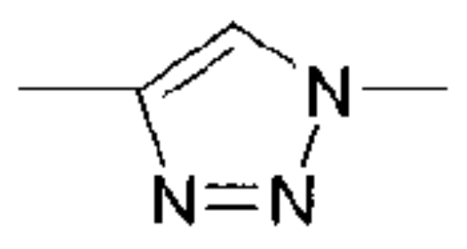
said thiolcarbamate fluorosilane group further represented by the formulae:

$(L^1)_d(L^2)_cSi–CH_2)_n–NH–C(O)–S–Q^1–R_f$ or

$(L^1)_d(L^2)_cSi–(CH_2)_n–S–C(O)–NH–Q^1–R_f$

wherein:

Q^1 is independently chosen from the group consisting of a C_2-C_{12} hydrocarbylene and a $C_2–C_{12}$ hydrocarbylene interrupted by at least one divalent moiety chosen from the group consisting of –S–, –S(O)–, $–S(O)_2–$, $–N(R^1)–C(O)–$,

$-C(O)-N(R^1)-$, $-(R^1)N-S(O)_2-$, and  .

9. The particles of claim 8 wherein R_f is chosen from a C_2–C_{12} perfluoroalkyl and Q^1 is independently chosen from the group consisting of a C_2-C_{12} hydrocarbylene interrupted by at least one divalent moiety chosen from the group consisting of $-S-$, $-S(O)-$, $-S(O)_2-$, and $-O-C(O)-NH-$.

10. The particles of claim 8 wherein R_f is chosen from a C_2–C_{12} perfluoroalkyl having one fluorine atom of the perfluoroalkyl replaced by hydrogen, a C_2–C_{12} perfluoroalkyl interrupted by at least one oxygen, methylene, or ethylene, or a C_2–C_{12} perfluoroalkyl having one fluorine atom of the perfluoroalkyl replaced by hydrogen which is interrupted by at least one oxygen, methylene, or ethylene.

11. The particles of claim 1 further comprising at least one particle having a surface covalently bonded to a N-sulfone urea fluorosilane group such that in Formula (1):

Z^1 is $-NH-$, and Z^2 is $-NH-S(O)_2-$; and

X^1 is O;

said N-sulfone urea fluorosilane group further represented by the formula:

$$(L^1)_d(L^2)_cSi-(CH_2)_n-NH-C(O)-NH-S(O)_2-Q^1-R_f$$

wherein:

Q^1 is independently chosen from the group consisting of an uninterrupted C_2-C_{12} hydrocarbylene.

12. The particles of claim 1 further comprising at least one particle having a surface covalently bonded to a N-formyl urea fluorosilane group such that in Formula (1):

a=1, x=1, and l=1; and

Z^1 is $-NH-$, and Z^2 is $-N[C(O)H]-$;

said N-formyl urea group further represented by the formula:

$(L^1)_d(L^2)_cSi{-}(CH_2)_n{-}NH{-}C(X^1){-}N[C(O)H]{-}Q^1{-}R_f$

wherein:

Q^1 is independently chosen from the group consisting of a C_2-C_{12} hydrocarbylene interrupted by at least one divalent moiety chosen from the group consisting of –S– and –NH–.

13. The particles of claim 1 further comprising at least one particle having a surface covalently bonded to a thioether succinamic acid fluorosilane group such that in Formula (1):

a=1, x=1, and l=1;

Z^1 is –NH– and Z^2 is $-[HC(COOH)(R^1)]CH{-}S{-}$ or $-(R^1)CH{-}[HC(COOH)]{-}S{-}$;

X^1 is O; and Q^1 is $-(CH_2)_2-$

said thioether succinamic acid group further represented by the formulae:

$(L)_3Si{-}(CH_2)_n{-}NH{-}C(O){-}[HC(COOH)(R^1)]CR^1{-}(CH_2)_m{-}S{-}(CH_2)_2{-}R_f$, or

$(L)_3Si{-}(CH_2)_n{-}NH{-}C(O){-}(R^1)CH{-}[CR^1(COOH)]{-}(CH_2)_m{-}S{-}(CH_2)_2{-}R_f$

wherein m is 1 or 0; wherein each R^1 is independently chosen from methyl or hydrogen.

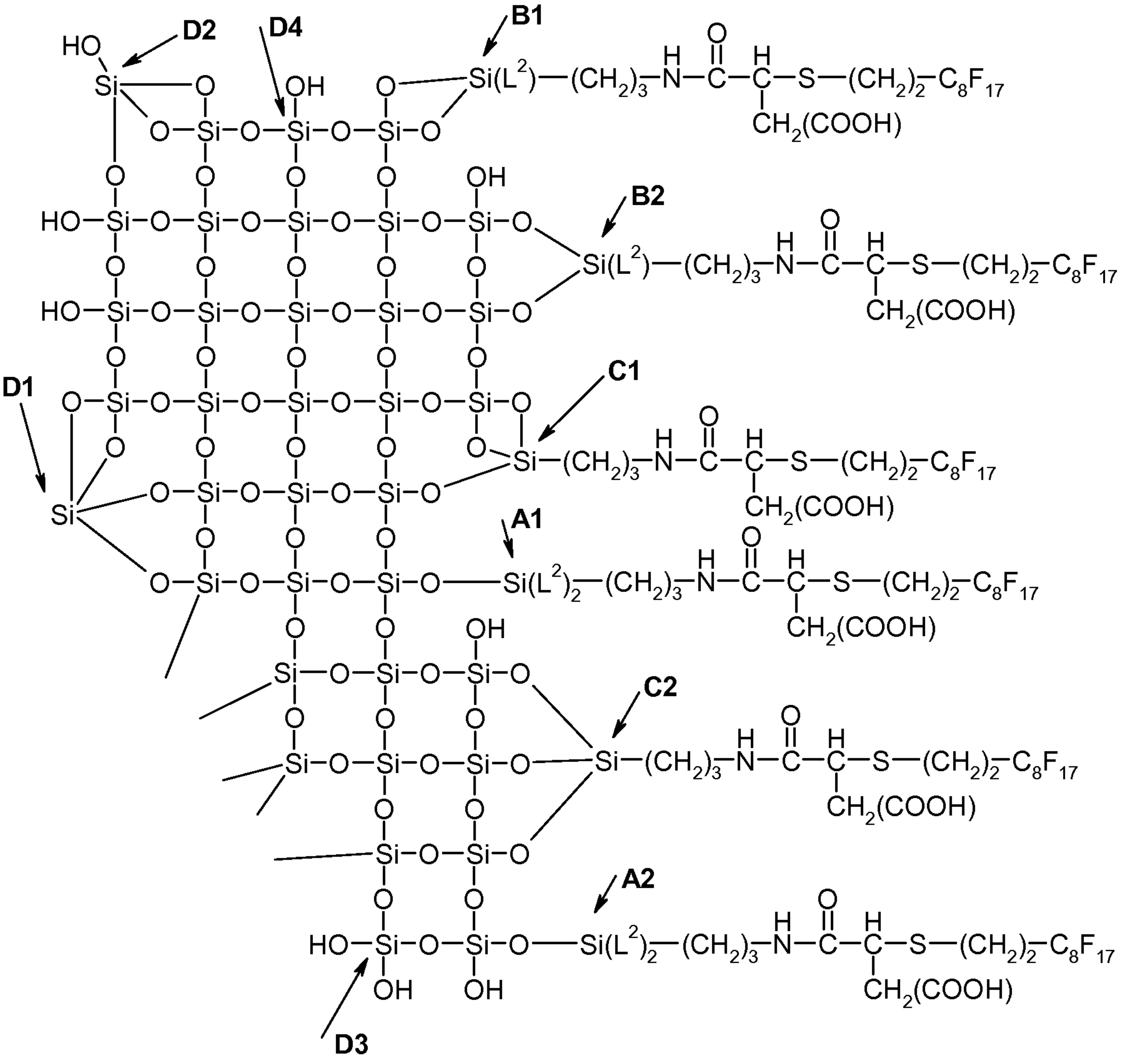

D2
D4
B1
B2
C1
D1
A1
C2
A2
D3
Si(L2)—(CH2)3—N(H)—C(=O)—C(H)—S—(CH2)2—C8F17
CH2(COOH)
Si(L2)2—(CH2)3—N(H)—C(=O)—C(H)—S—(CH2)2—C8F17
Si—(CH2)3—N(H)—C(=O)—C(H)—S—(CH2)2—C8F17
HO
OH

FIG. 1

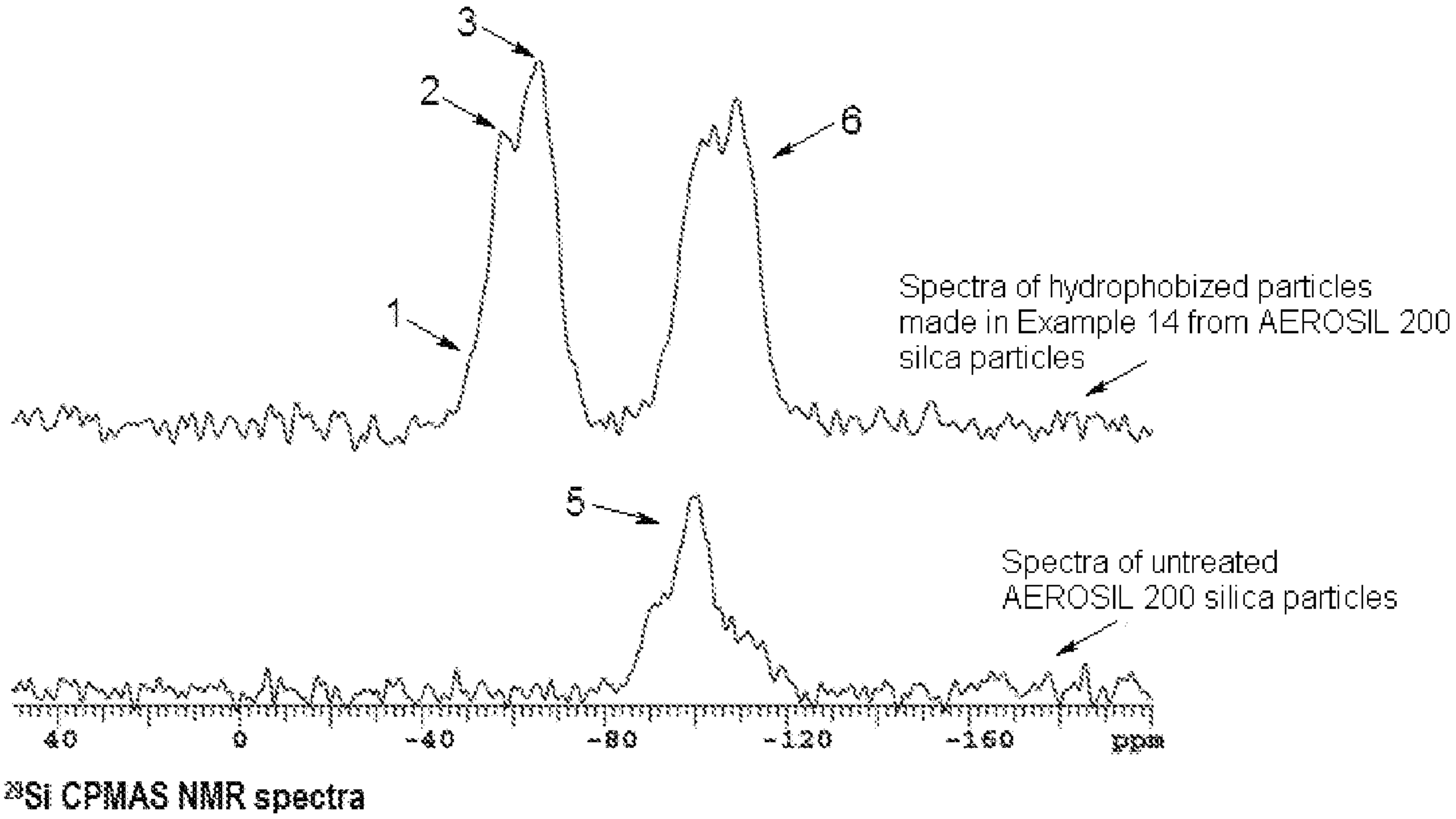
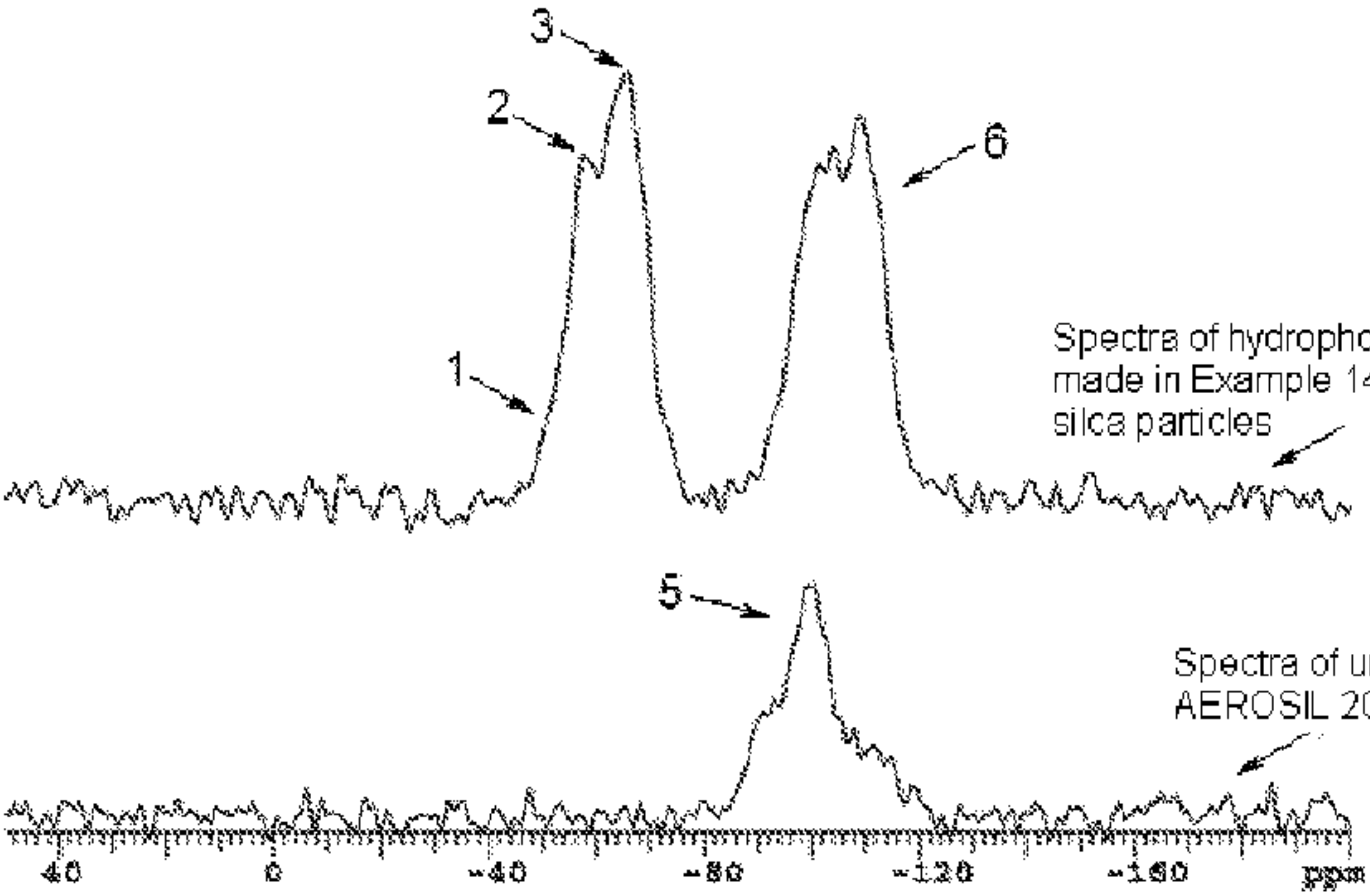

3
2
6
1
Spectra of hydrophobized particles made in Example 14 from AEROSIL 200 silca particles
5
Spectra of untreated AEROSIL 200 silica particles
40
0
-40
-80
-120
-160
ppm
29Si CPMAS NMR spectra

FIG. 2



Spectra of hydrophobized particles made in Example 14 from AEROSIL 200 silica particles

Spectra of untreated AEROSIL 200 silica particles

^{29}Si CPMAS NMR spectra