



(51) International Patent Classification:

C08G 77/42 (2006.01) *C08F* 290/14 (2006.01)
C08F 283/12 (2006.01) *C08L* 83/10 (2006.01)

(21) International Application Number:

PCT/US2014/020214

(22) International Filing Date:

4 March 2014 (04.03.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/862,611 6 August 2013 (06.08.2013) US

(71) Applicant: **DOW CORNING CORPORATION**
[US/US]; 2200 West Salzburg Road, Midland, MI 48686-0994 (US).

(72) Inventors: **SCHMIDT, Randall, Gene**; 813 Honeysuckle Circle, Midland, MI 48642 (US). **XU, Shengqing**; 3815 Aspen Way, Midland, MI 48642 (US).

(74) Agent: **BROWN, Catherine, U.**; Dow Corning Corporation, IP Department - CO1232, 2200 West Salzburg Road, Midland, MI 48686-0994 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,

DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report (Art. 21(3))

(54) Title: HYDROPHOBIC ORGANIC-SILICONE HYBRID POLYMERS AND METHODS FOR THEIR PREPARATION AND USE

(57) Abstract: A method of preparing a hydrophobic organic-silicone hybrid polymer having, per molecule, one or more reactive groups is disclosed. The method includes the steps of (1) combining ingredients including (a) a polyorganosiloxane having an average, per molecule, of one or more reactive groups, (b) a water insoluble, polymerizable, organic monomer, and optionally (c) an initiator to form a mixture; and (2) subjecting the mixture to polymerization conditions to form the hydrophobic organic-silicone hybrid polymer. The reaction product produced by the method includes the hydrophobic organic-silicone hybrid polymer.



HYDROPHOBIC ORGANIC-SILICONE HYBRID POLYMERS AND METHODS FOR THEIR PREPARATION AND USE

SUMMARY OF THE INVENTION

5 **[0001]** A method of preparing a hydrophobic organic-silicone hybrid polymer is disclosed. The method comprises preparing a mixture by combining ingredients comprising (a) 1wt% to 99 wt% of a polyorganosiloxane having an average, per molecule, of one or more reactive groups and (b) 1 wt% to 99 wt% of a water insoluble, polymerizable, organic monomer. The method further comprises subjecting the mixture to polymerization conditions to form the hydrophobic
10 organic-silicone hybrid polymer. The hydrophobic organic-silicone hybrid polymer has, per molecule, one or more reactive groups. The hydrophobic organic-silicone hybrid polymer may be combined with a catalyst and optionally other ingredients to form a composition. The composition may be reacted to form a solid article.

DETAILED DESCRIPTION

15 **[0002]** A method of preparing a hydrophobic organic-silicone hybrid polymer, which method comprises:

- (1) preparing a mixture by combining ingredients comprising
 - (a) a polyorganosiloxane having an average, per molecule, of one or more reactive groups,
 - 20 (b) a water insoluble, polymerizable, organic monomer, and
 - optionally (c) an initiator to form a mixture; and
- (2) subjecting the mixture to polymerization conditions to form the hydrophobic organic-silicone hybrid polymer, wherein the hydrophobic organic-silicone hybrid polymer has, per molecule, one or more reactive groups. When oxygen (O₂) is present before step (2), the
25 method may optionally further comprise removing oxygen before step (2). Without wishing to be bound by theory, it is thought that for reactions conducted in the presence of a free radical initiator, peroxide, and/or an azo-compound, performing the reaction in an inert atmosphere may prevent inhibition of the reaction by oxygen. This may be performed, for example, with a purge of one or more inert gases (*e.g.*, nitrogen or helium) for a sufficient period of time to
30 remove oxygen from the mixture, *e.g.*, > 10 minutes, so that the polymerization may be initiated and not be inhibited by oxygen.

[0003] In a first embodiment, the polymerizing in step (2) may be via a radical reaction mechanism. In this embodiment, ingredient (c) is optional. Some combinations of ingredients (a) and (b) will have reactive groups that allow the polymerizing in step (2) to occur via heating
35 or at room temperature of 25 °C, light exposure such as with ultraviolet (UV) or near UV light, irradiation, exposure to electrical energy, exposure to a magnetic field, or exposure to moisture.

Alternatively, ingredient (c) may be present and may be a radical initiator. The temperature for radical reaction will depend on various factors including whether ingredient (c) is present and the mechanism for initiation, however, temperature may be at, above, or below room temperature. Alternatively, temperature may range from 0 °C to 150 °C; alternatively 25 °C to 100 °C.

[0004] Alternatively, in a second embodiment, the polymerizing in step (2) may be via a step-growth polymerization mechanism. Step-growth polymerization includes polyaddition and polycondensation reaction mechanisms. In this embodiment, the reactive groups of ingredient (a) and/or reactive groups of ingredient (b) (which allow ingredient (b) to be polymerizable) may react via a polyaddition mechanism, polycondensation mechanism, or a combination thereof. The initiator selected for ingredient (c) in this embodiment will depend on various factors including the selection of reactive groups on ingredients (a) and/or (b). For example, in one polyaddition reaction mechanism the reactive groups are epoxy functional groups with hydroxy (-OH) functional groups or amine (-NH-) functional groups catalyzed by organofunctional tin compounds or amine compounds. In an alternative polyaddition reaction mechanism the reactive groups are isocyanate (-NCO) functional groups with hydroxy (-OH) functional groups or amine (-NH-) functional groups catalyzed by organofunctional tin compounds or amine compounds. In an alternative polyaddition mechanism (thiol-ene based Michael addition) the reactive groups are thiol (-SH) functional groups with (meth)acrylate ($\text{CH}_2=\text{C}(\text{H}/\text{Me})-\text{COO}-$) functional groups catalyzed by amines and phosphines (e.g., dimethylphenylphosphine, tris-(2-carboxyethyl) phosphine. In an alternative polyaddition mechanism, the reactive groups are azide ($-\text{N}_3$) functional groups with alkyne ($-\text{C}\equiv\text{C}$) functional group, which may occur as Huisgen cycloaddition by heat without any initiator (i.e., where ingredient (c) is absent), or this reaction may be catalyzed by compounds of copper (Cu) or ruthenium (Ru) or silver (Ag) as ingredient (c). Alternatively, in a polycondensation reaction mechanism, the functional groups may be silanol (-SiOH) with acyloxy such as acetoxy (-Si-OOC-R), or enoxy (-Si-OC(=CH₂)-R), or oxime (-Si-O-N=CRR'), or alkoxy (-Si-OR) or amine (-Si-NRR'), which is catalyzed by organic compounds of tin (Sn) or titanium (Ti) or bismuth (Bi). Some molecules may have combinations of two or more reactive groups. For example, an acrylate is both ester-functional and alkenyl-functional. Glycidoxo may be both ester-functional and epoxy-functional. In certain embodiments, ingredient (a) may contain one but not both functionalities. Alternatively, in certain embodiments ingredient (a) may contain both functionalities. In certain embodiments, ingredient (b) may contain one but not both functionalities. Alternatively, in certain embodiments ingredient (b) may contain both functionalities.

[0005] Alternatively, the hydrophobic organic-silicone hybrid polymer described herein may

be formed by 1) radical polymerization, 2) step-growth polymerization or 3) a combination of 1) and 2).

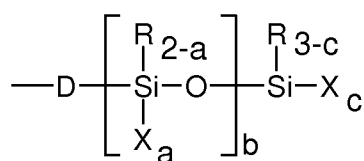
[0006] The method produces a hydrophobic organic-silicone hybrid polymer, which without wishing to be bound by theory is thought to be an organic- silicone interpenetrating network polymer. The hydrophobic organic-silicone hybrid polymer is reactive due to the presence of the one or more reactive groups present on the hydrophobic organic-silicone hybrid polymer produced by step (2). The one or more reactive groups present after step (2) may be the same as the reactive groups on ingredient (a), the same as reactive groups on ingredient (b) (*i.e.*, the groups that allow ingredient (b) to polymerize in step (2)), or both. The one or more reactive groups present after step (2) can come from a molar excess of the reactive groups on ingredient (a), a molar excess of reactive groups on ingredient (b) or both. Alternatively, an additional reactive group may be present on the hydrophobic organic-silicone hybrid polymer after step (2). The additional reactive group is different from the reactive groups on the polyorganosiloxane selected for ingredient (a) and the organic monomer selected for ingredient (b) used in the method to make the hydrophobic organic-silicone hybrid polymer, *i.e.*, the additional reactive groups may be such that they do not participate in the reaction to form the hydrophobic organic-silicone hybrid polymer, however, the additional reactive groups allow the hydrophobic organic-silicone hybrid polymer to react when formulated into a composition, described below.

[0007] The method described above may optionally further comprise adding (d) a solvent to the ingredients during step (1) and/or to the mixture after step (1). The method may optionally further comprise adding (e) a compatibilizer and/or ingredient (f) a crosslinker to the ingredients during step (1). The method may optionally further comprise adding (e) a compatibilizer to the ingredients during step (1). Ingredient (e) is optional when the reactive groups on ingredients (a) and (b) are radical polymerizable/reactive. Ingredient (e) may be added when the reactive groups on ingredients (a) and (b) are polycondensation or polyaddition reactive. The method may optionally further comprise adding (f) a crosslinker to the ingredients during step (1). Without wishing to be bound by theory, it is thought that adding ingredient (f) may be added, *e.g.*, when ingredient (a) has only one or two reactive groups per molecule, such as at the terminals; to branch the hydrophobic organic-silicone hybrid polymer and/or build a network structure of the hydrophobic organic-silicone hybrid polymer, because ingredient (f) may further entangle the polyorganosiloxane component supplied by ingredient (a) and the organic component supplied by ingredient (b).

[0008] Ingredient (a) is a polyorganosiloxane having an average, per molecule, of one or more reactive groups. In a first embodiment, the one or more reactive groups may be aliphatically unsaturated organic groups. Alternatively, ingredient (a) may have an average of two or more aliphatically unsaturated organic groups per molecule. The aliphatically

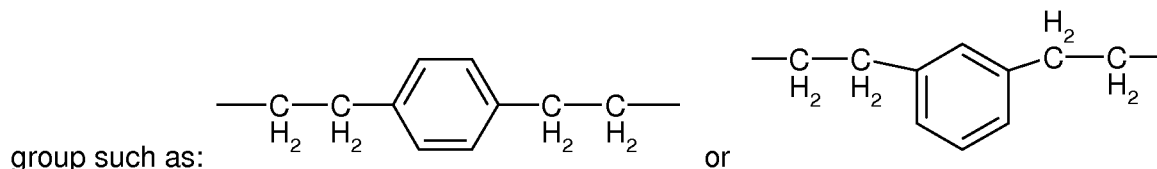
unsaturated organic groups may be alkenyl exemplified by, but not limited to, vinyl, allyl, propenyl, butenyl, and hexenyl. The unsaturated organic groups may be alkynyl groups exemplified by, but not limited to, ethynyl, propynyl, and butynyl. The unsaturated organic groups may be acrylate-functional groups such as acryloxyalkyl groups, or methacrylate functional groups such as methacryloxyalkyl groups, *e.g.*, methylmethacryloxy.

[0009] In an alternative embodiment, the one or more reactive groups are condensation and/or polyaddition reactive groups. The condensation and/or polyaddition reactive groups are exemplified by hydrogen atoms; halogen atoms; amido groups such as acetamido groups, benzamido groups, or methylacetamido groups; acyloxy groups such as acetoxy groups; hydrocarbonoxy groups such as alkoxy groups or alkenyloxy groups; amino groups; aminoxy groups; hydroxyl groups; mercapto groups; oximo groups; ketoximo groups; alkoxysilylhydrocarbylene groups; or a combination thereof. Alternatively, the condensation and/or polyaddition reactive groups are selected from amine groups, hydroxy groups, alcoholic groups, epoxy groups, isocyanate groups, and phenol groups. Alternatively, ingredient (a) may have the condensation and/or polyaddition reactive groups contained in groups of the formula:



, where each D independently represents an oxygen atom, a divalent organic group, a divalent silicone organic group, or a combination of a divalent hydrocarbon group and a divalent siloxane group; each X independently represents a condensation and/or polyaddition reactive group; each R independently represents a monovalent hydrocarbon group; subscript c represents 0, 1, 2, or 3; subscript a represents 0, 1, or 2; and subscript b has a value of 0 or greater, with the proviso that the sum of (a + c) is at least 1, such that, on average, at least one X is present in the formula. Alternatively, subscript b may have a value ranging from 0 to 18.

[0010] Alternatively, each D may be independently selected from an oxygen atom and a divalent hydrocarbon group. Alternatively, each D may be an oxygen atom. Alternatively, each D may be a divalent hydrocarbon group exemplified by an alkylene group such as ethylene, propylene, butylene, or hexylene; an arylene group such as phenylene, or an alkylarylene



Alternatively, an instance of D may be an oxygen atom while a different instance of D is a divalent hydrocarbon group.

[0011] Alternatively, each X may be a condensation and/or polyaddition reactive group independently selected from the group consisting of an alkoxy group; an alkenyloxy group; an amido group, such as an acetamido, a methylacetamido group, or benzamido group; an acyloxy group such as acetoxyl; an amino group; an aminoxyl group; a hydroxyl group; a mercapto group; an oximo group; a ketoximo group; and a halogen atom, or an organofunctional group containing a carboxylate, an isocyanate, an anhydride, or a metal atom. Alternatively, each X may be independently selected from the group consisting of an alkoxy group, an amido group, an acyloxy group, an amino group, a hydroxyl group, and an oximo group.

[0012] Alternatively, each R in the formula above may be independently selected from alkyl groups of 1 to 20 carbon atoms, aryl groups of 6 to 20 carbon atoms, and aralkyl groups of 7 to 20 carbon atoms.

[0013] Alternatively, subscript b may be 0.

[0014] Ingredient (a) may comprise the groups described by the formula above in an amount of the polyorganosiloxane ranging from 0.2 mol % to 10 mol %, alternatively 0.5 mol % to 5 mol %, alternatively 0.5 mol % to 2.0 mol %, alternatively 0.5 mol % to 1.5 mol %, and alternatively 0.6 mol % to 1.2 mol %.

[0015] The remaining silicon-bonded organic groups in the polyorganosiloxane for ingredient (a) may be monovalent organic groups free of aliphatic unsaturation (in the first embodiment) and/or free of condensation and/or polyaddition reactive groups (in the second embodiment). The silicon-bonded organic groups may be monovalent hydrocarbon groups or monovalent heteroatom containing groups such as halogenated hydrocarbon groups, or hydrocarbon groups containing one or more oxygen atoms, or hydrocarbon groups containing one or more nitrogen atoms. Examples of monovalent hydrocarbon groups include, but are not limited to, alkyl such as Me, Et, Pr, Bu, pentyl, hexyl, heptyl, octyl, decyl, dodecyl, undecyl, and octadecyl; cycloalkyl such as cyclopentyl and cyclohexyl; aryl such as Ph, tolyl, xylyl, and naphthyl; and aralkyl such as benzyl, 1-phenylethyl and 2-phenylethyl. Examples of monovalent halogenated hydrocarbon groups include, but are not limited to, chlorinated alkyl groups such as chloromethyl and chloropropyl groups; fluorinated alkyl groups such as fluoromethyl, 2-fluoropropyl, 3,3,3-trifluoropropyl, 4,4,4-trifluorobutyl, 4,4,4,3,3-pentafluorobutyl, 5,5,5,4,4,3,3-heptafluoropentyl, 6,6,6,5,5,4,4,3,3-nonafluorohexyl, and 8,8,8,7,7-pentafluorooctyl; chlorinated cycloalkyl groups such as 2,2-dichlorocyclopropyl, 2,3-dichlorocyclopentyl; and fluorinated cycloalkyl groups such as 2,2-difluorocyclopropyl, 2,3-difluorocyclobutyl, 3,4-difluorocyclohexyl, and 3,4-difluoro-5-methylcycloheptyl. Examples of other monovalent organic groups include, but are not limited to, hydrocarbon groups substituted with nitrogen atoms such as aminoalkyl and cyano-functional groups such as cyanoethyl and cyanopropyl. Examples of other

monovalent organic groups in (the first embodiment) include, but are not limited to, hydrocarbon groups substituted with oxygen atoms such as alkoxy and glycidoxymethyl.

[0016] In the first embodiment, ingredient (a) may comprise a polydiorganosiloxane of

Formula (I): $R^5_2R^4SiO(R^5_2SiO)_h(R^5R^4SiO)_iSiR^5_2R^4$,

5 Formula (II): $R^5_3SiO(R^5_2SiO)_f(R^5R^4SiO)_gSiR^5_3$, or a combination thereof.

[0017] In formulae (I) and (II), each R^5 is independently a hydrogen atom or a monovalent organic group free of aliphatic unsaturation and each R^4 is independently an aliphatically unsaturated organic group, exemplified by those described above. Subscript h may be 0 or a positive number. Alternatively, subscript h has an average value of at least 2. Alternatively

10 subscript h may have a value ranging from 2 to 2000. Subscript i may be 0 or a positive number. Alternatively, subscript i may have an average value ranging from 0 to 2000.

Subscript f may be 0 or a positive number. Alternatively, subscript f may have an average value ranging from 0 to 2000. Subscript g has an average value of at least 2. Alternatively

15 subscript g may have an average value ranging from 2 to 2000. Suitable monovalent organic groups for R^5 are as described above for ingredient (a). Alternatively, each R^5 is a monovalent hydrocarbon group exemplified by alkyl such as Me and aryl such as Ph. In the first embodiment, each R^4 is independently an aliphatically unsaturated monovalent organic group as described above for the first embodiment of ingredient (a). Alternatively, R^4 is exemplified

20 by alkenyl groups such as vinyl, allyl, butenyl, and hexenyl; and alkynyl groups such as ethynyl and propynyl.

[0018] In the first embodiment, ingredient (a) may comprise a polydiorganosiloxane such as i) dimethylvinylsiloxyl-terminated polydimethylsiloxane, ii) dimethylvinylsiloxyl-terminated poly(dimethylsiloxane/methylvinylsiloxane), iii) dimethylvinylsiloxyl-terminated polymethylvinylsiloxane, iv) trimethylsiloxyl-terminated

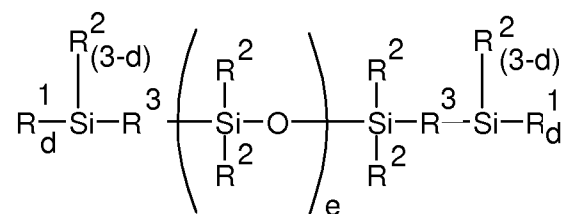
25 poly(dimethylsiloxane/methylvinylsiloxane), v) trimethylsiloxyl-terminated polymethylvinylsiloxane, vi) dimethylvinylsiloxyl-terminated

poly(dimethylsiloxane/methylvinylsiloxane), vii) dimethylvinylsiloxyl-terminated poly(dimethylsiloxane/methylphenylsiloxane), viii) dimethylvinylsiloxyl-terminated poly(dimethylsiloxane/diphenylsiloxane), ix) phenyl,methyl,vinyl-siloxyl-terminated

30 polydimethylsiloxane, x) dimethylhexenylsiloxyl-terminated polydimethylsiloxane, xi) dimethylhexenylsiloxyl-terminated poly(dimethylsiloxane/methylhexenylsiloxane), xii) dimethylhexenylsiloxyl-terminated polymethylhexenylsiloxane, xiii) trimethylsiloxyl-terminated poly(dimethylsiloxane/methylhexenylsiloxane), xiv) trimethylsiloxyl-terminated polymethylhexenylsiloxane, xv) dimethylhexenyl-siloxyl terminated

poly(dimethylsiloxane/methylhexenylsiloxane), xvi) dimethylvinylsiloxyl-terminated poly(dimethylsiloxane/methylhexenylsiloxane), or xvii) a combination thereof.

[0019] Alternatively, in a second embodiment, ingredient (a) may be a polyorganosiloxane having condensation and/or polyaddition reactive groups. Ingredient (a) in the second embodiment may have one or more condensation and/or polyaddition reactive groups. The condensation and/or polyaddition reactive groups may be selected from amine groups, hydroxy groups, alcoholic groups, epoxy groups, isocyanate groups, and phenol groups. Ingredient (a) may comprise a polydiorganosiloxane of formula (III):



, where each R^1 is independently a condensation

and/or polyaddition reactive group, each R² is independently a monovalent organic group, each R³ is independently an oxygen atom or a divalent hydrocarbon group, each subscript d is independently 1, 2, or 3, and subscript e is an integer having a value sufficient to provide the polydiorganosiloxane with a viscosity of at least 100 mPa·s at 25 °C and/or a DP of at least 87. DP may be measured by GPC using polystyrene standards calibration. Alternatively, subscript e may have a value ranging from 1 to 200,000.

[0020] Suitable condensation and/or polyaddition reactive groups for R¹ include, but are not limited to, the hydrolyzable substituents described above for group X. Alternatively, the hydrolyzable substituents for R¹ may be selected from amine groups, alcoholic groups, and epoxy groups, isocyanate groups. Alternatively, the alcoholic groups may be selected from hydroxy groups and phenol groups. Alternatively, the hydrolyzable substituents for R¹ may be selected from amine groups, hydroxy groups, alcoholic groups, epoxy groups, isocyanate groups, and phenol groups.

[0021] Suitable organic groups for R² include, but are not limited to, monovalent organic groups such as hydrocarbon groups and halogenated hydrocarbon groups. Examples of monovalent hydrocarbon groups for R² include, but are not limited to, alkyl such as methyl, ethyl, propyl, pentyl, octyl, decyl, dodecyl, undecyl, and octadecyl; cycloalkyl such as cyclopentyl and cyclohexyl; aryl such as phenyl, tolyl, xylyl, and benzyl; and aralkyl such as 2-phenylethyl. Examples of monovalent halogenated hydrocarbon groups for R² include, but are not limited to, chlorinated alkyl groups such as chloromethyl and chloropropyl groups; fluorinated alkyl groups such as fluoromethyl, 2-fluoropropyl, 3,3,3-trifluoropropyl, 4,4,4-trifluorobutyl, 4,4,4,3,3-pentafluorobutyl, 5,5,5,4,4,3,3-heptafluoropentyl, 6,6,6,5,5,4,4,3,3-

nonafluorohexyl, and 8,8,8,7,7-pentafluorooctyl; chlorinated cycloalkyl groups such as 2,2-dichlorocyclopropyl, 2,3-dichlorocyclopentyl; and fluorinated cycloalkyl groups such as 2,2-difluorocyclopropyl, 2,3-difluorocyclobutyl, 3,4-difluorocyclohexyl, and 3,4-difluoro-5-methylcycloheptyl. Examples of other monovalent organic groups for R^2 include, but are not limited to, hydrocarbon groups substituted with oxygen atoms such as glycidoxyalkyl, and hydrocarbon groups substituted with nitrogen atoms such as aminoalkyl and cyano-functional groups such as cyanoethyl and cyanopropyl. Alternatively, each R^2 may be an alkyl group such as methyl.

[0022] In the second embodiment, ingredient (a) may comprise an α,ω -difunctional-polydiorganosiloxane when, in formula (III) above, each subscript d is 1 and each R^3 is an oxygen atom. For example, ingredient (a) may have formula (IV): $R^1R^2_2SiO-(R^2_2SiO)_{e'}-SiR^2_2R^1$, where R^1 and R^2 are as described above and subscript e' is an integer having a value sufficient to give the polydiorganosiloxane of formula (IV) the viscosity described above. Alternatively, subscript e' may have a value ranging from 1 to 200,000, alternatively 50 to 1,000, and alternatively 200 to 700.

[0023] Alternatively, ingredient (a) may comprise a hydroxyl-functional polydiorganosiloxane of formula (IV) described above, in which each R^1 may be a hydroxyl group, each R^2 may be an alkyl group such as methyl, and subscript e' may have a value such that the hydroxyl functional polydiorganosiloxane has a viscosity of at least 100 mPa·s at 25 °C. Alternatively, subscript e' may have a value ranging from 50 to 700. Exemplary hydroxyl-endblocked polydiorganosiloxanes are hydroxyl-endblocked polydimethylsiloxanes. Hydroxyl-endblocked polydiorganosiloxanes suitable for use as ingredient (a) may be prepared by methods known in the art, such as hydrolysis and condensation of the corresponding organohalosilanes or equilibration of cyclic polydiorganosiloxanes.

[0024] Methods of preparing polydiorganosiloxane fluids suitable for use as ingredient (a), such as hydrolysis and condensation of the corresponding organohalosilanes or equilibration of cyclic polydiorganosiloxanes, are well known in the art.

[0025] In addition to, or instead of, the polydiorganosiloxane described above, ingredient (a) may further comprise a resin such as an MQ resin consisting essentially of $R^9_3SiO_{1/2}$ units and $SiO_{4/2}$ units, a TD resin consisting essentially of $R^9_3SiO_{3/2}$ units and $R^9_2SiO_{2/2}$ units, an MT resin consisting essentially of $R^9_3SiO_{1/2}$ units and $R^9SiO_{3/2}$ units, an MTD resin consisting essentially of $R^9_3SiO_{1/2}$ units, $R^9SiO_{3/2}$ units, and $R^9_2SiO_{2/2}$ units, or a combination thereof.

[0026] Each R⁹ is a monovalent organic group exemplified by those described above for ingredient (a). Alternatively, the monovalent organic groups represented by R⁹ may have 1 to 20 carbon atoms. Alternatively, examples of monovalent organic groups for R⁹ include, but are not limited to, monovalent hydrocarbon groups and monovalent halogenated hydrocarbon groups.

[0027] The resin may contain an average of 3 to 30 mole percent of aliphatically unsaturated organic groups, alternatively 0.1 to 30 mole percent, alternatively 0.1 to 5 mole percent, alternatively 3 to 100 mole percent. The aliphatically unsaturated organic groups may be alkenyl groups, alkynyl groups, or a combination thereof. The mole percent of aliphatically unsaturated organic groups in the resin is the ratio of the number of moles of unsaturated group-containing siloxane units in the resin to the total number of moles of siloxane units in the resin, multiplied by 100.

[0028] Methods of preparing resins are well known in the art. For example, resin may be prepared by treating a resin copolymer produced by the silica hydrosol capping process of Daudt, *et al.* with at least an alkenyl-containing endblocking reagent. The method of Daudt *et al.*, is disclosed in U.S. Patent 2,676,182.

[0029] The method of Daudt, *et al.* involves reacting a silica hydrosol under acidic conditions with a hydrolyzable triorganosilane such as trimethylchlorosilane, a siloxane such as hexamethyldisiloxane, or mixtures thereof, and recovering a copolymer having M-units and Q-units. The resulting copolymers generally contain from 2 to 5 percent by weight of hydroxyl groups. Such a resin may be useful, for example, in the second embodiment described herein.

[0030] Alternatively, a resin, which typically contains less than 2 % of silicon-bonded hydroxyl groups, may be prepared by reacting the product of Daudt, *et al.* with an unsaturated organic group-containing endblocking agent and an endblocking agent free of aliphatic unsaturation, in an amount sufficient to provide from 3 to 30 mole percent of unsaturated organic groups in the final product. Examples of endblocking agents include, but are not limited to, silazanes, siloxanes, and silanes. Suitable endblocking agents are known in the art and exemplified in U.S. Patents 4,584,355; 4,591,622; and 4,585,836. A single endblocking agent or a mixture of such agents may be used to prepare the resin. Such a resin may be useful, for example, in the first embodiment described herein.

[0031] Ingredient (a) may have a linear, branched, cyclic, or resinous structure. Alternatively, ingredient (a) may have a linear and/or branched structure. Alternatively, ingredient (a) may have a resinous structure. Ingredient (a) may be a homopolymer or a copolymer. Ingredient (a) may be one polyorganosiloxane. Alternatively, ingredient (a) may comprise two or more polyorganosiloxanes differing in at least one of the following properties: structure, viscosity,

average molecular weight, siloxane units, selection of reactive groups, and sequence. The reactive groups in the polyorganosiloxane may be located at terminal, pendant, or both terminal and pendant positions.

[0032] Ingredient (b) is a water insoluble, polymerizable, organic monomer.

5 **[0033]** In the first embodiment, ingredient (b) comprises a water insoluble, polymerizable, organic monomer, which is radical polymerizable. The radical polymerizable monomer for ingredient (b) may be selected from alkylalkenyl monomers, alkylallyl monomers, arylalkenyl monomers, arylacrylic-containing monomers, and alkylacrylic-containing monomers. The alkylalkenyl monomers may be alkylvinyl monomers. The alkylvinyl monomers may include α -olefins of 1 to 40 carbon atoms, such as ethylene, propylene, butene, hexene, octene, 10 dodecene, butadiene and/or isoprene. The arylalkenyl monomers may be arylvinyl monomers. Examples of arylvinyl monomers include those with one polymerizable group per molecule such as styrene. Alternatively, the radical polymerizable monomer for ingredient (b) may be selected from α -olefin, butadiene, isoprene, and styrene. Alternatively, the radical polymerizable group 15 for ingredient (b) may be a halogenated monomer, e.g., any one of those monomers discussed above, but having one or more halogen atoms per molecule. Alternatively, the radical polymerizable monomer for ingredient (b) may have two or more polymerizable groups per molecule such as divinylbenzene, trivinylcyclohexane, divinylketone, a conjugated diene such as butadiene, isoprene, and 2-chlorobutadiene. Any one or any combination of two or more of 20 the above radical polymerizable monomers may be used as ingredient (b).

[0034] In the second embodiment, ingredient (b) comprises a water insoluble, polymerizable, organic monomer is a condensation and/or polyaddition type monomer (*i.e.*, which is condensation and/or polyaddition polymerizable). Condensation / polyaddition type monomers for ingredient (b) are polyfunctional, *i.e.*, having two or more reactive groups per molecule. 25 Ingredient (b) may be selected from a polyisocyanate monomer, a polyol monomer, a polyamine monomer, a polyphenol monomer, and any combination of two or more of a polyol monomer, a polyisocyanate monomer, a polyamine monomer, a polyphenol monomer. Examples of suitable condensation and/or polyaddition polymerizable monomers for ingredient (b) include polyethylene glycol which is commercially available from Sigma-Aldrich, Inc. of St. 30 Louis, Missouri, U.S.A. and dicyclohexylmethane-4,4'-diisocyanate, which is commercially available from Bayer of Pittsburgh, Pennsylvania, U.S.A. as Desmodur W. Other examples of polyisocyanate monomers include aromatic diisocyanates such as methylene bis(phenyl isocyanate), meta-tetramethyl xylene diisocyanate (TMXDI), toluene diisocyanate (TDI), and methylene diphenyl diisocyanate; and aliphatic and cycloaliphatic isocyanates such as 35 hexamethylene diisocyanate (HDI), 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethyl-cyclohexane (isophorone diisocyanate, IPDI), and nonanetriisocyanate (TTI), phenylene

diisocyanate, xylene diisocyanate, 1,5-naphthalene diisocyanate, chlorophenylene 2,4-diisocyanate, bitoluene diisocyanate, dianisidine diisocyanate, toluidine diisocyanate and alkylated benzene diisocyanates generally; methylene-interrupted aromatic diisocyanates such as methylene-diphenyl-diisocyanate, especially the 4,4'-isomer (MDI) including alkylated
5 analogs such as 3,3'-dimethyl-4,4'-diphenyl-methane diisocyanate; such hydrogenated materials as cyclohexylene diisocyanate, 4,4'-methylenedicyclohexyl diisocyanate; mixed aralkyl diisocyanates such as the tetramethylxylyl diisocyanates, $\text{OCNC}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{C}(\text{CH}_3)_2\text{NCO}$, and polymethylene isocyanates such as 1,4-tetramethylene diisocyanate, 1,5-pentamethylene diisocyanate, 1,6-hexamethylene diisocyanate (HMDI), 1,7-
10 heptamethylene diisocyanate, 2,2,4- and 2,4,4-trimethylhexamethylene diisocyanate, 1,10-decamethylene diisocyanate, and 2-methyl-1,5-pentamethylene diisocyanate; vinylisocyanate; and combinations thereof.

[0035] Alternatively, ingredient (b) may be a polyol selected from a polyether polyol, such as dipropylene glycol or a poly(tetraalkylene ether) glycol such as glycerol propoxylate; a polyester
15 polyol; a polyester-amide polyol; a polyacetal polyol; a polycarbonate polyol; a polycaprolactone polyol; a polybutadiene polyol; a poly(propylene oxide)polyol; a poly(propylene oxide/ethylene oxide) copolymer; a polyether polyol; and a polysulfide polyol. Exemplary polyols include ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol (1,2-propylene glycol and/or 1,3-propylene glycol), 1,4-butylene glycol, 2,3-butylene glycol,
20 dipropylene glycol, tripropylene glycol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, neopentyl glycol, 1,6-hexanediol, 1,8-octanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, 2-methyl-1,3-propanediol, and a combination thereof. Exemplary polyols with three OH groups per molecule include glycerol, trimethylolpropane, 1,2,4-butanetriol, 1,2,6-hexanetriol, glycerol propoxylate, and a combination thereof.

[0036] Alternatively, ingredient (b) may be an epoxy functional resinous monomer, which may be commercially available from The Dow Chemical Company of Midland, MI, U.S.A. or Huntsman. Eponex® 1500 and 1510 are epoxy-functional cyclohexyl monomers from Momentive Specialty Chemicals, Inc. of Columbus, OH, U.S.A. Other epoxy functional
25 resinous monomers suitable for use as ingredient (b) are exemplified by diglycidyl ether resin, EPON™ Epoxy Novolac epoxy resin (from Momentive Specialty Chemicals of Houston, Texas, U.S.A.), o-cresol Novolac epoxy resins, phenol Novolac epoxy resins, cycloaliphatic epoxy resins, glycidyl ethers of polyvalent phenols such as diglycidyl ether of bisphenol A (DGEBA) and diglycidyl ether of bisphenol F (DGEF), glycidyl ethers of mononuclear diphenols such as glycidyl ethers of resorcinol, glycidyl ethers of hydroquinone, and glycidyl ethers of catechol,
30 polyglycidyl ethers of phenol Novolac epoxy resins such as phenol formaldehyde Novolac, alicyclic epoxy resins derived from the epoxidation of an olefin bond, the product of the reaction

of 2,2-bis-(hydroxy-phenyl)-propane (bisphenol A) and epichlorohydrin, triglycidyl isocyanurate, and products obtained from the reaction of bis-(4-hydroxy-phenyl)-methane (bisphenol F) and epichlorohydrin. Other examples include resorcinol diglycidyl ether {1,3-bis-(2,3-epoxypropoxy)benzene} marketed, for example, by Wilmington Chemical as HELOXY® 69; DER® 331 a diglycidyl ether of bisphenol A epoxy resin sold by The Dow Chemical Company of Midland, MI, U.S.A.; ERL® 4221D a cycloaliphatic epoxy resin also sold by The Dow Chemical Company; triglycidyl p-aminophenol {4-(2,3-epoxypropoxy)-N,N-bis{2,3-epoxypropyl}aniline}; diglycidyl ether of bromobisphenol A {2,2-bis(4-{2,3-epoxypropoxy}-3-bromo-phenyl)propane; diglycidylether of Bisphenol F (2,2-bis(p-(2,3-epoxypropoxy)phenyl)methane); triglycidyl ether of meta and/or para-aminophenol (3-(2,3-epoxypropoxy)phenyl)methane); triglycidyl ethers of epoxy N,N-bis(2,3-epoxypropyl)aniline); and tetraglycidyl methylene dianiline (N,N,N',N'-tetra(2,3-epoxypropyl) 4,4'-diaminodiphenyl methane) or combinations of two or more thereof.

[0037] Alternatively, ingredient (b) may be an amine functional monomer. Amine functional monomers are commercially available, for example, the Jeffamine® monomers are commercially available from Huntsman. Multifunctional primary or secondary polyamines and their adducts, anhydrides, or polyamides are suitable for use as ingredient (b) in this embodiment. The amine functional monomer can be any organic monomer with an active group capable of reacting with an epoxy group, and is exemplified by an aromatic diamine such as a diaminodiphenyl-sulfone, a methylenedianiline such as 4,4'-methylenedianiline, a diaminodiphenylether, benzidine, 4,4'-thiodianiline, 4-methoxy-6-m-phenylenediamine, 2,6-diaminopyridine, 2,4-toluenediamine, and dianisidine. Alicyclic amines such as menthane diamine and heterocyclic amines such as pyridine are also suitable. Some preferred commercial amine functional monomers are illustrated by Versamine® C-30 a cycloaliphatic amine curing agent sold by Cognis (Cincinnati, OH, U.S.A.) and Dytek® EP an aliphatic amine curing agent sold by DuPont, (Wilmington, DE, U.S.A.).

[0038] Ingredient (b) may be one organic monomer. Alternatively, ingredient (b) may be two or more organic monomers that differ in at least one of the following properties: structure, viscosity, average molecular weight, and selection of reactive groups. The reactive groups, which permit the organic monomer to polymerize, may be located at terminal, pendant, or both terminal and pendant positions.

[0039] The amount of ingredient (b) depends on various factors including the type of reactive groups selected for ingredient (a) and the type and amount of initiator selected for ingredient (c). However, the amount of ingredient (b) may be 1% to 99% based on the combined weights of ingredients (a) and (b). Alternatively, the amount of ingredient (b) may be 5% to 80% based on the combined weights of ingredients (a) and (b). Alternatively, the amount of ingredient (b)

may be 10% to 70% based on the combined weights of ingredients (a) and (b). Alternatively, the amount of ingredient (b) may be 20% to 60% % based on the combined weights of ingredients (a) and (b).

[0040] Alternatively, in a third embodiment, the first embodiment and the second embodiment described above may be combined. In this third embodiment, two or more of the reactions are used to form the hydrophobic organic-silicone hybrid polymer. For example, the ingredients in step (1) may be capable of reacting via polyaddition and radical mechanisms; or radical and polycondensation mechanisms. Ingredients (a) and (b) may be selected to have suitable reactive groups, as described above. Ingredient (c) is selected to catalyze the reaction of the reactive groups on ingredient (a) and/or ingredient (b).

[0041] Ingredient (c) is an initiator, which is capable of catalyzing polymerization of the reactive groups on ingredient (a) and/or the reactive groups that allow ingredient (b) to be polymerizable. The initiator may be capable of catalyzing polymerization of (a) the polyorganosiloxane, polymerization of (b) the water insoluble, polymerizable, organic monomer, and/or copolymerization of (a) the polyorganosiloxane and (b) the water insoluble, polymerizable, organic monomer. In the first embodiment, ingredient (c), when present, is a radical initiator; and (i) ingredient (b) has free radical reactive groups; or (ii) the one or more reactive groups on the polyorganosiloxane (a) is a free radical reactive group; or both (i) and (ii). The radical initiator may be a free radical initiator, a photoinitiator, or a combination of a free radical initiator and a photoinitiator. Suitable free radical initiators for ingredient (c) may be, for example, azo-compounds, peroxides, persulfates, disulfides, metal complexes that are decomposed to radicals by heat, light, or a redox process, any combination thereof. For example, the peroxide may be benzyl peroxide (BPO), diacryl peroxide (LPO), di-tert-butyl peroxyoxalates (DBPOX). Suitable azo-compounds may include, but are not limited to, azobisisobutyronitrile (AIBN) and di-tert butyl hyponitrite (DTBN). The photoinitiator is exemplified by, but not limited to, acetophenone such as 1-hydroxycyclohexyl phenyl ketone or 2,2-diethoxyacetophenone, benzil/benzoin compounds such as 4,4'-dimethylbenzil or benzoin methyl ether, benzophenone such as 4-hydroxybenzophenone, 4-benzoylbiphenyl, or 4-(dimethylamino)benzophenone, thioxanthenes such as thioxanthen-9-one or 10-methylphenothiazine, cationic photoinitiators such as boc-methoxyphenyldiphenylsulfonium triflate, (4-bromophenyl)diphenylsulfonium triflate, diphenyliodonium nitrate, (4-phenylthiophenyl)diphenylsulfonium triflate, and others such as 2-tert-butylanthraquinone, diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide.

[0042] In the second embodiment, ingredient (c) is a condensation and/or polyaddition reaction catalyst; and (i) ingredient (b) has condensation and/or polyaddition reactive groups; or (ii) the one or more reactive groups on ingredient (a) is a condensation and/or polyaddition

reactive group; or both (i) and (ii). The condensation and/or polyaddition reaction catalyst may be a tin compound, alkaline metal (Li, Na, K, Rb, Cs) compound, alkaline earth metal (Mg, Ca, Ba, Sr) compound, or an amine such as tertiary amine or secondary amine.

[0043] Suitable tin compounds for ingredient (c) include organotin compounds where the

5 valence of the tin is either +4 or +2, *i.e.*, Tin (IV) compounds or Tin (II) compounds. Examples of tin (IV) compounds include stannic salts of carboxylic acids such as dibutyl tin dilaurate, dimethyl tin dilaurate, di-(n-butyl)tin bis-ketonate, dibutyl tin diacetate, dibutyl tin maleate, dibutyl tin diacetylacetate, dibutyl tin dimethoxide, carbomethoxyphenyl tin tris-uberate, dibutyl tin dioctanoate, dibutyl tin diformate, isobutyl tin triceroate, dimethyl tin dibutyrate, 10 dimethyl tin di-neodeconoate, dibutyl tin di-neodeconoate, triethyl tin tartrate, dibutyl tin dibenzoate, butyltintri-2-ethylhexanoate, dioctyl tin diacetate, tin octylate, tin oleate, tin butyrate, tin naphthenate, dimethyl tin dichloride, a combination thereof, and/or a partial hydrolysis product thereof. Tin (IV) compounds are known in the art and are commercially available, such as Metatin® 740 and Fascat® 4202 from Acima Specialty Chemicals of Switzerland, Europe, 15 which is a business unit of The Dow Chemical Company. Examples of tin (II) compounds include tin (II) salts of organic carboxylic acids such as tin (II) diacetate, tin (II) dioctanoate, tin (II) diethylhexanoate, tin (II) dilaurate, stannous salts of carboxylic acids such as stannous octoate, stannous oleate, stannous acetate, stannous laurate, stannous stearate, stannous naphthanate, stannous hexanoate, stannous succinate, stannous caprylate, and a combination 20 thereof.

[0044] It is contemplated that any suitable amount of initiator may be used as long as there is a sufficient amount of initiator to accelerate a reaction between the reactive group(s) on ingredient (a) and/or ingredient (b) in the mixture at room temperature or at temperatures above room temperature. The exact amount of ingredient (c) depends on various factors including the 25 reactive groups present on ingredient (a) and/or ingredient (b) and the particular initiator selected. In some embodiments, the initiator is optional. Alternatively, the initiator may be added in an amount from 0.001 to 5 weight parts per one hundred parts of the mixture in step (1). Alternatively, ingredient (c) is added in an amount from 0.05 to 0.5 weight parts per 100 parts of the mixture.

30 **[0045]** The preparation of the hydrophobic organic-silicone hybrid polymer can be conducted neat or in the presence of ingredient (d) a solvent. The solvent may include, but is not limited to, an alcohol such as methanol, ethanol, isopropanol, butanol, or n-propanol, a ketone such as acetone, methylethyl ketone, or methyl isobutyl ketone, an aromatic hydrocarbon such as benzene, toluene, or xylene, an aliphatic hydrocarbon such as heptane, hexane, cyclohexane, 35 or octane, an ether such as dimethyl ether or tetrahydrofuran (THF), a glycol ether such as propylene glycol methyl ether, dipropylene glycol methyl ether, propylene glycol n-butyl ether,

propylene glycol n-propyl ether, or ethylene glycol n-butyl ether, a halogenated hydrocarbon such as dichloromethane, 1,1,1-trichloroethane or methylene chloride, chloroform, dimethyl sulfoxide, dimethyl acetonitrile, white spirits, mineral spirits, naphtha, or any combination thereof. Alternatively, the solvent comprises toluene, isopropanol, THF, xylene, hexane, cyclohexane, cyclohexanone, heptane, octane, or any combination of two or more thereof.

[0046] The amount of solvent can be up to 95% based on the combined weight of all ingredients in the mixture. Alternatively, when present, the amount of solvent may be 10% to 50% based on the combined weight of all ingredients in the mixture. The solvent and/or other volatile materials used or generated during the reaction may optionally be subsequently removed from the resulting hydrophobic organic-silicone hybrid polymer using any suitable method.

[0047] Ingredient (e) is a compatibilizer. The compatibilizer contains, per molecule, at least one first functional group that is capable of interacting with ingredient (a) and at least one second functional group that is capable of interacting with ingredient (b), wherein the first functional group and the second functional group may be the same as, or different from, one another. Each interaction may be physical or chemical. Alternatively, ingredient (e) may have more than one of the first functional group, more than one of the second functional group, or both. Without wishing to be bound by theory, it is thought that ingredient (e) can improve compatibility of polymer networks formed from ingredient (a) and ingredient (b) in the hydrophobic organic-silicone hybrid polymer through physical chain entanglement, and/or specific intermolecular interactions such as hydrogen bonding, ionic interaction, dipole-dipole interaction, and/or chemical reactions with the polymers into the networks formed by polymerizing ingredient (a) and/or ingredient (b). Without wishing to be bound by theory, it is thought that ingredient (e) may improve miscibility of ingredient (a) and ingredient (b). And, it is desirable that ingredient (e) is able to react, under the method conditions in step (2) during formation of the hydrophobic organic-silicone hybrid polymer. Without wishing to be bound by theory, it is thought that ingredient (e) reacts with at least one of ingredient (a) and ingredient (b), alternatively ingredient (e) may react with both ingredient (a) and ingredient (b). If two or more polyorganosiloxanes are used as ingredient (a), then the compatibilizer may react with one or more of them. If two or more monomers are used as ingredient (b), then the compatibilizer may react with one or more of them. Examples of compatibilizers include, but are not limited to 1,3-bis(3-methacryloxypropyl)tetramethyldisiloxane and 3-aminopropyltrimethoxysilane, which are commercially available from Gelest Inc. of Morrisville, Pennsylvania, U.S.A.; and divinyl benzene, allyl methacrylate, and glycerol ethoxylate, which are commercially available from Sigma-Aldrich, Inc. of St. Louis, Missouri, U.S.A. Without wishing to be bound by theory, it is thought that certain compatibilizers may have a physical

interaction with one ingredient due to compatibility a portion of each compound and a chemical interaction (reaction) with reactive groups on another ingredient. For example, 1,3-bis(3-methacryloxypropyl)tetramethyldisiloxane may have a physical interaction with ingredient (a) due to the compatibility of the siloxane portions of each compound and a chemical interaction (reaction) with reactive groups on ingredient (b), for example, when the organic monomer is radical polymerizable. An example of this is shown below, see example 3.

[0048] Ingredient (f) is a crosslinker. Ingredient (f) is multifunctional, having at least three reactive groups per molecule, which reactive groups are selected to react with one of ingredient (a) and ingredient (b). The crosslinker may be a hydrocarbonoxysilane, or a hydrolyzed and condensed product thereof. The hydrocarbonoxysilane may have formula $R^7_jSi(OR^6)_{(4-j)}$, where subscript j is 0 or 1. Alternatively, subscript j is 0. Each R^6 is independently a monovalent hydrocarbon group, such as an alkyl group or an alkenyl group. Alternatively, each R^6 is an alkyl group, such as Me, Et, Pr, or Bu; alternatively Me. Each R^7 is independently a functional group that may be reactive with the reactive groups of ingredient (a), with ingredient (b), or both. R^7 is exemplified by a monovalent hydrocarbon group that may be saturated or unsaturated. R^7 may be an alkyl group such as Me, Et, Pr, or Bu. Alternatively, R^7 may be an aliphatically unsaturated hydrocarbon group, such as alkenyl exemplified by vinyl, allyl and hexenyl or alkynyl such as ethynyl. Alternatively, ingredient (f) may be 1,3-bis(3-methoxypropyl)tetramethyl disiloxane, which is commercially available from Gelest, Inc. In the second embodiment, R^7 is exemplified by isocyanate functional groups such as isocyanato and isocyanatopropyl and amino-functional groups such as aminoalkyl, e.g., aminoethyl, aminomethyl, or aminopropyl. Alternatively, in the second embodiment, ingredient (f) may be isocyanatotrimethoxysilane, isocyanatopropyltrimethoxysilane, or aminopropyltrimethoxysilane, which are commercially available from Gelest, Inc.

[0049] The amounts of each ingredient used in step (1) will depend on various factors including the types and amounts of reactive groups on ingredient (a), the properties and structure of the polyorganosiloxane selected for ingredient (a), and the types and amounts of monomer selected for ingredient (b), however, the amounts of each ingredient may be:

1%-99%, alternatively 10%-90%, and alternatively 20-80%, of ingredient (a), based on the combined weights of all ingredients used in step (1);

1%-99%, alternatively 10%-90%, and alternatively 20%-80%, of ingredient (b), based on the combined weights of all ingredients used in step (1);

0-10%, alternatively 0.01%-10%, and alternatively 0.5%-5%, of ingredient (c), based on the combined weights of all ingredients used in step (1);

0-50%, and alternatively 0-10%, of ingredient (d), based on the combined weights of all

ingredients used in step (1);

0-50%, alternatively 0-20%, and alternatively 1%-10%, of ingredient (e), based on the combined weights of all ingredients used in step (1); and

0-70%, and alternatively 0-50%, of ingredient (f), based on the combined weights of all ingredients used in step (1). The total amount of ingredients (a), (b), (c), (d), (e), and (f) is 100%.

[0050] The method described above produces a reaction product comprising the hydrophobic organic-silicone hybrid polymer, described above. The hydrophobic organic-silicone hybrid polymer may comprise (I) a copolymer of repeating units based on the water insoluble, polymerizable, organic monomer (b) and the polyorganosiloxane (a); (II) a mixture of a homopolymer of repeating units based on the water insoluble, polymerizable organic monomer (b) and the polyorganosiloxane (a); or (III) a combination of both (I) and (II). The hydrophobic organic-silicone hybrid polymer has one or more reactive groups. The one or more reactive groups comprises one or more functional groups configured to be reacted to form a hydrophobic organic-silicone hybrid polymer having longer chains and/or a crosslinked network relative to the unreacted hydrophobic organic-silicone hybrid polymer (*i.e.*, the hydrophobic organic-silicone hybrid polymer formed by step (2) of the method described above). In the first embodiment, the one or more reactive groups comprises one or more aliphatically unsaturated organic groups capable of undergoing hydrosilylation reaction and/or radical initiated reaction. In the second embodiment, the one or more reactive groups comprises condensation and/or polyaddition reactive groups. Without wishing to be bound by theory, it is thought that the method described herein provides a benefit in that the hydrophobic organic-silicone hybrid polymer produced by the method herein is reactive; *i.e.*, the hydrophobic organic-silicone hybrid polymer has one or more reactive groups after performance of the method to form the reaction product comprising the hydrophobic organic-silicone hybrid polymer; and it is thought that this is distinct from previous methods for making silicone-organic IPNs, which produce silicone-organic IPNs that lack such reactive groups and are not reactive.

[0051] The reaction product may further comprise, in addition to the hydrophobic organic-silicone hybrid polymer, one or more other components, such as solvent, when ingredient (d) is used, and/or side products of the reaction. The method described above may optionally further comprise separating the reaction product, *e.g.*, by any convenient means such as stripping and/or distillation, to remove one or more of the other components from the hydrophobic organic-silicone hybrid polymer. The reaction product and/or the hydrophobic organic-silicone hybrid polymer are generally uniform and stable, which means that in a liquid form the hydrophobic organic-silicone hybrid polymer, and/or the reaction product of the method, is an opaque liquid that is uniform in appearance and does not visibly separate after three days at

room temperature of 25 °C. When placed in a container, the opaque liquid remains uniform in appearance upon visual inspection after the after container remains undisturbed for at least three days at room temperature of 25 °C, i.e., the opaque liquid visually appears the same throughout the container, without a separate, visually distinct phase on either the top or the bottom of the container. The hydrophobic organic-silicone hybrid polymer, which may be in the form of liquid, gel, solid, flake, or powder, may be solidified into a solid article by further reaction in a composition, which comprises the hydrophobic organic-silicone hybrid polymer, and a catalyst. This solid article produced by curing the composition may be in the form of gel, solid, film, a part, a slab, or porous foam with open cells or closed cells.

[0052] Because the hydrophobic organic-silicone hybrid polymer made by the method described above has one or more reactive groups, the hydrophobic organic-silicone hybrid polymer may be further reacted by combining the hydrophobic organic-silicone hybrid polymer with a catalyst and optionally one or more other reactive materials. For example, in the first embodiment the hydrophobic organic-silicone hybrid polymer may have one or more reactive groups such as hydrosilylation / radical initiatable groups, *e.g.*, the aliphatically unsaturated groups including vinyl, allyl, or acrylate-functional groups, described above. Alternatively, in the second embodiment, the hydrophobic organic-silicone hybrid polymer may have one or more condensation / polyaddition reactive groups. Alternatively, in the third embodiment, the hydrophobic organic-silicone hybrid polymer may have both one or more hydrosilylation / radical initiatable groups and one or more condensation / polyaddition reactive groups. The hydrophobic organic-silicone hybrid polymer may be combined with the one or more other reactive materials through their reactions. The one or more other reactive materials can be reacted with the one or more reactive groups in the hydrophobic organic-silicone hybrid polymer. The reaction may, for example, be between silyl-hydride (SiH) and a vinyl/allyl group, mercapto (SH) and an acrylate, silicon-bonded alkoxy (Si(OR)) and a silicon bonded hydroxy (SiOH) group, acetoxysilyl (Si(OOCCH₃)) and a SiOH group, enoxysilyl (CH₃C(=CH₂)O-Si) and a SiOH group, oxime (CH₃C₂H₅C=NO-Si) and a SiOH group, or aminosilyl ((CH₃)₂N-Si) and a SiOH group. The hydrophobic organic-silicone hybrid polymer and the one or more other reactive materials may be combined through physicochemical methods such as, for example, light, UV exposure, heating/cooling, radiation, moisture, ozone, high pressure, low pressure, magnetic fields, electric fields, and combinations thereof.

[0053] The hydrophobic organic-silicone hybrid polymer described above may be used in a composition. The composition may be reacted to form a solid article. The composition comprises:

(A) the hydrophobic organic-silicone hybrid polymer having one or more reactive groups per molecule, prepared as described above;

(B) a catalyst capable of catalyzing reaction of the one or more reactive groups of the hydrophobic organic-silicone hybrid polymer; and
optionally (C) a crosslinker.

[0054] In the first embodiment, the one or more reactive groups of ingredient (A) are

hydrosilylation and/or radical initiatable groups. The one or more reactive groups of ingredient (A), may be the same as the reactive groups on ingredient (a), the polyorganosiloxane used in the method described above for making the hydrophobic organic-silicone hybrid polymer. In this embodiment, the catalyst selected for ingredient (B) may be a radical initiator, which may be the same as or different from the radical initiator for ingredient (c), which may be used in the method for making the hydrophobic organic-silicone hybrid polymer described above. Without wishing to be bound by theory, it is thought that such a radical initiator may be present in the reaction product of the method described above. Alternatively, an additional amount of radical initiator, which may be the same as or different from the radical initiator selected for ingredient (c) used in the method for preparing the hydrophobic organic-silicone hybrid polymer, may be added to the composition. In this embodiment, the composition may optionally further comprise ingredient (C), a crosslinker having, per molecule, two or more two or more radical activatable unsaturated organic groups. The two or more radical activated unsaturated organic groups are selected from alkylvinyl groups, alkylalkenyl groups, alkylallyl groups, arylvinyl groups, arylalkenyl groups, arylacrylic-containing groups, and alkylacrylic-containing groups. The crosslinker selected for ingredient (C) may be a crosslinker described above as ingredient (f) (or alternatively a compatibilizer described above as ingredient (e)) used in the first embodiment of the method for making the hydrophobic organic-silicone hybrid polymer.

[0055] Alternatively, the catalyst selected for ingredient (B) may be a hydrosilylation catalyst. Hydrosilylation catalysts are commercially available. Suitable hydrosilylation catalysts can be a metal selected from platinum, rhodium, ruthenium, palladium, osmium, and iridium.

Alternatively, the hydrosilylation catalyst may be a compound of such a metal, for example, chloroplatinic acid, chloroplatinic acid hexahydrate, platinum dichloride, and complexes of said compounds with low molecular weight organopolysiloxanes or platinum compounds microencapsulated in a matrix or core/shell type structure. Complexes of platinum with low molecular weight organopolysiloxanes include 1,3-diethenyl-1,1,3,3 -tetramethyldisiloxane complexes with platinum. These complexes may be microencapsulated in a resin matrix.

[0056] The composition may optionally further comprise ingredient (C) a crosslinker. In the first embodiment, when the catalyst selected for ingredient (B) is a hydrosilylation catalyst, and no other ingredient in the composition other than ingredient (C) has silicon bonded hydrogen atoms, then ingredient (C) the crosslinker is present and has, per molecule, two or more silicon bonded hydrogen atoms.

[0057] Ingredient (C) in this embodiment of the composition is a SiH functional compound, *i.e.*, a compound having an average, per molecule, of one or more silicon bonded hydrogen atoms, alternatively 2 or more silicon bonded hydrogen atoms, and alternatively 3 or more silicon bonded hydrogen atoms. Ingredient (C) may comprise a silane and/or an organohydrogensilicon compound. The amount of ingredient (C) in the composition depends on various factors including the SiH content of ingredient (C), the unsaturated group content of ingredient (A), and the properties of the reaction product of the composition desired, however, the amount of ingredient (C) may be sufficient to provide a molar ratio of SiH groups in ingredient (C) to aliphatically unsaturated organic groups in ingredient (A) (commonly referred to as the SiH:Vi ratio) ranging from 0.3:1 to 5:1, alternatively 0.1:10 to 10:1. Ingredient (C) can have a monomeric or polymeric structure. When ingredient (C) has a polymeric structure, the polymeric structure may be linear, branched, cyclic, or resinous structure. When ingredient (C) is polymeric, then ingredient (C) can be a homopolymer or a copolymer. The silicon-bonded hydrogen atoms in ingredient (C) can be located at terminal, pendant, or at both terminal and pendant positions. Ingredient (C) may be one SiH functional compound. Alternatively, ingredient (C) may comprise a combination of two or more SiH functional compounds. Ingredient (C) may be two or more organohydrogenpolysiloxanes that differ in at least one of the following properties: structure, average molecular weight, viscosity, siloxane units, and sequence.

[0058] Ingredient (C) may comprise a silane of formula $R^{14}_mSiH_n$, where subscript m is 0, 1, 2, or 3; subscript n is 1, 2, 3, or 4, with the proviso that a sum of (m + n) is 4. Each R^{14} is independently a halogen atom or a monovalent organic group. Suitable halogen atoms for R^{14} are exemplified by chlorine, fluorine, bromine, and iodine; alternatively chlorine. Suitable monovalent organic groups for R^{14} include, but are not limited to, monovalent hydrocarbon and monovalent halogenated hydrocarbon groups. Monovalent hydrocarbon groups include, but are not limited to, alkyl such as Me, Et, Pr, Bu, pentyl, hexyl, heptyl, octyl, decyl, dodecyl, undecyl, and octadecyl; cycloalkyl such as cyclopentyl and cyclohexyl; aryl such as Ph, tolyl, xylyl, and naphthyl; and aralkyl such as benzyl, 1-phenylethyl and 2-phenylethyl. Examples of monovalent halogenated hydrocarbon groups include, but are not limited to, chlorinated alkyl groups such as chloromethyl and chloropropyl groups; fluorinated alkyl groups such as fluoromethyl, 2-fluoropropyl, 3,3,3-trifluoropropyl, 4,4,4-trifluorobutyl, 4,4,4,3,3-pentafluorobutyl, 5,5,5,4,4,3,3-heptafluoropentyl, 6,6,6,5,5,4,4,3,3-nonafluorohexyl, and 8,8,8,7,7-pentafluorooctyl; chlorinated cycloalkyl groups such as 2,2-dichlorocyclopropyl, 2,3-dichlorocyclopentyl; and fluorinated cycloalkyl groups such as 2,2-difluorocyclopropyl, 2,3-difluorocyclobutyl, 3,4-difluorocyclohexyl, and 3,4-difluoro-5-methylcycloheptyl. Examples of

other monovalent organic groups include, but are not limited to, hydrocarbon groups substituted with oxygen atoms such as glycidioxyalkyl, and alkoxy groups such as methoxy, ethoxy, propoxy, and butoxy; and hydrocarbon groups substituted with nitrogen atoms such as aminoalkyl and cyano-functional groups such as cyanoethyl and cyanopropyl. Examples of
 5 suitable silanes for ingredient (C) are exemplified by trichlorosilane (HSiCl_3), Me_2HSiCl , or MeHSi(OMe)_2 .

[0059] Alternatively, the organohydrogensilicon compound of ingredient (C) may comprise a polyorganohydrogensiloxane comprising siloxane units including, but not limited to,

$\text{HR}^5_2\text{SiO}_{1/2}$, $\text{R}^5_3\text{SiO}_{1/2}$, $\text{HR}^5\text{SiO}_{2/2}$, $\text{R}^5_2\text{SiO}_{2/2}$, $\text{R}^5\text{SiO}_{3/2}$, $\text{HSiO}_{3/2}$ and $\text{SiO}_{4/2}$ units. In

10 the preceding formulae, each R^5 is independently selected from the monovalent organic groups free of aliphatic unsaturation described above.

[0060] Ingredient (C) may comprise a polyorganohydrogensiloxane of

Formula (V): $\text{R}^{15}_3\text{SiO(R}^{15}_2\text{SiO)}_o(\text{R}^{15}\text{HSiO)}_p\text{SiR}^{15}_3$,

Formula (VI): $\text{R}^{15}_2\text{HSiO(R}^{15}_2\text{SiO)}_q(\text{R}^{15}\text{HSiO)}_r\text{SiR}^{15}_2\text{H}$, or a combination thereof.

15 **[0061]** In formulae (V) and (VI) above, subscript o has an average value ranging from 0 to 2000, subscript p has an average value ranging from 2 to 2000, subscript q has an average value ranging from 0 to 2000, and subscript r has an average value ranging from 0 to 2000. Each R^{15} is independently a monovalent organic group, as described above.

[0062] Polyorganohydrogensiloxanes for ingredient (C) are exemplified by:

- 20 a) dimethylhydrogensiloxy-terminated polydimethylsiloxane,
- b) dimethylhydrogensiloxy-terminated poly(dimethylsiloxane/methylhydrogensiloxane),
- c) dimethylhydrogensiloxy-terminated polymethylhydrogensiloxane,
- d) trimethylsiloxy-terminated poly(dimethylsiloxane/methylhydrogensiloxane),
- e) trimethylsiloxy-terminated polymethylhydrogensiloxane,
- 25 f) a resin consisting essentially of $\text{H(CH}_3)_2\text{SiO}_{1/2}$ units and $\text{SiO}_{4/2}$ units, and
- g) a combination thereof.

[0063] Methods of preparing linear, branched, and cyclic organohydrogenpolysiloxanes suitable for use as ingredient (C), such as hydrolysis and condensation of organohalosilanes, are known. Exemplary crosslinkers are disclosed, for example, in WO2013/043846,
 30 WO2003/093349 and WO2003/093369. Other organohydrogensilicon compounds suitable for ingredient (C) are commercially available and include, SYL-OFF® SL2 CROSSLINKER and SYL-OFF® SL12 CROSSLINKER, both of which are commercially available from Dow Corning Corporation of Midland, Michigan, U.S.A.

[0064] The exact amount of ingredient (C) in the first embodiment of composition depends on various factors including the selection of reactive groups of ingredient (A), the type and amount of ingredient (B), and the type and amount of any additional ingredient(s) (other than ingredient (C)), if present. However, the amount of ingredient (C) in the composition may range from 0% to 25%, alternatively 0.1% to 15%, and alternatively 1% to 5%, based on total weight of all ingredients in the composition.

[0065] In the second embodiment, the catalyst selected for ingredient (B) may be a condensation / polyaddition catalyst. The condensation and/or polyaddition reaction catalyst may be a tin compound, alkaline metal (Li, Na, K, Rb, Cs) compound, alkaline earth metal (Mg, Ca, Ba, Sr) compound, or an amine such as tertiary amine or secondary amine. Suitable tin compounds for ingredient (B) include organotin compounds where the valence of the tin is either +4 or +2, *i.e.*, Tin (IV) compounds or Tin (II) compounds. Examples of tin (IV) compounds include stannic salts of carboxylic acids such as dibutyl tin dilaurate, dimethyl tin dilaurate, di-(n-butyl)tin bis-ketionate, dibutyl tin diacetate, dibutyl tin maleate, dibutyl tin diacetylacetonate, dibutyl tin dimethoxide, carbomethoxyphenyl tin tris-uberate, dibutyl tin dioctanoate, dibutyl tin diformate, isobutyl tin triceroate, dimethyl tin dibutyrate, dimethyl tin di-neodeconoate, dibutyl tin di-neodeconoate, triethyl tin tartrate, dibutyl tin dibenzoate, butyltintri-2-ethylhexanoate, dioctyl tin diacetate, tin octylate, tin oleate, tin butyrate, tin naphthenate, dimethyl tin dichloride, a combination thereof, and/or a partial hydrolysis product thereof. Tin (IV) compounds are known in the art and are commercially available, such as Metatin® 740 and Fascat® 4202 from Acima Specialty Chemicals of Switzerland, Europe, which is a business unit of The Dow Chemical Company. Examples of tin (II) compounds include tin (II) salts of organic carboxylic acids such as tin (II) diacetate, tin (II) dioctanoate, tin (II) diethylhexanoate, tin (II) dilaurate, stannous salts of carboxylic acids such as stannous octoate, stannous oleate, stannous acetate, stannous laurate, stannous stearate, stannous naphthanate, stannous hexanoate, stannous succinate, stannous caprylate, and a combination thereof. The crosslinker selected for ingredient (C) in the second embodiment may be a crosslinker as described above for ingredient (f) in the method for making the hydrophobic organic-silicone hybrid polymer. Other suitable crosslinkers for a composition according to the second embodiment are known, and are described, for example, in WO 2013/009836.

[0066] The composition may optionally further comprise one or more additional ingredients, which are distinct from ingredients (A), (B), and (C), and which are selected from the group consisting of (D) a drying agent; (E) an extender; (F) a filler; (G) a filler treating agent; (H) a biocide; (I) a stabilizer; (J) a flame retardant; (K) a surface modifier; (L) a chain lengthener; (M) an endblocker; (N) a flux agent; (O) an anti-aging additive; (P) a pigment; (Q) an acid acceptor (R) a rheological additive; (S) a vehicle; (T) a surfactant; (U) a corrosion inhibitor, (V) a

polyorganosiloxane having two or more aliphatically unsaturated organic groups per molecule (which may be the same as or different from the polyorganosiloxane selected for ingredient (a) in the first embodiment of the method for preparing the hydrophobic organic-silicone hybrid polymer, described above), (W) a water release agent, (X) a polyorganosiloxane having two or more hydrolyzable groups per molecule (which may be the same as or different from the polyorganosiloxane selected for ingredient (a) in the second embodiment of the method for preparing the hydrophobic organic-silicone hybrid polymer, described above), and a combination thereof. Ingredients (D), (E), (F), (G), (H), (I), (J), (K), (L), (M), (N), (O), (P), (Q), (R), (S), (T), (U), and (V) are described and exemplified in for example, in WO 2013/009836 and WO2013/043846.

[0067] The composition described above may be prepared by any convenient means, such as mixing the ingredients at ambient or elevated temperature. Ingredient (I), when present, may be added before ingredient (B), for example, when the composition will be prepared at elevated temperature and/or the composition will be prepared as a one part composition.

[0068] When ingredient (G) is present, the composition may optionally be prepared by surface treating a particulate ingredient (*e.g.*, filler and/or spacer, if present) with ingredient (G), and thereafter mixing the product thereof with the other ingredients of the composition.

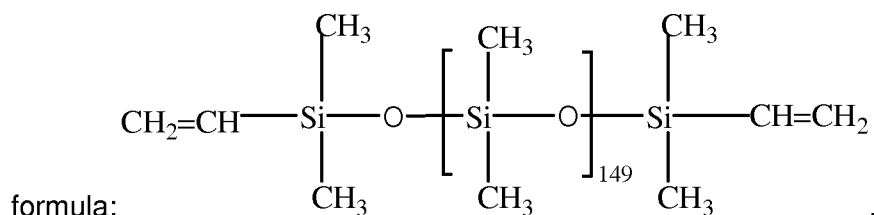
[0069] Alternatively, the composition may be prepared as a multiple part composition, for example, when ingredient (I) is absent, or when the composition will be stored for a long period of time before use. In the multiple part composition, ingredient (B) is stored in a separate part from any ingredient having a silicon bonded hydrogen atom, for example ingredient (C), and the parts are combined shortly before use of the composition. For example, a two part composition may be prepared by combining ingredients comprising (A), (B), (F), and optionally one or more other additional ingredients described above to form a base by any convenient means such as mixing. A curing agent may be prepared by combining ingredients comprising (A), (C), and optionally one or more other additional ingredients described above by any convenient means such as mixing. The ingredients may be combined at ambient or elevated temperature. When a two part composition is used, the weight ratio of amounts of base to curing agent may range from 1:1 to 10:1. The method for making the composition may comprise mixing ingredients comprising ingredient (A) and ingredient (B); or mixing ingredients comprising ingredients (A), (B), and (C); or mixing ingredients comprising ingredients (A) and (B), and one or more of (D), (E), (F), (G), (H), (I), (J), (K), (L), (M), (N), (O), (P), (Q), (R), (S), (T), (U), and (V); or mixing ingredients comprising ingredients (A), (B), and (C) and one or more of (D), (E), (F), (G), (H), (I), (J), (K), (L), (M), (N), (O), (P), (Q), (R), (S), (T), (U) and (V); so as to make the composition. In this method, where ingredient (C) is present, the composition may be a multiple part composition, and ingredient (B) and ingredient (C) are stored in separate parts. The

composition will cure to form a solid article. The solid article of the composition may have various forms, such as a gel, a rubber, or a resin.

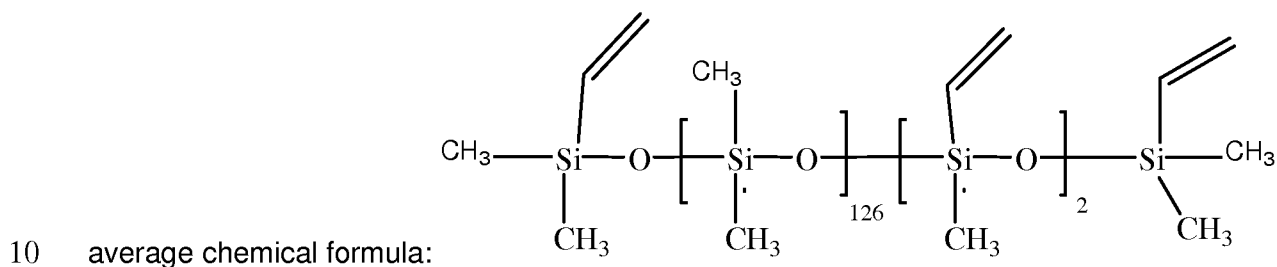
EXAMPLES

[0070] The examples below are intended to illustrate certain embodiments of the present invention and should not be interpreted as limiting the scope of the invention set forth in the claims. The following ingredients are used in the examples below.

- 5 **[0071]** The vinyl-terminated polydimethylsiloxane, "M^{Vi}D₁₄₉M^{Vi}", as referenced in the Examples below, was obtained from Dow Corning Corporation and has the average chemical

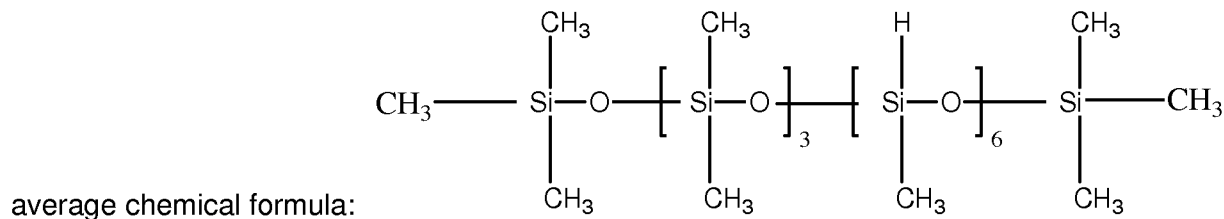


[0072] The polydimethylsiloxane with pedant and terminal vinyl groups, "M^{Vi}D₁₂₆D^{Vi}₂M^{Vi}", as referenced in the Examples below, was obtained from Dow Corning Corporation and has the

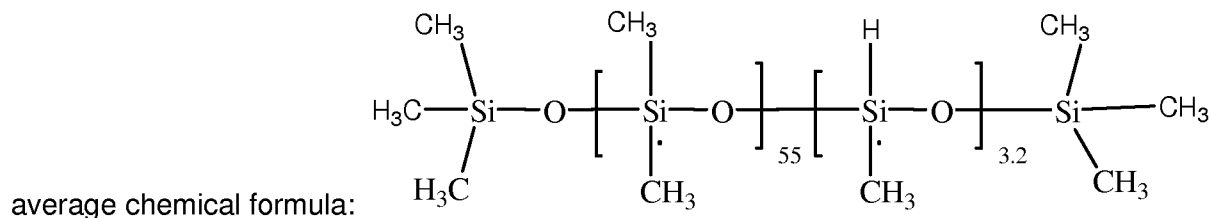


[0073] The D/T-vinyl polysiloxane: M_{0.025}D_{0.913}T_{0.054}M^{Vi}_{0.008}, having 2.5 mol% M units of formula (Me₃SiO_{0.5}), 91.3 mol% D units of formula (Me₂SiO), 5.4 mol% T units of formula (MeSiO_{1.5}), and 0.8 mol% units of formula (Me₂ViSiO_{0.5}), was obtained from Dow Corning Corporation.

- 15 **[0074]** The polydimethylsiloxane with pedant silicon-hydride (SiH) group, "MD₃D^H₆M", as referenced in the Examples below, was obtained from Dow Corning Corporation and has the

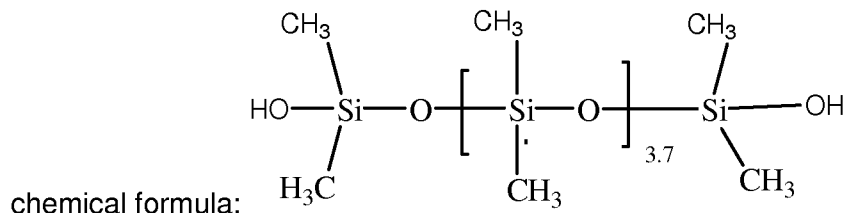


[0075] Another polydimethylsiloxane with pedant silicon-hydride (SiH) group, “MD₅₅D^H_{3.2}M”, as referenced in the Examples below, was obtained from Dow Corning Corporation and has the

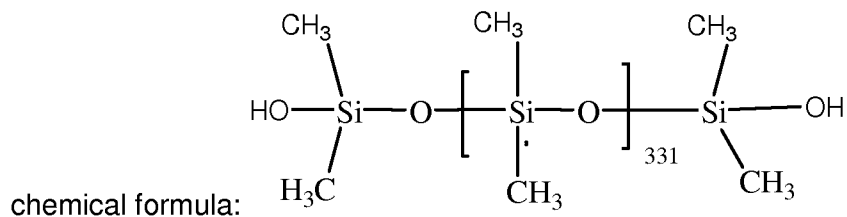


5

[0057] The silanol-terminated polydimethylsiloxane (DMS-S12), “MOHD_{3.7}MOH”, as referenced in the Examples below, was obtained from Gelest Inc. and has the average



[0057] The silanol-terminated polydimethylsiloxane (DMS-S32), “MOHD₃₃₁MOH”, as referenced in the Examples below, was obtained from Gelest Inc. and has the average



[0076] For purposes of these examples, viscosity was measured visually at room temperature of 25 °C by comparing a vial containing the product made in each example with vials of DOW CORNING® 200 FLUIDS of varying viscosities. “Low viscosity” means less than 10,000 cSt; “Moderate viscosity” means 10,000 cSt to 100,000 cSt; and “High viscosity” means greater than 100,000 cSt.

[0077] In example 1, the following ingredients were mixed in a container:

(a1) 112.8 g vinyl-terminated polydimethylsiloxane (M^{Vi}D₁₄₉M^{Vi}),

(b1) 33.83 g styrene (purchased from Sigma-Aldrich, Inc. of St. Louis, Missouri, U.S.A.),

(e1) 0.44 g 1,3-bis(3-methacryloxypropyl)tetramethyldisiloxane (purchased from Gelest Inc. of Morrisville, Pennsylvania, U.S.A.),

(c1) 1.32 g 2,5-di(tert-butylperoxy)2,5-dimethyl-3-hexyne (having 90% purity purchased from Sigma-Aldrich, Inc. of St. Louis, Missouri, U.S.A.), and

(d1) 58.45 g toluene (also from Sigma-Aldrich, Inc.).

[0078] The container was then purged with N₂ for 10 minutes to remove O₂. The mixture in the container was allowed to react for 5.5 hours at a temperature of 95 °C - 110 °C. The pressure in the container was reduced to 3 Torr and the container was heated at 80 °C to remove the solvent and any other volatile components that may have been present in the container. The resulting hydrophobic organic-silicone hybrid polymer was a white, opaque liquid with a moderate viscosity.

[0079] Without wishing to be bound by theory, it is thought that 2,5-di(tert-butylperoxy)2,5-dimethyl-3-hexyne may act as an initiator for crosslinking of ingredient (a1) and (co)polymerization for ingredient (b1) and ingredient (e1). While ingredient (e1) is a crosslinker for styrene polymerization, it is thought that the siloxane portion of the molecule will allow the polymer to interact with ingredient (a1), thereby improving compatibility of the ingredients. Without wishing to be bound by theory, it is thought that the hydrophobic organic-silicone hybrid polymer is formed via a radical reaction in which the methacryloxy groups of ingredient (e1) react with the vinyl groups of both ingredients (a1) and (b1). This example shows that a stable hydrophobic organic-silicone hybrid polymer can be formed via the reaction of ingredients (a) and (b) with one another and with a compatibilizer.

[0080] In example 2, the following ingredients were mixed in a container:

(a2) 114.76g D/T-vinyl polysiloxane (M_{0.025}D_{0.913}T_{0.054}M^{Vi}_{0.008}),

(b2) 23.21g isobutyl acrylate (purchased from Sigma-Aldrich, Inc.),

(c2) 0.60g t-butyl peroctoate (Esperox 28, purchased from Witco Chemicals Co.), and

(d2) 62.35g isopropanol.

[0081] The container was then purged with N₂ for 10 minutes to remove O₂. The mixture in the container was then allowed to react for 5.5 hours at a temperature of 80 °C - 85 °C. The pressure in the container was reduced to 3 Torr, and the container was heated at 108 °C to remove the solvent and any other volatile components that may have been present in the container. The resulting hydrophobic organic-silicone hybrid polymer was a white, opaque liquid with a high viscosity.

[0082] Without wishing to be bound by theory, it is thought that the hydrophobic organic-silicone hybrid polymer is formed via a radical reaction of two or more of the acrylate groups of ingredient (b2) and a radical reaction of two or more of the vinyl groups of ingredient (a2), and a radical reaction of an acrylate group of ingredient (b2) with a vinyl group of ingredient (a2). This example shows that a stable hydrophobic organic-silicone hybrid polymer can be formed via the reaction of ingredients (a) and (b) with themselves and/or with one another.

[0083] In example 3, the following ingredients were mixed in a container:

(a3-1) 133.65g vinyl-terminated polydimethylsiloxane (M^{Vi}D₁₄₉M^{Vi}),

(a3-2) 34.50g D/T-vinyl polysiloxane ($M_{0.025}D_{0.913}T_{0.054}M^{Vi}_{0.008}$),

(b3) 38.34g methylmethacrylate (purchased from Sigma-Aldrich, Inc.)

(e3) 1.96g 1,3-bis(3-methoxypropyl)tetramethyldisiloxane (purchased from Gelest, Inc.), and

(c3) 2.06g t-butyl peroctoate (Esperox 28, purchased from Witco Chemicals Co.).

5 **[0084]** The container was then purged with N_2 for 10 minutes to remove O_2 . The mixture in the container was allowed to react for 6.5 hours at a temperature of 90 °C - 97 °C. The resulting reaction product was the hydrophobic organic-silicone hybrid polymer; a white, opaque liquid with a moderate viscosity. The reaction product was able to be cured into a soft elastomer with $MD_3D^H_6M$ in presence of Pt-complex catalyst at 120 °C.

10 **[0085]** Without wishing to be bound by theory, it is thought that the hydrophobic organic-silicone hybrid polymer is formed via a radical reaction of the vinyl groups of ingredients (a3-1) and (a3-2), and a radical reaction of the methacrylate groups of ingredient (b3) and a radical reaction of vinyl groups with methacrylate groups. Without wishing to be bound by theory, it is thought that ingredient (e3) is reactive with both methacrylate groups and vinyl groups, thereby
15 allowing the (co)polymers of ingredient (a3-1) and ingredient (a3-2) and a (co)polymer from ingredient (b3) to be more compatible. This example shows that a stable hydrophobic organic-silicone hybrid polymer can be formed via the reaction of ingredients (a) and (b) with one another.

[0086] In example 4, the following ingredients were used mixed in a container:

20 (a4-1) 144.41g vinyl-terminated polydimethylsiloxane ($M^{Vi}D_{149}M^{Vi}$),

(a4-2) 42.95g D/T-vinyl polysiloxane ($M_{0.025}D_{0.913}T_{0.054}M^{Vi}_{0.008}$),

(b4) 14.42g styrene (purchased from Sigma-Aldrich, Inc.),

(e4) 0.31 g divinylbenzene (55% tech., purchased from Sigma-Aldrich, Inc.), and

(c4) 1.95g t-butyl peroctoate (Esperox 28, purchased from Witco Chemicals Co.).

25 **[0087]** The container was then purged with N_2 for 10 minutes to remove O_2 . The mixture in the container was allowed to react for 6.5 hours at a temperature of 90 °C - 100 °C. The resulting reaction product was a hydrophobic organic-silicone hybrid polymer; a white, opaque liquid with a moderate viscosity. The hydrophobic organic-silicone hybrid polymer was able to be cured into a hard elastomer with $MD_3D^H_6M$ in presence of Pt-complex catalyst at 120 °C.

30 **[0088]** Without wishing to be bound by theory, it is thought that the hydrophobic organic-silicone hybrid polymer is formed via radical reaction in which the vinyl groups of ingredient (e4) react with the vinyl groups of ingredients (b4) and also (a4-1) and (a4-2). This example shows that a stable hydrophobic organic-silicone hybrid polymer can be formed via the reaction of ingredients (a) and (b) with one another.

[0089] Examples 3 and 4 show that a hydrophobic organic-silicone hybrid polymer, which has reactive vinyl groups suitable for hydrosilylation may be formed by a simple method that does not require a separate recovery step. By providing a molar excess of vinyl groups in ingredient (a), the hydrophobic organic-silicone hybrid polymer may be formed by a radical reaction, and the hydrophobic organic-silicone hybrid polymer formed by the method described herein may have reactive vinyl groups. Furthermore, the hydrophobic organic-silicone hybrid polymer prepared in these examples can be formulated into compositions with an SiH crosslinker and a hydrosilylation reaction catalyst, and the compositions are curable.

[0090] In example 5, the following ingredients were mixed in a container:

- (a5-1) 93.42g vinyl-terminated polydimethylsiloxane ($M^{Vi}D_{149}M^{Vi}$),
- (a5-2) 10.5g polydimethylsiloxane with pendant silicon-hydride (SiH) group ($MD_{55}D^H_{3.2}M$),
- (b5) 20.87g methylmethacrylate (purchased from Sigma-Aldrich, Inc.),
- (e5) 2.13g allyl methacrylate (purchased from Sigma-Aldrich, Inc.),
- (c5-1) 0.92g SYL-OFF® 4000 (hydrosilylation catalyst available from, Dow Corning Corporation),
- (c5-2) 0.62g t-butyl peroctoate (Esperox 28, purchased from Witco Chemicals Co.), and
- (d5) 95.0 g THF (purchased from Sigma-Aldrich, Inc.).

[0091] The container was then purged with N_2 for 10 minutes to remove O_2 . The mixture in the container was allowed to react for 6 hours at a temperature of 70 °C - 74 °C. The pressure in the container was reduced to 3 Torr and the container was heated at 82 °C to then remove the solvent and any other volatile compounds that may have been present in the reaction product. The resulting hydrophobic organic-silicone hybrid polymer was a white, opaque liquid with a high viscosity. The hydrophobic organic-silicone hybrid polymer was able to be cured into a hard elastomer with $MD_3D^H_6M$ in presence of Pt-complex catalyst at 120 °C.

[0092] This example shows that a dual reaction system (polyaddition of the vinyl groups of (a5-1), the SiH of (a5-2), and the allyl groups of ingredient (e5); and radical reaction of the vinyl groups of (a5-1), the methacrylate groups of (b5), and the methacrylate groups of (e5)) may be used to prepare a hydrophobic organic-silicone hybrid polymer. Furthermore, the hydrophobic organic-silicone hybrid polymer prepared in this example can be formulated into a composition with an SiH crosslinker and a hydrosilylation reaction catalyst, and the composition is curable.

[0093] In example 6, the following ingredients were mixed in a container:

- (a6) 100.2g D/T-vinyl polysiloxane ($M_{0.025}D_{0.913}T_{0.054}M^{Vi}_{0.008}$),
- (c6-1) 0.30 g t-butyl peroctoate (Esperox 28 purchased from Witco Chemicals),
- (b6-1) 12.17g polyethylene glycol (MW=300, purchased from Sigma-Aldrich, Inc.),
- (b6-2) 10.81g dicyclohexylmethane-4,4'-diisocyanate (Desmodur W, purchased from Bayer),

(f6) 0.32g glycerol ethoxylate (MW=1000, purchased from Sigma-Aldrich, Inc.),
 (c6-2) 0.18g dibutyltin dilaurate (purchased from Gelest, Inc.), and
 (d6) 77.88g THF.

[0094] The container was then purged with N₂ for 10 minutes to remove O₂. The mixture in
 5 the container was allowed to react for 6 hours at a temperature of 70 °C - 73 °C. The pressure in
 the container was reduced to 3 Torr, and the container was heated at 82 °C to then remove the
 solvent and any other volatile compounds that may have been present in the reaction product.
 The resulting hydrophobic organic-silicone hybrid polymer was a white, opaque liquid with a
 high viscosity. The hydrophobic organic-silicone hybrid polymer was able to be cured into a soft
 10 elastomer with MD₃D^H₆M in presence of Pt-complex catalyst at 120 °C.

[0095] Without wishing to be bound by theory, it is thought that the hydrophobic organic-
 silicone hybrid polymer may be formed via two or more reactions; *i.e.*, polyaddition reaction of
 the isocyanate groups of ingredient (b6-2) with hydroxy groups of ingredients (b6-1) and (f6)
 initiated by ingredient (c6-2), and radical reaction of the vinyl groups of ingredient (a6) initiated
 15 by ingredient (c6-1). This example shows that a dual reaction system (polyaddition and radical)
 may be used to prepare a hydrophobic organic-silicone hybrid polymer. Furthermore, the
 hydrophobic organic-silicone hybrid polymer prepared in this example can be formulated into a
 composition with an SiH crosslinker and a hydrosilylation reaction catalyst, and the composition
 is curable. Without wishing to be bound by theory, it is thought that this hydrophobic organic-
 20 silicone hybrid polymer could be formulated into a composition with a multifunctional compound
 with 2 or more hydroxy or amine (-NH- or NH₂-) groups, and the resulting composition would be
 curable.

[0096] In example 7, the following ingredients were mixed in a container:

(a7-1) 135.3g vinyl-terminated polydimethylsiloxane (M^{Vi}D₁₄₉M^{Vi}),
 25 (17-2) 16.4g polydimethylsiloxane with pedant and terminal vinyl groups (M^{Vi}D₁₂₆D^{Vi}₂M^{Vi}),
 (c7-1) 0.75g t-butyl peroctoate (Esperox 28 purchased from Witco Chemicals),
 (b7-1) 18.9g polyethylene glycol (MW=300, purchased from Sigma-Aldrich, Inc.),
 (b7-2) 17.0g dicyclohexylmethane-4,4'-diisocyanate (Desmodur W, purchased from Bayer),
 (e7) 0.85g glycerol ethoxylate (MW=1000, purchased from Sigma-Aldrich, Inc.), and
 30 (c7-2) 0.35g dibutyltin dilaurate (purchased from Gelest, Inc.).

[0097] The container was then purged with N₂ for 10 minutes to remove O₂. The mixture in
 the container was allowed to react for 7 hours at a temperature of 90 °C - 97 °C. The resulting
 reaction product was a white, unclear liquid with a moderate viscosity, which contained the

hydrophobic organic-silicone hybrid polymer. The reaction product was able to be cured into a hard elastomer with $\text{MD}_3\text{D}^{\text{H}}_6\text{M}$ in presence of Pt-complex catalyst at 120 °C.

[0098] This example shows that a dual reaction (polyaddition of isocyanate groups of ingredient (b7-2) and hydroxy groups of ingredients (b7-1) and (f7) initiated by ingredient (c7-2); and radical reaction of ingredients (a7-1) and (a7-2) initiated by ingredient (c7-1)) may be used to prepare a hydrophobic organic-silicone hybrid polymer in a simple method that does not require recovery of the hydrophobic organic-silicone hybrid polymer when a solvent is not used. Furthermore, the hydrophobic organic-silicone hybrid polymer prepared in this example can be formulated into a composition with an SiH crosslinker and a hydrosilylation reaction catalyst, and the composition is curable.

[0099] In example 8, the following ingredients were mixed in a container:

(a8-1) 94.83g silanol-terminated polydimethylsiloxane (DMS-S32),

(a8-2) 10.54 g silanol-terminated polydimethylsiloxane (DMS-S12),

(e8) 2.14 g 3-isocyanatopropyltrimethoxysilane (purchased from Gelest, Inc.),

(b8-1) 12.8g polyethylene glycol (MW=300, purchased from Sigma-Aldrich, Inc.),

(b8-2) 14.62g dicyclohexylmethane-4,4'-diisocyanate (Desmodur W, purchased from Bayer),

(f8) 0.285g glycerol ethoxylate (MW=1000, purchased from Sigma-Aldrich, Inc.),

(c8) 0.22g dibutyltin dilaurate (purchased from Gelest), and

(d8) 91.1g THF.

[0100] The container was then purged with N_2 for 10 minutes to remove O_2 . The mixture in the container was allowed to react for 6 hours at a temperature of 70 °C - 74 °C. The pressure in the container was reduced to 3 Torr, and the container was heated at 82 °C to then remove the solvent and other volatile compounds from the reaction product. The resulting hydrophobic organic-silicone hybrid polymer was a white, opaque liquid with a moderate viscosity. The hydrophobic organic-silicone hybrid polymer was able to be cured into a hard elastomer with JEFFAMINE® D-230 polyetheramine (purchased from Huntsman) at 100 °C. The reaction product was also able to be cured into an elastomeric foam with JEFFAMINE® D-230 in presence of water at 80 °C.

[0101] Without wishing to be bound by theory, it is thought that the hydrophobic organic-silicone hybrid polymer is formed via dual reactions, *i.e.*, condensation and polyaddition, in which the isocyanate groups of ingredient (b8-2) react with the hydroxy groups of ingredients (b8-1), (e8), and (f8) via polyaddition reaction, and the silanol groups of ingredients (a8-1) and (a8-2) react with the methoxy groups of ingredient (e8). Ingredient (c8) is the initiator for both the polyaddition and condensation reactions. Ingredient (e8) allows the two polymer networks from polyaddition and condensation to be more compatible by its reactions into the two

networks. This example shows that a dual reaction system (polyaddition and condensation) may be used to prepare a hydrophobic organic-silicone hybrid polymer. Furthermore, the hydrophobic organic-silicone hybrid polymer prepared in this example can be formulated into a composition with an amine catalyst, and the composition is curable to a solid article in the form of a hard elastomer or a foam.

[0102] In example 9, the following ingredients were mixed in a container:

(a9-1) 90.12g silanol-terminated polydimethylsiloxane (DMS-S32),

(a9-2) 10.30 g silanol-terminated polydimethylsiloxane (DMS-S12),

(b9-1) 12.94g JEFFAMINE® D-2000 polyetheramine (purchased from Huntsman),

(b9-2) 14.88g D.E.R.331 (liquid epoxy resinous monomer, purchased from The Dow Chemical Company),

(e9) 2.09 g 3-aminopropyltrimethoxysilane (purchased from Gelest),

(c9) 0.56g 1,8-diazabicyclo[5,4,0] undec-7-ene (purchased from Sigma-Aldrich), and

(d9) 97.9g THF.

[0103] The container was then purged with N₂ for 10 minutes to remove O₂. The mixture in the container was allowed to react for 6.5 hours at a temperature of 70°C - 74°C. The pressure in the container was reduced to 3 Torr and the container was heated at 82°C to then remove the solvent and other volatile compounds. The resulting hydrophobic organic-silicone hybrid polymer was a white, unclear liquid with a moderate viscosity. The hydrophobic organic-silicone hybrid polymer was able to be cured into a hard elastomer with 3-isocyanatopropyltrimethoxysilane in presence of dibutyltin dilaurate at 120°C. The 3-isocyanatopropyltrimethoxysilane and dibutyl tin dilaurate were purchased from Gelest, inc.

[0104] Without wishing to be bound by theory, it is thought that the hydrophobic organic-silicone hybrid polymer is formed via dual reactions, *i.e.*, condensation and polyaddition, in which the epoxy groups on ingredient (b9-2) react with the amino groups (NH₂-) of ingredient (e9) via polyaddition reaction, and the silanol groups on ingredients (a9-1) and (a9-2) react via condensation reaction with the alkoxy groups on ingredient (e9). Without wishing to be bound by theory, it is thought that ingredient (c9) is the initiator for both the polyaddition and condensation reactions, and that ingredient (e9) allows the two polymer networks formed by polyaddition and condensation to more compatible by its reactions into the two networks. This example shows that a dual reaction system (polyaddition and condensation) may be used to prepare a hydrophobic organic-silicone hybrid polymer. Furthermore, the hydrophobic organic-silicone hybrid polymer prepared in this example can be formulated into a composition with a condensation reaction catalyst and crosslinker and cured to form a solid article.

[0105] In example 10, the following ingredients were mixed in a container:

(a10-1) 79.72g silanol-terminated polydimethylsiloxane (DMS-S32),

(a10-2) 19.80 g silanol-terminated polydimethylsiloxane (DMS-S12),
(f10-1) 2.04 g vinyltrimethoxysilane (purchased from Gelest), (b10-1) 12.37g polyethylene glycol (MW=300, purchased from Sigma-Aldrich, Inc),
(b10-2) 12.44g dicyclohexylmethane-4,4'-diisocyanate (Desmodur W, purchased from Bayer),
5 (f10-2) 0.42g glycerol ethoxylate (MW=1000, purchased from Sigma-Aldrich, Inc),
(c10) 0.22g dibutyltin dilaurate (purchased from Gelest), and
(d10) 99.27g THF.

[0106] The container was then purged with N₂ for 10 minutes to remove O₂. The mixture in the container was allowed to react for 6.5 hours at a temperature of 70°C - 72°C. The pressure
10 in the container was reduced to 3 Torr and the container was heated at 84°C to then remove the solvent and other volatile compounds. The resulting hydrophobic organic-silicone hybrid polymer was a white, opaque liquid with a moderate viscosity. The hydrophobic organic-silicone hybrid polymer was able to be cured into a hard elastomer with MD₃DH₆M in presence of Pt-complex catalyst at 120°C.

[0107] Without wishing to be bound by theory, it is thought that the hydrophobic organic-silicone hybrid polymer of example 10 forms by dual reactions, *i.e.*, condensation and polyaddition, in which the silanol groups of ingredients (a10-1) and (a10-2) react with the methoxy groups of ingredient (f10-1) via condensation reaction, and the isocyanate groups of ingredient (b10-2) react with the hydroxy groups of ingredients (b10-1) and (f10-2) via
20 polyaddition reaction, with ingredient (c10) being the initiator for both the polyaddition and condensation reactions. This example shows that a stable hydrophobic organic-silicone hybrid polymer can be formed using two separate crosslinkers, without a compatibilizer.

[0108] All of the hydrophobic organic-silicone hybrid polymers prepared in examples 1-10 was stable. These examples show that stable reaction products can be formed by the method
25 described herein, and that the reaction products formed by the method contain reactive groups that allow the reaction products to be formulated into compositions and further reacted to form solid articles.

[0109] All amounts, ratios, and percentages are by weight unless otherwise indicated by the context of the specification. The following definitions are provided to further describe the
30 method herein. The articles "a", "an", and "the" each refer to one or more, unless otherwise indicated by the context of the specification.

[0110] "Alkyl" means an acyclic, branched or unbranched, saturated monovalent hydrocarbon group. Examples of alkyl groups include Me, Et, Pr, 1-methylethyl, Bu, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, 1-methylbutyl, 1-ethylpropyl, pentyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl, hexyl, heptyl, 2-ethylhexyl, octyl, nonyl, and
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decyl; and as well as other branched saturated monovalent hydrocarbon groups with 6 or more carbon atoms. Alkyl groups have at least one carbon atom. Alternatively, alkyl groups may have 1 to 12 carbon atoms, alternatively 1 to 10 carbon atoms, alternatively 1 to 6 carbon atoms, alternatively 1 to 4 carbon atoms, alternatively 1 to 2 carbon atoms, and alternatively 1 carbon atom.

[0111] “Aralkyl” and “alkaryl” each refer to an alkyl group having a pendant and/or terminal aryl group or an aryl group having a pendant alkyl group. Exemplary aralkyl groups include benzyl, tolyl, xylyl, phenylethyl, phenyl propyl, and phenyl butyl. Aralkyl groups have at least 6 carbon atoms. Monocyclic aralkyl groups may have 6 to 12 carbon atoms, alternatively 6 to 9 carbon atoms, and alternatively 6 to 7 carbon atoms. Polycyclic aralkyl groups may have 7 to 17 carbon atoms, alternatively 7 to 14 carbon atoms, and alternatively 9 to 10 carbon atoms.

[0112] “Alkenyl” means an acyclic, branched, or unbranched unsaturated monovalent hydrocarbon group, where the monovalent hydrocarbon group has a double bond. Alkenyl groups include Vi, allyl, propenyl, and hexenyl. Alkenyl groups have at least 2 carbon atoms. Alternatively, alkenyl groups may have 2 to 12 carbon atoms, alternatively 2 to 10 carbon atoms, alternatively 2 to 6 carbon atoms, alternatively 2 to 4 carbon atoms, and alternatively 2 carbon atoms.

[0113] “Alkynyl” means an acyclic, branched, or unbranched unsaturated monovalent hydrocarbon group, where the monovalent hydrocarbon group has a triple bond. Alkynyl groups include ethynyl and propynyl. Alkynyl groups have at least 2 carbon atoms. Alternatively, alkynyl groups may have 2 to 12 carbon atoms, alternatively 2 to 10 carbon atoms, alternatively 2 to 6 carbon atoms, alternatively 2 to 4 carbon atoms, and alternatively 2 carbon atoms.

[0114] “Aryl” means a cyclic, fully unsaturated, hydrocarbon group. Aryl is exemplified by, but not limited to, Ph and naphthyl. Aryl groups have at least 5 carbon atoms. Monocyclic aryl groups may have 5 to 9 carbon atoms, alternatively 6 to 7 carbon atoms, and alternatively 6 carbon atoms. Polycyclic aryl groups may have 10 to 17 carbon atoms, alternatively 10 to 14 carbon atoms, and alternatively 12 to 14 carbon atoms.

[0115] “Carbocycle” and “carbocyclic” refer to a hydrocarbon ring. Carbocycles may be monocyclic or alternatively may be fused, bridged, or spiro polycyclic rings. Carbocycles have at least 3 carbon atoms. Monocyclic carbocycles may have 3 to 9 carbon atoms, alternatively 4 to 7 carbon atoms, and alternatively 5 to 6 carbon atoms. Polycyclic carbocycles may have 7 to 17 carbon atoms, alternatively 7 to 14 carbon atoms, and alternatively 9 to 10 carbon atoms. Carbocycles may be saturated or partially unsaturated.

[0116] “Cycloalkyl” refers to a saturated hydrocarbon group including a carbocycle. Cycloalkyl groups are exemplified by cyclobutyl, cyclopentyl, cyclohexyl, and methylcyclohexyl.

Cycloalkyl groups have at least 3 carbon atoms. Monocyclic cycloalkyl groups may have 3 to 9 carbon atoms, alternatively 4 to 7 carbon atoms, and alternatively 5 to 6 carbon atoms.

Polycyclic cycloalkyl groups may have 7 to 17 carbon atoms, alternatively 7 to 14 carbon atoms, and alternatively 9 to 10 carbon atoms.

5 **[0117]** "Halogenated hydrocarbon" means a hydrocarbon where one or more hydrogen atoms bonded to a carbon atom have been formally replaced with a halogen atom. Halogenated hydrocarbon groups include haloalkyl groups, halogenated carbocyclic groups, and haloalkenyl groups. Haloalkyl groups include fluorinated alkyl groups such as trifluoromethyl (CF₃), fluoromethyl, trifluoroethyl, 2-fluoropropyl, 3,3,3-trifluoropropyl, 4,4,4-trifluorobutyl, 4,4,4,3,3-
10 pentafluorobutyl, 5,5,5,4,4,3,3-heptafluoropentyl, 6,6,6,5,5,4,4,3,3-nonafluorohexyl, and 8,8,8,7,7-pentafluorooctyl; and chlorinated alkyl groups such as chloromethyl and 3-chloropropyl. Halogenated carbocyclic groups include fluorinated cycloalkyl groups such as 2, 2-difluorocyclopropyl, 2, 3-difluorocyclobutyl, 3, 4-difluorocyclohexyl, and 3, 4-difluoro-5-methylcycloheptyl; and chlorinated cycloalkyl groups such as 2, 2-dichlorocyclopropyl, 2, 3-
15 dichlorocyclopentyl. Haloalkenyl groups include allyl chloride.

[0118] "Heteroatom" means any of the Group 13-17 elements of the IUPAC Periodic Table of the Elements at http://www.iupac.org/fileadmin/user_upload/news/IUPAC_Periodic_Table-1Jun12.pdf, except carbon. "Heteroatom" includes, for example, N, O, P, S, Br, Cl, F, and I.

[0119] "Heteroatom containing group" means an organic group comprising a carbon atom
20 and at least one heteroatom. Heteroatom containing groups may include, for example, one or more of acyl, amide, amine, carboxyl, cyano, epoxy, hydrocarbonoxy, imino, ketone, ketoxime, mercapto, oxime, and/or thiol. For example, when the heteroatom containing group contains one or more halogen atoms, then the heteroatom containing group may be a halogenated hydrocarbon group as defined above. Alternatively, when the heteroatom is oxygen, then the
25 heteroatom containing group may be a hydrocarbonoxy group such as an alkoxy group or an alkylalkoxy group. Alternatively, when the heteroatom is nitrogen, then the heteroatom containing group may be cyano or a cyano-functional group such as cyanoalkyl or cyanoalkenyl.

[0120] "Heteroalkyl" group means an acyclic, branched or unbranched, saturated monovalent
30 hydrocarbon group that also includes at least one heteroatom. "Heteroalkyl" includes haloalkyl groups and alkyl groups in which at least one carbon atom has been replaced with a heteroatom such as N, O, P, or S, *e.g.*, when the heteroatom is O, the heteroalkyl group may be an alkoxy group.

[0121] "Heterocycle" and "heterocyclic" each mean a ring group comprised of carbon atoms
35 and one or more heteroatoms in the ring. The heteroatom in the heterocycle may be N, O, P, S, or a combination thereof. Heterocycles may be monocyclic or alternatively may be fused,

bridged, or spiro polycyclic rings. Monocyclic heterocycles may have 3 to 9 member atoms in the ring, alternatively 4 to 7 member atoms, and alternatively 5 to 6 member atoms. Polycyclic heterocycles may have 7 to 17 member atoms, alternatively 7 to 14 member atoms, and alternatively 9 to 10 member atoms. Heterocycles may be saturated or partially unsaturated.

5 **[0122]** "Heteroaromatic" means a fully unsaturated ring containing group comprised of carbon atoms and one or more heteroatoms in the ring. Monocyclic heteroaromatic groups may have 5 to 9 member atoms, alternatively 6 to 7 member atoms, and alternatively 5 to 6 member atoms. Polycyclic heteroaromatic groups may have 10 to 17 member atoms, alternatively 10 to 14 member atoms, and alternatively 12 to 14 member atoms. Heteroaromatic includes
10 heteroaryl groups such as pyridyl. Heteroaromatic includes heteroaralkyl, *i.e.*, an alkyl group having a pendant and/or terminal heteroaryl group or a heteroaryl group having a pendant alkyl group. Exemplary heteroaralkyl groups include methylpyridyl and dimethylpyridyl.

[0123] "Hydrophobicity" and its derivatives such as 'hydrophobic' refers to the association of non-polar groups or molecules in an aqueous environment which arises from the tendency of
15 water to exclude non-polar molecules. For example, a hydrophobic material will absorb < 2% water (have <2 % increase in weight) when immersed in liquid water for one day at 25°C. For clarity, the hydrophobic organic-silicone hybrid polymer described herein may have reactive groups that are reactive with water even though said hydrophobic organic-silicone hybrid polymer is hydrophobic in nature.

20 **[0124]** "Water insoluble" means that an amount of a compound that dissolves into water is < 1 g of the compound per 100 g of water at 20°C.

[0125] Abbreviations used herein are defined as follows. The abbreviation "cP" means centiPoise, and "cSt" means centiStokes. "DP" means the degree of polymerization. "FTIR" means Fourier transform infrared spectroscopy. "GC" means gas chromatography. "GPC"
25 means gel permeation chromatography. "Mn" means number average molecular weight. Mn may be measured using GPC. "Mw" means weight average molecular weight. "NMR" means nuclear magnetic resonance. "Pa·s" means Pascal seconds, and "ppm" means parts per million. "Et" means ethyl. "Me" means methyl. "Ph" means phenyl. "Pr" means propyl and includes various structures such as iPr and nPr. "iPr" means isopropyl. "nPr" means normal
30 propyl. "Bu" means butyl and includes various structures including nBu, sec-butyl, tBu, and iBu. "iBu" means isobutyl. "nBu" means normal butyl. "tBu" means tert-butyl. "Vi" means vinyl.

[0126] The disclosure of ranges includes the range itself and also anything subsumed therein, as well as endpoints. For example, disclosure of a range of 2.0 to 4.0 includes not only the range of 2.0 to 4.0, but also 2.1, 2.3, 3.4, 3.5, and 4.0 individually, as well as any other
35 number subsumed in the range. Furthermore, disclosure of a range of, for example, 2.0 to 4.0

includes the subsets of, for example, 2.1 to 3.5, 2.3 to 3.4, 2.6 to 3.7, and 3.8 to 4.0, as well as any other subset subsumed in the range.

[0127] With respect to any Markush groups relied upon herein for describing particular features or aspects of various embodiments, different, special, and/or unexpected results may be obtained from each member of the respective Markush group independent from all other Markush members. Each member of a Markush group may be relied upon individually and or in combination with any other member or members of the group, and each member provides adequate support for specific embodiments within the scope of the appended claims. For example, disclosure of the Markush group: alkyl, aryl, and carbocyclic includes the member alkyl individually; the subgroup alkyl and aryl; and any other individual member and subgroup subsumed therein.

[0128] Any ranges and subranges relied upon in describing various embodiments of the present disclosure independently and collectively fall within the scope of the appended claims, and are understood to describe and contemplate all ranges including whole and/or fractional values therein, even if such values are not expressly written herein. The enumerated ranges and subranges sufficiently describe and enable various embodiments of the present disclosure, and such ranges and subranges may be further delineated into relevant halves, thirds, quarters, fifths, and so on. As just one example, a range "of 200 to 1400" may be further delineated into a lower third, *i.e.*, from 200 to 600, a middle third, *i.e.*, from 600 to 1000, and an upper third, *i.e.*, from 1000 to 1400, which individually and collectively are within the scope of the appended claims, and may be relied upon individually and/or collectively and provide adequate support for specific embodiments within the scope of the appended claims. In addition, with respect to the language which defines or modifies a range, such as "at least," "greater than," "less than," "no more than," and the like, it is to be understood that such language includes subranges and/or an upper or lower limit. As another example, a range of "at least 0.1%" inherently includes a subrange from 0.1% to 35%, a subrange from 10% to 25%, a subrange from 23% to 30%, and so on, and each subrange may be relied upon individually and/or collectively and provides adequate support for specific embodiments within the scope of the appended claims. Finally, an individual number within a disclosed range may be relied upon and provides adequate support for specific embodiments within the scope of the appended claims. For example, a range of "1 to 9" includes various individual integers, such as 3, as well as individual numbers including a decimal point (or fraction), such as 4.1, which may be relied upon and provide adequate support for specific embodiments within the scope of the appended claims.

[0129] When selecting ingredients for use in the method and composition described above, there may be overlap between types of ingredients because certain ingredients described herein may have more than one function. For example, certain alkoxysilanes may be useful as

filler treating agents and as adhesion promoters, and certain plasticizers such as fatty acid esters may also be useful as filler treating agents. Certain particulates may be useful as fillers and as pigments, and even as flame retardants, *e.g.*, carbon black. Certain crosslinkers for ingredient (f) and certain compatibilizers for ingredient (e) in the method may be useful as crosslinkers for the composition containing the hydrophobic organic-silicone hybrid polymer. Certain crosslinkers for ingredient (f) may also be useful as compatibilizers, for example, when the reactive groups of ingredients (a) and (b) are the same. When adding additional ingredients to the composition, the additional ingredients are distinct from one another.

[0130] The subject matter of all combinations of independent and dependent claims, both singly and multiply dependent, is expressly contemplated but is not described in detail for the sake of brevity. The disclosure has been described in an illustrative manner, and the terminology which has been used is intended to be in the nature of words of description rather than of limitation. Many modifications and variations of the present disclosure are possible in light of the above teachings, and the disclosure may be practiced otherwise than as specifically described. The aspects of the invention of appended claims 1-29 are hereby incorporated by reference.

Embodiments of the invention

[0131] In a first embodiment, a method of preparing a hydrophobic organic-silicone hybrid polymer is disclosed. The method comprises:

- (1) preparing a mixture by combining ingredients comprising
 - (a) 1 wt% to 99 wt% of a polyorganosiloxane having an average, per molecule, of one or more reactive groups,
 - (b) 1 wt% to 99 wt% of a water insoluble, polymerizable, organic monomer, and
 - (c) 0 to 10 wt% of an initiator; and
- (2) subjecting the mixture to polymerization conditions to form the hydrophobic organic-silicone hybrid polymer, wherein the hydrophobic organic-silicone hybrid polymer has, per molecule, one or more reactive groups.

[0132] In a second embodiment, the method of the first embodiment further comprises at least one of:

- adding (d) a solvent to the ingredients during step (1) and/or to the mixture after step (1), and/or
- adding (e) a compatibilizer to the ingredients during step (1), and/or
- adding (f) a crosslinker to the ingredients during step (1).

[0133] In a third embodiment, in the method of any preceding embodiments, oxygen may be present before step (2) and the method further comprises removing some or all of the oxygen before step (2).

[0134] In a fourth embodiment, the initiator is present, and the initiator is capable of catalyzing polymerization of (a) the polyorganosiloxane, or polymerization of (b) the water insoluble, polymerizable, organic monomer, and/or copolymerization of (a) and (b).

[0135] In a fifth embodiment, the fourth embodiment further includes where the initiator is a radical initiator; and one of:

(i) ingredient (b), the water insoluble, polymerizable, organic monomer, has free radical reactive groups; or

(ii) the one or more reactive groups on ingredient (a), the polyorganosiloxane, is a free radical reactive group; or

(iii) both (i) and (ii).

[0136] In a sixth embodiment, the fourth or fifth embodiment further includes that the initiator is a free radical initiator, a photoinitiator, or a combination of a free radical initiator and a photoinitiator.

[0137] In a seventh embodiment, the fourth embodiment further includes that the initiator is a condensation and/or polyaddition reaction catalyst; and one of

(i) ingredient (b), the water insoluble, polymerizable, organic monomer, has condensation and/or polyaddition reactive groups; or

(ii) the one or more reactive groups on ingredient (a), the polyorganosiloxane, is a condensation and/or polyaddition reactive group; or

(iii) both (i) and (ii).

[0138] In an eighth embodiment, any one of the preceding embodiments further includes that the hydrophobic organic-silicone hybrid polymer comprises

(I) a copolymer of repeating units based on the water insoluble, polymerizable, organic monomer (b) and the polyorganosiloxane (a); or

(II) a mixture of a homopolymer of repeating units based on the water insoluble, polymerizable, organic monomer (b) and the polyorganosiloxane (a); or

(III) a combination of both (I) and (II).

[0139] In a ninth embodiment, the method of any one of the preceding embodiments further includes that the one or more reactive groups of the hydrophobic organic-silicone hybrid polymer comprises one or more functional groups configured to be reacted to form a hydrophobic organic-silicone hybrid polymer having longer chains and/or a crosslinked network relative to the unreacted hydrophobic organic-silicone hybrid polymer.

[0140] In a tenth embodiment, the method of the first embodiment further includes that the one or more reactive groups of ingredient (a) comprises one or more aliphatically unsaturated organic groups capable of undergoing hydrosilylation reaction and/or radical initiated reaction.

[0141] In an eleventh embodiment, the tenth embodiment further includes that the water insoluble, polymerizable, organic monomer is a radical polymerizable monomer.

[0142] In a twelfth embodiment, the eleventh embodiment further includes that the radical polymerizable monomer is selected from alkylvinyl monomers, alkylalkenyl monomers, alkylallyl monomers, arylvinyl monomers, arylalkenyl monomers, and alkylacrylic-containing monomers.

[0143] In a thirteenth embodiment, the twelfth embodiment further includes that the radical polymerizable monomer is selected from α -olefin, butadiene, isoprene, and styrene.

[0144] In a fourteenth embodiment, the method of the first embodiment further includes that the one or more reactive groups of ingredient (a) comprises one or more condensation and/or polyaddition reactive groups.

[0145] In a fifteenth embodiment, the method of the fourteenth embodiment further includes that the condensation and/or polyaddition reactive groups are selected from amine groups, hydroxy groups, alcoholic groups, epoxy groups, isocyanate groups, and phenol groups.

[0146] In a sixteenth embodiment, the method of the fourteenth or fifteenth embodiment further includes that the water insoluble, polymerizable, organic monomer is a condensation and/or polyaddition type monomer.

[0147] In a seventeenth embodiment, the method of the sixteenth embodiment further includes that the water insoluble, polymerizable, organic monomer is selected from a polyisocyanate monomer, a polyol monomer, a polyamine monomer, a polyphenol monomer, and any combination of two or more of a polyol monomer, a polyisocyanate monomer, a polyamine monomer, a polyphenol monomer.

[0148] In an eighteenth embodiment, the method of any one of the second to the ninth embodiments further includes that the solvent comprises toluene, isopropanol, tetrahydrofuran, xylene, hexane, cyclohexane, cyclohexanone, heptane, octane, or any combination of two or more thereof.

[0149] A nineteenth embodiment is a hydrophobic, organic-silicone hybrid polymer prepared by the method of any one of the embodiments described above.

[0150] The twentieth embodiment is a hydrophobic, organic-silicone hybrid polymer of the nineteenth embodiment, where the hydrophobic, organic-silicone hybrid polymer is an opaque liquid that is uniform in appearance and does not visibly separate after three days at 25 °C.

[0151] The twenty-first embodiment is a composition comprising: (A) the hydrophobic organic-silicone hybrid polymer of the nineteenth or twentieth embodiments; (B) a catalyst capable of catalyzing reaction of the one or more reactive groups of the hydrophobic organic-silicone hybrid polymer; and optionally (C) a crosslinker; optionally (D) a drying agent; optionally (E) an extender; optionally (F) a filler; optionally (G) a filler treating agent; optionally (H) a biocide; optionally (I) a stabilizer, optionally (J) a flame retardant; optionally (K) a surface

modifier; optionally (L) a chain lengthener; optionally (M) an endblocker; optionally (N) a flux agent; optionally (O) an anti-aging additive; optionally (P) a pigment; optionally (Q) an acid acceptor; optionally (R) a rheological additive; optionally (S) a vehicle; optionally (T) a surfactant; optionally (U) a corrosion inhibitor; optionally (V) a polyorganosiloxane having two or more aliphatically unsaturated organic groups per molecule; optionally (W) a water release agent; and optionally (X) a polyorganosiloxane having two or more hydrolyzable groups per molecule.

[0152] The twenty-second embodiment is a composition according to the twenty-first embodiment, where (B) the catalyst is a radical initiator, and the composition optionally further comprises (C) a crosslinker having, per molecule, two or more two or more radical activatable unsaturated organic groups.

[0153] The twenty-third embodiment is a composition according to the twenty-second embodiment, where the two or more radical activated unsaturated organic groups are selected from alkylvinyl groups, alkylalkenyl groups, alkylallyl groups, arylvinyl groups, arylalkenyl groups, and alkylacrylic-containing groups.

[0154] The twenty-fourth embodiment is a composition according to the twenty-second or twenty-third embodiments, where (B) the catalyst is a hydrosilylation catalyst, and with the proviso that when no ingredient in the composition other than ingredient (C) has silicon bonded hydrogen atoms, then ingredient (C) the crosslinker is present and has, per molecule, two or more silicon bonded hydrogen atoms.

[0155] The twenty-fifth embodiment is a composition according to any one of the twenty-first to twenty-fourth embodiments, where the composition further comprises one or more additional ingredients, which are distinct from ingredients (A), (B), and (C), and which are selected from the group consisting of (D) the drying agent; (E) the extender; (F) the filler; (G) the filler treating agent; (H) the biocide; (I) the stabilizer; (J) the flame retardant; (K) the surface modifier; (L) the chain lengthener; (M) the endblocker; (N) the flux agent; (O) the anti-aging additive; (P) the pigment; (Q) the acid acceptor (R) the rheological additive; (S) the vehicle; (T) a surfactant; (U) the corrosion inhibitor; (V) the polyorganosiloxane having two or more aliphatically unsaturated organic groups per molecule, (W) the water release agent; (X) the polyorganosiloxane having two or more hydrolyzable groups per molecule, and a combination thereof.

[0156] The twenty-sixth embodiment is a method for making the composition of any one of the twenty-first to twenty-fifth embodiments. This method comprises:

mixing ingredients comprising ingredient (A) and ingredient (B); or

mixing ingredients comprising ingredients (A), (B), and (C); or

mixing ingredients comprising ingredients (A) and (B), and one or more of (D), (E), (F), (G), (H), (I), (J), (K), (L), (M), (N), (O), (P), (Q), (R), (S), (T), (U), and (V); or

mixing ingredients comprising ingredients (A), (B), and (C) and one or more of (D), (E), (F), (G), (H), (I), (J), (K), (L), (M), (N), (O), (P), (Q), (R), (S), (T), (U) and (V);
so as to make the composition.

[0157] The twenty-seventh embodiment is a method according to the twenty-sixth
5 embodiment, where ingredient (C) is present, the composition is a multiple part composition,
and ingredient (B) and ingredient (C) are stored in separate parts.

[0158] The twenty-eight embodiment is a solid article prepared by a method comprising
reacting the composition of any one of the twenty-first through twenty-fifth embodiments.

CLAIMS

1. A method of preparing a hydrophobic organic-silicone hybrid polymer, which method comprises:

(1) preparing a mixture by combining ingredients comprising

(a) 1 wt% to 99 wt% of a polyorganosiloxane having an average, per molecule, of one or more reactive groups,

(b) 1 wt% to 99 wt% of a water insoluble, polymerizable, organic monomer, and

(c) 0 to 10 wt% of an initiator; and

(2) subjecting the mixture to polymerization conditions to form the hydrophobic organic-silicone hybrid polymer, wherein the hydrophobic organic-silicone hybrid polymer has, per molecule, one or more reactive groups.

2. The method of claim 1, further comprising adding (d) a solvent to the ingredients during step (1) and/or to the mixture after step (1).

3. The method of claim 1 or claim 2, further comprising adding (e) a compatibilizer and/or (f) a crosslinker to the ingredients during step (1).

4. The method of any one of claims 1-3, where oxygen is present before step (2) and the method further comprises removing oxygen before step (2).

5. The method of any one of claims 1-4, where the initiator is present, and the initiator is capable of catalyzing polymerization of (a) the polyorganosiloxane, or polymerization of (b) the water insoluble, polymerizable, organic monomer, and/or copolymerization of (a) and (b).

6. The method of claim 5, where the initiator is a radical initiator; and (i) ingredient (b), the water insoluble, polymerizable, organic monomer, has free radical reactive groups; or (ii) the one or more reactive groups on ingredient (a), the polyorganosiloxane, is a free radical reactive group; or both (i) and (ii).

7. The method of claim 5, where the initiator is a condensation and/or polyaddition reaction catalyst; and (i) ingredient (b), the water insoluble, polymerizable, organic monomer, has condensation and/or polyaddition reactive groups; or (ii) the one or more reactive groups on ingredient (a), the polyorganosiloxane, is a condensation and/or polyaddition reactive group; or both (i) and (ii).

8. The method of any one of claims 1-7, wherein the hydrophobic organic-silicone hybrid polymer comprises (I) a copolymer of repeating units based on the water insoluble, polymerizable, organic monomer (b) and the polyorganosiloxane (a); (II) a mixture of a homopolymer of repeating units based on the water insoluble, polymerizable, organic monomer (b) and the polyorganosiloxane (a); or (III) a combination of both (I) and (II).
9. The method of any one of claims 1-8, where the one or more reactive groups of the hydrophobic organic-silicone hybrid polymer comprises one or more functional groups configured to be reacted to form a hydrophobic organic-silicone hybrid polymer having longer chains and/or a crosslinked network relative to the unreacted hydrophobic organic-silicone hybrid polymer.
10. The method of claim 1, where the one or more reactive groups of ingredient (a) comprises one or more aliphatically unsaturated organic groups capable of undergoing hydrosilylation reaction and/or radical initiated reaction.
11. The method of any one of claims 10, where the water insoluble, polymerizable, organic monomer is a radical polymerizable monomer.
12. The method of claim 11, where the radical polymerizable monomer is selected from alkylvinyl monomers, alkylalkenyl monomers, alkylallyl monomers, arylvinyl monomers, arylalkenyl monomers, and alkylacrylic-containing monomers.
13. The method of claim 1, where the one or more reactive groups of ingredient (a) comprises one or more condensation and/or polyaddition reactive groups.
14. The method of claim 13, where the condensation and/or polyaddition reactive groups are selected from amine groups, hydroxy groups, alcoholic groups, epoxy groups, isocyanate groups, and phenol groups.
15. The method of claim 14, where the water insoluble, polymerizable, organic monomer is selected from a polyisocyanate monomer, a polyol monomer, a polyamine monomer, a polyphenol monomer, and any combination of two or more of a polyol monomer, a polyisocyanate monomer, a polyamine monomer, a polyphenol monomer.

16. A hydrophobic, organic-silicone hybrid polymer prepared by the method of any one of claims 1-15, where the hydrophobic, organic-silicone hybrid polymer is an opaque liquid that is uniform in appearance and does not visibly separate after three days at 25 °C.

17. A composition comprising: (A) the hydrophobic organic-silicone hybrid polymer of claim 16; (B) a catalyst capable of catalyzing reaction of the one or more reactive groups of the hydrophobic organic-silicone hybrid polymer; and optionally (C) a crosslinker; optionally (D) a drying agent; optionally (E) an extender; optionally (F) a filler; optionally (G) a filler treating agent; optionally (H) a biocide; optionally (I) a stabilizer, optionally (J) a flame retardant; optionally (K) a surface modifier; optionally (L) a chain lengthener; optionally (M) an endblocker; optionally (N) a flux agent; optionally (O) an anti-aging additive; optionally (P) a pigment; optionally (Q) an acid acceptor; optionally (R) a rheological additive; optionally (S) a vehicle; optionally (T) a surfactant; optionally (U) a corrosion inhibitor; optionally (V) a polyorganosiloxane having two or more aliphatically unsaturated organic groups per molecule; optionally (W) a water release agent; and optionally (X) a polyorganosiloxane having two or more hydrolyzable groups per molecule.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/020214

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G77/42 C08F283/12 C08F290/14 C08L83/10
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 C08F C08L

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013/096332 A1 (DOW CORNING [US]; DOW CORNING TAIWAN INC) 27 June 2013 (2013-06-27) paragraphs [0006], [0014], [0020], [0022], [0028], [0029], [0038], [0040], [0047] example 1 -----	1-3,7-9, 13,16,17
X	EP 2 599 847 A1 (DOW CORNING [US]; DOW CORNING FRANCE SAS [FR]) 5 June 2013 (2013-06-05) paragraphs [0002], [0015], [0019], [0020], [0045], [0052], [0054], [0057] example 7 -----	1-6, 8-12,16, 17
X	US 2012/029111 A1 (CHANG FRANK [US] ET AL) 2 February 2012 (2012-02-02) example 2 ----- -/-	1-5,7-9, 13-17



Further documents are listed in the continuation of Box C.



See patent family annex.

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

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"&" document member of the same patent family

Date of the actual completion of the international search

16 May 2014

Date of mailing of the international search report

23/05/2014

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

International application No

PCT/US2014/020214

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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