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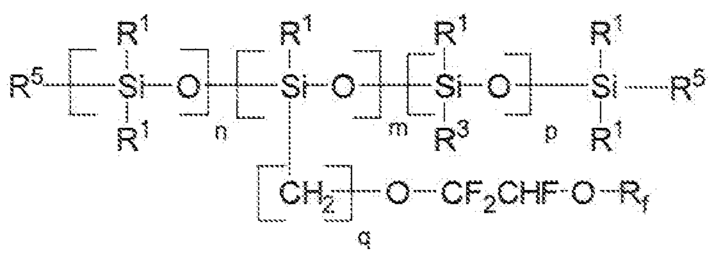
(54) **Title**: FLUOROALKYL SILICONE COMPOSITIONS



(I)

(57) **Abstract**: Provided is fluoroalkyl silicone of the formula (I): wherein each R^1 is independently an alkyl or aryl; R_f is a perfluoroalkyl group, optionally substituted by one or more in-chain --0-, · S- or— NR_f^1- heteroatorns, where R_f^1 is a perfluoroalkyl preferably a C_1-C_6 perfluoroalkyl; R^3 is -H, -OR^4; where R^4 is a C_1-C_4 alkyl n is 0 to 2000; m may be zero; p may be zero, n + m + p is at least one; q is at least 3; R^5 is H, alkyl, aryl-$(CH_2)_n$-O-CF_2CHF-O-R_f, or R^3; wherein the fluoroalkyl silicone has at least one fluorinated group of the formula $(CH_2)_q$-O-CF_2CHF-O-R_f.

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FLUOROALKYL SILICONE COMPOSITIONS

Background

Pressure sensitive adhesives (PSAs) are an important class of materials. Generally, PSAs adhere to a substrate with light pressure (e.g., finger pressure) and typically do not require any post-curing (e.g., heat or radiation) to achieve their maximum bond strength. A wide variety of PSA chemistries are available. PSAs, particularly silicone PSAs offer one or more of the following useful characteristics: adhesion to low surface energy (LSE) surfaces, quick adhesion with short dwell times, wide use temperature (i.e., performance at high and low temperature extremes), moisture resistance, weathering resistance (including resistance to ultraviolet (UV) radiation, oxidation, and humidity), reduced sensitivity to stress variations (e.g., mode, frequency and angle of applied stresses), gentleness to skin, and resistance to chemicals (e.g., solvents and plasticizers) and biological substances (e.g., mold and fungi).

Fluorinated release coatings are often used with PSAs, particularly silicone PSAs, to provide desired release properties. In some embodiments, the desired release force is no greater than 50 g/25 mm, e.g., no greater than 30 g/25 mm at 180 degrees peel angle and 230 cm/min (90 inches/min). However, the selection of fluorinated release coatings available to achieve the desired release performance is limited, particularly for wet-cast (e.g., solvent-based, water-based, and hot melt coated) PSAs. For example, few release materials provide stable, consistent, smooth release of an adhesive.

The most common fluorinated release coatings are fluorosilicone materials with pendent $R_fCH_2CH_2$- group made from R_f-$CH{=}CH_2$, wherein R_f is typically a CF_3- or a $CF_3CF_2CF_2CF_2$- group. However, commercially available fluorosilicone release coatings are typically more expensive. The reasons for high cost of commonly used fluorosilicone release materials are believed to related a) the lower reactivity of $R_fCH{=}CH_2$ to low yield hydrosilylation reactions, and b) the preparation from expensive R_f-I with two steps, i) addition to ethylene to form R_f-CH_2CH_2-I and ii) elimination of HI.

The present disclosure provides novel fluoroalkyl silicones that can be used as release materials or can also be blended with one or more additional low surface energy materials (e.g., fluoropolymers, polyacrylates with pendent R_f group, lower cost fluoroalkyl silicones and non-fluorinated silicones) while maintaining the desired low release characteristics of the instant fluorosilicone material. In addition, in some embodiments, high blend ratios of low surface energy materials may be used without detrimentally affecting the re-adhesion force of the adhesive after removal of the blended release materials comprising the present fluorosilicones.

Applicants have identified high reactive fluorinated alkenes for high yield of hydrosilylation products (from hydrosilicones) and subsequently providing novel fluoroalkyl silicones having similar or better performance to current products at reduced cost.

Summary

The present disclosure relates to novel fluoroalkyl silicones and use thereof as release materials. In another aspect, the present disclosure provides release liners comprising a substrate and the release material according to the present disclosure bonded to a major surface of the substrate. In another aspect, the present disclosure providers a crosslinked or uncrosslinked coating comprising the fluoroalkyl silicone release material.

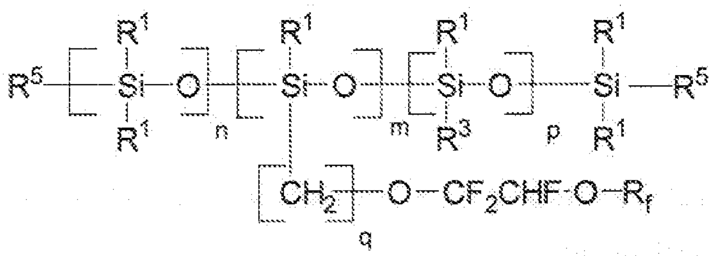
In yet another aspect, the present disclosure provides adhesive articles comprising an adhesive having a first major surface and a second major surface, wherein the first major surface of the adhesive is in contact with a release material according to the present disclosure. In some embodiments, the adhesive articles further comprise a first substrate (or backing) having a first major surface and a second major surface, wherein the release material is bonded to the first major surface of the first substrate. In some embodiments, the second major surface of the adhesive is in contact with the second major surface of the first substrate. In some embodiments, the second major surface of the adhesive is in contact with a second, independently selected release material bonded to the second major surface of the first substrate. In some embodiments, the adhesive articles further comprise a second substrate, wherein the second major surface of the adhesive is in contact with a major surface of the second substrate.

In some embodiments, the adhesive comprises a silicone adhesive. In some embodiments, the silicone adhesive comprises a poly(diorganosiloxane). In some embodiments, the silicone adhesive comprises a polydiorganosiloxane-polyurea block copolymer. In some embodiments, the silicone adhesive comprises a polydiorganosiloxane-polyoxamide copolymer. In some embodiments, the silicone adhesive further comprises a tackifier. In other embodiments, the adhesive comprises an acrylate adhesive.

In another aspect the present disclosure provides a method of making the fluoroalkyl silicones by the hydrosilylation reaction between a perfluoroalkyl alkenyl ether and a hydrosilicone.

Detailed Description

The present disclosure provides novel fluoroalkyl silicones of the formula:



I

wherein

each R^1 is independently an alkyl or aryl;

R_f is a perfluoroalkyl group, optionally substituted by one or more in-chain –O-, -S- or –NR_f^1- heteroatoms, where R_f^1 is a perfluoroalkyl, preferably a C_1-C_6 perfluoroalkyl;

R^3 is -H, -OR^4; where R^4 is a C_1-C_4 alkyl

n is 0 to 2000;

m may be zero, preferably at least 2;

p may be zero, preferably 10 to 2000;

n + m + p is at least one;

q is at least 3;

R^5 is H, alkyl, aryl, –$(CH_2)_n$-O-CF_2CHF-O-R_f, or R^3;

wherein the fluoroalkyl silicone has at least one R_f group of the formula –$(CH_2)_q$-O-CF_2CHF-O-R_f, preferably at least two R_f groups , either as R^5 and/or in the siloxane unit with the subscript m. In some embodiments p is at least one, preferably at least 2. R_f may contain 1 to 8, preferably 1 to 6, most preferably 3 to six, perfluorinated carbon atoms.

In some embodiment the ratio of m to p is from 100:0 to 5:95, preferably the ratio of m to p is from 50:50 to 20 : 80.

The disclosed fluoroalkyl silicones contain pendent or terminal $-(CH_2)_q$-O-CF_2CHF-O-R_f, group, which may further contain reactive hydrosilane groups (H-Si), alkoxysilane groups (R^4O-Si), alkyl silane groups (Si-R^1), either as R^5 and/or in the siloxane unit with the subscript p. In some embodiments the alkyl and alkoxy groups of the silicone can be long chains (e.g. C_{16}-C_{50}) , either as R^5 and/or in the siloxane unit with the subscript p.

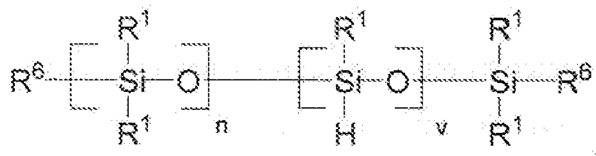
The novel fluoroalkyl silicone of Formula I may be prepared by hydrosilylation in the presence of a hydrosilylation catalyst, of a perfluoroalkyl alkenyl ether compound of the formula:

R_f-O-$CHFCF_2$-O-$(CH_2)_{q-2}CH{=}CH_2$, II

wherein

R_f is a perfluoroalkyl group, optionally substituted by one or more in-chain –O-, -S- or –NR_f^1- heteroatoms, where R_f^1 is a perfluoroalkyl;

with a hydrosilicone of the formula:



, III

where

each R^1 is independently an alkyl or aryl;

n is 0 to 2000; preferably at least 10;

v may be zero;

R^6 is H, alkyl or aryl;

with the proviso that the hydrosilicone contains at least one Si-H group, preferably at least two Si-H groups. Thus the silicone unit with the subscript "v" of Formula III may be at least one, preferably at least 2, and/or R^6 can be H.

All or a portion of the Si-H groups of the hydrosilicone may be reacted with the alkenyl ether of Formula II. In some embodiments, unreacted hydrosilyl (Si-H) groups may be converted to other useful functional groups, as described herein.

The fluoroalkyl silicone of Formula I have a M_w of at least 400, preferably at least 1000. In some embodiments, the M_w may be 2000 or greater. In some embodiments, the M_w may be limited to 1,000,000 or less; preferably limited to 500,000 or less. In some embodiments n, m and p are each greater than one and where the ratio of n to m is greater than one, preferably the ratio of n to m is greater than 10. In some embodiments, R^3 is H, and the ratio of m to p is from 100 : 0 to 5:95. In some embodiments, R^3 is OR^4 (prepared as described herein).

The fluoroalkyl silicone of Formula I is prepared, in part, with at least one hydrosilicone having a plurality of Si-H groups as represented by Formula III. Examples of useful Si-H group containing silicones include hydride terminated polydimethylsiloxanes having the formula $HMe_2SiO(SiMe_2O)_nSiMe_2H$ (CAS 70900-21-9); hydride terminated methylhydrosiloxane-dimethylsiloxane copolymers having the formula $HMe_2SiO(SiMe_2O)_n(SiMeHO)_qSiMe_2H$ (CAS 69013-23-6); trimethylsiloxane terminated polyethylhydrosiloxanes having the formula $Me_3SiO(SiMeHO)_qSiMe_3$ (CAS 63148-57-2); trimethylsiloxane terminated methylhydrosiloxane-dimethylsiloxane copolymers having the formula $Me_3SiO(SiMe_2O)_n(SiMeHO)_qSiMe_3$ (CAS 68037-59-2); triethylsiloxane terminated polyethylhydrosiloxanes having the formula $Et_3SiO(SiEtHO)_qSiEt_3$ (CAS 24979-95-1); hydride terminated poly(phenyl-dimethylhydrosiloxysiloxanes) having the formula $HSiMe_2O(SiPh(OSiMe_2H)O)_qSiMe_2H$; all commercially available from vendors such as, for example, Gelest, Inc. or Dow Corning Corp. with different molecular weights.

It will be appreciated that the R_f group of the fluoroalkyl compound of Formula II may be linear or branched or a combination thereof. The perfluoroalkyl alkenyl ether compounds of Formula II, in turn, may be prepared by reaction of a perfluoro(alkyl vinyl ether) compound of the formula:

R_f-O-CF=CF_2 IV

with a compound of the formula:

H-O-$(CH_2)_{q-2}$CH=CH_2, VI

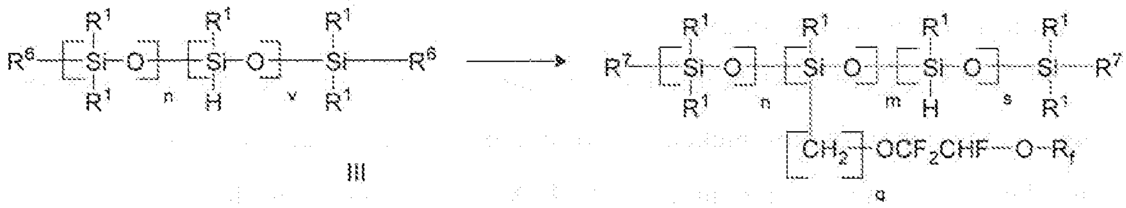
where q and R_f are as previously defined.

The reaction between compounds IV and VI is described in US 2005/0113609 (Furakawa et al.) incorporated herein by reference. The perfluoro(alkyl ether) of Formula IV, in turn, may be prepared by fluoride ion catalyzed addition of a perfluorinated acid fluoride to hexafluoropropylene oxide, followed by decarboxylation, according to the techniques describe in US 6255536 (Worm et al.), incorporated herein by reference. Perfluorinated acid fluoride may be obtained from hexafluoropropene oxide by reaction with MF or by electrochemical fluorination process as described in US6482979 (Hintzer et al.), incorporated herein by reference. Alternatively, the perfluorinated acid fluorides may be prepared by electrochemical fluorination of alcohols, acids or esters as known in the art.

Commercial available perfluorovinyl ethers of Formula IV are, for example, $CF_3OCF{=}CF_2$, $CF_3CF_2CF_2OCF{=}CF_2$ and $CF_3OCF_2CF_2CF_2OCF{=}CF_2$.

In the presence of the hydrosilylation catalyst, the compounds of Formula II are hydrosilated by the hydrosilicone of Formula III to produce the fluoroalkyl silicones of Formula I. All or a portion of the Si-H groups may undergo the hydrosilylation with the compound of Formula II. In the following Scheme I, subscription "q" represent the number of original in-chain hydrosilane units, m the number of those in-chain units substituted by hydrosilylation, and subscript s is the number of in-chain Si-H groups remaining. In addition, where R^6 is H, all or a portion of those terminal Si-H groups may undergo hydrosilylation to provide terminal R_f groups in the R^7. In some embodiments, all of the Si-H groups, whether terminal or in-chain, will be converted to $-(C_3H_6)$-OCF_2CHFOR_f groups. It will further be understood that hydrosilylation of the fluoroalkyl alkenyl ether of Formula II can yield two propyl isomers: propylene (Si-$(CH_2)_3$-) and isopropylene (Si-$CH(CH_3)CH_2$-) when q = 3. These two isomers are illustrated generically as $-C_3H_6-$ as part of $-(CH_2)_q-$.

Scheme I



III

V

where

each R^1 is independently an alkyl or aryl;

n is 0 to 2000;

m may be zero, preferably at least 1;

s may be zero;

R^6 is H, alkyl or aryl;

R^7 is H, alkyl, aryl or $-(C_3H_6)$-OCF_2CHF-O-R_f;

q is at least 3; and

R_f is a perfluoroalkyl group, optionally substituted by one or more in-chain –O-, -S- or –NR_f^1- heteroatoms, where R_f^1 is a perfluoroalkyl;

with the proviso that the starting material of Formula III contain at least one, preferably at least two Si-H groups, and with the proviso that the product of Formula V contains at least one, preferably at least two $-(C_3H_6)$-OCF_2CHFOR_f groups, whether in-chain represented by the units with subscript m, and/or one or both of the R^7 groups may be $-(C_3H_6)$-OCF_2CHFOR_f groups. Additionally, where there is partial hydrosilylation of the compounds of Formula II, the product of Scheme 1 will further contain in-chain Si-H groups, represented by the units with subscript s, and/or one or both of the R^7 groups may be H. It will be understood that the unit with the subscript "s" represents the propotion of Si-H groups not reacted by hydrosilation (i.e. m + s = v).

Alternatively, the fluoroalkyl silicones of the formula I can be made by hydrosilylation of perfluoroalkyl alkenyl ether compound of the formula II with either H-$Si(R^1)X_2$ to form R_f-O-$CHFCF_2$-O-$(CH_2)_q SiR^1X_2$, wherein X is a hydrolysable group (e.g. Cl, $CH_3C(O)O$- CH_3O- and CH_3CH_2O-), following hydrolysis condensation polymerization; or cyclic hydrosilane, -[O-SiR^{1}H]w-, to form cyclic silane substituted with R_f-O-CHFCF$_2$-O-(CH$_2$)$_q$-, wherein w is 3 or 4, following by ring opening polymerization, as known from reported literatures.

Regarding the hydrosilylation reaction, numerous patents teach the use of various complexes of cobalt, rhodium, nickel, palladium, or platinum as catalysts for hydrosilylation reactions. For example, U.S. 4,288,345 (Ashby et al) discloses as a catalyst for hydrosilylation reactions a platinum-siloxane complex. Additional platinum-siloxane complexes are disclosed as catalysts for hydrosilylation reactions in U.S. Pat. Nos. 3,715,334, 3,775,452, and 3,814,730 (Karstedt et al). U.S. 3,470,225 (Knorre et al) discloses production of organic silicon compounds by addition of a compound containing silicon- bonded hydrogen to organic compounds containing at least one non-aromatic double or triple carbon-to-carbon bond using a platinum compound of the empirical formula $PtX_2(RCOCR'COR'')_2$ wherein X is halogen, R is alkyl, R' is hydrogen or alkyl, and R" is alkyl or alkoxy.

The catalysts disclosed in the foregoing patents are characterized by their high catalytic activity. Other platinum complexes for accelerating the aforementioned thermally-activated addition reaction include: a platinacyclobutane complex having the formula $(PtCl_2C_3H_6)_2$ (U.S. 3,159,662, Ashby); a complex of a platinous salt and an olefin (U.S. 3,178,464, Pierpoint); a platinum-containing complex prepared by reacting chloroplatinic acid with an alcohol, ether, aldehyde, or mixtures thereof (U.S. 3,220,972, Lamoreaux); a platinum compound selected from trimethylplatinum iodide and hexamethyldiplatinum (U.S. 3,313,773, Lamoreaux); a hydrocarbyl or halohydrocarbyl nitrile-platinum (II) halide complex (U.S. 3,410,886, Joy); a hexamethyl-dipyridine-diplatinum iodide (U.S. 3,567,755, Seyfried et al); a platinum curing catalyst obtained from the reaction of chloroplatinic acid and a ketone having up to 15 carbon atoms (U.S. 3,814,731, Nitzsche et al); a platinum compound having the general formula $(R')PtX_2$ where R' is a cyclic hydrocarbon radical or substituted cyclic hydrocarbon radical having two aliphatic carbon-carbon double bonds, and X is a halogen or alkyl radical (U.S. 4,276,252, Kreis et al); platinum alkyne complexes (U.S. 4,603,215, Chandra et al.); platinum alkenylcyclohexene complexes (U.S. 4,699,813, Cavezzan); and a colloidal hydrosilylation catalyst provided by the reaction between a silicon hydride or a siloxane hydride and a platinum (0) or platinum (II) complex (U.S. 4,705,765, Lewis).

Although these platinum complexes and many others are useful as catalysts in processes for accelerating the hydrosilylation, processes for promoting the ultraviolet or visible radiation-activated addition reaction between these compounds may be preferable in some instances. Platinum complexes that can be used to initiate ultraviolet radiation-activated hydrosilylation reactions have been disclosed, e.g., platinum azo complexes (U.S. Pat. No. 4,670,531, Eckberg); (η^4-cyclooctadiene)diarylplatinum complexes (U.S. 4,530,879, Drahnak); and (η^5-cyclopentadienyl)trialkylplatinum complexes (U.S. 4,510,094, Drahnak). Other compositions that are curable by ultraviolet radiation include those described in U.S. 4,640,939 and 4,712,092 and in European Patent Application No. 0238033. U.S. 4,916,169 (Boardman et al) describes hydrosilylation reactions activated by visible radiation. U.S. 6,376,569 (Oxman et al.) describes a process for the actinic radiation-activated addition reaction of a compound containing silicon-bonded hydrogen with a compound containing aliphatic unsaturation, said addition being referred to as hydrosilylation, the improvement comprising using, as a platinum hydrosilylation catalyst, an (η^5-cyclopentadienyl)tri(σ-aliphatic)platinum complex, and, as a reaction accelerator, a free-radical photoinitiator capable of absorbing actinic radiation, i.e., light having a wavelength ranging from about 200 nm to about 800 nm. The process can also employ, as a sensitizer, a compound that absorbs actinic radiation, and that is capable of transferring energy to the aforementioned platinum complex or platinum complex/free-radical photoinitiator combination, such that the hydrosilylation reaction is initiated upon exposure to actinic radiation. The process is applicable both to the synthesis of low molecular weight compounds and to the curing of high molecular weight compounds, i.e., polymers.

Combinations of the hydrosilylation catalysts and photocatalysts and/or curing methods may also be used.

The catalyst is typically present in an amount that is effective to catalyze the hydrosilylation reaction. More typically, the catalyst is present in amounts sufficient to provide as little as one part of catalyst, or less, per million parts of the Si-H groups of the silicone polymer. On the other hand, amounts of the catalyst sufficient to provide as high as 1 to 10, or more, parts of catalyst per 1,000 parts of the Si-H groups of the silicone polymer may also be used. All or a portion of the Si-H groups may be functionalized with the perfluoroalkyl group.

In the presence of the hydrosilylation catalyst, hydrosilylation of hydrosilicone of Formula III with the compounds of Formula II readily produce the fluoroalkyl silicones of Formula I in high yield under mild conditions, such as at room temperature. The fluoroalkyl allyl ether of formula II demonstrated high reactivity to hydrosilicones, and the reaction may be controlled by slowly addition of hydrosilicone into the solution of fluoroalkyl allyl ether and catalyst - with or without solvent. In contrary, almost no product was observed from $C_4F_9CH=CH_2$ under similar conditions, indicating the significantly higher reactivity of perfluoroalkyl alkenyl ether in comparison with perfluoroalkylethylene.

Regarding the product of Formula V of Scheme I, the Si-H functional fluoroalkyl silicones may be used as a crosslinking agent, such as to thermally crosslink with silicones or fluorinated silicones having a plurality of ethylenically unsaturated bonds in a subsequent hydrosilylation reaction. In some embodiments, the fluoroalkyl silicone may be subsequently crosslinked by vinyl substituted silicones: i.e. silicone having a plurality of vinyl groups.

The non-fluorinated organopolysiloxane polymers (vinyl silicones) comprising an average of at least two ethylenically unsaturated organic groups may be formulated with the fluoroalkyl silicone of Formula V. In some embodiments, the non-fluorinated organopolysiloxane polymer has a vinyl equivalent weight of no greater than 60,000 grams per equivalent, e.g., no greater than 20,000, or even no greater than 10,000 grams per equivalent. In some embodiments, the non-fluorinated organopolysiloxane polymer has a vinyl equivalent weight of 2000 to 5000 grams per equivalent, e.g., 2000 to 4000 grams per equivalent, or even 2500 to 3500 grams per equivalent.

Exemplary non-fluorinated organopolysiloxane polymers include those comprising a triorganosiloxy endblocked polydiorganosiloxane polymer. In some embodiments, the non-fluorinated organopolysiloxane polymer comprises $R_2SiO_{2/2}$ units (i.e., "D" units) and $R_3SiO_{1/2}$ units (i.e., "M" units), wherein each R group independently represents a saturated or ethylenically unsaturated, substituted or unsubstituted hydrocarbon radical, provided that at least two R groups contain terminal ethylenic unsaturation.

The ethylenically unsaturated radicals are independently selected from the group consisting of the vinyl radical and higher alkenyl radicals represented by the formula -R'-CH=CH wherein R' denotes $-(CH_2)_w-$; and w has the value of 1-48.

In some embodiments, trace amounts of non-linear siloxane units, i.e., $SiO_{4/2}$ units (i.e., "Q" units) and $RSiO_{3/2}$, units (i.e., "T" units); may be present wherein R is as described above. In some embodiments, trace amounts of other silicon-bonded radicals, such as hydroxyl and alkoxyl may also be present.

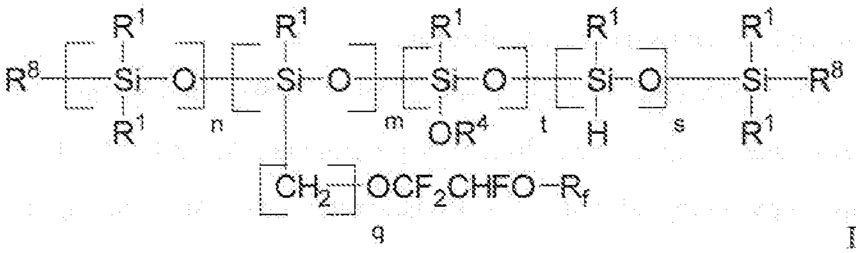
Exemplary non-fluorinated organopolysiloxane polymer comprising an average of at least two ethylenically unsaturated organic groups include those having the formula $M^{vi}D_xM^{vi}$, wherein M represents M units, D represents D units, the superscript "vi" indicates the presence of vinyl-functional groups, and x is the degree of polymerization. Commercially available $M^{vi}D_xM^{vi}$, non-fluorinated organopolysiloxane polymers include those available under the trade designations DMS-V from Gelest Inc. (e.g., DMS-V03, DMS-V05, DMS-V21, DMS-V22, DMS-V25, DMS-V35, and DMS-V41).

Examples of useful silicone having a plurality of vinyl groups include vinyl terminated polydimethylsiloxanes having the formula $H_2C{=}CHSiMe_2O(SiMe_2O)_nSiMe_2CH{=}CH_2$ (CAS 68083-19-2); vinyl terminated dimethylsiloxane-diphenylsiloxane copolymers having the formula $H_2C{=}CHSiMe_2O(SiMe_2O)_n(SiPh_2O)mSiMe_2CH{=}CH_2$ (CAS: 68951-96-2); vinyl terminated polyphenylmethylsiloxanes having the formula $H_2C{=}CHSiMePhO(SiMePhO)_nSiMePhCH{=}CH_2$ (CAS: 225927-21-9); vinyl-phenylmethyl terminated vinylphenylsiloxane-methylphenylsiloxane copolymers (CAS: 8027-82-1); vinyl terminated trifluoropropylmethylsiloxane-dimethylsiloxane copolymers having the formula $H_2C{=}CHSiMePhO(SiMe_2O)_n(SiMe(CH_2CH_2CF_3)O)_mSiMePhCH{=}CH_2$ (CAS: 68951-98-4); $H_2C{=}CHSiMe_2O\text{-}(SiMe_2O)_n(SiMe(CH_2CH_2CF_3)O)_mSiMe_2CH{=}CH_2$, $H_2C{=}CHSiMe_2O\text{-}(SiMe_2O)_n(SiMe(CH_2CH_2C_4F_9)O)_mSiMe_2CH{=}CH_2$, vinyl terminated dimethylsiloxane-diethylsiloxane copolymers having the formula $H_2C{=}CHSiMe_2O(SiMe_2O)_n(SiEt_2O)_nSiMe_2CH{=}CH_2$; trimethylsiloxy terminated vinylmethylsiloxane-dimethylsiloxane copolymers

$Me_3SiO(SiMe_2O)_n(SiMe(CH{=}CH_2)O)_mSiMe_3$ (CAS: 67762-94-1); vinyl terminated vinylmethylsiloxane-dimethylsiloxane copolymers having the formula $H_2C{=}CH(SiMe_2O)_n(SiMeCH{=}CH_2O)_mSiMe_2CH{=}CH_2$ (CAS: 68063-18-1); vinylmethylsiloxane homopolymers (cyclic and linear) having the formula $Me_3SiO(SiMe(CH{=}CH_2)O)_nSiMe3$; and vinyl T-structure polymers having the formula $MeSi[O(SiMe_2O)_mSiMe_2CH{=}CH_2]_3$; all commercially available from vendors such as, for example, Gelest, Inc., Morrisville, Pa. or Dow Corning Corp., Midland, Mich. Additional useful silicones having a plurality of vinyl groups include a vinyl-terminated fluorosilicone that is commercially available under the trade designations "SYL-OFF Q2-7785" and "SYL-OFF Q2-7786" from Dow Corning Corp.

In some embodiments, the Si-H group of Formula V, Scheme I may be converted to alkyl groups by subsequent hydrosilylation of an olefin of the formula: $CH_2{=}CHCH_2$-R^4, where R^4 is H or C_1-C_{50} alkyl in the presence of a hydrosilylation catalyst.

Again with regard to the silicone of Formula V, Scheme I, the Si-H groups may be converted to alkoxide groups (Si-H → Si-OR^4) and the alkoxy-functional fluoroalkyl silicone can be subsequently hydrolysis-condensation crosslinked by siloxane formation. Generally, the hydrides are reacted with an alcohol of the formula R^4-OH to convert all or a portion of the Si-H groups to Si-OR^4 groups, where R^4 is a C_1-C_{50} alkyl, preferably a short alkyl group for easy hydrolysis. Thus the present disclosure provides crosslinkable, fluoroalkyl silicones of the formula:



IV

wherein

n is 0 to 2000;,

m may be zero, preferably at least one;

s may be zero;

t may be zero, preferably at least one;

R^8 is H, alkyl or aryl, $-(CH_2)_q$-OCF_2CHFOR_f or OR^4, where R^4 is C_1-C_{50} alkyl;

q is at least 3; and

R_f is a perfluoroalkyl group, optionally substituted by one or more in-chain –O-, -S- or –NR_f^1- heteroatoms, where R_f^1 is a perfluoroalkyl;

with the proviso that the silicone contains at least one, preferably at least two Si-OR^4 groups and the silicone contains at least one –$(CH_2)_q$-O-CF_2CHF-O-R_f group. In Formula IV, the unit with the subscript t may be at least one, preferably at least two, and/or R^8 may be –OR^4. Further, if only a portion of the Si-H groups are converted to alkoxysilane groups (Si-OR^4), then s may be at least one, and/or a potion of R^8 may be H. Further, the unit with the subscript m may be at least one, and/or a portion of the R^8 groups may be –$(CH_2)_q$-O-CF_2CHF-O-R_f. In some embodiments R^4 is lower-chain alkyl (C_1-C_{16}, preferably C_1-C_4). In other embodiments R^4 is long-chain alkyl (C_{18}-C_{50})

Subsequently, these alkoxide groups (Si-OR^4) may be hydrolyzed by moisture, then crosslinked by dehydration, which can be catalyzed by a acid, or acid from a photoacid generator (PAG) initiated by photo irradiation, or a thermal acid generator initiated by heating to form siloxane Si-O-Si crosslinked polymers. The acid generator is preferably free of amines or ammonium compounds. The crosslinking of the alkoxide substituted silicones by photo irradiation in the presence of PAG is described in US 6129980 or WO 9840439 (Liu et al.), incorporated herein by reference.

The conversion of all or a portion of the Si-H groups in the silicone to alkoxide groups by reacting the hydropolysiloxane with an alcohol in the presence of at least one of a Pd(0) and Pt(0) catalyst according to the methods of U.S.S.N 61/739277(Rathore et al.) filed 19 Dec 2012 and incorporated herein by reference.

A wide variety of acid generating materials can be used in the practice of the invention to catalyze the moisture curing reaction, including onium salts such as sulfonium and iodonium salts. Activating the acid generating material liberates an acid that initiates and accelerates crosslinking of the moisture-curable composition through the formation of Si-O-Si crosslinks. Activation may be accomplished by irradiating the composition with, for example, ultraviolet, visible light, electron beam or microwave radiation. While heat may be used to activate the acid generating material, the compositions of the invention advantageously do not require this and thereby can avoid undesirable damage to heat sensitive substrates.

Although the acid generating material described above is preferred due to the controlled curability it provides, it has been found that condensation catalysts, such as strong organic acids, weak Lewis acids, weak organic bases and metal chelates can also be used in the preparation of the novel silicone pressure-sensitive adhesive. Another preferred class of condensation catalyst is the strong organic acids having pKa values of less than about 3 and the anhydrides and ammonium salts thereof described in U.S. Patent No. 5,286,815. Examples of useful strong organic acids and derivatives include trichloroacetic acid, cyanoacetic acid, malonic acid, nitroacetic acid, dichloroacetic acid, difluoroacetic acid, trichloroacetic anhydride, dichioroacetic anhydride, difluoroacetic arthydride, triethylammonium trichloroacetate, trimethylammonium trichloroacetate, and mixtures thereof.

The condensation catalyst or an acid generating material is used in amounts of about 0.5 to about 20 parts by weight, based on 100 parts by weight of the alkoxy functional silicone.

The fluoroalkyl silicone of Formula IV contains both Si-OR^4 and Si-H functional groups are dual curable, which may be controllably cured initially via Si-H with a vinyl silicone, then moisture or photo-acid cured from Si-OR^4 or vice versa.

The fluoroalkyl silicone release materials of Formula I can be blended with one or more additional low surface energy materials (e.g., a fluoropolymer or silicone) while maintaining the desired low release characteristics of the fluorosilicone material, even when the additional low surface energy material itself is not a release material. In addition, in some embodiments, high blend ratios may be used without detrimentally affecting the readhesion force of the adhesive after removal for the blended release materials of the present disclosure.

Exemplary low surface energy materials that may be blended with the fluoroalkyl silicone release polymer of Formula I include additional fluorosilicone polymers, including those described herein, as well as non-fluorinated silicones and fluoropolymers.

Fluoropolymers can be prepared from a wide variety of fluorinated ethylenes and non-fluorinated monomers. As used herein, the term "fluorinated" includes both perfluorinated and partially-fluorinated materials.

Generally, any known fluorosilicone release polymer may be used. The term "fluorosilicone" means a silicone material comprising at least some fluorine atoms on a pendent groups (i.e. fluoroalkyl). Exemplary fluorosilicone release coatings include release coating compositions derived from organopolysiloxanes having fluorine containing organic groups and alkenyl groups an organohydrogensiloxane crosslinking agent and a platinum-containing catalyst. Other fluorosilicone release coatings may be derived from, e.g., organopolysiloxanes having fluorine containing organic groups and silicon-bonded hydrogen groups, an alkenyl functional organopolysiloxane and a platinum-containing catalyst.

A number of useful commercially available fluorosilicone polymers are available from Dow Corning Corp. (Midland, Mich.) under the SYL-OFF and the SYL-OFF ADVANTAGE series of trade designations including, e.g., SYL-OFF Q2-7785 and SYL-OFF Q2-7786. These fluorosilicone polymers are particularly useful in forming release coating compositions when combined with a suitable crosslinking agent. One useful crosslinking agent is available under the SYL-OFF Q2-7560 trade designation from Dow Corning Corp. Other useful crosslinking agents are disclosed in U.S. Pat. Nos. 5,082,706 (Tangney) and 5,578,381 (Hamada et al.). Other fluorosilicone polymers are commercially available from General Electric Co. (Albany, N.Y.), Wacker Chemie (Germany), Akrosil (Menasha, Wis.), and Loparex (Willowbrook, Ill.). Other fluorosilicone polymers are available from Momentive (FSR2000), and Siliconature (Scotchpak 9741 and M117)

One class of fluoropolymers is based upon fluorinated olefinic monomers such as tetrafluoroethylene (TFE), hexafluoropropylene (HFP), vinyl fluoride (VF), vinylidene and fluoride (VDF). In some embodiments, the fluoroolefin-based fluoropolymers may be homopolymers or copolymers of fluorinated olefinic monomers. In some embodiments, the fluoroolefin-based fluoropolymers may be copolymers of one or more fluorinated olefinic monomers and one or more other monomers, including, e.g., non-fluorinated olefins such as ethylene, chlorinated olefins such as chlorotrifluoroethylene, and fluorinated vinyl ethers such as trifluoromethylvinylether.

In some embodiments, the fluoroolefin-based polymers may be amorphous fluoropolymers. As used herein, amorphous fluoropolymers are materials that exhibit essentially no crystallinity or possess no significant melting point as determined for example by differential scanning calorimetry (DSC). In some embodiments, the amorphous fluoropolymers are elastomeric. In some embodiments the elastomeric fluoropolymers may comprise, e.g., interpolymerized units derived from VDF, HFP, and, optionally, TFE monomers. Examples of such are commercially available from 3M Company under the trade names Dyneon™ Fluoroelastomer FC 2145 and FT 2430. Additional amorphous fluoropolymers include, e.g., VDF-chlorotrifluoroethylene copolymers, commercially available under the trade name Kel-F™ 3700, from 3M Company.

In some embodiments, the fluoroolefin-based polymers may be homopolymers and copolymers that do exhibit crystalline melting point. Exemplary crystalline fluoropolymers include those based on fluorinated monomers such as TFE or VDF such as polyvinylidene fluoride (PVDF), available commercially from 3M Company as Dyneon™ PVDF, or thermoplastic copolymers of TFE such as those based on the crystalline microstructure of TFE-HFP-VDF, e.g., those available from 3M under the trade name Dyneon™ Fluoroplastic THV™ 220.

In some embodiments, the fluoroolefin-based polymers may include PVDF-containing fluoroplastic materials having very low molar levels of HFP such as those sold under the trade name Dyneon™ PVDF 6010 or 3100, available from Dyneon LLC, of St. Paul, Minn.; and Kynar™ 740, 2800, 9301, available from Elf Atochem North America Inc.

A separate class of fluoropolymers useful in some embodiments of the present disclosure are fluoroacrylate polymers, which are based upon (meth)acrylates (i.e., acrylates and/or methacrylates) having pendant fluoroalkyl groups. Fluoroacrylate polymers derived from fluoroacrylate monomers and multi-(meth)acrylates such a polyethylene glycol diacrylate (PEGDA) or 1,6-hexanediol diacrylate (HDDA) will form nonlinear (e.g., branched and/or crosslinked) fluoropolymers. Fluoroacrylate polymers derived from fluoroacrylate monomers and mono-(meth)acrylates such as C_1-C_{50} acrylates (e.g., C_4-C_{20} acrylates such as butyl acrylate, isooctyl acrylate, 2-ethylhexyl acrylate, and octadecyl acrylate) form linear fluoropolymers.

Such fluoroacrylate monomers can be polymerized to yield a fluorinated acrylic polymer as described in US 7199197 (Caldwell et al.) and US 7297210 (Qui et al.). The fluoroacrylate monomers can also be copolymerized with one or more comonomers such as mono-(meth)acrylate monomers to produce linear fluoropolymers according to some embodiments of the present disclosure. In some embodiments, the comonomer may be an alkyl mono-(meth)acrylate. In some embodiments, the alkyl mono-(meth)acrylate is a C_1-C_{50}, e.g., a C_4 to C_{20}, alkyl mono-(meth)acrylate. Representative examples of useful alkyl mono-(meth)acrylates include methyl(meth)acrylate, butyl(meth)acrylate, isobutyl (meth)acrylate, hexyl(meth)acrylate, dodecyl(meth)acrylate, octadecyl(meth)acrylate, and 2-ethylhexyl(meth)acrylate.

The ratio of fluoroalkyl silicone release composition to fluoropolymer (e.g., linear fluoroacrylate polymer or fluoroolefinic polymer) can vary widely. For example, in some embodiments, the weight ratio of the fluoroalkyl silicone release polymer of Formula I to the linear fluoropolymer is no greater than 10:1, no greater than 5:1, or even no greater than 3:1. In some embodiments, it may be desirable to minimize the amount of the relatively expensive fluoroalkyl silicone release polymer of Formula I, while retaining the required release and readhesion properties. In some embodiments, the weight ratio of the fluoroalkyl silicone release polymer of Formula I to the linear fluoropolymer is no greater than 1:1, no greater than 1:5, no greater than 1:10, or even no greater than 1:20. For example, in some embodiments the weight ratio of the fluoroalkyl silicone release polymer of Formula I to the linear fluoropolymer is between 10:1 and 1:20, e.g., between 3:1 and 1:20, inclusive; between 2:1 and 1:10, inclusive (e.g., between 1:1 and 1:10, inclusive), or even between 2:1 and 1:3.

In other embodiments, the fluoroalkyl silicone of Formula I may be blended with non-fluorinated silicone polymers, including vinyl-substituted (described *supra*), hydrogen (Si-H) substituted silicone polymers, and non-functional silicone polymers. As previous described for the vinyl-substituted silicone polymers, the hydrogen-substituted and non-functional silicone polymers may comprise M, D, T and Q units. Vinyl-substituted and hydrogen-substituted (Si-H) silicone polymers are described in US 7279210 (Qiu et al.), incorporated herein by reference.

Coatings

The present disclosure further provides coating compositions comprising the fluoroalkyl silicone of Formula I in a suitable solvent. In some embodiments, the disclosure provides crosslinkable coating compositions comprising the fluoroalkyl silicone of Formula I and a crosslinking agent in a stable solvent. In other embodiments, the fluoroalkyl silicone of Formula IV, containing hydrolysable Si-OR^4 groups, is self-crosslinking by formation of siloxane bonds.

The term "coatable" or "coatable composition" means that the composition is soluble or dispersible in solvents or water and is substantially gel-free and, that it can be applied to a substrate using standard coating methods, and that it forms a film upon heating or curing. The coatable compositions of the invention can be used to impart release properties to a wide variety of substrates.

The coatable compositions are preferably diluted or dispersed in a liquid (for example, water and/or an organic solvent) before coating a substrate. Preferably, the coating compositions contain from about 5 to about 15 percent solids (more preferably, about 2 to about 10 percent), based upon the weight of the coating composition.

The coatable compositions can be applied to fibrous substrates (for example, woven, knit, and non-woven fabrics, textiles, carpets, leather, or paper) to impart water- and oil-repellency. The coatable compositions can be applied to a substrate (or articles comprising a substrate) by standard methods such as, for example, spraying, padding, dipping, roll coating, brushing, or exhaustion.

The composition can then be dried to remove any remaining water or solvent. Preferably, the coated composition is heated to a temperature between about 100°C. and about 175°C. The coatable compositions are useful as release coatings, and can be applied to surfaces requiring release properties from adhesives. Surprisingly, dried coatable compositions of the invention show significant solvent resistance. The coatable compositions can therefore be used as release coatings for solvent cast adhesives.

Substrates suitable for release coatings include, for example, paper, metal sheets, foils, non-woven fabrics, polyolefin coated paper, and films of thermoplastic resins such as polyesters, polyamides, polyolefins, polycarbonates, and polyvinyl chloride. Release coating compositions can be applied to suitable substrates by conventional coating techniques such as, for example, wire-wound rod, direct gravure, offset gravure, reverse roll, air-knife, and trailing blade coating. The resulting release coating compositions can provide effective release for a wide variety of pressure sensitive adhesives such as, for example, natural rubber based adhesives, silicone based adhesives, acrylic adhesives, and other synthetic film-forming elastomeric adhesives.

Examples

Materials:

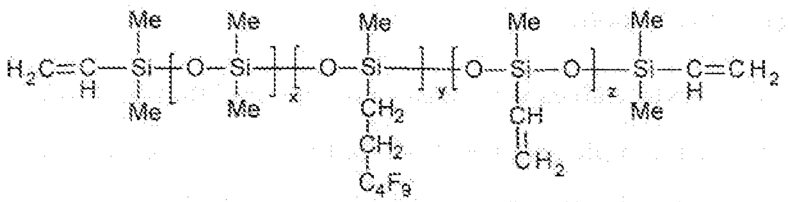
$C_3F_7OCHFCF_2OCH_2CH=CH_2$ (PE5) was made from $C_3F_7OCF=CF_2$ and $HOCH_2CH=CH_2$ by similar procedures described in US Patent Publication No. 2005/0113609, except that 1,2-dimethoxyethane (from GFS Chemicals, Inc.) was used as solvent.

1,2-dimethoxyethane was obtained from GFS Chemicals, Inc., Powell, OH.

"Syl-Off 7048" is a 100 weight percent solids silane crosslinker (said to comprise methylhydrogen cyclosiloxane, Viscosity- 30 centistokes) having H-Si equivalent weight of 60, obtained from Dow Corning Corporation, Midland, MI, under the trade designation "Syl-Off® 7048".

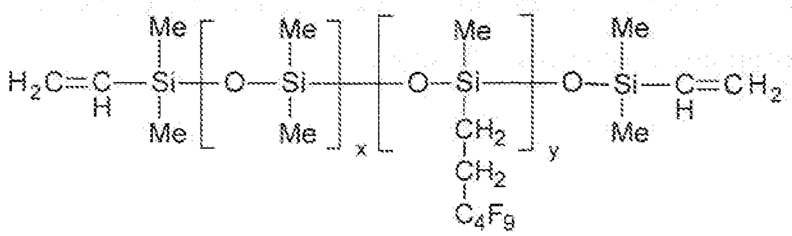
"Pt-Cat" (Karstedt catalyst) was bis(1,3-divinyl-1,1,3,3-tetrametyldisiloxane) platinum(0) (2 wt% platinum in xylene), purchased from Gelest, Inc., Morrisville, PA and kept in the dark before use.

"Q2-7785", is an 80 wt% solution of fluorosilicone polymer dispersed in heptane, obtained from Dow Corning Corporation, Midland, Michigan, under the trade designation of "Syl-Off® Q2-7785", having the following structure:



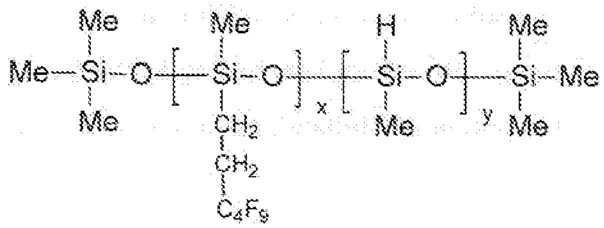
(X = 490; Y = 210; Z = 3)

"Q2-7786" is a 100 wt% fluorosilicone polymer obtained from Dow Corning Corporation, Midland, Michigan, under the trade designation of "Syl-Off® Q2-7786", having the following structure:



(X = Y =45)

"Q2-7560" is a 100 wt% crosslinker, obtained from Dow Corning Corporation, Midland, Michigan, under trade designation "Syl-Off® Q2-7560" having the following structure:



(X=12, Y=28)

Test Methods

Method for % Extractable Silicone Test

The silicone coat weight of a 3.69 centimeter diameter sample of coated substrate was determined by comparing samples of coated and uncoated substrates using an EDXRF spectrophotometer (obtained from Oxford Instruments, Elk Grove Village, IL under trade designation OXFORD LAB X3000).

Unreacted silicone extractables were measured on cured thin film formulations of Example and Comparative Example samples described below to ascertain the extent of silicone crosslinking immediately after the coatings were cured. The percent extractable silicone, (i.e., the unreacted silicone extractables), a measure of the extent of silicone cure on a release liner, was measured by the following method: The coated substrate sample was cured at then immersed in and shaken with methyl isobutyl ketone (MIBK) for 5 minutes, removed, and allowed to dry. The silicone coating weight was measured again.

Silicone extractables were attributed to the weight difference between the silicone coat weight before and after extraction with MIBK as a percent using the following formula:

Extractable Silicone% = (a - b) / a * 100%

Where a = initial coating weight (before extraction with MIBK); and
b = final coating weight (after extraction with MIBK).

Every number is the average of at least two tests.

Method for Release Test

Release Test:

An IMASS SP2000 slip peel tester (obtained from IMASS Inc., Accord, MA) was used for all release tests. Tests were performed at 21°C at 50% RH. A piece of 2.54 cm wide 3M Tape 610 (commercially available from 3M Company, St. Paul, MN under trade designation "**Scotch® Premium Cellophane Tape 610"**) was laminated to the sample coatings with a 2 kg rubber roller, then peeled at an angle of 180° at the speed of 2.29 m per minute in 5 seconds. Typically, 3 measurements were made and the mean reported.

Re-adhesion Test on Stainless Steel

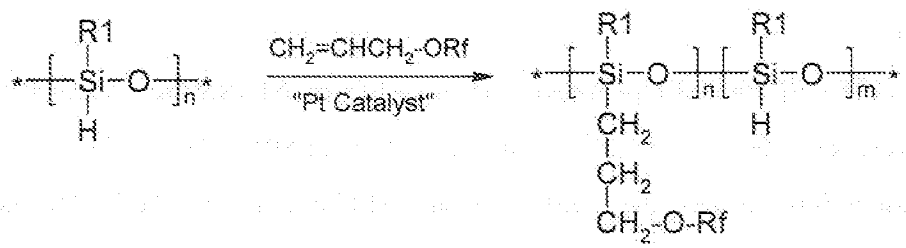
The 3M Tape 610 strips peeled in the Release test were laminated to a steel plate with a 2 kg rubber roller. An IMASS SP2000 slip peel tester was used to peel the tape at an angle of 180° at the speed of 30 cm per minute in 10 seconds. Typically, 3 measurements were made and the mean reported. When measuring re-adhesion for a sample, re-adhesion value of a pristine sample of 3M Tape 610 which was not contacted with release coatings was also determined (as an internal control) and the data for the control was reported along with the data for corresponding samples.

Method for Determining Contact Angle

Coated films prepared in Examples and Coated Examples described below were rinsed for 1 minute with hand agitation in an isopropanol (IPA) bath prior to water and hexadecane (HD) contact angles measurements. Measurements were made using a VCA-2500XE video contact angle analyzer (available from AST Products, Billerica, MA). Reported values are the average of at least 3 drops; each drop was measured twice. Drop volumes were 5 µL for static measurements and 1-3 µL for advancing and receding. For HD, only advancing and receding contact angles are reported because static and advancing values were found to be nearly equal.

Preparative Example 1 (PE1)

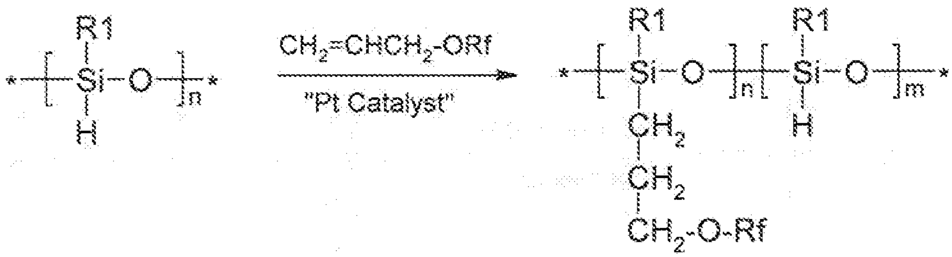
Preparation of $-[SiMe(C_3H_6OCHFCF_2OC_3F_7)n\text{-}O]\text{-}[SiMeH\text{-}O]m\text{-}$, $n/m = 33/67$:



Pt-Cat [40 ppm] and $C_3F_7OCF_2CHFOCH_2CH{=}CH_2$ (8.3 g) was mixed together in a 100 mL round bottom flask followed by dropwise addition of the Syl-Off 7048 (5 g) through a dropping funnel at room temperature. The addition of Syl-Off 7048 resulted in the evolution of heat after 20-60 seconds of stirring. The mixture was stirred for an additional 30 minutes followed by the analysis of the mixture by FT-IR (Si-H at ~2160 cm^{-1} reduced) and ^1H NMR (Si-H at 4.5 ppm reduced). To isolate the product, any unreacted/residual $C_3F_7OCF_2CHFOCH_2CH{=}CH_2$ was then evaporated using vacuum. Yield- 99% and the ratio of n:m was 33:67. Chemical shift of ^1H-NMR: 5.8-5.9 (broad split peak); 4.57 (-Si*H*); 3.9 (b); 1.76 (b), 1.47 (b), 1.02 (broad), 0.63 (broad); 0.24 (broad, -SiCH_3) ppm.

Preparative Example 2 (PE2)

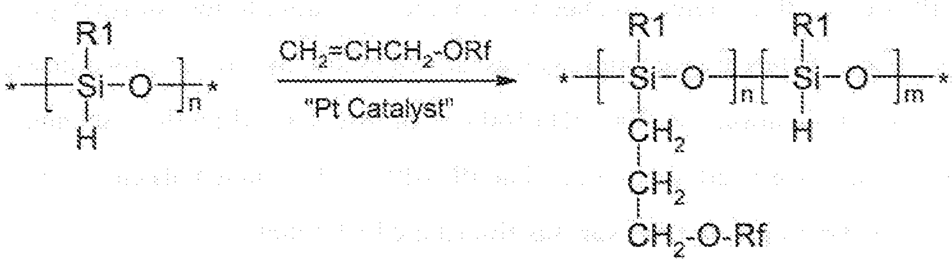
Preparation of –[SiMe($C_3H_6OCHFCF_2OC_3F_7$)n-O]-[SiMeH-O]m-, n/m = 100/0:



PE2 was prepared in the same manner as PE1 except that Pt-Cat [40 ppm] and $C_3F_7OCF_2CHFOCH_2CH{=}CH_2$ (28 g) was mixed together in a 100 mL round bottom flask followed by drop wise addition of the Syl-Off 7048 (5 g) through a dropping funnel at room temperature. Yield- 99% and the ratio of n:m is 100:0. Chemical shift of ^{1}H-NMR: 5.8-5.9 (broad split peak); 3.9 (b); 1.76 (b), 1.47 (b), 1.02 (broad), 0.63 (broad); 0.24 (broad, -SiCH_3) ppm.

Preparative Example 3 (PE3)

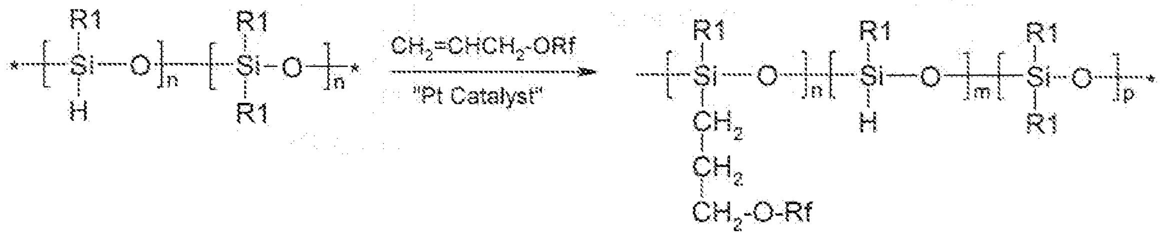
Preparation of –[SiMe($C_3H_6OCHFCF_2OC_3F_7$)n-O]-[SiMeH-O]m-, n/m = 33/67:



PE3 was prepared in the same manner as PE1 except that Pt-Cat [40 ppm] and $C_3F_7OCF_2CHFOCH_2CH{=}CH_2$ (16 g) was mixed together in a 100 mL round bottom flask followed by drop wise addition of the Syl-Off 7048 (5 g) through a dropping funnel at room temperature. Yield- 99% and the ratio of n:m is 67:33. Chemical shift of ^{1}H-NMR: 5.8-5.9 (broad split peak); 4.57 (-SiH); 3.9 (b); 1.76 (b), 1.47 (b), 1.02 (broad), 0.63 (broad); 0.24 (broad, -SiCH_3) ppm.

Preparative Example 4 (PE4)

Preparation of –[SiMe($C_3H_6OCHFCF_2OC_3F_7$)n-O]-[SiMeH-O]m-[SiMe$_2$-O]$_p$-, n/m/p = 0.3/0.37/0.33:



PE4 was prepared in the same manner as PE1 except that Pt-Cat [40 ppm] and $C_3F_7OCF_2CHFOCH_2CH{=}CH_2$ (5.4 g) was mixed together in a 100 mL round bottom flask followed by drop wise addition of the Syl-Off 7048 (5 g) through a dropping funnel at room temperature. Yield- 99% and the ratio of n/m/p = 0.30/0.37/0.33. Chemical shift of ^{1}H-NMR: 5.8-5.9 (broad split peak); 4.57 (-Si*H*); 3.9 (b); 1.76 (b), 1.47 (b), 1.02 (broad), 0.63 (broad); 0.24 (broad, -SiCH_3) ppm.

Preparative Examples 5-13 (PE5-PE13)

Preparation of fluorinated alkenes:

PE5-PE13 fluorinated alkenes were made according to the following reaction with different R_f and different space linkages as shown below by similar procedures described in US Patent Publication No. 2005/0113609, except that 1,2-dimethoxyethane (from GFS Chemicals, Inc.) was used as solvent. The PE5-PE13 fluorinated alkenes were consequently useful for making various fluorinated silicones.

$R_f\text{-}OCF{=}CF_2 + HO\text{-}(CH_2)x\text{-}CH{=}CH_2 \rightarrow R_f\text{-}OCHFCF_2\text{-}O\text{-}(CH_2)x\text{-}CH{=}CH_2$

PE5: $C_3F_7OCHFCF_2OCH_2CH{=}CH_2$, b.p. 112-115°C

PE6: $C_3F_7OCHFCF_2O(CH_2)_2CH{=}CH_2$, b.p. 136-139°C

PE7: $C_3F_7OCHFCF_2O(CH_2)_3CH{=}CH_2$, b.p. 70-72.5°C/39 mmHg

PE8: $C_3F_7OCHFCF_2O(CH_2)_4CH{=}CH_2$, b.p. 93-94°C/26 mmHg

PE9: $C_3F_7OCHFCF_2O(CH_2)_7CH{=}CH_2$, b.p. 95-97°C/5.3 mmHg

PE10: $C_3F_7OCHFCF_2O(CH_2)_9CH{=}CH_2$, b.p. 101-103°C/3.2 mmHg

PE11: $CF_3O(CF_2)_3OCHFCF_2O(CH_2)_2CH{=}CH_2$, b.p. 151-154°C

PE12: $CF_3O(CF_2)_3OCHFCF_2O(CH_2)_4CH{=}CH_2$, b.p. 92-94 °C/26 mmHg

PE13: $C_3F_7OCF(CF_3)CF_2OCHFCF_2O(CH_2)_2CH{=}CH_2$, b.p. 75-78°C/16mmHg

Examples 1- 19 (EX1-EX19) and Comparative Examples 1-12 (CE1-CE12)

EX1-EX19 coating solutions were prepared by first dissolving PE1, Q2-7785, and Q2-7786 thoroughly in a mixture of heptane/ethyl acetate (80:20 mixture by weight) to result in 10 or 20 wt % solutions then mixing PE1 solution with either Q2-7785 solution or Q2-7786 solution thoroughly. The concentration of the PE1/Q2-7785 mixture or PE1/Q2-7786 mixture in the coating solution was either 10 or 20% by weight.

CE1-CE12 coating solutions were prepared by first dissolving Q2-7560, Q2-7785, and Q2-7786 thoroughly in a mixture of heptane/ethyl acetate (80:20 mixture by weight) to result in 10 or 20 wt % solutions then mixing Q2-7560 solution with either Q2-7785 solution or Q2-7786 solution thoroughly. The concentration of the Q2-7560/Q2-7785 mixture or Q2-7560/Q2-7786 mixture in the coating solution was either 10 or 20% by weight.

The resulting EX1-EX19 and CE1-CE12 coating solutions were then coated on a 2-mil (0.058 millimeter (mm)) thick polyester terephthalate (PET) film (obtained from Mitsubishi Polyester Film, Greer, SC, under the trade designation "Hostaphan™ 3SAB", which has one side chemically treated or primed to improve the adhesion of silicone coatings) with different size of Mayer bars for different coating weights. All coatings were cured at 120 °C for 2 minutes in an oven equipped with solvent exhaust. Table 1, below, summarizes the compositions of the coating solutions as well as the size number of Meyer bars used for preparing the coatings.

Table 1

Example	Ratio of components in coating solution (parts by weight)				Solution concentration (wt.%)	Meyer bar used
	PE1	Q2-7560	Q2-7785	Q2-7786		
EX1	1	0	16	0	10	6
EX2	1	0	8	0	20	6
EX3	1	0	16	0	20	12
EX4	1	0	0	16	10	6
CE1	0	1	32	0	10	6
CE2	0	1	32	0	20	6
CE3	0	1	32	0	20	12
CE4	0	1	0	16	10	6
CE5	0	1	32	0	20	6
CE6	0	1	32	0	20	12
EX5	1	0	8	0	20	3
EX6	1	0	8	0	20	6
EX7	1	0	8	0	20	12
CE7	0	1	0	15	10	6
CE8	0	1	0	15	10	3
EX8	1	0	0	8	20	6
EX9	1	0	0	8	20	12
CE9	0	1	32	0	20	6
CE10	0	1	32	0	20	12

EX10	1	0	16	0	10	6
EX11	1	0	8	0	10	6
EX12	1	0	16	0	20	6
EX13	1	0	16	0	20	12
EX14	1	0	8	0	20	6
EX15	1	0	8	0	20	12
EX16	1	0	0	8	20	6
EX17	1	0	0	8	20	12
EX18	1	0	0	15	10	6
EX19	1	0	0	15	10	3
CE11	0	1	0	15	10	6
CE12	0	1	0	15	10	3

The % Extractable Silicone test was run for the EX1-4 and CE1-CE4 samples using the method described above. The results are summarized below in Table 2.

Table 2

Example	Initial coating weight (gsm)	After extraction coating weight (gsm)	% Extractable silicone
EX1	0.309	0.282	8.6
EX2	0.627	0.601	4.1
EX3	1.245	1.137	8.7
EX4	0.238	0.232	2.5
CE1	0.318	0.298	6.2
CE2	0.638	0.607	4.8
CE3	1.240	1.197	3.4
CE4	0.239	0.226	5.4

The water and hexadecane contact angle measurements were done for EX5-EX9 and CE5-CE8 samples using the methods described above. The results are summarized below in Table 3.

Table 3

Example	Water Contact Angle (degrees)						Hexadecane Contact Angles (degrees)					
	Advancing		Receding		Static		Advancing		Receding		Static	
	Left	Right	Left	Right	Left	Right	Left	Right	Left	Right	Left	Right
CE5	121.2	121.2	108.0	108.0	118.4	118.4	49.0	49.0	35.2	35.2	45.0	45.0
CE6	121.7	121.7	109.2	109.2	117.5	117.5	49.8	49.8	36.3	36.3	44.7	44.7
EX5	122.9	122.9	100.9	100.9	118.8	118.8	47.4	47.4	33.8	33.8	43.5	43.5
EX6	117.3	117.3	105.7	105.7	115.8	115.8	46.6	46.6	35.0	35.0	42.6	42.6
EX7	118.4	118.4	105.0	105.0	114.2	114.2	47.7	47.7	36.1	36.1	42.0	42.0
CE7	114.3	114.3	100.7	100.7	111.1	111.1	49.2	49.2	41.8	41.8	46.4	46.4
CE8	114.9	114.9	99.7	99.7	110.4	110.4	50.1	50.1	42.0	42.0	47.8	47.8
EX8	116.3	116.3	103.6	103.6	112.7	112.7	45.5	45.5	36.9	36.9	40.2	40.2
EX9	117.2	117.2	102.8	102.8	113.2	113.2	46.0	46.0	37.6	37.6	40.5	40.5

Release testing of EX10-EX19 and CE9-CE12 were done using the methods described above. The results are summarized below in Table 4.

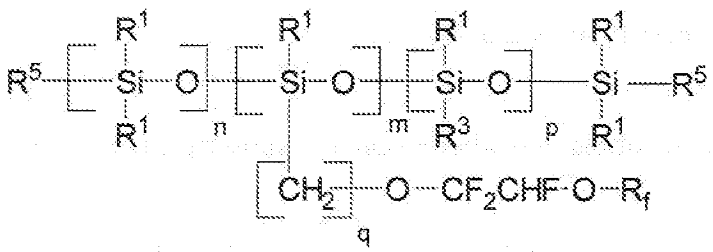
Table 4

Example	Coating weight (g)	Release (g/cm)	Readhesion (g/cm)	Release type
Control tape for CE9-CE10	N/A	N/M	344.17	N/M
CE9	0.638	2.68	319.8	Smooth
CE10	1.240	3.07	329.6	Smooth
Control tape for EX10-EX11	N/A	N/M	341.3	N/M
EX10	0.324	5.55	285.3	Smooth
EX11	0.309	4.45	313.1	Smooth
Control tape for EX12-EX17	N/A	N/M	331.3	N/M
EX12	0.631	4.88	290.2	Smooth
EX13	1.245	4.84	289.7	Smooth
EX14	0.627	3.38	304.9	Smooth
EX15	1.294	3.07	314.1	Smooth
EX16	0.613	1.54	281.2	Smooth
EX17	1.290	1.65	275.2	Smooth
Control tape for EX18-EX19 and CE11-CE12	N/A	N/M	262.0	N/M
EX18	N/M	1.30	143.5	Smooth
EX19	N/M	1.42	168.4	Smooth
CE11	N/M	1.46	187.5	Smooth
CE12	N/M	2.01	207.1	Smooth

N/A means not applicable, N/M means not measured.

What is claimed is:

1. A fluoroalkyl silicone of the formula:



wherein

each R^1 is independently an alkyl or aryl;

R_f is a perfluoroalkyl group, optionally substituted by one or more in-chain –O-, -S- or –NR_f^1- heteroatoms, where R_f^1 is a perfluoroalkyl, preferably a C_1-C_6 perfluoroalkyl;

R^3 is -H, -OR^4; where R^4 is a C_1-C_4 alkyl

n is 0 to 2000;

m may be zero;

p may be zero,

n + m + p is at least one;

q is at least 3;

R^5 is H, alkyl, aryl –$(CH_2)_n$-O-CF_2CHF-O-R_f, or R^3;

wherein the fluoroalkyl silicone has at least one fluorinated group of the formula –$(CH_2)_q$-O-CF_2CHF-O-R_f.

2. The fluoroalkysilane of claim 1 wherein R_f is a C_1-C_6 perfluorolkyl group.

3. The fluoroalkyl silicone of claim 1, wherein R_f is selected from -CF_3, -CF_2CF_3, -C_3F_7, -C_4F_9, -C_5F_{11}, -C_6F_{13}, $CF_3O(CF_2)_2CF_2$-, $(CF_3)_2N(CF_2)_2CF_2$-, -$CF_2CF(CF_3)_2$ and $C_3F_7OCF(CF_3)CF_2$-.

4. The fluoroalkyl silicone of claim 1 wherein R_f is of the formula C_rF_{2r+1}-$(O$-$C_sF_{2s})_t$-, where r is at least 1, s is at least 2, and t is from 1 to 10.

5. The fluoroalkyl silicone of claim 4 wherein each of subscripts r and s are 3 to 6.

6. The fluoroalkyl silicone of claim 1 wherein R_f is of the formula $C_rF_{2r+1}N(C_rF_{2r+1})$-$C_sF_{2s}$-, where r is at least 1, and s is at least 2.

7. The fluoroalkyl silicone of claim 6 wherein each of subscripts r, and s are 3 to 6.

8. The fluoroalkyl silicone of any of the previous claims where the ratio of m to p is from 100 : 0 to 5:95.

9. The fluoroalkyl silicone of any of the previous claims where the ratio of m to p is from 50:50 to 20:80.

10. The fluoroalkyl silicone of any of the previous claims having a M_w of at least 400.

11. The fluoroalkyl silicone of any of the previous claims wherein m is at least 2.

12. The fluoroalkyl silicone of any of the previous claims wherein R^5 is $-(CH_2)_q$-O-CF_2CHF-O-R_f where q is at least 3 and R_f is a perfluoroalkyl group, optionally substituted by one or more in-chain –O-, -S- or –NR_f^1- heteroatoms.

13. The fluoroalkyl silicone of any of claims 1 to 12 wherein p is at least 1 and R^3 is H.

14. The fluoroalkyl silicone of any of claims 1 to 12 wherein p is at least 1 and R^3 is –O-R^4, where R^4 is C_1-C_4 alkyl.

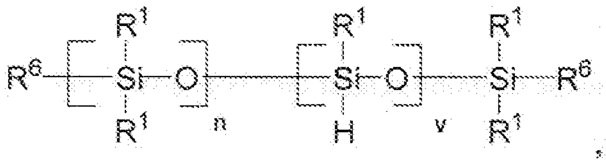
15. The fluoroalkyl silicone of any of the previous claims wherein p is 10 to 2000.

16. A method of making the fluoroalkyl silicone of claim 1, comprising hydrosilylation of a perfluoroalkyl alkenyl ether of the formula:

R_f-O-$CHFCF_2$-O-$(CH_2)_{q-2}CH{=}CH_2$, wherein

R_f is a perfluoroalkyl group, optionally substituted by one or more in-chain –O-, -S- or –NR_f^1- heteroatoms, where R_f^1 is a perfluoroalkyl;

with a with a hydrosilicone of the formula:



, where

each R^1 is independently an alkyl or aryl;

n is 0 to 2000; and

v may be zero;

R^6 is H, alkyl, or aryl,

said hydrosilylation in the presence of a hydrosilylation catalyst;

with the proviso that the hydrosilicone contains at least one Si-H group.

17. The method of claim 16 wherein the perfluoroalkyl alkenyl ether is prepared by reaction of a perfluoro(vinyl ether) of the formula:

R_f-O-CF=CF_2 with a compound of the formula:

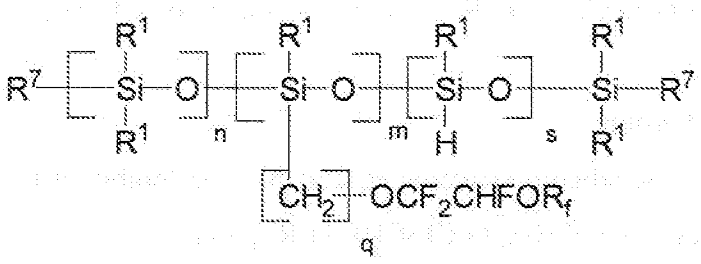
H-O-$(CH_2)_{q-2}$CH=CH_2,

q is at least 3; and

R_f is a perfluoroalkyl group;

in the presence of a base catalyst.

18. The method of claim 16 wherein the hydrosilylation product is of the formula:



where

R^1 is independently an alkyl or aryl

n is 0 to 2000;

m may be zero when R^7 is -$CH_2)_q$-O-CF_2CHF-O-R_f;

s may be zero when R^7 is H;

R^7 is H, R1 or $-CH_2)_q-O-CF_2CHF-O-R_f$

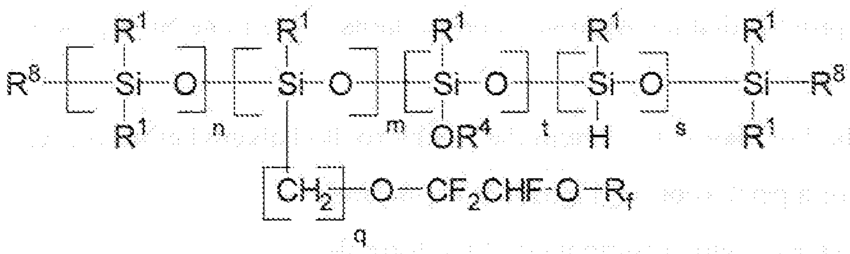
q is at least 3;

R_f is a perfluoroalkyl group;

with the proviso that the silicone contains at least one Si-H group and at least one $-(CH_2)_q-O-CF_2CHF-R_f$ group.

19. The method of claim 18 comprising the further step of alkoxylation of the Si-H groups with an alcohol of the formula R^4-OH, where R^4 is C_1-C_4 alkyl.

20. The product of claim 19 of the formula:



wherein

n is 0 to 2000;

q is at least 3;

m may be zero when R^8 is $-(CH_2)_q-O-CF_2CHF-O-R_f$;

s may be zero;

t may be zero when R^8 is OR^4;

R^8 is H, alkyl or aryl or OR^4, where R^4 is H or C_1-C_4 alkyl or $-(CH_2)_q-O-CF_2CHF-O-R_f$;

R_f is a perfluoroalkyl group;

with the proviso that the silicone contains at least one, preferably at least two Si-OR^4 groups and at least one $-CH_2)_q-O-CF_2CHF-O-R_f$ group.

21. A release liner comprising a backing and a layer of the cured coating of the fluoroalkyl silicone of any of claims 1-15 on at least one major surface of the backing.

22. The release liner of claim 21 wherein at least one of R^5 and R^3 of the fluoroalkyl silicone is $-OR^4$, where R^4 is C_1-C_4 alkyl.

23. The release liner of claim 22, wherein the fluoroalkyl silicone is moisture cured.

24. The release liner of claim 21, wherein at least one of R^5 and R^3 of the fluoroalkyl silicone is H, cured with a vinyl silicone.

25. The release liner of claim 24, wherein the fluoroalkyl silicone is hydrosilylation cured in the presence of a hydrosilylation catalyst.

26. The release liner of claim 24 wherein at least one of R^5 and R^3 of the fluoroalkyl silicone is H, and at least one of R^5 and R^3 of the fluoroalkyl silicone is -OR4 and is cured by hydrosilylation with a vinyl silicone , and moisture or photo-acid cured from Si-OR^4 .

27. The release liner of claim 22, wherein the fluoroalkyl silicone is photo irradiation cured in the presence of a photoacid generator.

28. An adhesive article comprising (I) a release liner comprising a backing and a cured release coating comprising the fluoroalkyl silicone any of claims 1-15 on at least one surface of the backing, and (II) a pressure-sensitive adhesive in contact with a surface of the release liner.

29. The adhesive article of claim 28, further comprising a second backing adhered to the adhesive surface on the opposite surface of the release liner.

30. The adhesive article according to any one of claims 28 to 29, wherein the adhesive comprises a silicone adhesive.

31. The adhesive article according to any one of claims 28 to 29, wherein the adhesive comprises an acrylate adhesive.

32. A coatable release solution comprising the fluoroalkyl silicone of any of claims 1 to 15 and a solvent.

33. The coatable release solution of claim 32 further comprising a non-fluorinated organopolysiloxane polymer.

34. The coatable release solution of claim 32 further comprising a linear fluoropolymer.

35. The coatable release solution of claim 34 wherein the linear fluoropolymer is a fluoroalkyl acrylate polymer.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/058529

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G77/385 C08L83/08 C09J7/02
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)
C08G C08L C09J

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	US 2005/113609 A1 (FURUKAWA YUTAKA [JP]) 26 May 2005 (2005-05-26) cited in the application	1-3,16, 17
A	paragraphs [0064] - [0065]; examples 1-3	4-15, 18-35

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

☒ See patent family annex.

* Special categories of cited documents :

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 December 2014	12/12/2014

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2014/058529

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2005113609 A1	26-05-2005	NONE	