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(54) Title: SILICON-CONTAINING POLYMER AND METHOD OF MAKING A SILICON-CONTAINING POLYMER

$$A-[Q]_x-[Z]_y-I$$

(I)

(57) **Abstract**: A silicon-containing polymer is represented by the general formula:(I) wherein A, Q, Z, x, and y are as defined in the specification, and I is iodine. Group Q includes a hydrolyzable silane group and group A is fluorinated. A method of making the silicon-containing polymer is also disclosed.

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SILICON-CONTAINING POLYMER AND METHOD OF MAKING A SILICON-CONTAINING POLYMER

TECHNICAL FIELD

The present disclosure broadly relates to silicon-containing polymers and methods of making them.

BACKGROUND

Over the years, various protective coatings have been developed that provide resistance to mechanical damage, corrosion, marine organisms, and/or graffiti. Often these coatings are based on silicone and/or organofluorine chemistry.

Many protective coatings have a high concentration of fluorine in order to achieve a desired level of moisture, chemical, and/or graffiti resistance. However, such compositions typically sacrifice hardness and durability in their quest for repellency. There remains a need for new materials that can be used to make protective coatings on substrates.

SUMMARY

In one aspect, the present disclosure provides a silicon-containing polymer represented by the general formula:

$$A\text{-}[Q]_x\text{-}[Z]_y\text{-}I$$

wherein:

A represents a monovalent group represented by the formula

$$R_f^2\, R_f^1 R_h-$$

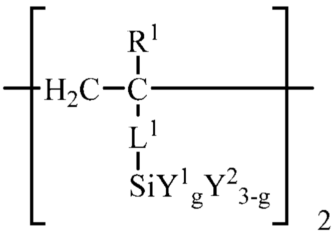
wherein

R_h represents a covalent bond or an alkylene group having from 1 to 18 carbon atoms,

R_f^1 represents a covalent bond or a divalent group selected from the group consisting of $-(CF_2O)_a-$, $-(CF_2CF_2O)_b-$, $-(CF_2CF_2CF_2O)_c-$, $-(CF_2CF_2CF_2CF_2O)_d-$, $-(CF_2CF(CF_3)O)_e-$, and combinations thereof, wherein a, b, c, d, and e represent integers in the range of from 0 to 130, and wherein $1 \leq a + b + c + d + e \leq 130$, and

R_f^2 represents a perfluoroalkyl or perfluoroalkoxy group having from 1 to 8 carbon atoms;

each Q independently represents at least one divalent monomeric unit represented by the formula



$$\left[-H_2C-\underset{\underset{\underset{\displaystyle SiY^1{}_gY^2{}_{3-g}}{|}}{\underset{\displaystyle L^1}{|}}}{\overset{\overset{\displaystyle R^1}{|}}{C}}- \right]_2$$

wherein

R^1 represents H or methyl,

L^1 represents a covalent bond or a divalent aliphatic group having from 1 to 10 carbon atoms,

each Y^1 independently represents a hydrocarbyl group having from 1 to 6 carbon atoms,

each Y^2 independently represents a hydrolyzable group, and

g is 0, 1, or 2; and

each Z independently represents a divalent residue of a non-halogenated free-radically polymerizable ethylenically-unsaturated monomer having from 2 to 18 carbons,

wherein x represents an integer greater than or equal to 3, and y represents an integer greater than or equal to zero.

In another aspect the present disclosure provides a method of making a silicon-containing polymer, the method comprising:

i) combining components comprising:

a) a first molar amount of an iodocompound represented by the formula

$$R_f^2\,R_f^1R_h\text{-I}$$

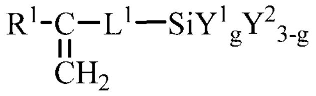
wherein

R_h represents a covalent bond or an alkylene group having from 1 to 18,

R_f^1 represents a covalent bond or a divalent group selected from the group consisting of $-(CF_2O)_a-$, $-(CF_2CF_2O)_b-$, $-(CF_2CF_2CF_2O)_c-$, $-(CF_2CF_2CF_2CF_2O)_d-$, $-(CF_2CF(CF_3)O)_e-$, and combinations thereof, wherein a, b, c, d, and e represent integers in the range of from 0 to 130, and wherein $1 \leq a + b + c + d + e \leq 130$, and

R_f^2 is a perfluoroalkyl or perfluoroalkoxy group having from 1 to 8 carbon atoms;

b) a second molar amount of a free-radically polymerizable silane compound represented by the formula



$$R^1\text{-}C(=CH_2)\text{-}L^1\text{—}SiY^1_gY^2_{3-g}$$

wherein

R^1 represents H or methyl,

L^1 represents a covalent bond or a divalent aliphatic group having from 1 to 10 carbon atoms,

each Y^1 independently represents a hydrocarbyl group having from 1 to 6 carbon atoms,

each Y^2 independently represents a hydrolyzable group,

g is 0, 1, or 2; and

wherein the second molar amount is at least three times the first molar amount; and

c) a free-radical initiator; and

ii) free-radically interpolymerizing at least components a) and b) to provide the silicon-containing polymer.

Silicon-containing polymers according to the present disclosure are moisture- curable and are useful, for example, for providing protective coatings on substrates. Moreover, they can be readily prepared according to the method of the present disclosure.

Features and advantages of the present disclosure will be further understood upon consideration of the detailed description as well as the appended claims.

DETAILED DESCRIPTION

As used herein:

the term "aliphatic" includes the term alicyclic and refers to any organic group or molecule that contains carbon, hydrogen, and optionally one or more of N, O, S, and halogen, but does not contain an aromatic moiety;

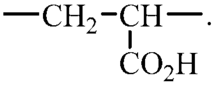
the term "alkene" refers to an ethylenically-unsaturated compound consisting of carbon and hydrogen atoms;

the term "fluorinated alkene" refers to an alkene wherein one or more hydrogen atoms have been replaced by fluorine atom(s);

the term "hydrocarbyl" refers to a monovalent radical composed entirely of carbon and hydrogen;

the prefix "(meth)acryl" means "acryl" and/or "methacryl"; and

the term "residue of a polymerizable monomer or monomer" in reference to a polymer or oligomer refers to atoms resulting from incorporation of the polymerizable monomer in the polymer or oligomer; for example, a residue of acrylic acid (i.e., $CH_2{=}CHCO_2H$) would be the divalent radical



$$—CH_2-\underset{\displaystyle CO_2H}{\underset{|}{CH}}—.$$

Silicon-containing polymers according to the present disclosure are represented by the following general formula

$$A\text{-}[Q]_x\text{-}[Z]_y\text{-}I$$

wherein I represents iodine.

A represents a monovalent group represented by the formula $R_f^2\ R_f^1R_h$–.

R_h represents a covalent bond or an alkylene group having from 1 to 18 carbon atoms, preferably from 1 to 12 carbon atoms, more preferably 1 to 6 carbon atoms, and even more preferably 1 to 4 carbon atoms. Examples of suitable alkylene groups include: methylene, ethylene (i.e., ethane-1,2-diyl), propane-1,3-diyl, propane-1,2-diyl, butane-1,4-diyl, cyclohexane-1,4-diyl, hexane-1,6-diyl, octane-1,8-diyl, decane-1,10-diyl, and octadecane-1,18-diyl.

R_f^1 represents a covalent bond or a divalent group selected from the group consisting of $-(CF_2O)_a-$, $-(CF_2CF_2O)_b-$, $-(CF_2CF_2CF_2O)_c-$, $-(CF_2CF_2CF_2CF_2O)_d-$, $-(CF_2CF(CF_3)O)_e-$, and combinations thereof, wherein a, b, c, d, and e represent integers in the range of from 0 to 130, and wherein $1 \leq a + b + c + d + e \leq 130$.

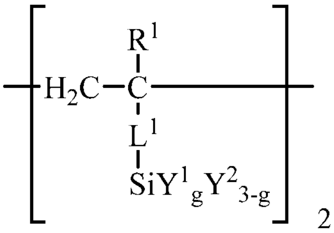
In some embodiments, $1 \leq a + b + c + d + e \leq 130$. In some embodiments, $2 \leq a + b + c + d + e \leq 130$. In some embodiments, at least one of a, b, c, d, or e represents an integer in the range of from 1 or 2 to 130, preferably 1 or 2 to 80, more preferably 1or 2 to 50, and more preferably 1 or 2 to 40. In some embodiments, at least one of a, b, c, d, or e represents an integer in the range of from 1 or 2 to 10, preferably 1 or 2 to 5. In some embodiments, $1 \leq a + b + c + d + e \leq 50$. In some embodiments, $2 \leq a + b + c + d + e \leq 50$. In some embodiments, $10 \leq a + b + c + d + e \leq 130$. In some embodiments, $10 \leq a + b + c + d + e \leq 50$. In some embodiments, $30 \leq a + b + c + d + e \leq 60$. In some embodiments, $4 \leq a + b + c + d + e \leq 130$, preferably $4 \leq a + b + c + d + e \leq 80$, more preferably $4 \leq a + b + c + d + e \leq 50$, more preferably $4 \leq a + b + c + d + e \leq 40$, and even more preferably $4 \leq a + b + c + d + e \leq 40$.

Some examples of R^1_f include $-(CF_2O)_{20\text{-}30}-$, $-(CF_2CF_2O)_{30\text{-}40}-$, $-(CF_2CF_2CF_2O)_{40\text{-}50}-$, $-(CF_2CF_2CF_2CF_2O)_{20\text{-}30}$, $-(CF_2CF(CF_3)O)_{4\text{-}8}-$, $-(CF_2CF(CF_3)O)_{30\text{-}40}-$, $-(CF_2CF_2O)_{30\text{-}40}(CF_2CF(CF_3)O)_{30\text{-}40}-$, and

$-(CF_2O)_{20\text{-}30}(CF_2CF_2O)_{85\text{-}100}-$. When present in combination, the units $-(CF_2O)-$, $-(CF_2CF_2O)-$, $-(CF_2CF_2CF_2O)-$, $-(CF_2CF_2CF_2CF_2O)-$, and $-(CF_2CF(CF_3)O)-$, may be present in a random or pseudorandom order and/or in blocks.

R_f^2 represents a perfluoroalkyl or perfluoroalkoxy group having from 1 to 8 carbon atoms, preferably from 1 to 6 carbon atoms, more preferably 1 to 4 carbon atoms, and still more preferably from 1 to 3 carbon atoms. Examples include perfluoromethyl, perfluoroethyl, perfluoro-n-propyl, perfluoroisopropyl, perfluorobutyl, perfluoropentyl, perfluorohexyl, and perfluorooctyl, perfluoromethoxy, perfluoroethoxy, perfluoro-n-propoxy, perfluoroisopropoxy, perfluorobutoxy, perfluoropentoxy, perfluorohexoxy, and perfluorooctoxy.

Each Q independently represents at least one divalent monomeric unit represented by the formula



$$\left[\!-H_2C-\overset{\displaystyle R^1}{\underset{\underset{\displaystyle SiY^1_gY^2_{3-g}}{\displaystyle L^1}}{C}}-\!\right]_2$$

wherein the free valences are indicate by the lines extending through the square brackets.

R^1 represents H or methyl, preferably H.

L^1 represents a covalent bond or a divalent aliphatic group having from 1 to 10 carbon atoms, preferably 1 to 8 carbon atoms, more preferably 1 to 6 carbon atoms, and more preferably 1 to 4 carbon atoms. In some preferred embodiments, L^1 is composed of entirely of carbon and hydrogen. Examples of suitable divalent aliphatic groups include: methylene, ethylene (i.e., ethane-1,2-diyl), propane-1,3-diyl, propane-1,2-diyl, butane-1,4-diyl, cyclohexane-1,4-diyl, hexane-1,6-diyl, octane-1,8-diyl, and decane-1,10-diyl, carbonyloxyethylene, and carbonyloxypropylene.

Each Y^1 independently represents a hydrocarbyl group having from 1 to 6 carbon atoms, preferably 1 to 3 carbon atoms, and more preferably 1 or 2 carbon atoms. Examples of Y^1 include methyl, ethyl, propyl, butyl, pentyl, cyclohexyl, and phenyl.

Each Y^2 independently represents a hydrolyzable group. Such groups are well known in the art and include, for example, chlorine, bromine, alkoxyl groups having 1 to 4 carbon atoms (e.g., methoxy, ethoxy), and alkanecarboxylates having 1 to 4 carbon atoms (e.g., acetate, propionate).

g represents 0, 1, or 2. In some preferred embodiments g is zero.

Each Z independently represents a divalent residue of a non-halogenated free-radically polymerizable ethylenically-unsaturated monomer having from 2 to 18 carbons, preferably having from 2 to 12 carbon atoms, more preferably from 2 to 6 carbon atoms, a more preferably from 2 to 4 carbon atoms. Examples of suitable non-halogenated free-radically polymerizable ethylenically-unsaturated monomer giving rise to such residues include: polymerizable ethylenically-unsaturated monomers include: alpha olefins having from 2 to 18 carbon atoms (e.g., ethylene, propylene, isobutylene, 1-butene, 1-isobutene, 1-hexene, 1-dodecene, and 1-octadecene), styrene a substituted styrenes, vinyl esters (e.g., vinyl acetate), maleic anhydride, N-vinylformamide, N-vinylacetamide, N-vinyl-2-pyrrolidone, vinylphosphonic acid, (meth)acrylonitrile, (meth)acrylamide and N-substituted derivatives thereof, 2-methylvinylphosphonic acid, (meth)acrylic acid, acrylic acid esters having from 4 to 15 carbon atoms (preferably having from 4 to 11 carbon atoms, and more preferably from 5 to 8 carbon atoms), methacrylic acid esters having from 5 to 16 carbon atoms (preferably having from 2 to 12 carbon atoms, and more preferably from 6 to 9 carbon atoms), and combinations thereof. Examples of suitable acrylates and methacrylates include octyl (meth)acrylate, nonylphenol ethoxylate (meth)acrylate, isononyl (meth)acrylate, isobornyl(meth)acrylate, 2-(2-ethoxyethoxy)ethyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, beta-carboxyethyl (meth)acrylate, isobutyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, isodecyl (meth)acrylate, dodecyl(meth)acrylate, n-butyl(meth)acrylate, methyl(meth)acrylate, hexyl(meth)acrylate, stearyl (meth)acrylate, hydroxy functional caprolactone ester (meth)acrylate, isooctyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, hydroxyisopropyl (meth)acrylate, hydroxybutyl (meth)acrylate, hydroxyisobutyl (meth)acrylate, and tetrahydrofurfuryl (meth)acrylate.

The subscript x represents an integer greater than or equal to 3 (e.g., 3, 4, 5, 10, 25, 50, 100), while y represents an integer greater than or equal to zero (e.g., 1, 2, 3, 25, 50, 100).

Silicon-containing polymers such as those described above can be made for example by free-radical mediated polymerization of ethylenically-unsaturated free-radically polymerizable monomers in the presence of an iodocompound. As used herein, the term "polymerization" includes oligomerization unless contrary to the context.

Accordingly, silicon-containing polymers according to the present disclosure can be made, for example, by combining components comprising an iodocompound
with a free-radically polymerizable silane compound, and a free-radical initiator, and at least partially decomposing the free-radical initiator to form free-radicals thereby causing free-radical polymerization (which may be a "living" free-radical polymerization) resulting in chain growth, and ultimately termination with iodine.

The iodocompound is represented by the formula

$$R_f^2\ R_f^1 R_h\text{-}I$$

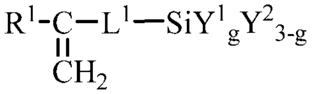
wherein R_h, R_f^1, and R_f^2 are as previously defined. In the above formula, I represents iodine. Examples of suitable iodocompounds include $CF_3CF_2CF_2CF_2CH_2CH_2I$, $CF_3CF_2CF_2O\text{-}[CF(CF_3)CF_2O]_kCFICF_3$ where k ranges from 4 to 100 or more (e.g., $CF_3CF_2CF_2O\text{-}[CF(CF_3)CF_2O]_{4\text{-}8}CFICF_3$ and $CF_3CF_2CF_2O\text{-}[CF(CF_3)CF_2O]_{30\text{-}40}CFICF_3$).

Additional examples of suitable iodocompounds include (wherein v is an integer from 1 to 18): $(CF_3)_2CF(CH_2)_vI$, $(CF_3)_2CFCH_2I$, $(CF_3)_2CF(CH_2)_vI$, $(CF_3)_3C(CH_2)_vI$, $C_4F_9C_2H_4I$, $CF_3OC_2F_4(CH_2)_vI$, $CF_3(CH_2)_vI$, $CF_3CF_2CF_2(CH_2)_vI$, $CF_3CF_2(CH_2)_vI$, $CF_3O(CF_2O)_{20\text{-}30}(CH_2)_vI$, $CF_3CF_2O(CF_2CF_2O)_{30\text{-}40}(CH_2)_vI$, $CF_3O(CF_2CF_2CF_2O)_{40\text{-}50}(CH_2)_vI$,

$(CF_2CF_2CF_2CF_2O)_{20-30}(CH_2)_vI$, $CF_3O(CF_2CF(CF_3)O)_{4-8}(CH(CH_3))_vI$, $CF_3O(CF_2CF(CF_3)O)_{30-40}(CH_2)_vI$, $CF_3CF_2O(CF_2CF_2O)_{30-40}(CH_2)_vI$, $CF_3CF_2O(CF_2CF(CF_3)O)_{30-40}(CH_2)_vI$, and $(CF_3)_2CFOCF_2CF_2I$.

The above-described iodocompounds can be prepared by known methods. For example, the fluoroalkyl iodides can be prepared by displacement of a leaving group (on the fluoroalkyl moiety) by iodide, and the perfluoroalkyl iodides can be prepared by the reaction of a perfluoroolefin (e.g., tetrafluoroethylene or hexafluoropropylene) with IF_5 or by decarbonylation of perfluoroacyl halides. Further details and methods are disclosed in U.S. Pat. No. 7,893,186 (Yu et al.). Suitable iodocompounds can also be prepared as generally described by Howell et al. in "The preparation of primary poly-hexafluoropropylene oxide halides (poly-HFPO-CF_2X where X = I, Br, Cl and F)", Journal of Fluorine Chemistry (2004), vol. 125, pages 1513-1518. Many suitable iodocompounds are commercially available.

The free-radically polymerizable silane compound is represented by the formula



$$R^1\text{-}\underset{\underset{CH_2}{\|}}{C}-L^1-SiY^1{}_gY^2{}_{3-g}$$

wherein R^1, L^1, Y^1, Y^2, and g are as previously defined. Examples of commercially available free-radically polymerizable silane compounds include: (acryloxymethyl)phenethyltrimethoxysilane, (acryloxymethyl)trimethoxysilane, (3-acryloxypropyl)methyldichlorosilane, (3-acryloxypropyl)methyldiethoxysilane, (3-acryloxypropyl)methyldimethoxysilane, (3-acryloxypropyl)trichlorosilane, (3-acryloxypropyl)trimethoxysilane, (3-acryloxypropyl)trimethoxysilane, (3-acryloxypropyl)tris(trimethylsiloxy)silane, allylmethyldichlorosilane, allylmethyldimethoxysilane, 11-allyloxyundecyltrimethoxysilane, 3-(3-methacryloxy-2-hydroxypropoxy)propylbis-(trimethylsiloxy)methylsilane, n-(3-methacryloxy-2-hydroxypropyl)-3-aminopropyltriethoxysilane, (methacryloxymethyl)bis(trimethylsiloxy)methylsilane, (methacryloxymethyl)dimethylethoxysilane, (methacryloxymethyl)methyldiethoxysilane, (methacryloxymethyl)methyldimethoxysilane, (methacryloxymethyl)phenyldimethylsilane, methacryloxymethylphenethyltris(trimethylsiloxy)silane, methacryloxymethyltriethoxysilane, methacryloxymethyltrimethoxysilane, methacryloxymethyltrimethylsilane, methacryloxymethyltris(trimethylsiloxy)silane, methacryloxypentamethyldisiloxane, 3-methacryloxypropylbis(trimethylsiloxy)methylsilane, 3-methacryloxypropyldimethylchlorosilane, methacryloxypropyldimethylethoxysilane, methacryloxypropyldimethylmethoxysilane, methacryloxypropylmethyldichlorosilane, methacryloxypropylmethyldiethoxysilane, methacryloxypropylmethyldimethoxysilane, 3-methacryloxypropyltriacetoxysilane, methacryloxypropyltrichlorosilane, methacryloxypropyltriethoxysilane, methacryloxypropyltriisopropoxysilane, methacryloxypropyltrimethoxysilane, methacryloxypropyltris(methoxyethoxy)silane, methacryloxypropyltris(trimethylsiloxy)silane, methacryloxypropyltris(trimethylsiloxy)silane, methacryloxypropyltris(trimethylsiloxy)silane, methacryloxypropyltris(vinyldimethylsiloxy)silane, vinyl(chloromethyl)dimethoxysilane, vinyldimethylchlorosilane, vinyldimethylethoxysilane, vinyldiphenylchlorosilane, vinyldiphenylethoxysilane, vinylmethylbis(trimethylsiloxy)silane, vinylmethyldiacetoxysilane, vinylmethyldichlorosilane, vinylmethyldiethoxysilane, vinylmethyldimethoxysilane, vinyloctyldichlorosilane, vinylphenyldichlorosilane, vinylphenyldiethoxysilane, vinylphenylmethylchlorosilane, vinylphenylmethylmethoxysilane, vinyltriacetoxysilane, vinyltrichlorosilane, vinyltriethoxysilane, vinyltriisopropenoxysilane, vinyltriisopropoxysilane, vinyltrimethoxysilane, vinyltris(1-methoxy-2-propoxy)silane, vinyltris(2-methoxyethoxy)silane, vinyltris(dimethylsiloxy)silane, and vinyltris(trimethylsiloxy)silane, all of which are available from Gelest, Inc., Morrisville, Pennsylvania.

The molar amount of the free-radically polymerizable silane compound should be at least three times the molar amount of the iodocompound. In some embodiments, the molar amount of the free-radically polymerizable silane compound should be at least 4, 5, 6, 7, 8, 10, 20, 20, 50, or even at least 100 times the molar amount of the iodocompound, or more.

Examples of suitable free-radical initiators include thermal free-radical initiators (e.g., organic peroxides and certain azo compounds) and photoinitiators. Thermal free-radical initiators are generally preferred. The free-radical initiator(s) is preferably included in an effective amount (i.e., an amount sufficient to carry out the polymerization) although any quantity may be used. Examples of suitable free-radical initiators include Thermal initiators for free-radical polymerization are generally used in effective amounts (e.g., from about 0.01 to 5 percent by weight). Useful thermal initiators include, for example, azo and peroxide initiators. Examples of suitable azo initiators include 2,2'-azobis(2,4-dimethylvaleronitrile); 2,2'-azobis(isobutyronitrile); 2,2'-azobis-2-methylbutyronitrile; and (1,1'-azobis(1-cyclohexanecarbonitrile); 2,2'-azobis(methyl isobutyrate); 2,2'-azobis(2-amidinopropane) dihydrochloride; and 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile). Examples of suitable peroxide initiators include benzoyl peroxide, acetyl peroxide, lauroyl peroxide, decanoyl peroxide, dicetyl peroxydicarbonate, di(4-t-butylcyclohexyl) peroxydicarbonate, di(2-ethylhexyl) peroxydicarbonate, t-butyl peroxypivalate, t-butyl peroxy-2-ethylhexanoate, and dicumyl peroxide.

Polymerization is effected by decomposition of the free-radical initiator (e.g., by heating and/or ultraviolet radiation).

In some embodiments, the components further include a non-halogenated free-radically polymerizable ethylenically-unsaturated monomer having from 2 to 18 carbons, preferably, having from 2 to 12 carbon atoms, more preferably from 2 to 6 carbon atoms, a more preferably from 2 to 4 carbon atoms. Examples of suitable non-halogenated free-radically polymerizable ethylenically-unsaturated monomers include: alpha olefins having from 2 to 18 carbon atoms (e.g., ethylene, propylene, isobutylene, 1-butene, 1-isobutene, 1-hexene, 1-dodecene, and 1-octadecene), styrene a substituted styrenes, vinyl esters (e.g., vinyl acetate), maleic anhydride, N-vinylformamide, N-vinylacetamide, N-vinyl-2-pyrrolidone, vinylphosphonic acid, (meth)acrylonitrile, (meth)acrylamide and N-substituted derivatives thereof, 2-methylvinylphosphonic acid, (meth)acrylic acid, acrylic acid esters having from 4 to 15 carbon atoms (preferably having from 4 to 11 carbon atoms, and more preferably from 5 to 8 carbon atoms), methacrylic acid esters having from 5 to 16 carbon atoms (preferably having from 2 to 12 carbon atoms, and more preferably from 6 to 9 carbon atoms), and combinations thereof. Examples of suitable acrylates and methacrylates include octyl (meth)acrylate, nonylphenol ethoxylate (meth)acrylate, isononyl (meth)acrylate, isobornyl(meth)acrylate, 2-(2-ethoxyethoxy)ethyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, beta-carboxyethyl (meth)acrylate, isobutyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, isodecyl (meth)acrylate, dodecyl(meth)acrylate, n-butyl(meth)acrylate, methyl(meth)acrylate, hexyl(meth)acrylate, stearyl (meth)acrylate, hydroxy functional caprolactone ester (meth)acrylate, isooctyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, hydroxyisopropyl (meth)acrylate, hydroxybutyl (meth)acrylate, hydroxyisobutyl (meth)acrylate, and tetrahydrofurfuryl (meth)acrylate.

If desired, solvent may be used in during polymerization to facilitate mixing and/or reaction. Examples of suitable solvents include: aliphatic hydrocarbons (e.g., hexane, heptane, cyclohexane); aromatic solvents (e.g., benzene, toluene, xylene); ethers (e.g., diethyl ether, glyme, diglyme, diisopropyl ether); esters (e.g., ethyl acetate, butyl acetate); alcohols (e.g., ethanol, isopropyl alcohol); ketones (e.g., acetone, methyl ethyl ketone, methyl isobutyl ketone); sulfoxides (e.g., dimethyl sulfoxide); amides (e.g., N,N-dimethylformamide, N,N-dimethylacetamide); halogenated solvents (e.g., ethylchloroform, dichloroethylene, trifluorotoluene); and combinations thereof.

Silicon-containing compounds according to the present disclosure are moisture curable due to hydrolysis of the hydrolyzable groups bound to silicon, followed by cross-linking to form Si-O-Si linkages. Typically, this occurs spontaneously upon standing and/or solvent evaporation of the coating in air containing water vapor to form a crosslinked reaction product. Heat and/or steam (e.g., superheated steam) may be used to accelerate and/or advance curing of the moisture-curable composition.

The resultant crosslinked product may have good mechanical durability (e.g., hardness and/or abrasion resistance), adhesion, and/or repellency properties. It used as a protective coating, the thickness of the protective coating may be, for example, from 10 nanometers to 1 millimeter (mm) or more, more typically from 0.01 mm to 0.3 mm.

Suitable substrates on which the moisture curable composition (and resultant cured composition) may be disposed include, for example, aluminum, stainless steel, glass, copper, silver, kitchen tile, restroom fixtures, plastic film, molded plastic parts, painted and/or clearcoated automotive body panels, marine surfaces (e.g., hulls and trim), motorcycle parts, and cover glasses for electronic displays,

SELECT EMBODIMENTS OF THE PRESENT DISCLOSURE

In a first embodiment, the present disclosure provides a silicon-containing polymer represented by the general formula:

$$A\text{-}[Q]_x\text{-}[Z]_y\text{-}I$$

wherein:

A represents a monovalent group represented by the formula

$$R_f^2 R_f^1 R_h-$$

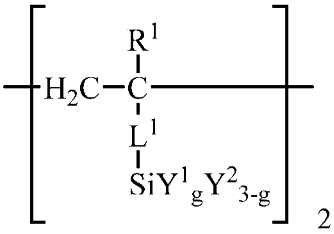
wherein

R_h represents a covalent bond or an alkylene group having from 1 to 18 carbon atoms,

R_f^1 represents a covalent bond or a divalent group selected from the group consisting of $-(CF_2O)_a-$, $-(CF_2CF_2O)_b-$, $-(CF_2CF_2CF_2O)_c-$, $-(CF_2CF_2CF_2CF_2O)_d-$, $-(CF_2CF(CF_3)O)_e-$, and combinations thereof, wherein a, b, c, d, and e represent integers in the range of from 0 to 130, and wherein $1 \leq a + b + c + d + e \leq 130$, and

R_f^2 represents a perfluoroalkyl or perfluoroalkoxy group having from 1 to 8 carbon atoms;

each Q independently represents at least one divalent monomeric unit represented by the formula



$$\left[H_2C-\overset{\displaystyle R^1}{\underset{\displaystyle \underset{\displaystyle SiY^1_gY^2_{3-g}}{L^1}}{C}} \right]_2$$

wherein

R^1 represents H or methyl,

L^1 represents a covalent bond or a divalent aliphatic group having from 1 to 10 carbon atoms,

each Y^1 independently represents a hydrocarbyl group having from 1 to 6 carbon atoms,

each Y^2 independently represents a hydrolyzable group, and

g is 0, 1, or 2; and

each Z independently represents a divalent residue of a non-halogenated free-radically polymerizable ethylenically-unsaturated monomer having from 2 to 18 carbons,

wherein x represents an integer greater than or equal to 3, and y represents an integer greater than or equal to zero.

In a second embodiment, the present disclosure provides a silicon-containing polymer according to the first embodiment, wherein R_h has from 1 to 4 carbon atoms.

In a third embodiment, the present disclosure provides a silicon-containing polymer according to the first or second embodiment, wherein R_f^1 represents a covalent bond.

In a fourth embodiment, the present disclosure provides a silicon-containing polymer according to any one of the first to third embodiments, wherein R_f^2 has from 1 to 4 carbon atoms.

In a fifth embodiment, the present disclosure provides a silicon-containing polymer according to any one of the first to fourth embodiments, wherein L^1 has from 1 to 4 carbon atoms.

In a sixth embodiment, the present disclosure provides a silicon-containing polymer according to any one of the first to fifth embodiments, wherein each Z independently represents a divalent residue of a non-halogenated free-radically polymerizable ethylenically-unsaturated monomer having from 2 to 8 carbons.

In a seventh embodiment, the present disclosure provides a method of making a silicon-containing polymer, the method comprising:

i) combining components comprising:

a) a first molar amount of an iodocompound represented by the formula

$$R_f^2\ R_f^1R_h\text{-}I$$

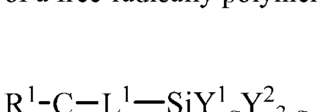
wherein

R_h represents a covalent bond or an alkylene group having from 1 to 18,

R_f^1 represents a covalent bond or a divalent group selected from the group consisting of $-(CF_2O)_a-$, $-(CF_2CF_2O)_b-$, $-(CF_2CF_2CF_2O)_c-$, $-(CF_2CF_2CF_2CF_2O)_d-$, $-(CF_2CF(CF_3)O)_e-$, and combinations thereof, wherein a, b, c, d, and e represent integers in the range of from 0 to 130, and wherein $1 \leq a + b + c + d + e \leq 130$, and

R_f^2 is a perfluoroalkyl or perfluoroalkoxy group having from 1 to 8 carbon atoms;

b) a second molar amount of a free-radically polymerizable silane compound represented by the formula



$$R^1\text{-}\underset{\underset{\displaystyle CH_2}{\|}}{C}-L^1-SiY^1{}_gY^2{}_{3-g}$$

wherein

R^1 represents H or methyl,

L^1 represents a covalent bond or a divalent aliphatic group having from 1 to 10 carbon atoms, each Y^1 independently represents a hydrocarbyl group having from 1 to 6 carbon atoms,

each Y^2 independently represents a hydrolyzable group,

g is 0, 1, or 2; and

wherein the second molar amount is at least three times the first molar amount; and

c) a free-radical initiator; and

ii) free-radically interpolymerizing at least components a) and b) to provide the silicon-containing polymer.

In an eighth embodiment, the present disclosure provides a method of making a silicon-containing polymer according to the seventh embodiment, wherein the components further comprise:

d) a non-halogenated free-radically polymerizable ethylenically-unsaturated monomer having from 2 to 18 carbons, and wherein step ii) comprises free-radically interpolymerizing at least components a), b), and c) to provide the silicon-containing polymer.

In a ninth embodiment, the present disclosure provides a method of making a silicon-containing polymer according to the seventh or eighth embodiment, wherein the non-halogenated free-radically polymerizable ethylenically-unsaturated monomer is selected from the group consisting of N-vinylformamide, N-vinylacetamide, vinylphosphonic acid, 2-methylvinylphosphonic acid, acrylic acid, methacrylic acid, acrylic acid esters having from 4 to 15 carbon atoms, acrylic acid esters having from 5 to 16 carbon atoms, alpha olefins having from 2 to 18 carbon atoms, and combinations thereof.

In a tenth embodiment, the present disclosure provides a method of making a silicon-containing polymer according to any one of the seventh to ninth embodiments, wherein R_h has from 1 to 4 carbon atoms.

In an eleventh embodiment, the present disclosure provides a method of making a silicon-containing polymer according to any one of the seventh to tenth embodiments, wherein R_f^1 represents a covalent bond.

In a twelfth embodiment, the present disclosure provides a method of making a silicon-containing polymer according to any one of the seventh to eleventh embodiments, wherein R_f^2 has from 1 to 4 carbon atoms.

In a thirteenth embodiment, the present disclosure provides a method of making a silicon-containing polymer according to any one of the seventh to twelfth embodiments, wherein L^1 has from 1 to 4 carbon atoms.

Objects and advantages of this disclosure are further illustrated by the following non-limiting examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this disclosure.

EXAMPLES

Unless otherwise noted, all parts, percentages, ratios, etc. in the Examples and the rest of the specification are by weight. Unless otherwise indicated, materials used in the examples may be obtained from Sigma-Aldrich Company, LLC, Saint Louis, Missouri, or other general chemical suppliers, and/or may be made according to known methods.

Preparation of Oligomeric Hexafluoropropylene Oxide Iodide $CF_3CF_2CF_2O[CF(CF_3)CF_2O]_nCFICF_3$, n = 4-8 ($HFPOI_{1400}$),

A 500-ml three neck round bottom flask equipped with a mechanical stirrer and nitrogen bubbler was charged with 25 g (0.19 mol) of lithium iodide and 220 g (0.17) mol of oligomeric HFPO acid fluoride, $CF_3CF_2CF_2O[CF(CF_3)CF_2O]_nCF(CF_3)C(=O)F$, n=4-8, Mn (1300 g/mol) prepared generally as described in U.S. Pat. No. 3,322,826 (Moore) and heated to 186°C with an oil bath. At 180°C the mixture turned purple and decarbonylation occurred. The liquid was decanted from the solid and vacuum distilled from a head temperature of 97-210°C at 1 mm. Oligomeric iodide C_3F_7O-$[CF(CF_3)CF_2O]_nCFICF_3$, n = 4-8 having molecular weight M_n = 1400 g/mol ($HFPOI_{1400}$) was isolated (212 g yield).

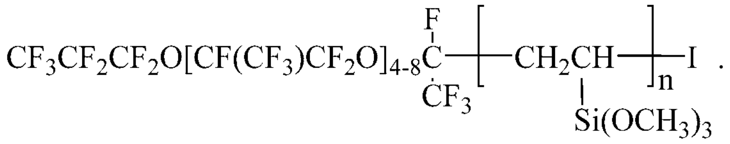
Preparation of Oligomeric Hexafluoropropylene Oxide Iodide $CF_3CF_2CF_2O[CF(CF_3)CF_2O]_nCFICF_3$, n = 30-40 ($HFPOI_{6000}$)

A 1-L three neck round bottom flask equipped with a mechanical stirrer and nitrogen bubbler was charged with 100 g (0.02 mol) oligomeric HFPO acid, $CF_3CF_2CF_2O[CF(CF_3)CF_2O]_nCF(CF_3)CO_2H$, n=30-40 obtained as KRYTOX 157FSH from E.I. du Pont de Nemours and Co., Wilmington, Delaware, 100 g of FLUORINERT ELECTRONIC LIQUID FC-770 from 3M Company (Saint Paul, Minnesota) and converted to the acid chloride by reaction with 7.5 g (0.06 mol) of thionyl chloride and 1 g of N,N-dimethylformamide at 82°C over two hours. The reaction resulted in the acid chloride, and was exchanged to the acid fluoride by the addition of 5 g of potassium fluoride (0.08 mol) and heating for 24 hours at 98°C. The reaction was followed by FTIR as the C(=O)Cl 1808 cm^{-1} functional group was converted to C(=O)F 1883cm^{-1}. Conversion to the iodide was done by the addition of 11 g (0.08 mol) of lithium iodide and distilling out the FC-770 before decarbonylation to a temperature of 240°C for ten minutes. To the reaction product mixture was added 200 g FC770 and 10 g of filtering agent and filtered. The solution was vacuum stripped to obtain 78.5 g of oligomeric iodide

$CF_3CF_2CF_2O[CF(CF_3)CF_2O]_nCF(CF_3)CF_2I$, n = 30-40 ($HFPOI_{6100}$) in 80% yield, molecular weight $M_n = 6100$ g/mol.

EXAMPLE 1

This example describes the preparation of POLYMER 1,



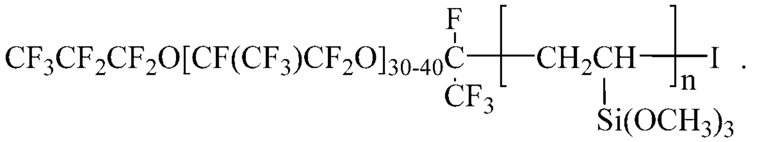
$$CF_3CF_2CF_2O[CF(CF_3)CF_2O]_{4\text{-}8}\underset{CF_3}{\overset{F}{C}}\left[CH_2\underset{Si(OCH_3)_3}{CH}\right]_n I\ .$$

Vinyltrimethoxysilane (50 g, 0.34 mol), 2.5 g of $HFPOI_{1400}$ ($M_n = 1400$ g/mol, 0.0014 mol), and 1.1 of dicumyl peroxide were charged into a 250 ml Parr pressure reactor. The reactor was purged with nitrogen for 2 minutes, and then heated at 150°C for 5 hours. A viscous liquid was thus prepared (POLYMER 1).

Coating preparation: 0.2 g of POLYMER 1, 9.8 g of isopropyl alcohol, and 0.03 g of 5% aqueous hydrochloric acid were mixed in a vial. The resultant solution was coated onto a glass slide using a No. 12 Meyer rod (27.4 microns nominal wet thickness, RD Specialties, Webster, New York). The slide was cured at 120°C for 10 minutes in an oven resulting in a hydrophobic coating. Contact Angles: advancing water = 114°, receding water = 112°, advancing hexadecane = 76°, receding hexadecane = 63°.

EXAMPLE 2

This example describes the preparation of POLYMER 2,

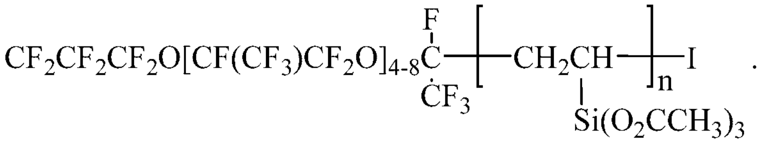


$$CF_3CF_2CF_2O[CF(CF_3)CF_2O]_{30\text{-}40}\underset{CF_3}{\overset{F}{C}}\left[CH_2\underset{Si(OCH_3)_3}{CH}\right]_n I\ .$$

Vinyltrimethoxysilane (44 g, 0.30 mol), 15 g of $HFPOI_{6100}$ ($M_n = 6100$ g/mol, 0.0025 mol), 19 g of NOVEC ENGINEERED FLUID HFE-7200 from 3M Company, and 0.36 of dicumyl peroxide were charged into a 50 ml Parr pressure reactor. The reactor was purged with nitrogen for 2 minutes, and then heated at 132°C for 5 hours. After evaporation of the HFE-7200, a viscous liquid was isolated (POLYMER 2).

EXAMPLE 3

This example describes the preparation of POLYMER 3,

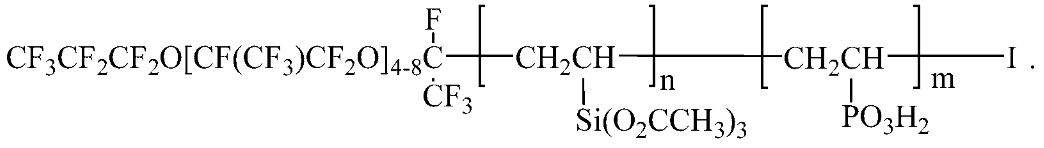


$$CF_2CF_2CF_2O[CF(CF_3)CF_2O]_{4\text{-}8}\underset{CF_3}{\overset{F}{C}}\left[CH_2\underset{Si(O_2CCH_3)_3}{CH}\right]_n I\ .$$

Vinyltriacetoxysilane (50 g, 0.22 mol), 2.5 g of $HFPOI_{1400}$ (0.0018 mol), and 1.1 of dicumyl peroxide were charged into a 250 ml Parr pressure reactor. The reactor was purged with nitrogen for 2 minute, and then heated at 150°C for 5 hours, after which a light viscous liquid was obtained (POLYMER 3).

EXAMPLE 4

This example describes the preparation of POLYMER 4,



$$CF_3CF_2CF_2O[CF(CF_3)CF_2O]_{4\text{-}8}\underset{CF_3}{\overset{F}{C}}-\left[CH_2\underset{Si(O_2CCH_3)_3}{CH}\right]_n-\left[CH_2\underset{PO_3H_2}{CH}\right]_m-I\ .$$

Vinyltrimethoxysilane (50 g, 0.34 mol), 2.5 g (0.23 mol) of vinylphosphoric acid, 2.5 g of $HFPOI_{1400}$ (0.0018 mol), and 1.1 of dicumyl peroxide were charged into a 250 ml Parr pressure reactor. The reactor was purged with nitrogen for 2 minutes, and then heated at 150°C for 5 hours, resulting in a viscous liquid (POLYMER 4).

Coating preparation: 0.2 g of POLYMER 4, 9.8 g of isopropyl alcohol, and 0.03 g of 5% aqueous hydrochloric acid were mixed in a vial. The resultant solution was coated onto an aluminum plate using a No. 12 Meyer rod (27.4 microns nominal wet thickness). The slide was cured at 120°C for 10 minutes in an oven resulting in a hydrophobic coating. Contact Angles: advancing water = 114°, receding water = 106°, advancing hexadecane = 75°, receding hexadecane = 59°.

All cited references, patents, and patent applications in the above application for letters patent are herein incorporated by reference in their entirety in a consistent manner. In the event of inconsistencies or contradictions between portions of the incorporated references and this application, the information in the preceding description shall control. The preceding description, given in order to enable one of ordinary skill in the art to practice the claimed disclosure, is not to be construed as limiting the scope of the disclosure, which is defined by the claims and all equivalents thereto.

What is claimed is:

1. A silicon-containing polymer represented by the general formula:

$$A\text{-}[Q]_x\text{-}[Z]_y\text{-}I$$

wherein:

A represents a monovalent group represented by the formula

$$R_f^2\,R_f^1R_h-$$

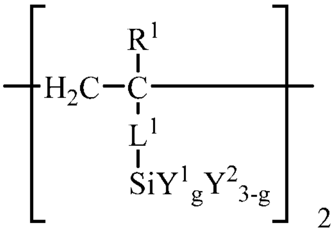
wherein

R_h represents a covalent bond or an alkylene group having from 1 to 18 carbon atoms,

R_f^1 represents a covalent bond or a divalent group selected from the group consisting of $-(CF_2O)_a-$, $-(CF_2CF_2O)_b-$, $-(CF_2CF_2CF_2O)_c-$, $-(CF_2CF_2CF_2CF_2O)_d-$, $-(CF_2CF(CF_3)O)_e-$, and combinations thereof, wherein a, b, c, d, and e represent integers in the range of from 0 to 130, and wherein $1 \leq a + b + c + d + e \leq 130$, and

R_f^2 represents a perfluoroalkyl or perfluoroalkoxy group having from 1 to 8 carbon atoms;

each Q independently represents at least one divalent monomeric unit represented by the formula



$$\left[-H_2C-\underset{\underset{SiY^1_gY^2_{3-g}}{|}}{\underset{L^1}{\underset{|}{\overset{R^1}{\overset{|}{C}}}}}- \right]_2$$

wherein

R^1 represents H or methyl,

L^1 represents a covalent bond or a divalent aliphatic group having from 1 to 10 carbon atoms,

each Y^1 independently represents a hydrocarbyl group having from 1 to 6 carbon atoms,

each Y^2 independently represents a hydrolyzable group, and

g is 0, 1, or 2; and

each Z independently represents a divalent residue of a non-halogenated free-radically polymerizable ethylenically-unsaturated monomer having from 2 to 18 carbons,

wherein x represents an integer greater than or equal to 3, and y represents an integer greater than or equal to zero.

2. The silicon-containing polymer of claim 1, wherein R_h has from 1 to 4 carbon atoms.

3. The silicon-containing polymer of claim 1, wherein R_f^1 represents a covalent bond.

4. The silicon-containing polymer of claim 1, wherein R_f^2 has from 1 to 4 carbon atoms.

5. The silicon-containing polymer of claim 1, wherein L^1 has from 1 to 4 carbon atoms.

6. The silicon-containing polymer of claim 1, wherein each Z independently represents a divalent residue of a non-halogenated free-radically polymerizable ethylenically-unsaturated monomer having from 2 to 8 carbons.

7. A method of making a silicon-containing polymer, the method comprising:
   - i) combining components comprising:
     - a) a first molar amount of an iodocompound represented by the formula

$$R_f^2 R_f^1 R_h\text{-I}$$

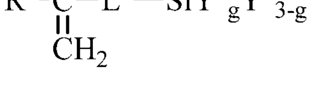
wherein

R_h represents a covalent bond or an alkylene group having from 1 to 18,

R_f^1 represents a covalent bond or a divalent group selected from the group consisting of $-(CF_2O)_a-$, $-(CF_2CF_2O)_b-$, $-(CF_2CF_2CF_2O)_c-$, $-(CF_2CF_2CF_2CF_2O)_d-$, $-(CF_2CF(CF_3)O)_e-$, and combinations thereof, wherein a, b, c, d, and e represent integers in the range of from 0 to 130, and wherein $1 \leq a + b + c + d + e \leq 130$, and

R_f^2 is a perfluoroalkyl or perfluoroalkoxy group having from 1 to 8 carbon atoms;

     - b) a second molar amount of a free-radically polymerizable silane compound represented by the formula



$$R^1\text{-}\underset{\underset{\displaystyle CH_2}{\|}}{C}\text{—}L^1\text{—}SiY^1{}_gY^2{}_{3\text{-}g}$$

wherein

R^1 represents H or methyl,

L^1 represents a covalent bond or a divalent aliphatic group having from 1 to 10 carbon atoms,

each Y^1 independently represents a hydrocarbyl group having from 1 to 6 carbon atoms,

each Y^2 independently represents a hydrolyzable group,

g is 0, 1, or 2; and

wherein the second molar amount is at least three times the first molar amount; and

c) a free-radical initiator; and

ii) free-radically interpolymerizing at least components a) and b) to provide the silicon-containing polymer.

8. The method of claim 7, wherein the components further comprise:

d) a non-halogenated free-radically polymerizable ethylenically-unsaturated monomer having from 2 to 18 carbons, and wherein step ii) comprises free-radically interpolymerizing at least components a), b), and c) to provide the silicon-containing polymer.

9. The method of claim 8, wherein the non-halogenated free-radically polymerizable ethylenically-unsaturated monomer is selected from the group consisting of N-vinylformamide, N-vinylacetamide, vinylphosphonic acid, 2-methylvinylphosphonic acid, acrylic acid, methacrylic acid, acrylic acid esters having from 4 to 15 carbon atoms, acrylic acid esters having from 5 to 16 carbon atoms, alpha olefins having from 2 to 18 carbon atoms, and combinations thereof.

10. The method of claim 8, wherein R_h has from 1 to 4 carbon atoms.

11. The method of claim 8, wherein R_f^1 represents a covalent bond.

12. The method of claim 8, wherein R_f^2 has from 1 to 4 carbon atoms.

13. The method of claim 8, wherein L^1 has from 1 to 4 carbon atoms.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/035472

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F230/08 C08F283/06 C09D143/04
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09D C08F C08G

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 343 526 A2 (DAIKIN IND LTD [JP]) 29 November 1989 (1989-11-29) examples 1-6 -----	1-9, 11-13
A	WO 2011/005443 A2 (3M INNOVATIVE PROPERTIES CO [US]) 13 January 2011 (2011-01-13) examples 9-12 -----	1-13
A	WO 2011/082063 A1 (3M INNOVATIVE PROPERTIES CO [US]; HANSEN RICHARD G [US]; GUERRA MIGUEL) 7 July 2011 (2011-07-07) the whole document -----	1-13
A	EP 1 607 427 A1 (WACKER CHEMIE GMBH [DE]) 21 December 2005 (2005-12-21) the whole document -----	1-13

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search 28 July 2015	Date of mailing of the international search report 04/08/2015
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Queste, Sébastien

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2015/035472

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