

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(10) International Publication Number

WO 2019/005710 A1

(43) International Publication Date
03 January 2019 (03.01.2019)

(51) International Patent Classification:
C08G 77/08 (2006.01) *C08G 77/18* (2006.01)
C08G 77/04 (2006.01) *C08L 83/04* (2006.01)
C08G 77/12 (2006.01)

(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, ST, 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).

(21) International Application Number:
PCT/US2018/039377

(22) International Filing Date:
26 June 2018 (26.06.2018)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/524,636 26 June 2017 (26.06.2017) US

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

(72) Inventors: OLSEN, Matthew; 1509 Taylor Way, Collegeville, PA 19426 (US). GOHNDRONE, John; 2304 Parkwood Drive, Midland, MI 48642 (US). ZHOU, Xiaoyuan; 3112 Abigail Lane, Midland, MI 48640 (US). JOHNSON, William; 1315 Ellys Lane, Midland, MI 48642 (US). MARCHAND, Christine; 5904 Partridge Lane, Midland, MI 48640 (US).

(74) Agent: BROWN, Catherine U.; The Dow Chemical Company, Intellectual Property: 2040 Bldg., The Dow Chemical Company, 2211 H.H. Dow Way, Midland, MI 48674 (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, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, 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.

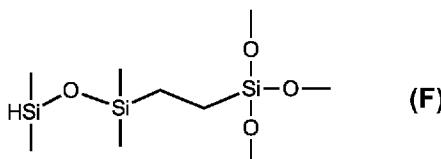
Declarations under Rule 4.17:

- 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))

Published:

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

(54) Title: METHOD FOR HYDROSILYLATION OF ALIPHATICALLY UNSATURATED ALKOXY SILANES AND HYDROGEN TERMINATED ORGANOSILOXANE OLIGOMERS TO PREPARE ALKOXY SİLYL TERMINATED POLYMERS USEFUL FOR FUNCTIONALIZING POLYORGANOSILOXANES USING A RHODIUM CATALYST



(57) Abstract: A method for preparing a product includes combining starting materials including, A) a siloxane oligomer having silicon bonded hydrogen atoms, B) an alkoxy silane having at least one aliphatically unsaturated group capable of undergoing hydrosilylation reaction and C) a dirhodium complex catalyst. The method can be used to produce a compound of formula (Formula (F)). This compound can be used in a hydrosilylation reaction with a vinyl-functional polyorganosiloxane. The resulting product includes an ethyltrimethoxysilyl functional polyorganosiloxane useful in condensation reaction curable sealant compositions.

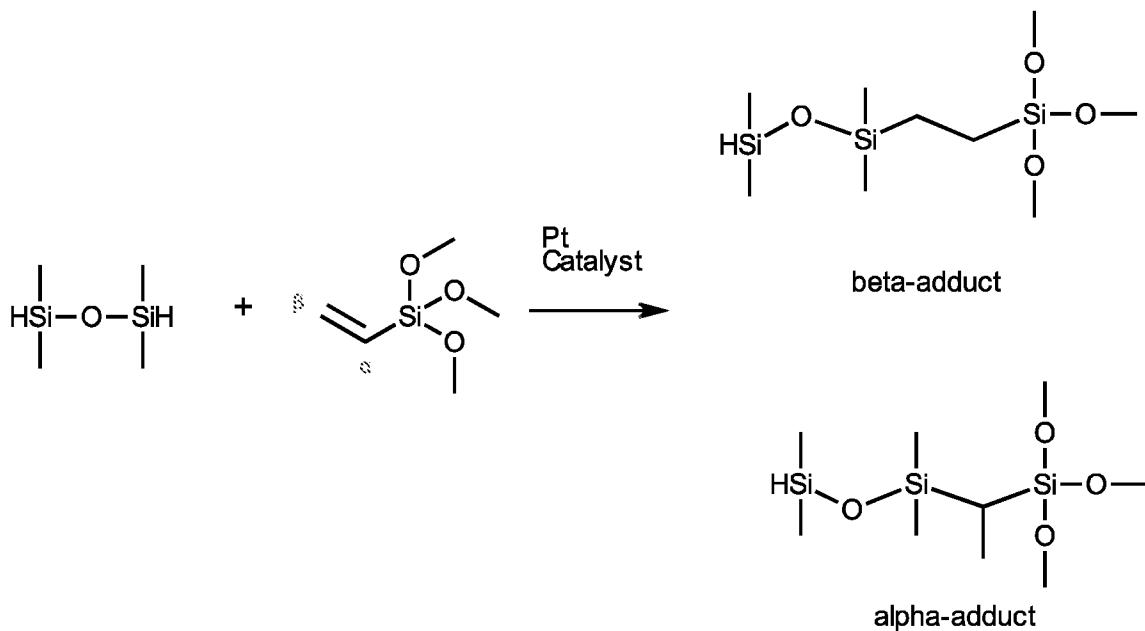
METHOD FOR HYDROSILYLATION OF ALIPHATICALLY UNSATURATED
ALKOXYSILANES AND HYDROGEN TERMINATED ORGANOSILOXANE
OLIGOMERS TO PREPARE ALKOXYSILYL TERMINATED POLYMERS USEFUL FOR
FUNCTIONALIZING POLYORGANOSILOXANES USING A RHODIUM CATALYST

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 62/524636 filed June 26, 2017 under 35 U.S.C. §119 (e). U.S. Provisional Patent Application No. 62/524636 is hereby incorporated by reference.

BACKGROUND

[0002] In the reaction scheme shown below, hydrosilylation reaction of vinyltrimethoxysilane with 1,1,3,3-tetramethyldisiloxane using a platinum catalyst yields a mixture including the α -adduct branched isomer and β -adduct linear isomer as reaction products.



[0003] However, this method suffers from the drawback that selectivity results in a 65/35 mole ratio of β -adduct/ α -adduct. In addition, without prompt removal or deactivation of the Pt catalyst, “over hydrosilylation” will occur, leading to side products in which both hydrogen atoms on the hydrogen terminated organosiloxane oligomer have reacted with a vinyltrimethoxysilane molecule, *i.e.*, $\alpha\alpha$ adduct, $\alpha\beta$ adduct, $\beta\alpha$ adduct, and/or $\beta\beta$ adduct. One method for minimizing the formation of these side products is to use a molar excess of 1,1,3,3-tetramethyldisiloxane. However, this

method suffers from the drawback of process inefficiency and the need to recover relatively large amounts of unreacted 1,1,3,3-tetramethyldisiloxane.

[0004] There is an industry need to provide a method to produce the beta-adduct with high selectivity and/or high yield.

BRIEF SUMMARY OF THE INVENTION

[0005] A method for selectively preparing a product comprising an alkoxy-functional organohydrogensiloxane oligomer comprises:

1) reacting starting materials comprising:

(A) a polyorganohydrogensiloxane oligomer of unit formula (I):

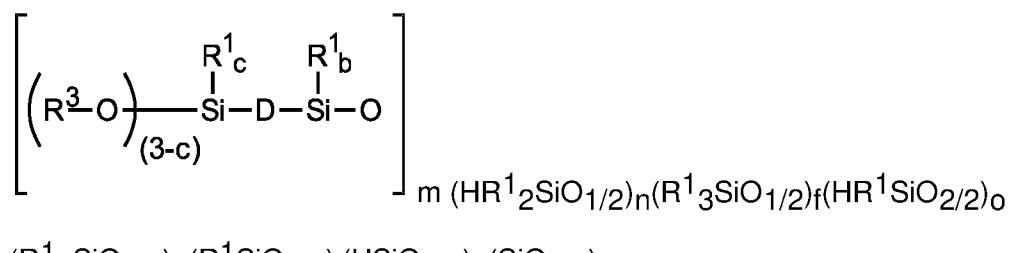
$(HR^1_2SiO_{1/2})^e(R^1_3SiO_{1/2})^f(HR^1SiO_{2/2})^g(R^1_2SiO_{2/2})^h(R^1SiO_{3/2})^i(HSiO_{3/2})^j(SiO_{4/2})^k$
where subscripts e, f, g, h, i, j, and k have values such that $5 \geq e \geq 0$, $5 \geq f \geq 0$, $10 \geq g \geq 0$, $5 \geq h \geq 0$, subscript i is 0 or 1, $5 \geq j \geq 0$, subscript k is 0 or 1, with the proviso that a quantity $(e + g + j) \geq 2$, and a quantity $(e + f + g + h + i + j + k) \leq 50$; and each R^1 is independently a monovalent hydrocarbon group of 1 to 18 carbon or a monovalent halogenated hydrocarbon group of 1 to 18 carbon atoms;

(B) an aliphatically unsaturated alkoxy silane of formula (II):

$$R^2-Si\begin{array}{c} R^1 \\ | \\ c \end{array}-OR^3$$
, where R^1 is as described above, each R^2 is independently an aliphatically unsaturated monovalent hydrocarbon group of 2 to 18 carbon atoms, each R^3 is independently a monovalent hydrocarbon group of 1 to 18 carbon atoms, subscript c is 0 or 1; and

(C) a rhodium diphosphine chelate, thereby preparing the reaction product comprising the alkoxy-functional organohydrogensiloxane oligomer; and optionally 2) isolating the alkoxy-functional organohydrogensiloxane oligomer prepared in step 1).

[0006] The alkoxy-functional organohydrogensiloxane oligomer has unit formula:



R^1 , R^3 , and subscripts c, f, h, i, and k are as described above, subscript b is 0 to 2, m > 0, and a quantity $(m + n + o + p) = (e + g + j)$, and each D is independently a divalent hydrocarbon group of 2 to 18 carbon atoms, with the proviso that > 90 mol% of all D groups produced in step 1) are linear.

[0007] The alkoxy-functional organohydrogensiloxane oligomer is useful in a method for preparing a poly-alkoxy functional polyorganosiloxane. The method for preparing the poly-alkoxy functional polyorganosiloxane comprises:

(1) reacting starting materials comprising:

- (a) an alkoxy-functional organohydrogensiloxane oligomer described above,
- (b) a polyorganosiloxane having, per molecule, an average of at least two aliphatically unsaturated monovalent hydrocarbon groups; and
- (c) a hydrosilylation reaction catalyst.

DETAILED DESCRIPTION OF THE INVENTION

[0008] The method for selectively preparing a product comprising an alkoxy-functional organohydrogensiloxane oligomer comprises:

1) reacting starting materials comprising:

(A) a polyorganohydrogensiloxane oligomer of unit formula (I):

$(HR^1_2SiO_{1/2})^e(R^1_3SiO_{1/2})^f(HR^1_2SiO_{2/2})^g(R^1_2SiO_{2/2})^h(R^1SiO_{3/2})^i(HSiO_{3/2})^j(SiO_{4/2})^k$
where subscripts e, f, g, h, i, j, and k have values such that $5 \geq e \geq 0$, $5 \geq f \geq 0$, $10 \geq g \geq 0$, $5 \geq h \geq 0$, subscript i is 0 or 1, $5 \geq j \geq 0$, subscript k is 0 or 1, with the proviso that a quantity $(e + g + j) \geq 2$, and a quantity $(e + f + g + h + i + j + k) \leq 50$; and each R^1 is independently a monovalent hydrocarbon group of 1 to 18 carbon or a monovalent halogenated hydrocarbon group of 1 to 18 carbon atoms;

(B) an aliphatically unsaturated alkoxy silane of formula (II):

$$R^2-\overset{R^1}{\underset{c}{\overset{|}{\text{Si}}}}-(OR^3)^{(3-c)}$$
, where each R^2 is independently an aliphatically unsaturated monovalent hydrocarbon group of 2 to 18 carbon atoms, each R^3 is independently a monovalent hydrocarbon group of 1 to 18 carbon atoms, subscript c is 0 or 1; and

(C) a rhodium diphosphine chelate, thereby preparing the reaction product comprising the alkoxy-functional organohydrogensiloxane oligomer; and
optionally 2) isolating the alkoxy-functional organohydrogensiloxane oligomer prepared in step 1).

[0009] Ingredient (A) useful in the method described above is a polyorganohydrogensiloxane oligomer of unit formula (III):

$(HR^1_2SiO_{1/2})_e(R^1_3SiO_{1/2})_f(HR^1SiO_{2/2})_g(R^1_2SiO_{2/2})_h(R^1SiO_{3/2})_i(HSiO_{3/2})_j(SiO_{4/2})_k$

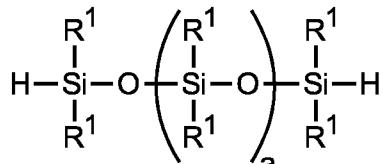
where subscripts e, f, g, h, i, j, and k have values such that $5 \geq e \geq 0$, $5 \geq f \geq 0$, $10 \geq g \geq 0$, $5 \geq h \geq 0$, subscript i is 0 or 1, $5 \geq j \geq 0$, subscript k is 0 or 1, with the proviso that a quantity $(e + g + j) \geq 2$, and a quantity $(e + f + g + h + i + j + k) \leq 50$; and each R^1 is independently a monovalent hydrocarbon group of 1 to 18 carbon or a monovalent halogenated hydrocarbon group of 1 to 18 carbon atoms. Alternatively, monovalent hydrocarbon groups for R^1 have 1 to 12 carbon atoms, and alternatively 1 to 10 carbon atoms.

[0010] Suitable monovalent hydrocarbon groups for R^1 include, but are not limited to, an alkyl group of 1 to 6 carbon atoms and an aryl group of 6 to 10 carbon atoms.

Suitable alkyl groups for R^1 are exemplified by, but not limited to, methyl, ethyl, propyl (e.g., iso-propyl and/or n-propyl), butyl (e.g., isobutyl, n-butyl, tert-butyl, and/or sec-butyl), pentyl (e.g., isopentyl, neopentyl, and/or tert-pentyl), hexyl, as well as branched saturated hydrocarbon groups of 6 carbon atoms. Suitable aryl groups for R^1 are exemplified by, but not limited to, phenyl, tolyl, xylol, naphthyl, benzyl, and dimethyl phenyl. Suitable monovalent halogenated hydrocarbon groups for R^1 include, but are not limited to, a halogenated alkyl group of 1 to 6 carbon atoms, or a halogenated aryl group of 6 to 10 carbon atoms. Suitable halogenated alkyl groups for R^1 are exemplified by, but not limited to, the alkyl groups described above where one or more hydrogen atoms is replaced with a halogen atom, such as F or Cl. For example, 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, 2,2-difluorocyclopropyl, 2,3-difluorocyclobutyl, 3,4-difluorocyclohexyl, and 3,4-difluoro-5-methylcycloheptyl, chloromethyl, chloropropyl, 2-dichlorocyclopropyl, and 2,3-dichlorocyclopentyl are examples of suitable halogenated alkyl groups. Suitable halogenated aryl groups for R^1 are exemplified by, but not limited to, the aryl groups described above where one or more hydrogen atoms is replaced with a halogen atom, such as F or Cl. For example, chlorobenzyl and fluorobenzyl are suitable halogenated aryl groups. Alternatively, each R^1 is independently methyl, ethyl or propyl. Each

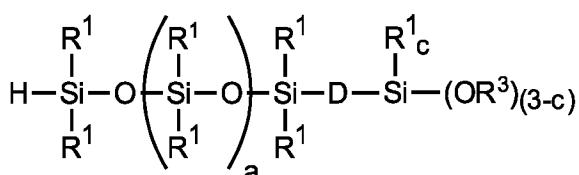
instance of R^1 may be the same or different. Alternatively, each R^1 is a methyl group. Examples of suitable hydridosilanes include trimethylsilane and trimethoxysilane.

[0011] In an alternative embodiment, ingredient (A) is an α,γ -hydrogen terminated organohydrogensiloxane oligomer of formula (IV):



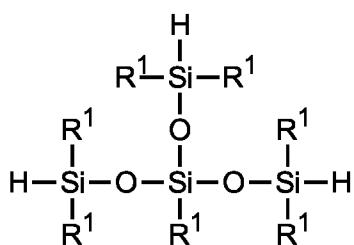
, where each R^1 is independently an alkyl group of 1 to 6 carbon atoms, an aryl group of 6 to 10 carbon atoms, a halogenated alkyl group of 1 to 6 carbon atoms, or a halogenated aryl group of 6 to 10 carbon atoms; and subscript a is an integer up to 20. Alternatively, subscript a is 0 to 20, alternatively subscript a is 0 to 10; alternatively subscript a is 0 to 5; and alternatively subscript a is 0 or 1. Alternatively, subscript a may be 2 to 10; alternatively subscript a is 2 to 5. Examples of suitable organohydrogensiloxane oligomers include 1,1,3,3,5,5-hexamethyltrisiloxane, 1,1,3,3-tetramethyldisiloxane, 1,1,3,3,5,5-hexaethyltrisiloxane, and 1,1,3,3-tetraethyldisiloxane. Alternatively, ingredient (A) may be 1,1,3,3-tetramethyldisiloxane.

[0012] When the organohydrogensiloxane oligomer of formula (IV) is used in the method, the product comprises an alkoxy-functional organohydrogensiloxane oligomer produced of formula (V):



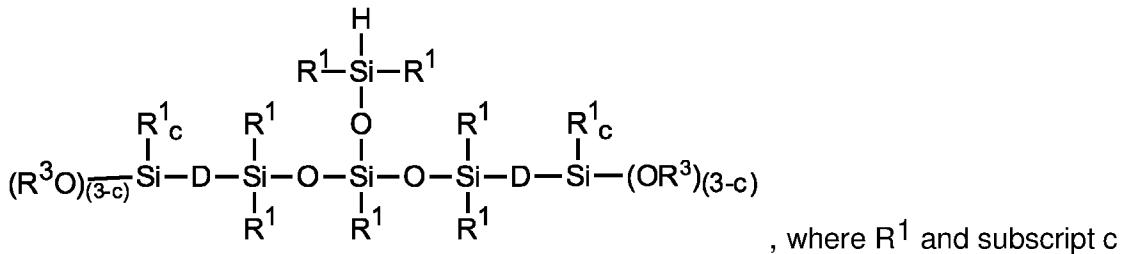
, where R^1 and subscripts a and c are as described above, D is a divalent hydrocarbon group of 2 to 18 carbon atoms, with the proviso that > 90 mol% of D are linear divalent hydrocarbon groups.

[0013] In an alternative embodiment, ingredient (A) the organohydrogensiloxane oligomer has unit formula (VI): $(HR^1_2SiO_{1/2})_3(R^1_2SiO_{2/2})_q(R^1SiO_{3/2})$, where subscript q is 0 to 3. The polyorganohydrogensiloxane oligomer of this unit formula may have formula (VII):



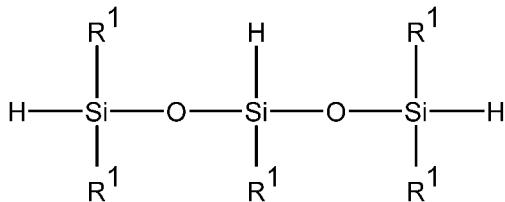
, where R^1 is as described above. Examples of such organohydrogensiloxane oligomers include siloxanes of formula $(\text{Me}_2\text{HSiO}_{1/2})_3(\text{PrSiO}_{3/2})$, where Me represents a methyl group and Pr represents a propyl group.

[0014] When the organohydrogensiloxane oligomer used for ingredient A) in the method described above has unit formula (VII), the product comprises an alkoxy-functional organohydrogensiloxane oligomer of formula (VIII) where formula (VIII) is:

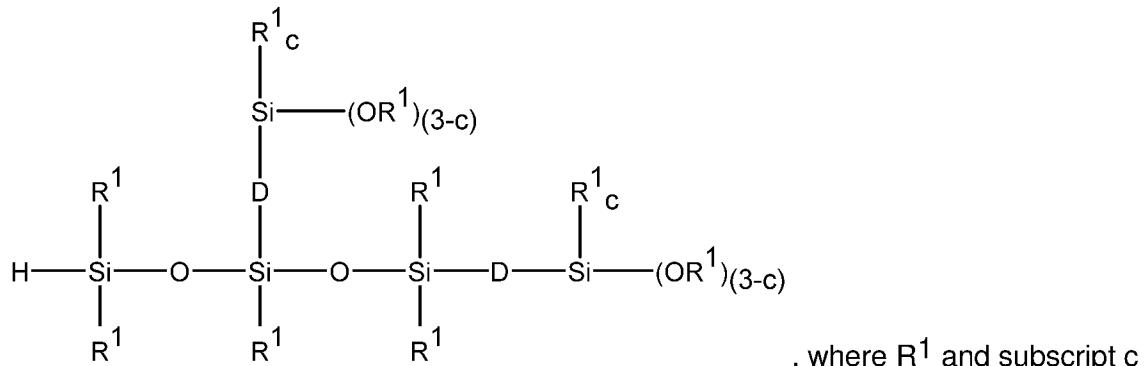
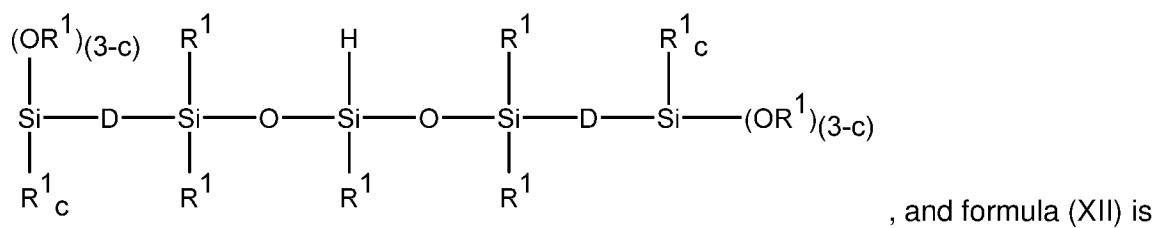


[0015] In an alternative embodiment of the invention, ingredient (A) the organohydrogensiloxane oligomer may have unit formula (IX):

$(\text{HR}^1_2\text{SiO}_{1/2})_2(\text{R}^1_2\text{SiO}_{2/2})_q(\text{HR}^1\text{SiO}_{2/2})_r$, where R^1 is as described above, subscript q is 0 to 3, and subscript r is 0 to 3. In this embodiment, the organohydrogensiloxane oligomer may have formula (X):

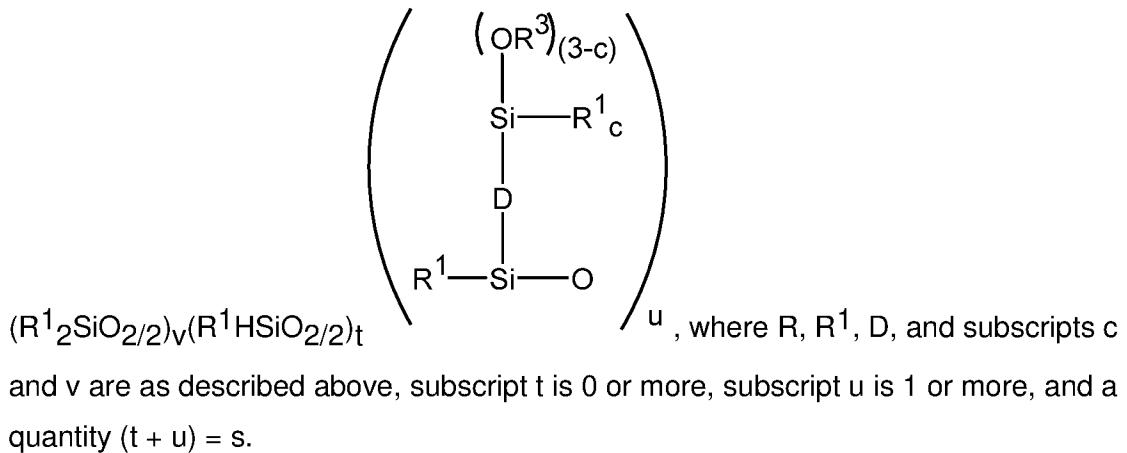


, where R^1 is as described above. Examples of such organohydrogensiloxane oligomers include 1,1,3,5,5- pentamethyltrisiloxane. In this embodiment, the product comprises an alkoxy-functional organohydrogensiloxane oligomer of formula (XI), formula (XII), or a combination thereof, where formula (XI) is



are as described above.

[0016] In an alternative embodiment ingredient (A) the organohydrogensiloxane oligomer is cyclic. The cyclic organohydrogensiloxane oligomer may have unit formula (XIII): $(\text{R}^1_2\text{SiO}_2/2)_v(\text{R}^1\text{HSiO}_2/2)_s$, where R^1 is as described above, subscript $s \geq 3$, and subscript $v \geq 0$. Alternatively, subscript s may be 3 to 14; alternatively 3 to 9, alternatively 3 to 6, alternatively 3 to 5, and alternatively 4. Alternatively, subscript v may be 0 to 14; alternatively 0 to 9, alternatively 0 to 6, alternatively 0 to 5, and alternatively 0. When this cyclic organohydrogensiloxane oligomer is used as ingredient (A), then the product may comprises an alkoxy-functional organohydrogensiloxane oligomer of unit formula (XIV):



[0017] Ingredient (B) useful in the method described above is an aliphatically unsaturated alkoxy silane of formula (XV): $R_1^d R_2^2 Si(OR_3^3)(3-d)$, where each R_1^1 is independently a monovalent hydrocarbon group or a monovalent halogenated hydrocarbon group (as described above), each R_2^2 is independently an aliphatically unsaturated hydrocarbon group, each R_3^3 is independently a monovalent hydrocarbon group, subscript d is 0 or 1. The aliphatically unsaturated hydrocarbon group for R_2^2 may be an alkenyl group or an alkynyl group. Suitable alkenyl groups include vinyl, allyl, propenyl, butenyl and hexenyl; alternatively vinyl, allyl or hexenyl; and alternatively vinyl. The monovalent hydrocarbon group for R_3^3 may be a monovalent hydrocarbon group as described above for R_1^1 .

[0018] Ingredient (B) may comprise an aliphatically unsaturated alkoxy silane exemplified by a dialkoxy silane, such as a dialkenyldialkoxy silane; a trialkoxy silane, such as an alkenyltrialkoxy silane; or a combination thereof. Examples of suitable aliphatically unsaturated alkoxy silanes include vinyltrimethoxysilane, allyltriethoxysilane, allyltrimethoxysilane, vinyltriethoxysilane, hexenyltrimethoxysilane, vinylmethyldimethoxysilane, hexenylmethyldimethoxysilane, hexenyltriethoxysilane, and a combination thereof, and alternatively vinyltrimethoxysilane.

[0019] Ingredient (A) and ingredient (B) are present in relative molar amounts of ingredient (A):ingredient (B) of 1:1 to > 1:1, alternatively greater than or equal to 1, *i.e.*, (A):(B) ratio $\geq 1:1$. Alternatively, (A):(B) ratio may range from 5:1 to 1:1, alternatively 2:1 to 1:1; and alternatively 1.5:1 to 1:1. Without wishing to be bound by theory, it is thought that a molar excess of ingredient (A) relative to ingredient (B) may favorably affect yield in the product.

[0020] Ingredient (C) useful in the method and composition described herein is a chelated rhodium diphosphine complex. The chelated rhodium diphosphine complex may have formula (C1): $[R^4(R^5_2P)_2RhR^6]_2$, formula (C2): $[R^4(R^5_2P)_2Rh(R^6)]R^7$, or a mixture thereof. In each of formula (C1) and formula (C2), each R^4 is independently a divalent hydrocarbon group, each R^5 is independently a monovalent hydrocarbon group, and each R^6 is independently a negatively charged ligand, and each R^7 is independently an anion. The divalent hydrocarbon group for R^4 may be an alkane-diyl, such as an alkane-diyl group of 1 to 6 carbon atoms. Alternatively, R^4 may be methane-diyl, ethane-1,2-diyl, or hexane-1,6-diyl; and alternatively R^4 may be ethane-1,2-diyl.

[0021] The monovalent hydrocarbon group for R⁵ may be an alkyl group or an aryl group. Suitable alkyl groups for R⁵ are exemplified by, but not limited to, methyl, ethyl, propyl (e.g., iso-propyl and/or n-propyl), butyl (e.g., isobutyl, n-butyl, tert-butyl, and/or sec-butyl), pentyl (e.g., isopentyl, neopentyl, and/or tert-pentyl), hexyl, as well as branched saturated hydrocarbon groups of 6 carbon atoms. Alternatively, the alkyl group for R⁵ may be methyl, ethyl or propyl. Suitable aryl groups for R⁵ are exemplified by, but not limited to, phenyl, tolyl, xylyl, benzyl, and 2-phenylethyl. Alternatively, R⁵ may be an ethyl group or a phenyl group.

[0022] Examples of negatively charged ligand suitable for R⁶ include a halogen atom, an alkoxy ligand, an aryl ligand, and a heteroaryl ligand. Examples of suitable halogen atoms include bromine (Br), chlorine (Cl) and iodine (I). Alternatively, the halogen atom may be Cl. Examples of alkoxy ligands include methoxy, ethoxy, and propoxy. Alternatively the alkoxy ligand may be methoxy. Examples of suitable aryl ligands include phenyl, benzyl, or indenyl.

[0023] R⁷ is an anion. Alternatively, the anion may be what is referred to by those skilled in the art as a 'weakly coordinating anion' or a 'non-coordinating anion', including perchlorate, trifluoromethylsulfonate, tetrafluoroborate, tetrakisphenylborate, tetrakis(pentafluorophenyl)borate, methyltris(pentafluorophenyl)borate, tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, hexafluoroantimonate, hexafluorophosphate, [Al(C(CF₃)₃)₄]⁻, carboranes such as [HCB₁₁Me₅Br₆]⁻, (where Me represents a methyl group).

[0024] In formula (C2), X represents a donor ligand. Appropriate donor ligands are nitriles such as acetonitrile, cyclized or non-cyclized ethers such as tetrahydrofuran or diethylether, dimethylsulfoxide, olefins such as 1,2-cis-cyclooctene or 1-octene or ethylene, dienes such as 1,5-cyclooctadiene or 2,5-norbornadiene or 1,5-hexadiene, ketones such as acetone, or alkynes such as acetylene or 1,2-diphenylacetylene.

[0025] Examples suitable catalysts for ingredient (C) include, but are not limited to [1,2-bis(diphenylphosphino)ethane]dichlorodirhodium and [1,2-bis(diethylphosphino)ethane]dichlorodirhodium, and mixtures thereof.

[0026] The amount of ingredient (C) used in step (1) of the method described above depends on various factors including the specific organohydrogensiloxane oligomer selected for ingredient (A), the specific alkoxy silane selected for ingredient (B), and the temperature to which the mixture can be heated without boiling away the

organohydrogensiloxane oligomer selected for ingredient (A). However, the amount of ingredient (C) may be sufficient to provide a molar amount of rhodium metal of 1 parts per million (ppm) to 100 ppm, alternatively 5 ppm to 80 ppm, alternatively 5 ppm to 20 ppm based on combined weights of ingredients (A) and (B). The method may optionally further comprise deactivation or removal of the catalyst. However, with appropriate catalyst loading, the step of deactivation or removal of the catalyst may be omitted.

[0027] The method described herein may be performed at 1 atmosphere of pressure or higher. Alternatively, the method may be performed at 1 atmosphere to 1.5 atmosphere. Step 1) may be performed at 0°C to 150°C, alternatively 50°C to 150°C, alternatively 60°C to 150°C, and alternatively 50°C to 100°C. The temperature for heating in step 1) depends on various factors including the pressure selected, however, heating may be performed at least 70°C to ensure the reaction proceeds quickly enough to be practical. The upper limit for temperature during heating is not critical and depends on the ingredients selected, *i.e.*, the upper limit should be such that the ingredients do not vaporize out of the reactor selected for performing the method. Alternatively, heating may be from 70°C to 150°C, alternatively 70°C to 100°C.

[0028] Step (1) of the method described above produces a product comprising an alkoxy-functional organohydrogensiloxane oligomer. The alkoxy-functional organohydrogensiloxane oligomer has unit formula (XVI):



$(R^1_2SiO_{2/2})_h(R^1SiO_{3/2})_i(HSiO_{3/2})_p(SiO_{4/2})_k$, where

R^1 , R^3 , and subscripts c , f , h , i , and k are as described above, subscript b is 0 to 2, subscript $m > 0$, and subscripts m , n , o , and p have values such that a quantity $(m + n + o + p) = (e + g + j)$, and each D is independently a divalent hydrocarbon group of 2 to 18 carbon atoms, with the proviso that > 90 mol% of all D groups produced in step 1) are linear. Subscripts e , g , and j are as described above in formula (I). The method described herein provides the benefit that this alkoxy-functional organohydrogensiloxane oligomer is produced with high selectivity to the β -adduct compound, *i.e.*, where D is linear, with either none or lower amounts of the corresponding α -adduct compound than existing methods using other catalysts.

[0029] The ingredients in step 1) of the method described above form a mixture, which may be homogeneous or heterogeneous. One or more additional ingredients, *i.e.*, in addition to ingredients (A), (B), and (C) described above, may optionally be used in the method and composition described herein. The additional ingredient, when present, may be (D) a solvent.

[0030] Ingredient (D) is a solvent that may be added to the mixture used in step 1) of the method described herein. One or more of ingredients (A), (B), and/or (C) may be provided in a solvent. For example, the ingredient (C) may be dissolved in a solvent that is added to the mixture in step 1). The solvent may facilitate contacting of reactants and catalyst, flow of the mixture and/or introduction of certain ingredients, such as the catalyst. Solvents used herein are those that help fluidize the ingredients of the mixture but essentially do not react with any of these ingredients. Solvents may be selected based on solubility the ingredients in the mixture and volatility. The solubility refers to the solvent being sufficient to dissolve ingredients of the mixture. Volatility refers to vapor pressure of the solvent. If the solvent is too volatile (having too high vapor pressure) the solvent may not remain in solution during heating. However, if the solvent is not volatile enough (too low vapor pressure) the solvent may be difficult to remove from the product or isolate from the alkoxy-functional organohydrogensiloxane oligomer.

[0031] The solvent may be an organic solvent. The organic solvent can be an aromatic hydrocarbon such as benzene, toluene, or xylene, or a combination thereof. Ingredient (D) may be one solvent. Alternatively, ingredient (D) may comprise two or more different solvents.

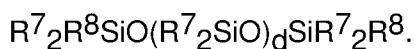
[0032] The amount of solvent can depend on various factors including the specific solvent selected and the amount and type of other ingredients selected for the mixture. However, the amount of solvent may range from 0 % to 99 %, or when present, 1 % to 99 %, and alternatively 2 % to 50 %, based on the weight of the mixture.

[0033] The method may optionally further comprise one or more additional steps. The method may further comprise a step of: recovering a fraction containing the alkoxy-functional organohydrogensiloxane oligomer from the product. Because the alkoxy-functional organohydrogensiloxane oligomer may comprise a β -adduct compound (*i.e.*, where D is linear) and a corresponding α -adduct compound (*i.e.*, where D is not linear) are difficult and/or costly to separate from one another, a fraction comprising both β -adduct compound and α -adduct compound may be recovered from the product after step 1) described above. It is desirable that this fraction contain > 90% β -adduct

compound, alternatively > 90% to 100% β -adduct compound, alternatively 92% to 100%, alternatively > 90% to < 100%, alternatively 92% to < 100%, and alternatively 95% to < 100% β -adduct compound, based on the combined amounts of β -adduct compound and α -adduct compound in the fraction. Recovering this fraction may be performed by any convenient means, such as stripping or distillation, with heating or under vacuum, or a combination thereof.

[0034] The fraction described above comprising the β -adduct compound alkoxy-functional organohydrogensiloxane oligomer above is useful for functionalization of polyorganosiloxanes, including oligomers and longer chain polymers, containing aliphatically unsaturated functionality. For example, a hydrosilylation reaction of the SiH group in the alkoxy-functional organohydrogensiloxane oligomer of formula (X) with an aliphatically unsaturated group bonded to silicon in a polyorganosiloxane (such as a polydiorganosiloxane having aliphatically unsaturated terminal groups) can produce an alkoxy-functional polyorganosiloxane. The polyorganosiloxane having aliphatically unsaturated terminal groups may have unit formula (XVII):

$(R^7R^8SiO_{1/2})_e(R^7R^8SiO_{2/2})_f(R^7SiO_{3/2})_g(SiO_{4/2})_h$, where each R^7 is independently a hydrogen atom, an alkyl group, an aryl group, a halogenated alkyl group, or a halogenated aryl group (such as those described above for R^1), and each R^8 is independently an aliphatically unsaturated hydrocarbon group such as an alkenyl group exemplified by alkenyl groups such as vinyl, allyl, butenyl, and hexenyl; and alkynyl groups such as ethynyl and propynyl. Subscript e is an integer of 0 or more, subscript f is an integer of 0 or more, subscript g is an integer of 0 or more, and subscript h is an integer of 0 or more, with the proviso that a quantity $(f + g) > 1$. Alternatively, the polyorganosiloxane may be a polydiorganosiloxane. The polydiorganosiloxane having aliphatically unsaturated terminal groups may have formula (XVIII):



[0035] In formula (XVIII), R^7 and R^8 are as described above. Subscript d may be 0 or a positive number. Alternatively, each R^7 may be an alkyl group or an aryl group as described above for R^1 . Alternatively, subscript d has an average value of at least 2. Alternatively subscript d may have a value ranging from 2 to 2000.

[0036] The compound of formula (XVIII) may comprise a polydiorganosiloxane such as i) dimethylvinylsiloxy-terminated polydimethylsiloxane,
ii) dimethylvinylsiloxy-terminated poly(dimethylsiloxane/methylphenylsiloxane),

- iii) dimethylvinylsiloxy-terminated poly(dimethylsiloxane/diphenylsiloxane),
- iv) phenyl,methyl,vinyl-siloxy-terminated polydimethylsiloxane, or
- v) dimethylhexenylsiloxy-terminated polydimethylsiloxane.

The alkoxy-functional polyorganosiloxane may be produced by combining the product or fraction including the β -adduct compound alkoxy-functional organohydrogensiloxane oligomer with a polydiorganosiloxane of formula (XVIII) as described above.

[0037] The hydrosilylation reaction to prepare the alkoxy-functional polyorganosiloxane may be performed by a method comprising: combining starting materials comprising

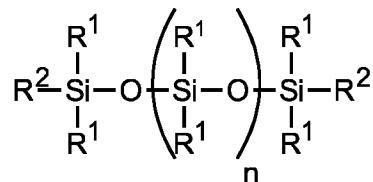
- (a) the product (or fraction) comprising the β -adduct compound alkoxy-functional organohydrogensiloxane oligomer as described above,
- (b) the polyorganosiloxane having at least one aliphatically unsaturated silicon bonded group per molecule as described above, and
- (c) a hydrosilylation catalyst other than the rhodium diphosphine catalyst complex described above. Suitable catalysts for catalyzing hydrosilylation reaction are known in the art and are commercially available. Such hydrosilylation catalysts can be a platinum group metal, such as platinum. 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. Exemplary hydrosilylation catalysts are described in U.S. Patents 3,159,601; 3,220,972; 3,296,291; 3,419,593; 3,516,946; 3,814,730; 3,989,668; 4,784,879; 5,036,117; and 5,175,325 and EP 0 347 895 B. Microencapsulated hydrosilylation catalysts and methods of preparing them are known in the art, as exemplified in U.S. Patents 4,766,176 and 5,017,654. Combining the starting materials may be performed at elevated temperature, such as heating at 50°C to 250°C.

[0038] The polyalkoxy-functional polyorganosiloxanes produced by the hydrosilylation of described above may have formula:

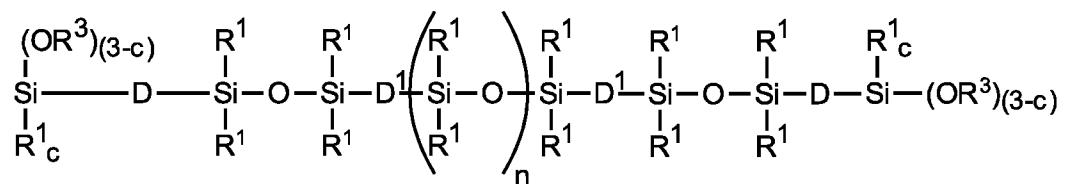
(XIX): $R_2^7R^{11}SiO(R_2^7SiO)_dSiR_2^7R^{11}$, where R^7 and subscript d are as described above, and each R^{11} is polyalkoxyfunctional group, with the proviso that > 90 mol% of

R^{11} are β -adduct. Alternatively, in formula (XIX), > 90 mol% to 100 mol% of R^{11} are β -adduct groups. Alternatively, in formula (XIX), 92% to < 100% % of R^{11} are β -adduct groups.

[0039] For example, when (b) the polyorganosiloxane having aliphatically unsaturated terminal groups is a polydiorganosiloxane of formula (XX):

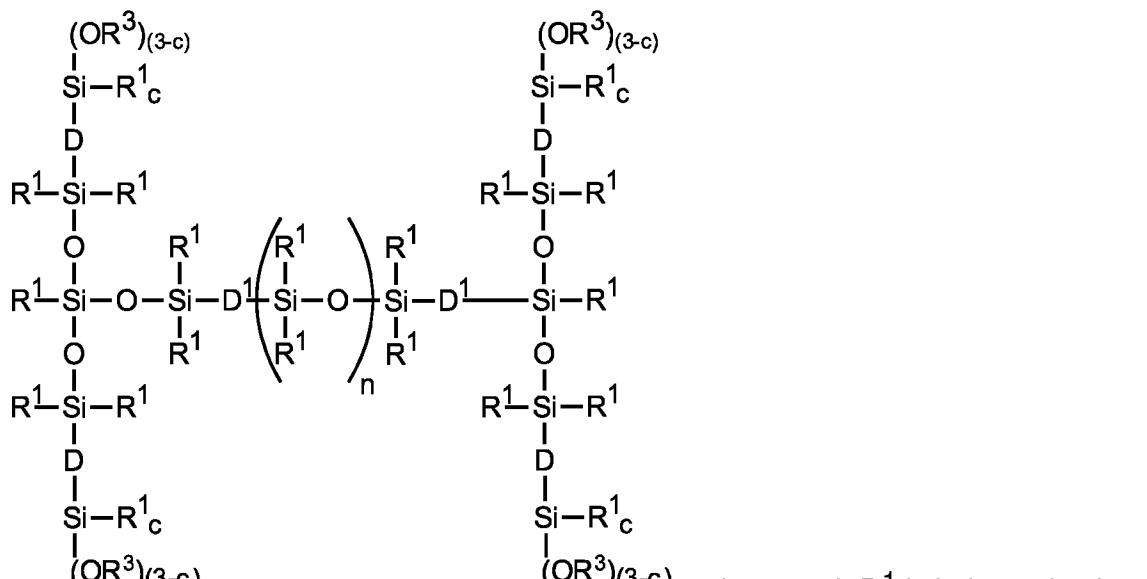


polyorganosiloxane may have formula (XXI):



where each D^1 is independently a divalent hydrocarbon group; where R^1 , R^2 , D and subscript c are as described above.

[0040] Alternatively, the poly-alkoxy functional polyorganosiloxane may have formula (XXII):



divalent hydrocarbon group; where R^1 , R^2 , D and subscript c are as described above.

[0041] The poly-alkoxy functional polyorganosiloxanes, such as polyalkoxy-functional polydimethylsiloxanes, prepared as described above can be used in any application that utilizes reactivity of the alkoxy groups.

[0042] For example, the poly-alkoxy functional polyorganosiloxane prepared as described above is useful in condensation reaction curable compositions, such as sealant compositions. Suitable condensation reaction curable compositions can be prepared by mixing starting materials comprising:

(i) the alkoxy-functional polyorganosiloxane prepared as described above, and

(ii) condensation reaction catalyst. Without wishing to be bound by theory, it thought that a condensation reaction curable composition including (i) the poly-alkoxy functional polyorganosiloxane will cure faster than a similar condensation reaction curable composition containing a different poly-alkoxy functional polyorganosiloxane (prepared using a conventional endblocker having higher branched isomer content).

[0043] Starting material (ii) is a condensation reaction catalyst. Suitable condensation reaction catalysts include tin catalysts and titanium catalysts. Suitable tin catalysts 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-ketonate, dibutyl tin diacetate, dibutyl tin maleate, dibutyl tin diacetylacetone, 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. Exemplary titanium catalysts include titanium esters such as tetra-n-butyltitanate tetraisopropyltitanate, tetra-2-ethylhexyltitanate, tetraphenyltitanate, triethanolamine titanate, organosiloxytitanium

compounds, and dicarbonyl titanium compounds, such as titanium ethyl acetoacetate and bis(acetoacetyl)-diisopropoxy titanium (IV). A titanium catalyst may be used when the composition will be formulated as a room temperature vulcanizing sealant composition. The amount of condensation reaction catalyst depends on various factors including the amount of starting material (i) and the types and amounts of any additional starting materials added to the composition, however the amount of condensation reaction catalyst may be 0.2 to 6, alternatively 0.5 to 3, parts by weight based on the weight of starting material (i).

[0044] The condensation reaction curable composition may further comprise one or more additional ingredients distinct from ingredients (i) and (ii). Suitable additional ingredients are exemplified by (iii) a filler; (iv) a filler treating agent; (v) a crosslinker; (vi) a surface modifier, (vii) a drying agent; (viii) an extender, a plasticizer, or a combination thereof; (ix) a biocide; (x) a flame retardant; (xi) a chain lengthener; (xii) an endblocker; (xiii) a nonreactive binder; (xiv) an anti-aging additive; (xv) a water release agent; (xvi) a pigment; (xvii) a rheological additive; (xviii) a vehicle (such as a solvent and/or a diluent); (xix) a tackifying agent; (xx) a corrosion inhibitor; and a combination of two or more thereof. These additional ingredients and their amounts for use in a condensation reaction curable composition are exemplified by those disclosed, for example, in U.S. Patent 9,156,948.

[0045] Starting material (iii) that may be added to the composition is a filler. The filler may comprise a reinforcing filler, an extending filler, or a combination thereof. For example, the composition may optionally further comprise ingredient (iii-1), a reinforcing filler, which when present may be added in an amount ranging from 0.1 % to 95 %, alternatively 1 % to 60 %, based on the weight of the composition. The exact amount of starting material (iii-1) depends on various factors including the form of the reaction product of the composition and whether any other fillers are added. Examples of suitable reinforcing fillers include precipitated calcium carbonates and reinforcing silica fillers such as fume silica, silica aerogel, silica xerogel, and precipitated silica. Suitable precipitated calcium carbonates include Winnofil® SPM from Solvay and Ultrapflex® and Ultrapflex® 100 from Specialty Minerals, Inc. Fumed silicas are known in the art and commercially available; e.g., fumed silica sold under the name CAB-O-SIL by Cabot Corporation of Massachusetts, U.S.A.

[0046] The composition may optionally further comprise starting material (iii-2) an extending filler in an amount ranging from 0.1 % to 95 %, alternatively 1 % to 60 %, and

alternatively 1 % to 20 %, based on the weight of the composition. Examples of extending fillers include crushed quartz, aluminum oxide, magnesium oxide, ground calcium carbonate, zinc oxide, talc, diatomaceous earth, iron oxide, clays, mica, chalk, titanium dioxide, zirconia, sand, carbon black, graphite, or a combination thereof.

Extending fillers are known in the art and commercially available; such as a ground quartz sold under the name MIN-U-SIL by U.S. Silica of Berkeley Springs, WV.

Examples of extending calcium carbonates include CS-11 from Imerys, G3T from Huber, and Omyacarb 2T from Omya.

[0047] The composition may optionally further comprise starting material (iv) a treating agent. The amount of starting material (iv) can vary depending on factors such as the type of treating agent selected and the type and amount of particulates to be treated, and whether the particulates are treated before being added to the composition, or whether the particulates are treated *in situ*. However, starting material (iv) may be used in an amount ranging from 0.01 % to 20 %, alternatively 0.1 % to 15 %, and alternatively 0.5 % to 5 %, based on the weight of the composition. Particulates, such as the filler, the physical drying agent, certain flame retardants, certain pigments, and/or certain water release agents, when present, may optionally be surface treated with starting material (iv). Particulates may be treated with starting material (iv) before being added to the composition, or *in situ*. Starting material (iv) may comprise an alkoxy silane, an alkoxy-functional oligosiloxane, a cyclic polyorganosiloxane, a hydroxyl-functional oligosiloxane such as a dimethyl siloxane or methyl phenyl siloxane, or a fatty acid. Examples of fatty acids include stearates such as calcium stearate.

[0048] Some representative organosilicon filler treating agents that can be used as starting material (iv) include compositions normally used to treat silica fillers such as organochlorosilanes, organosiloxanes, organodisilazanes such as hexaalkyl disilazane, and organoalkoxysilanes such as $C_6H_{13}Si(OCH_3)_3$, $C_8H_{17}Si(OC_2H_5)_3$, $C_{10}H_{21}Si(OCH_3)_3$, $C_{12}H_{25}Si(OCH_3)_3$, $C_{14}H_{29}Si(OC_2H_5)_3$, and $C_6H_5CH_2CH_2Si(OCH_3)_3$. Other treating agents that can be used include alkylthiols, fatty acids, titanates, titanate coupling agents, zirconate coupling agents, and combinations thereof.

[0049] Alternatively, starting material (iv) may comprise an alkoxy silane having the formula (XXIII): $R^{13}_pSi(OR^{14})_{(4-p)}$, where subscript p may have a value ranging from 1 to 3, alternatively subscript p is 3. Each R^{13} is independently a monovalent organic

group, such as a monovalent hydrocarbon group of 1 to 50 carbon atoms, alternatively 8 to 30 carbon atoms, alternatively 8 to 18 carbon atoms. R¹³ is exemplified by alkyl groups such as hexyl, octyl, dodecyl, tetradecyl, hexadecyl, and octadecyl; and aromatic groups such as benzyl and phenylethyl. R¹³ may be saturated or unsaturated, and branched or unbranched. Alternatively, R¹³ may be saturated and unbranched.

[0050] Each R¹⁴ is independently a saturated hydrocarbon group of 1 to 4 carbon atoms, alternatively 1 to 2 carbon atoms. Starting material (iv) is exemplified by hexyltrimethoxysilane, octyltriethoxysilane, decyltrimethoxysilane, dodecyltrimethoxysilane, tetradecyltrimethoxysilane, phenylethyltrimethoxysilane, octadecyltrimethoxysilane, octadecyltriethoxysilane, and combinations thereof.

[0051] Alkoxy-functional oligosiloxanes may also be used as treating agents. For example, suitable alkoxy-functional oligosiloxanes include those of the formula (XXIV): (R¹⁵O)_qSi(OSiR¹⁶)₂R¹⁷)_(4-q). In this formula, subscript q is 1, 2 or 3, alternatively subscript q is 3. Each R¹⁵ may be an alkyl group. Each R¹⁶ may be an unsaturated monovalent hydrocarbon group of 1 to 10 carbon atoms. Each R¹⁷ may be an unsaturated monovalent hydrocarbon group having at least 10 carbon atoms.

[0052] Alternatively, a polyorganosiloxane capable of hydrogen bonding is useful as a treating agent. This strategy to treating surface of a filler takes advantage of multiple hydrogen bonds, either clustered or dispersed or both, as the means to tether the compatibilization moiety to the filler surface. The polyorganosiloxane capable of hydrogen bonding has an average, per molecule, of at least one silicon-bonded group capable of hydrogen bonding. The group may be selected from: an organic group having multiple hydroxyl functionalities or an organic group having at least one amino functional group. The polyorganosiloxane capable of hydrogen bonding means that hydrogen bonding is the primary mode of attachment for the polyorganosiloxane to a filler. The polyorganosiloxane may be incapable of forming covalent bonds with the filler. The polyorganosiloxane may be free of condensable silyl groups e.g., silicon bonded alkoxy groups, silazanes, and silanols. The polyorganosiloxane capable of hydrogen bonding may be selected from the group consisting of a saccharide-siloxane polymer, an amino-functional polyorganosiloxane, and a combination thereof. Alternatively, the polyorganosiloxane capable of hydrogen bonding may be a saccharide-siloxane polymer.

[0053] Starting material (v) is a crosslinker. Starting material (v) may comprise a silane crosslinker having hydrolyzable groups or partial or full hydrolysis products thereof. Starting material (v) has an average, per molecule, of greater than two substituents reactive with the alkoxy groups on starting material (i). Examples of suitable silane crosslinkers for starting material (v) may have general formula (XXV): $R^{10}_kSi(R^9)_{(4-k)}$, where each R^{10} is independently a monovalent hydrocarbon group such as an alkyl group; each R^9 is a hydrolyzable substituent, for example, a halogen atom, an acetamido group, an acyloxy group such as acetoxy, an alkoxy group, an amido group, an amino group, an aminoxy group, a hydroxyl group, an oximo group, a ketoximo group, or a methylacetamido group; and each instance of subscript k may be 0, 1, 2, or 3. For starting material (v), subscript k has an average value greater than 2. Alternatively, subscript k may have a value ranging from 3 to 4. Alternatively, each R^9 may be independently selected from hydroxyl, alkoxy, acetoxy, amide, or oxime. Alternatively, starting material (v) may be selected from an acyloxysilane, an alkoxysilane, a ketoximosilane, and an oximosilane.

[0054] Starting material (v) may comprise an alkoxysilane exemplified by a dialkoxy silane, such as a dialkyldialkoxy silane; a trialkoxysilane, such as an alkyltrialkoxy silane; a tetraalkoxysilane; or partial or full hydrolysis products thereof, or another combination thereof. Examples of suitable trialkoxysilanes include methyltrimethoxysilane, methyltriethoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, isobutyltrimethoxysilane, isobutyltriethoxysilane, and a combination thereof, and alternatively methyltrimethoxysilane. Examples of suitable tetraalkoxysilanes include tetraethoxysilane. The amount of the alkoxysilane that is used in the composition may range from 0.5 to 15, parts by weight per 100 parts by weight of starting material (i).

[0055] Starting material (v) may comprise an acyloxysilane, such as an acetoxy silane. Acetoxy silanes include a tetraacetoxysilane, an organotriacetoxysilane, a diorganodiacetoxysilane, or a combination thereof. The acetoxy silane may contain alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, and tertiary butyl; alkenyl groups such as vinyl, allyl, or hexenyl; aryl groups such as phenyl, tolyl, or xylyl; aralkyl groups such as benzyl or 2-phenylethyl; and fluorinated alkyl groups such as 3,3,3-trifluoropropyl. Exemplary acetoxy silanes include, but are not limited to, tetraacetoxysilane, methyltriacetoxysilane, ethyltriacetoxysilane, vinyltriacetoxysilane,

propyltriacetoxysilane, butyltriacetoxysilane, phenyltriacetoxysilane, octyltriacetoxysilane, dimethyldiacetoxysilane, phenylmethyldiacetoxysilane, vinylmethyldiacetoxysilane, diphenyl diacetoxysilane, tetraacetoxysilane, and combinations thereof. Alternatively, starting material (v) may comprise organotriacetoxysilanes, for example mixtures comprising methyltriacetoxysilane and ethyltriacetoxysilane. The amount of the acetoxysilane that is used in the curable silicone composition may range from 0.5 to 15 parts by weight per 100 parts by weight of starting material (i); alternatively 3 to 10 parts by weight of acetoxysilane per 100 parts by weight of starting material (i).

[0056] Examples of silanes suitable for starting material (v) containing both alkoxy and acetoxyl groups that may be used in the composition include methyldiacetoxymethoxysilane, methylacetoxymethoxysilane, vinylacetoxymethoxysilane, vinylacetoxymethoxysilane, methyldiacetoxyethoxysilane, methylacetoxymethoxysilane, and combinations thereof.

[0057] Aminofunctional alkoxy silanes suitable for starting material (v) are exemplified by $\text{H}_2\text{N}(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$, $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$, $\text{CH}_3\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, $\text{CH}_3\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$, $\text{CH}_3\text{NH}(\text{CH}_2)_5\text{Si}(\text{OCH}_3)_3$, $\text{CH}_3\text{NH}(\text{CH}_2)_5\text{Si}(\text{OCH}_2\text{CH}_3)_3$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$, $\text{CH}_3\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, $\text{CH}_3\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$, $\text{C}_4\text{H}_9\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, $\text{C}_4\text{H}_9\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{SiCH}_3(\text{OCH}_3)_2$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{SiCH}_3(\text{OCH}_2\text{CH}_3)_2$, $\text{H}_2\text{N}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_3)_2$, $\text{H}_2\text{N}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_2\text{CH}_3)_2$, $\text{CH}_3\text{NH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_3)_2$, $\text{CH}_3\text{NH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_2\text{CH}_3)_2$, $\text{CH}_3\text{NH}(\text{CH}_2)_5\text{SiCH}_3(\text{OCH}_3)_2$, $\text{CH}_3\text{NH}(\text{CH}_2)_5\text{SiCH}_3(\text{OCH}_2\text{CH}_3)_2$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_3)_2$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_2\text{CH}_3)_2$, $\text{CH}_3\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_3)_2$, $\text{CH}_3\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_2\text{CH}_3)_2$, $\text{C}_4\text{H}_9\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_3)_2$, $\text{C}_4\text{H}_9\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_2\text{CH}_3)_2$, and a combination thereof.

[0058] Suitable oximosilanes for starting material (v) include alkyltrioximosilanes such as methyltrioximosilane, ethyltrioximosilane, propyltrioximosilane, and

butyltrioximosilane; alkoxytrioximosilanes such as methoxytrioximosilane, ethoxytrioximosilane, and propoxytrioximosilane; or alkenyltrioximosilanes such as propenyltrioximosilane or butenyltrioximosilane; alkenyloximosilanes such as vinyloximosilane; alkenylalkyldioximosilanes such as vinyl methyl dioximosilane, vinyl ethyldioximosilane, vinyl methyldioximosilane, or vinyl ethyldioximosilane; or combinations thereof.

[0059] Suitable ketoximosilanes for starting material (v) include methyl tris(dimethylketoximo)silane, methyl tris(methylethylketoximo)silane, methyl tris(methylpropylketoximo)silane, methyl tris(methylisobutylketoximo)silane, ethyl tris(dimethylketoximo)silane, ethyl tris(methylethylketoximo)silane, ethyl tris(methylpropylketoximo)silane, ethyl tris(methylisobutylketoximo)silane, vinyl tris(dimethylketoximo)silane, vinyl tris(methylethylketoximo)silane, vinyl tris(methylpropylketoximo)silane, vinyl tris(methylisobutylketoximo)silane, tetrakis(dimethylketoximo)silane, tetrakis(methylethylketoximo)silane, tetrakis(methylpropylketoximo)silane, tetrakis(methylisobutylketoximo)silane, methylbis(dimethylketoximo)silane, methylbis(cyclohexylketoximo)silane, triethoxy(ethylmethylketoxime)silane, diethoxydi(ethylmethylketoxime)silane, ethoxytri(ethylmethylketoxime)silane, methylvinylbis(methylisobutylketoximo)silane, or a combination thereof.

[0060] Alternatively, starting material (v) may be polymeric. For example, starting material (v) may comprise a disilane such as bis(trimethoxysilyl)hexane, 1,4-bis(trimethoxysilyl(ethyl)]benzene, and bis[3-(trimethoxysilyl)propyl] tetrasulfide.

[0061] Starting material (v) can be one single crosslinker or a combination comprising two or more crosslinkers that differ in at least one of the following properties: hydrolyzable substituents and other organic groups bonded to silicon, and when a polymeric crosslinker is used, siloxane units, structure, molecular weight, and sequence. Starting material (vi) is an adhesion promoter. Suitable adhesion promoters for starting material (vi) may comprise a hydrocarbonoxysilane such as an alkoxy silane, a combination of an alkoxy silane and a hydroxy-functional polyorganosiloxane, an aminofunctional silane, a mercaptofunctional silane, or a combination thereof. Adhesion promoters are known in the art and may comprise silanes having the formula (XXVI): $R^{24}_t R^{25}_u Si(OR^{26})_{4-(t+u)}$ where each R^{24} is independently a monovalent organic group having at least 3 carbon atoms; R^{25} contains at least one SiC bonded substituent having an adhesion-promoting group, such as amino, epoxy, mercapto or acrylate

groups; subscript t has a value ranging from 0 to 2; subscript u is either 1 or 2; and the sum of (t + u) is not greater than 3. Alternatively, the adhesion promoter may comprise a partial condensate of the above silane. Alternatively, the adhesion promoter may comprise a combination of an alkoxy silane and a hydroxy-functional polyorganosiloxane.

[0062] Alternatively, the adhesion promoter may comprise an unsaturated or epoxy-functional compound. The adhesion promoter may comprise an unsaturated or epoxy-functional alkoxy silane. For example, the functional alkoxy silane can have the formula (XXVII): $R^{27}_v Si(OR^{28})_{(4-v)}$, where subscript v is 1, 2, or 3, alternatively subscript v is 1.

Each R^{27} is independently a monovalent organic group with the proviso that at least one R^{27} is an unsaturated organic group or an epoxy-functional organic group. Epoxy-functional organic groups for R^{27} are exemplified by 3-glycidoxypropyl and (epoxycyclohexyl)ethyl. Unsaturated organic groups for R^{27} are exemplified by 3-methacryloyloxypropyl, 3-acryloyloxypropyl, and unsaturated monovalent hydrocarbon groups such as vinyl, allyl, hexenyl, undecenyl. Each R^{28} is independently a saturated hydrocarbon group of 1 to 4 carbon atoms, alternatively 1 to 2 carbon atoms. R^{28} is exemplified by methyl, ethyl, propyl, and butyl.

[0063] Examples of suitable epoxy-functional alkoxy silanes include 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropyltriethoxysilane, (epoxycyclohexyl)ethyldimethoxysilane, (epoxycyclohexyl)ethyldiethoxysilane and combinations thereof. Examples of suitable unsaturated alkoxy silanes include vinyltrimethoxysilane, allyltrimethoxysilane, allyltriethoxysilane, hexenyltrimethoxysilane, undecenyltrimethoxysilane, 3-methacryloyloxypropyl trimethoxysilane, 3-methacryloyloxypropyl triethoxysilane, 3-acryloyloxypropyl trimethoxysilane, 3-acryloyloxypropyl triethoxysilane, and combinations thereof.

[0064] Alternatively, the adhesion promoter may comprise an epoxy-functional siloxane such as a reaction product of a hydroxy-terminated polyorganosiloxane with an epoxy-functional alkoxy silane, as described above, or a physical blend of the hydroxy-terminated polyorganosiloxane with the epoxy-functional alkoxy silane. The adhesion promoter may comprise a combination of an epoxy-functional alkoxy silane and an epoxy-functional siloxane. For example, the adhesion promoter is exemplified by a mixture of 3-glycidoxypropyltrimethoxysilane and a reaction product of hydroxy-terminated methylvinylsiloxane with 3-glycidoxypropyltrimethoxysilane, or a mixture of 3-glycidoxypropyltrimethoxysilane and a hydroxy-terminated methylvinylsiloxane, or a

mixture of 3-glycidoxypropyltrimethoxysilane and a hydroxy-terminated methylvinyl/dimethylsiloxane copolymer.

[0065] Alternatively, the adhesion promoter may comprise an aminofunctional silane, such as an aminofunctional alkoxy silane exemplified by $\text{H}_2\text{N}(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$, $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$, $\text{CH}_3\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, $\text{CH}_3\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$, $\text{CH}_3\text{NH}(\text{CH}_2)_5\text{Si}(\text{OCH}_3)_3$, $\text{CH}_3\text{NH}(\text{CH}_2)_5\text{Si}(\text{OCH}_2\text{CH}_3)_3$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$, $\text{CH}_3\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$, $\text{C}_4\text{H}_9\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, $\text{C}_4\text{H}_9\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{SiCH}_3(\text{OCH}_3)_2$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{SiCH}_3(\text{OCH}_2\text{CH}_3)_2$, $\text{H}_2\text{N}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_2\text{CH}_3)_2$, $\text{CH}_3\text{NH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_3)_2$, $\text{CH}_3\text{NH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_2\text{CH}_3)_2$, $\text{CH}_3\text{NH}(\text{CH}_2)_5\text{SiCH}_3(\text{OCH}_2\text{CH}_3)_2$, $\text{CH}_3\text{NH}(\text{CH}_2)_5\text{SiCH}_3(\text{OCH}_3)_2$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_2\text{CH}_3)_2$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_3)_2$, $\text{CH}_3\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_2\text{CH}_3)_2$, $\text{C}_4\text{H}_9\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_3)_2$, $\text{C}_4\text{H}_9\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_2\text{CH}_3)_2$, N-(3-(trimethoxysilyl)propyl)ethylenediamine, and a combination thereof.

[0066] Alternatively, the adhesion promoter may comprise a mercaptofunctional alkoxy silane, such as 3-mercaptopropyltrimethoxysilane or 3-mercaptopropyltriethoxysilane.

[0067] The exact amount of starting material (vi) depends on various factors including the type of adhesion promoter selected and the end use of the composition and its reaction product. However, starting material (vi), when present, may be added to the composition in an amount ranging from 0.01 to 50 weight parts based on the weight of the composition, alternatively 0.01 to 10 weight parts, and alternatively 0.01 to 5 weight parts. Starting material (vi) may be one adhesion promoter. Alternatively, starting material (vi) may comprise two or more different adhesion promoters that differ in at least one of the following properties: structure, viscosity, average molecular weight, polymer units, and sequence.

[0068] When selecting ingredients for the condensation reaction curable composition described above, there may be overlap between types of starting materials because certain starting materials described herein may have more than one function. For example, certain alkoxy silanes may be useful as filler treating agents, as adhesion promoters, and as crosslinkers.

[0069] Alternatively, the crosslinker, the filler, and the adhesion promoter may each be present in the composition. In this embodiment, the crosslinker may comprise an alkyl trialkoxysilane, such as methyltrimethoxysilane; the filler may comprise an extending filler such as calcium carbonate; and the adhesion promoter may comprise an alkoxy silane other than the crosslinker, such as N-(3-(trimethoxysilyl)propyl)ethylenediamine, 3-mercaptopropyltrimethoxysilane, or both.

[0070] The composition described above may be prepared as a one part composition, for example, by combining all ingredients by any convenient means, such as mixing. For example, a one-part composition may be made by optionally combining (e.g., premixing) (i) the alkoxy-functional polyorganosiloxane with all or part of (iii) the filler, when present; and mixing this with a pre-mix comprising the catalyst (ii) and, when present (v) the crosslinker. Other additives such as an anti-aging additive and a pigment may be added to the mixture at any desired stage. A final mixing step may be performed under substantially anhydrous conditions, and the resulting compositions are generally stored under substantially anhydrous conditions, for example in sealed containers, until ready for use.

[0071] Alternatively, the composition may be prepared as a multiple part (e.g., 2 part) composition when a crosslinker is present. In this instance the catalyst and crosslinker are stored in separate parts, and the parts are combined shortly before use of the composition. For example, a two part curable composition may be prepared by combining ingredients comprising the alkoxy-functional polyorganosiloxane and the crosslinker to form a first (curing agent) part by any convenient means such as mixing. A second (base) part may be prepared by combining starting materials comprising a catalyst and the alkoxy-functional polyorganosiloxane by any convenient means such as mixing. The starting materials may be combined at ambient or elevated temperature and under ambient or anhydrous conditions, depending on various factors including whether a one part or multiple part composition is selected. The base part and curing agent part may be combined by any convenient means, such as mixing, shortly before

use. The base part and curing agent part may be combined in relative amounts of base: curing agent ranging from 1:1 to 10:1.

[0072] The equipment used for mixing the starting materials is not specifically restricted. Examples of suitable mixing equipment may be selected depending on the type and amount of each ingredient selected. For example, agitated batch kettles may be used for relatively low viscosity compositions, such as compositions that would react to form gums or gels. Alternatively, continuous compounding equipment, *e.g.*, extruders such as twin screw extruders, may be used for more viscous compositions and compositions containing relatively high amounts of particulates. Exemplary methods that can be used to prepare the compositions described herein include those disclosed in, for example, U.S. Patent Publications US 2009/0291238 and US 2008/0300358.

[0073] These compositions made as described above may be stable when stored in containers that protect the compositions from exposure to moisture, but these compositions may react via condensation reaction when exposed to atmospheric moisture.

EXAMPLES

[0074] These examples are intended to illustrate some embodiments of the invention and should not be interpreted as limiting the scope of the invention set forth in the claims. In the examples below, the examples for preparing alkoxy-functional organohydrogensiloxane oligomers were performed under inert conditions, *i.e.*, the flask was purged with nitrogen before adding starting materials. The disiloxane, trisiloxane, and siloxane oligomers starting materials were purified by contacting with basic Al₂O₃ to decrease acid concentration, such as disclosed in U.S. Patent 5,026,890 (see example 15). The following starting materials and abbreviations are defined as follows:

Abbreviation	Definition
Me	methyl
TMDS	1,1,3,3-tetramethyldisiloxane, example of starting material A)
M'D'M'	1,1,3,5,5-pentamethyltrisiloxane, example of starting material A)
M'TPr	Siloxane oligomer having 3 (Me ₂ HSiO _{1/2}) units and having one (PrSiO _{3/2}) unit, where Me represents a methyl group and Pr represents a propyl group.
VTMS	Vinyltrimethoxysilane, example of starting material B)

Abbreviation	Definition
ETM	HSiMe ₂ OSiMe ₂ CH ₂ CH ₂ Si(OMe) ₃ , including other isomers such as HSiMe ₂ OSiMe ₂ CMeHSi(OMe) ₃
Pr-T EHM	PrSi(OSiMe ₂ CH ₂ CH ₂ Si(OMe) ₃) ₂ (OSiMe ₂ H) including others isomers, where Pr represents a propyl group
M'D'M' EHM	(OMe) ₃ SiCH ₂ CH ₂ SiMe ₂ OSiMeHOSiCH ₂ CH ₂ Si(OMe) ₃ , including other isomers
[Rh(dppe)Cl]2	bis(diphenylphosphino)ethane dirhodium dichloride, example of starting material C)
THF	Tetrahydrofuran, example of a solvent
GC-FID	Gas chromatography with flame ionization detection
GC-MS	Gas chromatography, mass spectrometry
MeSi(OMe) ₃	Methyl trimethoxysilane
Ti(OiPr) ₂ (EAA)2	Titanium Diisopropoxide Di(Ethyl Acetoacetate)
Ti(OBu) ₄	Titanium tetrabutoxide
(MeO) ₃ Si(CH ₂)SH	Thiopropyl Trimethoxysilane
(MeO) ₃ Si(CH ₂) ₃ NH(CH ₂) ₂ NH ₂	Aminoethylaminopropyl Trimethoxysilane

[0075] “Yield” means molar amount alkoxy-functional organohydrogensiloxane oligomer produced / molar amount alkoxy-functional organohydrogensiloxane oligomer possible based on the amount of limiting reagent (the aliphatically unsaturated alkoxy silane). “Selectivity” means the ratio of linear isomer/branched isomer of the alkoxy-functional organohydrogensiloxane (where isomers have the same molecular weight).

Example 1:

[0076] A 250 mL round bottom flask containing a stirbar was loaded with 80 g of TMDS, and to it was affixed an addition funnel containing 82.77 g of VTMS. The apparatus was thoroughly purged with nitrogen and then pre-heated to 50 °C. A steady addition of the VTMS was initiated (~1 drop/sec) and then 2.38 mL of a 0.005 M solution of [Rh(dppe)Cl]2 in THF was added. The addition was continued at such a rate that the reaction mixture temperature did not exceed 70 °C after the first 50% of VTMS was added, and then 80 °C for the second half of the addition. Following the addition, the reaction mixture was allowed to react for 16 h at 80 °C. The reaction mixture was then purified by vacuum distillation, which resulted in a light fraction (solvents, unreacted reagents, and light byproducts), a desired product fraction (approximately distilling at 1.25 Torr (0.1666 kPa) and 55-60 °C), and a heavy fraction which was left behind in the

distillation flask. The yield of the desired product fractions was 103.8 g (65% yield), and this fraction contained ~96% of the linear isomer and 4% of the branched isomers. Upon repetition, the yield of the minor byproducts varied, and sometimes contained additional species such as the dehydrogenative silylation product, however the linear isomer was always the major product in >90% yield.

Example 2 (comparative):

[0077] In an air-free glovebox, a mixture of 1.1 g of VTMS, 1 g of TMDS, and 0.25 g of dodecane (internal standard) was added to a 20 mL scintillation vial containing a stirbar. Then 30 μ L of a 0.01 M solution of $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ in THF was added (this reagent solution was heated to ~60 °C with stirring in order to dissolve the poorly soluble catalyst). After stirring at room temperature for 30 min, the reaction mixture was heated to 50 °C for 16h. At this stage, an aliquot (~150 μ L) of the reaction mixture was withdrawn and injected into a GC vial, and diluted with ~1 mL of xylene. The reaction was analyzed by GC-FID and GC-MS. Analysis indicated an overall yield of 62% of ETM with a selectivity ratio of 87:13 of the linear: branched isomers. A small amount of unreacted starting materials were observed. This example 3 shows less selectivity than example 1 to the desired beta-adduct in the product. As will be shown in Example 20, this lower selectivity has a detrimental effect on sample curing performance.

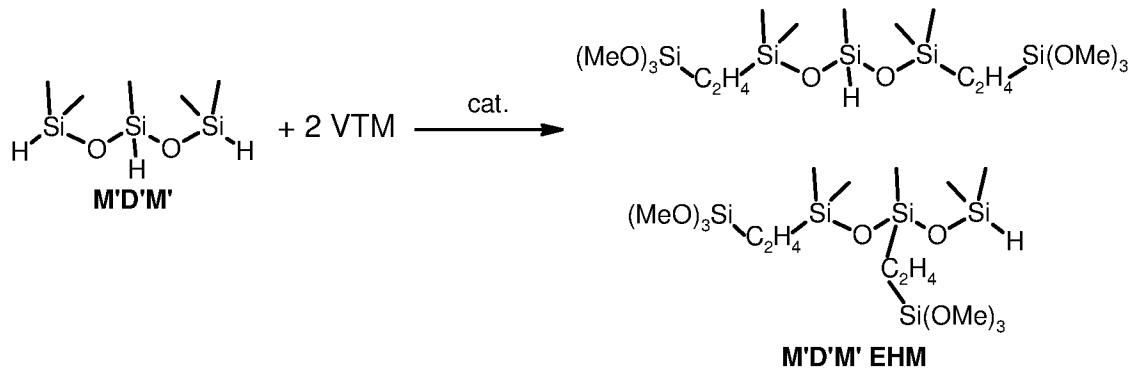
Example 3 (comparative) – Preparation of Ethyltrimethoxysilyl-terminated tetramethyldisiloxane

[0078] In an air-free glovebox, a mixture of 1.1 g of VTMS, 1 g of TMDS, and 0.25 g of dodecane (internal standard) was added to a 20 mL scintillation vial containing a stirbar. Then 30 μ L of a 0.01 M solution of Pt in THF in the form of Karstedt's catalyst (supplied as 2% in xylene, Sigma Aldrich) was added (this reagent solution was heated to ~60 °C with stirring in order to dissolve the poorly soluble catalyst). After stirring at room temperature for 30 min, the reaction mixture was heated to 50 °C for 16h. At this stage, an aliquot (~150 μ L) of the reaction mixture was withdrawn and injected into a GC vial, and diluted with ~1 mL of xylene. The reaction was analyzed by GC-FID and GC-MS. Analysis indicated 72% overall yield of the ETM products, with a selectivity ratio of 64:36 of the linear: branched isomers. A small amount of unreacted tetramethyldisiloxane was observed but all of the vinyltrimethoxysilane was observed.

Example 4 (comparative)

[0079] A solution of 1% Pt catalyst in toluene was prepared. VTM in an amount of 18.05 g was added at a rate of 275 μ L/min to a flask containing 11.97 g M'D'M' in at a

temperature of 40 °C under N₂ with rapid stirring while cooling the flask, by means of a syringe pump. 5% of the total VTM was initially added, followed by 10 pm Pt catalyst (39 μ L of the 1% solution Pt in toluene) to start the exotherm, and then the addition of the remaining VTM was begun. The temperature was monitored by a thermocouple and kept below 80 °C by controlling the addition rate. After the complete addition of VTM, the reaction solution was stirred at 75°C for 0.5 h, allowed to cool, and characterized by GC which showed the product mixture contained 10% monofunctional oligomer, 68% difunctional oligomer, and 20% trifunctional oligomer. The sample was purified by distillation under 1Torr (0.1333kPa) to give 16.9 g M'D'M' EHM (yield: 56%) with a boiling point of 135-137°C at 1 Torr (0.1333kPa). The sample was characterized by GC, ¹H, and ²⁹Si NMR. The final product was composed of 66% β isomer and 34% α isomer; 60% D-H isomer (first product structure in the reaction scheme shown below) and 40% M-H isomer (second product structure in the reaction scheme shown below). ¹H NMR (CDCl₃): δ 4.69 (M-H), 4.62 (D-H), 3.55 (-OCH₃), 1.06 (-CH₃ from α isomer), 0.56 (-CH₂CH₂- from β isomer), 0.25 to 0 (-CH₃ and -CH(Me)-). ²⁹Si NMR (CDCl₃): δ 11 to 9 (M-D'), 9 to 7 (M-D), -6 to -8 (M'), -19 to -23 (D), -35 to -38 (D'), -40 to -43 (T).



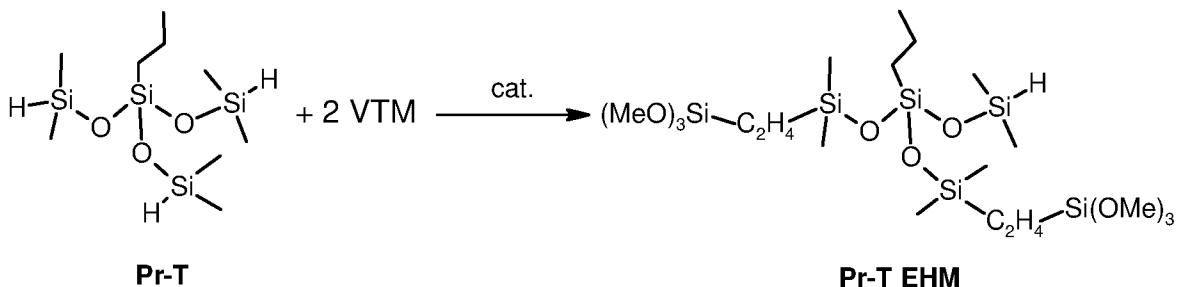
Example 5

[0080] A rhodium diphosphine catalyst, [Rh 1,2-bis(diphenylphosphino)ethane Cl]₂ was dissolved in THF to prepare a 1 millimolar (mM) catalyst solution. A three-neck round bottom flask fitted with a thermocouple and a cold water condenser was charged with 9.96 g M'D'M' and 15.04 g VTM. The flask was purged with N₂, and the mixture in the flask was heated to 80°C, followed by the addition of [Rh(dppe)Cl]₂ solution (1 mL). A slight exotherm was observed, with the temperature elevated to 96 °C within 5 minutes of addition. After 17 h stirring at 80°C under N₂, the reaction mixture was allowed to cool to

room temperature of 25°C and analyzed by GC which showed it contained 13% monofunctional oligomer, 63% difunctional oligomer, and 12% trifunctional oligomer. The sample was purified by distillation under 1 Torr (0.1333kPa) to generate 14.4 g difunctional oligomer product (yield: 57%) that was characterized by GC, ^1H , and ^{29}Si NMR. According to ^1H NMR, this oligomer was composed of 98% M'D'M' EHM (shown below) and 2% dehydrogenative species. The M'D'M' EHM comprised 97% β isomer and 3% α isomer, as well as 53% D-H isomer (top product structure) and 47% M-H isomer (bottom product structure, shown in the reaction scheme above). ^1H NMR (CDCl_3): δ 6.88 (- $\text{CH}=\text{CH}-$), 6.33 (- $\text{CH}=\text{CH}-$), 4.69 (M-H), 4.62 (D-H), 3.55 (- OCH_3), 1.06 (- CH_3 from α isomer), 0.56 (- CH_2CH_2- from β isomer), 0.20 to 0 (- CH_3). ^{29}Si NMR (CDCl_3): δ 11 to 9 (M-D'), 9 to 7 (M-D), -6 to -8 (M), -19 to -21 (D), -35 to -37 (D'), -40 to -43 (T), -57 to -58 (T-CH=CH-).

Example 6 (comparative)

[0081] The procedure of Example 4 was repeated, except that M'TPr (15.0 g), VTM (15.0 g), and platinum catalyst solution in toluene (39 μL) were used as starting materials. The crude product contained 14% monofunctional oligomer, 54% difunctional oligomer, and 31% trifunctional oligomer by GC (FID). The sample was purified by distillation under 1 Torr (0.1333kPa) to give 13.5 g pure Pr-T EHM (yield: 45%). This was characterized by GC (retention time: 30.8-31.1 min), ^1H , and ^{29}Si NMR. This sample was composed of 70% β isomer and 30% α isomer. ^1H NMR (CDCl_3): δ 4.69 (Si-H), 3.55 (- OCH_3), 1.36 ($\text{CH}_3\text{CH}_2\text{CH}_2-$), 1.09 (- CH_3 from α isomer), 0.92 ($\text{CH}_3\text{CH}_2\text{CH}_2-$), 0.56 (- CH_2CH_2- from β isomer), 0.45 ($\text{CH}_3\text{CH}_2\text{CH}_2-$), 0.2 to 0 (- SiCH_3). ^{29}Si NMR (CDCl_3): δ 10 to 7 (M), -6 to -8 (M'), -40 to -43 (T-OMe), -63 to -65 (T-Pr).



Example 7

[0082] The procedure of example 5 was repeated, except that M'T^{Pr} (29.7 g), VTM (29.7 g), and [Rh(dppe)Cl]₂ (4 mM in THF, 0.5 mL, 2 μ mol) were used as starting materials. The reaction was conducted at 80 °C for 7 h. The crude product contained 18% monofunctional oligomer, 63% difunctional oligomer, and 18% trifunctional oligomer by GC (FID). The sample was purified by distillation under 1 Torr (0.1333kPa) to give 25.8 g pure difunctional Pr-T EHM (yield: 44%). The Pr-T EHM was characterized by GC (retention time: 30.5, 30.8 and 31.0 min), ¹H, and ²⁹Si NMR. This sample was composed of 99% β isomer and 1% α isomer. ¹H NMR (CDCl₃): δ 4.69 (m, 1H, Si-H), 3.55 (s, 18H, -OCH₃), 1.35 (m, 2H, CH₃CH₂CH₂-) 1.08 (d, 0.07H, -CH₃ from α isomer), 0.92 (t, 3H, CH₃CH₂CH₂-), 0.55 (s, 8H, -CH₂CH₂- from β isomer), 0.45 (m, 2H, CH₃CH₂CH₂-), 0.17 (d, 6H, -SiMe₂H), 0.06 (s, 12H, -SiMe₂-C₂H₄). ²⁹Si NMR (CDCl₃): δ 8.5 (M), -6.9 (M), -41.6 (T-OMe), -64.8 (T-Pr).

β/α ratio	Platinum catalyst (comparative)	[Rh(dppe)Cl] ₂
M'D'M' EHM	66/34	97/3
Pr-T EHM	70/30	99/1

Example 8

[0083] A mixture of 4.00 g of HSi(OMe)₂Me (38 mmol) and 5.58 g ViSi(OMe)₃ (38 mmol) was added to a 20 mL glass vial containing a stirbar and to the mixture was added 188 μ L of 0.005 M [Rh(dppe)Cl]₂ (0.01 M in Rh) in THF. The mixture was stirred at 70°C for 16h. The reaction mixture was then analyzed by GC-MS and GC-FID, which indicated that a reaction had only occurred to a slight extent. However, the hydrosilylation product fraction was entirely composed of (OMe)₃SiCH₂CH₂SiMe(OMe)₂ (4.8% yield) with no branched isomer observed.

[0084] The overall yields are shown below in Table 15.

Reagent/Product	Mass Balanced Based on HSi(OMe) ₂ Me
(OMe) ₃ SiCH ₂ CH ₂ SiMe(OMe) ₂	4.8%
HSi(OMe) ₂ Me	95.0%
Unidentified byproduct	0.2%

Example 9

[0085] A mixture of 4.00 g of $C_3H_5Si(OMe)_3$ (25 mmol) and 3.31 g of $HSiMe_2OSiMe_2H$ (25 mmol) was added to a 20 mL glass vial containing a stirbar and to the mixture was added 123 μ L of 0.005 M $[Rh(dppe)Cl]_2$ (0.01 M in Rh) in THF. The mixture was stirred at 70°C for 16 h. The reaction mixture was then analyzed by GC-MS and GC-FID, which indicated that a reaction was partially complete and that the ratio of linear to branched to other unidentified isomers was 98.5 : 1.0 : 0.5.

[0086] The overall yields are shown below in Table 16.

Reagent/Product	Mass Balance Based on $HSiMe_2OSiMe_2H$
$HSiMe_2OSiMe_2(CH_2)_3Si(OMe)_3$	45.1%
$HSiMe_2OSiMe_2CH_2CMeHSi(OMe)_3$	0.5%
$(OMe)_3Si(CH_2)_3SiMe_2OSiMe_2(CH_2)_3Si(OMe)_3$ and trace other double addition products	5.5%
$HSiMe_2OSiMe_2H$	47.2%
Unidentified byproducts	1.7%

Example 10

[0087] A mixture of 4.00 g of (5-hexenyl)Si(OMe)₃ (20 mmol) and 2.63 g of $HSiMe_2OSiMe_2H$ (20 mmol) was added to a 20 mL glass vial containing a stirbar and to the mixture was added 98 μ L of 0.005 M $[Rh(dppe)Cl]_2$ (0.01 M in Rh) in THF. The mixture was stirred at 70°C for 16h. The reaction mixture was then analyzed by GC-MS and GC-FID, which indicated that a reaction was partially complete and that the ratio of the linear hydrosilylation product to other isomers was 99.5 : 0.5.

[0088] The overall yields are shown below in Table 17.

Reagent/Product	Mass Balance Based on $HSiMe_2OSiMe_2H$
$HSiMe_2OSiMe_2(CH_2)_6Si(OMe)_3$	69.2%
Other non-linear isomers of $HSiMe_2OSiMe_2(CH_2)_4CMeHSi(OMe)_3$	0.4%
$(OMe)_3Si(CH_2)_6SiMe_2OSiMe_2(CH_2)_6Si(OMe)_3$	1.0%
$HSiMe_2OSiMe_2H$	24.1%
Unidentified byproducts	5.3%

Example 11

[0089] To a mixture of 5.00 g of $\text{HSiMe}_2(\text{OSiMe}_2)_x\text{OSiMe}_2\text{H}$ (~6.8 mmol of Si-H) and 1.01 g of $\text{ViSi}(\text{OMe})_3$ (6.8 mmol Si-Vi) was added 34 μL of 0.005 M $[\text{Rh}(\text{dppe})\text{Cl}]_2$ (0.01 M in Rh) in THF ($x = 16\text{-}24$). The mixture was then heated at 70°C for 16h, at which point the mixture was analyzed by ^1H NMR, which indicated that 97.9% of the Si-H endgroups had reacted, and of the converted endgroups there was a ratio of linear : branched hydrosilylation products of 93.7 : 6.3. The remainder of the mass-balance was composed of unreacted reagents.

Example 12 (Reference) – Compounding Procedure for Composition Samples 1-4

[0090] To a speed mixer cup was added 210.88g of a trimethoxy-functional polydimethylsiloxane prepared by hydrosilylation reaction of an ethyltrimethoxysilyl-terminated tetramethyldisiloxane and an α,ω -vinyl-terminated polydimethylsiloxane. A mixture of i) methyltrimethoxysilane, ii) tetra-n-butoxy titanate, iii) 3-mercaptopropyltrimethoxysilane, iv) mixture of 80% titanium ethyl acetoacetate and 20% methyltrimethoxysilane, and v) N-(3-(trimethoxysilyl)propyl)ethylenediamine was prepared in a ratio equivalent to the ratio shown in a table below. From this mixture, 13.16g was added to the speed mixer cup. The cup was mixed in a DAC 600.2 VAC-P Speedmixer for 30 seconds at 800 revolutions per minute (rpm), then 30 seconds at 1500 rpm. Next, 149.2 g of precipitated calcium carbonate was added to the cup and mixed 30 seconds at 800 rpm, and 30 seconds at 1500 rpm. The sides and bottom of the cup were then scraped by hand with a spatula. Next 26.76 g of ground calcium carbonate was added to the cup and it was mixed for 30 seconds at 800 rpm and 30 seconds at 1500 rpm. Again, the sides and bottom of the cup were hand scraped with a spatula. Finally, the cup was fitted with a cap that contained a hole as to allow the contents of the cup to be exposed to a vacuum environment. The cup was de-aired by mixing 30 seconds at 800 rpm and 5 pounds per square inch (psi) (34.5kPa), 30 seconds at 1500 rpm and 5 psi (34.5kPa), and 30 seconds at 800 rpm and 14.7 psi (101.35kPa). The resulting sealant composition was transferred to Semco® tubes via a hand operated cup press.

Samples 1 and 3 (comparative)	Starting Materials	Amount (g)
	Polydimethylsiloxane 100% end capped with 70% β ethyltrimethoxysilyl group 30% α ethyltrimethoxy (using the ethyltrimethoxysilyl-terminated tetramethyldisiloxane of comparative example 4)	210.88
	Precipitated Calcium Carbonate	149.2
	Ground Calcium Carbonate	26.76
	Methyltrimethoxysilane	7.36
	Tetra-n-butoxy titanate	1.32
	3-Mercaptopropyltrimethoxysilane	0.76
	Mixture 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	3.52
N-(3-(Trimethoxysilyl)propyl)ethylenediamine		0.2

Samples 2 and 4	Starting Materials	Amount (g)
	Polydimethylsiloxane 100% end capped with $\geq 95\%$ β ethyltrimethoxy (using the ethyltrimethoxysilyl-terminated tetramethyldisiloxane of example 1)	210.88
	Precipitated Calcium Carbonate	149.2
	Ground Calcium Carbonate	26.76
	Methyltrimethoxysilane	7.36
	Tetra-n-butoxy titanate	1.32
	3-Mercaptopropyltrimethoxysilane	0.76
	Mixture 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	3.52
N-(3-(Trimethoxysilyl)propyl)ethylenediamine		0.2

Reference Example 13 - Compounding Procedure for Composition Samples 5 and 6

[0091] To a one gallon Ross double planetary mixer pot was added 900g of a trimethoxy-functional polydimethylsiloxane prepared by hydrosilylation reaction of an ethyltrimethoxysilyl-terminated tetramethyldisiloxane and an α,ω -vinyl-terminated polydimethylsiloxane. A mixture of i) methyltrimethoxysilane, ii) tetra-n-butoxy titanate, iii) 3-mercaptopropyltrimethoxysilane, iv) mixture of 80% titanium ethyl acetoacetate and 20% methyltrimethoxysilane, and v) N-(3-(trimethoxysilyl)propyl)ethylenediamine was prepared in a ratio equivalent to the ratio shown in the tables below. From this mixture, 56.15g was added to the pot. The pot was fitted to the mixer, and was voided of air via

vacuum pump and filled with N₂ three times to create an inert atmosphere. The pot was mixed five minutes at 50 rpm. Next, 636.76g of precipitated calcium carbonate was added to the pot. The pot was then voided of air via vacuum pump and filled with N₂ three times to create an inert atmosphere. The pot was mixed five minutes at 50 rpm. Next 114.21g of ground calcium carbonate was added to the pot. The pot was then voided of air via vacuum pump and filled with N₂ three times to create an inert atmosphere. The pot was mixed five minutes at 50 rpm. Next, the sides and bottom of the pot, and the blades were scraped down with a spatula. The pot was closed and again voided of air via vacuum pump and filled with plant N₂ three times to create an inert atmosphere. The pot was then mixed for ten minutes at 50 rpm, then mixed for five minutes at 30 rpm and -27mmHg (3.599 kPa). The resulting sealant was packaged into Semco® tubes via the mixer's hydraulic pot press.

Sample 5 (comparative)	Component	Amount (g)
	Polydimethylsiloxane 100% end capped with 70% β ethyltrimethoxysilyl group 30% α ethyltrimethoxy converter (ethyltrimethoxysilyl-terminated tetramethyldisiloxane of Example 4)	900.00
	Precipitated Calcium Carbonate	636.76
	Ground Calcium Carbonate	114.21
	Methyltrimethoxysilane	31.41
	Tetra-n-butoxy titanate	5.63
	3-Mercaptopropyltrimethoxysilane	3.24
	Mixture 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	15.02
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	0.85

Sample 6	Ross Mixer Component	Amount (g)
	Polydimethylsiloxane 100% end capped with $\geq 95\%$ β ethyltrimethoxy converter (ethyltrimethoxysilyl-terminated tetramethyldisiloxane of Example 1	900.00
	Precipitated Calcium Carbonate	636.76
	Ground Calcium Carbonate	114.21
	Methyltrimethoxysilane	31.41
	Tetra-n-butoxy titanate	5.63
	3-Mercaptopropyltrimethoxysilane	3.24
	Mixture 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	15.02
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	0.85

Reference Example 14 - Compounding procedure for samples 7 and 8

[0092] To a 500g Speedmixer cup was added 258.35g of a hexamethoxy-functional polydimethylsiloxane prepared by hydrosilylation reaction of a di-ethyltrimethoxysilyl-terminated tetramethyldisiloxane and an α,ω -vinyl-terminated polydimethylsiloxane. A mixture of i) methyltrimethoxysilane, ii) mixture of 80% titanium ethyl acetoacetate and 20% methyltrimethoxysilane, iii) tetra-n-butoxy titanate, iv) 3-mercaptopropyltrimethoxysilane, and v) N-(3-(trimethoxysilyl)propyl)ethylenediamine was prepared in a ratio equivalent to the ratio seen in the above formulations. To the cup was added 21.05g of this mixture. The cup was then mixed in a DAC 600.2 VAC-P Speedmixer one minute at 2000rpm. Next, 194.5g of precipitated calcium carbonate was added to the cup and mixed 30 seconds at 2000 rpm. Next, 26.10g of ground calcium carbonate was added to the cup and mixed 30 seconds at 2000rpm. The sides and bottom of the cup were hand scraped with a spatula. Finally, the cup was fitted with a cap that contained a hole as to allow the contents of the cup to be exposed to a vacuum environment. The cup was de-aired by mixing 30 seconds at 800 rpm and 5 psi (34.5kPa), 30 seconds at 1500 rpm and 5 psi (34.5kPa), and 30 seconds at 800 rpm and 14.7 psi (101.35kPa). The resulting sealant was transferred to Semco® tubes via a hand operated cup press.

Sample 7	Component	Amount (g)
	Polydimethylsiloxane 80% end capped with ~70% β 30% α di-ethyltrimethoxysilyl groups made as described above in Example 7	258.35
	Precipitated Calcium Carbonate	194.50
	Ground Calcium Carbonate	26.10
	Methyltrimethoxysilane	13.80
	Mixture 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	4.90
	Tetra-n-butoxy titanate	1.15
	3-Mercaptopropyltrimethoxysilane	0.65
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	0.55

Sample 8	Component	Amount (g)
	Polydimethylsiloxane 80% end capped with $\geq 95\%$ β di-ethyltrimethoxysilyl groups made as described above in Example 8	258.35
	Precipitated Calcium Carbonate	194.50
	Ground Calcium Carbonate	26.10
	Methyltrimethoxysilane	13.80
	Mixture 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	4.90
	Tetra-n-butoxy titanate	1.15
	3-Mercaptopropyltrimethoxysilane	0.65
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	0.55

Reference Example 15 - Compounding Procedure for Samples 9-12

[0093] To a one gallon Ross double planetary mixer pot was added 1033.40g of trimethoxy-functional polydimethylsiloxane prepared by hydrosilylation reaction of an ethyltrimethoxysilyl-terminated tetramethyldisiloxane and an α,ω -vinyl-terminated polydimethylsiloxane. A mixture of i) methyltrimethoxysilane, ii) mixture of 80% titanium ethyl acetoacetate and 20% methyltrimethoxysilane, iii) tetra-n-butoxy titanate, iv) 3-mercaptopropyltrimethoxysilane, and v) N-(3-(trimethoxysilyl)propyl)ethylenediamine was prepared in a ratio equivalent to the ratio seen in the above formulations. From this mixture, 84.20g was added to the pot. The pot was fitted to the mixer, and was voided of air via vacuum pump and filled with N₂ three times to create an inert atmosphere. The

pot was mixed five minutes at 50 rpm. Next, 778.00g of precipitated calcium carbonate was added to the pot. The pot was then voided of air via vacuum pump and filled with N₂ three times to create an inert atmosphere. The pot was mixed five minutes at 50 rpm. Next 104.40g of ground calcium carbonate was added to the pot. The pot was then voided of air via vacuum pump and filled with N₂ three times to create an inert atmosphere. The pot was mixed five minutes at 50 rpm. Next, the sides and bottom of the pot, and the blades were scraped down with a spatula. The pot was closed and again voided of air via vacuum pump and filled with N₂ three times to create an inert atmosphere. The pot was then mixed for ten minutes at 50 rpm, then mixed for five minutes at 30 rpm and -27mmHg (3.599 kPa). The resulting sealant was packaged into Semco® tubes via the mixer's hydraulic pot press.

Sample 9	Component	Amount (g)
	Polydimethylsiloxane 80% end capped with ~70% β 30% α ethyltrimethoxy converter made as described above in Example 4	1033.40
	Precipitated Calcium Carbonate	778.00
	Ground Calcium Carbonate	104.40
	Methyltrimethoxysilane	55.20
	Mixture 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	19.60
	Tetra-n-butoxy titanate	4.60
	3-Mercaptopropyltrimethoxysilane	2.60
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	2.20

Sample 10	Component	Amount (g)
	Polydimethylsiloxane 80% end capped with $\geq 95\%$ β ethyltrimethoxy converter made as described above in Example 1	1033.40
	Precipitated Calcium Carbonate	778.00
	Ground Calcium Carbonate	104.40
	Methyltrimethoxysilane	55.20
	Mixture 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	19.60
	Tetra-n-butoxy titanate	4.60
	3-Mercaptopropyltrimethoxysilane	2.60
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	2.20

Sample 11	Component	Amount (g)
	Polydimethylsiloxane 100% end capped with ~70% β 30% α ethyltrimethoxy converter made as described above in Example 4	1033.40
	Precipitated Calcium Carbonate	778.00
	Ground Calcium Carbonate	104.40
	Methyltrimethoxysilane	55.20
	Mixture 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	19.60
	Tetra-n-butoxy titanate	4.60
	3-Mercaptopropyltrimethoxysilane	2.60
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	2.20

Sample 12	Component	Amount (g)
	Polydimethylsiloxane 100% end capped with $\geq 95\%$ β ethyltrimethoxy converter made as described above in Example 1	1033.40
	Precipitated Calcium Carbonate	778.00
	Ground Calcium Carbonate	104.40
	Methyltrimethoxysilane	55.20
	Mixture 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	19.60
	Tetra-n-butoxy titanate	4.60
	3-Mercaptopropyltrimethoxysilane	2.60
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	2.20

[0094] The composition samples prepared as described above were evaluated using the following test methods.

Tack-Free Time Procedure

[0095] A 100 mil slab of sealant was drawn down on a piece of polyethylene terephthalate (PET). A small strip of PET is then lightly pressed onto the surface of the sealant to check for cure. When no sealant is transferred to the strip of PET, the sealant is considered tack free.

Skin-Over Time Procedure

[0096] A 100 mil slab of sealant was drawn down on a piece of PET. A sealant is considered to have become skinned over when no sealant transfers to a gloved or bare finger when lightly touched.

Creep and Recovery

[0097] The table below shows testing done on some of the composition samples prepared as described above. On an 8 millimeter (mm) parallel plate constant stress rheometer, a dollop of uncured sealant was pressed to 1.829 mm and trimmed with a razor blade. The sealant was cured in place for the time specified. Next, a constant stress of 0.5 psi (3.45 kPa) was applied for the time specified. The stress was then released and the sealant was allowed to recover for five minutes. Sealant with a faster cure will creep less during the stress period, and will recover more closely to zero during the recovery period. In each case listed below, the sample with higher percentage of beta-adduct had the benefits of less creep and better recovery (recovered more).

Creep and Recovery Data

Sample	Cure Time	Stress Time	Creep (%)	Recovery (%)
5 (comparative)	2 hours	10 seconds	5.76	0.14
6	2 hours	10 seconds	1.86	0.03
7 (comparative)	3 hours	10 seconds	3.04	0.13
8	3 hours	10 seconds	1.89	0.05
11 (comparative)	1 hour	2 minutes	121.76	24.74
12	1 hour	2 minutes	20.73	2.3

Table 13. Initial Cure

Sample #	Description	Tack-free time (min)	Skin-over time (min)
1 (comparative)	Speedmixer 70% β 30% α ETM	40	19
2	Speedmixer \geq 95% β ETM	20	9
3 (comparative)	Speedmixer 70% β 30% α ETM	36	22
4	Speedmixer \geq 95% β ETM	20	15
5 (comparative)	Ross Mixer 70% β 30% α ETM	19	14
6	Ross Mixer \geq 95% β ETM	12	8
7 (comparative)	Speedmixer 70% β 30% α EHM	47	15
8	Speedmixer \geq 95% β EHM	22	15
9 (comparative)	Ross Mixer 70% β 30% α ETM	46	20
10	Ross Mixer \geq 95% β ETM	31	17
11 (comparative)	Ross Mixer 70% β 30% α ETM	23	13
12	Ross Mixer \geq 95% β ETM	15	8

[0098] The table above shows that that each sealant composition compounded with \geq 95% of the beta-adduct ethyltrimethoxysilyl group containing polydimethylsiloxane

cured faster than its sealant composition counterpart, which contained the same starting materials except that a 70% β 30% α adduct ethyltrimethoxysilyl group containing polydimethylsiloxane was used. In each instance the tack-free time is faster with the sealant composition containing the polydimethylsiloxane with the higher content ($\geq 95\%$) of the beta adduct when compared to a sealant composition containing the same starting materials except for a polydimethylsiloxane with a mixture of 70% β 30% α isomers of the ethyltrimethoxysilyl group. In all but one instance the skin over time was faster, where samples 7 and 8 have the same skin over time. All samples were tested side by side to eliminate the temperature and humidity variable on cure.

Example 16

[0099] A mixture of 3.56 g of $\text{ViSi}(\text{OMe})_2\text{Me}$ (where Vi represents vinyl and Me represents methyl) and 4.00 g $\text{HSiMe}_2\text{OSiMe}_2\text{H}$ was added to a 20 mL glass vial containing a stirbar and to the mixture was added 135 microliters (μL) of 0.005 M $[\text{Rh}(\text{dppe})\text{Cl}]_2$ (0.01 M in Rh) in THF. The mixture was stirred at 70°C for 16 h. At this stage, all of the vinyl reagent was consumed and the reaction was judged to be complete. The reaction mixture was then analyzed by GC-MS and GC-FID, which indicated that the ratio of linear to branched to other unidentified isomers was 94 : 5 : 1.

[0100] The overall yields are shown below in Table 14.

Reagent/Product	Mass Balance Based on $\text{HSiMe}_2\text{OSiMe}_2\text{H}$
$\text{MeSi}(\text{OMe})_2\text{CH}_2\text{CH}_2\text{SiMe}_2\text{OSiMe}_2\text{H}$	62.3%
$\text{MeSi}(\text{OMe})_2\text{CH}_3\text{CHSiMe}_2\text{OSiMe}_2\text{H}$	2.9%
$\text{MeSi}(\text{OMe})_2\text{CH}_2\text{CH}_2\text{SiMe}_2\text{OSiMe}_2\text{CH}_2\text{CH}_2\text{SiMe}(\text{OMe})_2$ (and other trace double addition products)	8.6%
$\text{HSiMe}_2\text{OSiMe}_2\text{H}$	23.7%
Unidentified byproducts	2.5%

Example 17

[0101] A mixture of 4.00 g of $\text{HSi}(\text{OMe})_2\text{Me}$ (38 mmol) and 5.58 g $\text{ViSi}(\text{OMe})_3$ (38 mmol) was added to a 20 mL glass vial containing a stirbar and to the mixture was added 188 μL of 0.005 M $[\text{Rh}(\text{dppe})\text{Cl}]_2$ (0.01 M in Rh) in THF. The mixture was stirred at 70°C for 16h. The reaction mixture was then analyzed by GC-MS and GC-FID, which indicated that a reaction had only occurred to a slight extent. However, the hydrosilylation product fraction was entirely composed of $(\text{OMe})_3\text{SiCH}_2\text{CH}_2\text{SiMe}(\text{OMe})_2$ (4.8% yield) with no branched isomer observed.

[0102] The overall yields are shown below in Table 15.

Reagent/Product	Mass Balanced Based on HSi(OMe) ₂ Me
(OMe) ₃ SiCH ₂ CH ₂ SiMe(OMe) ₂	4.8%
HSi(OMe) ₂ Me	95.0%
Unidentified byproduct	0.2%

Example 18

[0103] A mixture of 4.00 g of C₃H₅Si(OMe)₃ (25 mmol) and 3.31 g of HSiMe₂OSiMe₂H (25 mmol) was added to a 20 mL glass vial containing a stirbar and to the mixture was added 123 μ L of 0.005 M [Rh(dppe)Cl]₂ (0.01 M in Rh) in THF. The mixture was stirred at 70°C for 16 h. The reaction mixture was then analyzed by GC-MS and GC-FID, which indicated that a reaction was partially complete and that the ratio of linear to branched to other unidentified isomers was 98.5 : 1.0 : 0.5.

[0104] The overall yields are shown below in Table 16.

Reagent/Product	Mass Balance Based on HSiMe ₂ OSiMe ₂ H
HSiMe ₂ OSiMe ₂ (CH ₂) ₃ Si(OMe) ₃	45.1%
HSiMe ₂ OSiMe ₂ CH ₂ CMeHSi(OMe) ₃	0.5%
(OMe) ₃ Si(CH ₂) ₃ SiMe ₂ OSiMe ₂ (CH ₂) ₃ Si(OMe) ₃ and trace other double addition products	5.5%
HSiMe ₂ OSiMe ₂ H	47.2%
Unidentified byproducts	1.7%

Example 19

[0105] A mixture of 4.00 g of (5-hexenyl)Si(OMe)₃ (20 mmol) and 2.63 g of HSiMe₂OSiMe₂H (20 mmol) was added to a 20 mL glass vial containing a stirbar and to the mixture was added 98 μ L of 0.005 M [Rh(dppe)Cl]₂ (0.01 M in Rh) in THF. The mixture was stirred at 70°C for 16h. The reaction mixture was then analyzed by GC-MS and GC-FID, which indicated that a reaction was partially complete and that the ratio of the linear hydrosilylation product to other isomers was 99.5 : 0.5.

[0106] The overall yields are shown below in Table 17.

Reagent/Product	Mass Balance Based on HSiMe ₂ OSiMe ₂ H
HSiMe ₂ OSiMe ₂ (CH ₂) ₆ Si(OMe) ₃	69.2%
Other non-linear isomers of HSiMe ₂ OSiMe ₂ (CH ₂) ₄ CMeHSi(OMe) ₃	0.4%
(OMe) ₃ Si(CH ₂) ₆ SiMe ₂ OSiMe ₂ (CH ₂) ₆ Si(OMe) ₃	1.0%
HSiMe ₂ OSiMe ₂ H	24.1%
Unidentified byproducts	5.3%

Reference Example 20 – Compounding Procedure for Sealant Samples 17 to 46, below
(Prophetic)

[0107] To a Speedmixer cup was added the polymer referenced in a table below. A slurry of methyltrimethoxysilane, slurry of 80% titanium ethyl acetoacetate 20% methyltrimethoxysilane, tetra-n-butoxy titanate, 3-mercaptopropyltrimethoxysilane, and N-(3-(trimethoxysilyl)propyl)ethylenediamine was prepared in a ratio equivalent to the ratio seen in the above formulations. Note that not all starting materials were in every slurry. To the cup was added this slurry equivalent to the sum of its starting materials. The cup was then mixed in a DAC 600.2 VAC-P Speedmixer one minute at 1500rpm. Next, the allotment of precipitated calcium carbonate and ground calcium carbonate, where used, was added to the cup and mixed 30 seconds at 2000 rpm. Finally, the cup was fitted with a cap that contained a hole as to allow the contents of the cup to be exposed to a vacuum environment. The cup was de-aired by mixing 30 seconds at 800 rpm and 5 psi (34.5kPa), 30 seconds at 1500 rpm and 5 psi (34.5kPa), and 30 seconds at 800 rpm and 14.7 psi (101.35kPa). The resulting sealant was transferred to Semco® tubes via a hand operated cup press. A reasonable variance was allowed when adding starting materials.

Sample	Speedmixer	Amount (g)
	Component	
Sample 17	Polydimethylsiloxane 100% end capped with 66.4% β ethyltrimethoxy tetramethyldisiloxane	207.19
	Precipitated Calcium Carbonate	150.04
	Methyltrimethoxysilane	8.88
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	3.70
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	0.19
Sample 18	Speedmixer	Amount (g)
	Component	
	Polydimethylsiloxane 100% end capped with 76.6% β ethyltrimethoxy tetramethyldisiloxane	207.19
	Precipitated Calcium Carbonate	150.04
	Methyltrimethoxysilane	8.88
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	3.70
Sample 19	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	0.19
	Speedmixer	Amount (g)
	Component	
	Polydimethylsiloxane 100% end capped with 86.8% β ethyltrimethoxy tetramethyldisiloxane	207.19
	Precipitated Calcium Carbonate	150.04
	Methyltrimethoxysilane	8.88
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	3.70
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	0.19
Sample 20		
	Speedmixer	Amount (g)
	Component	
	Polydimethylsiloxane 100% end capped with 96.4% β ethyltrimethoxy tetramethyldisiloxane	207.19
	Precipitated Calcium Carbonate	150.04
	Methyltrimethoxysilane	8.88
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	3.70
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	0.19

Sample	Speedmixer	Amount (g)
	Component	
Sample 21	Polydimethylsiloxane 80% end capped with 65% β Pr-T EHM	207.19
	Precipitated Calcium Carbonate	150.04
	Methyltrimethoxysilane	8.88
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	3.70
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	0.19
Sample 22	Speedmixer	Amount (g)
	Component	
	Polydimethylsiloxane 100% end capped with 95% β Pr-T EHM	207.19
	Precipitated Calcium Carbonate	150.04
	Methyltrimethoxysilane	8.88
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	3.70
Sample 23	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	0.19
	Speedmixer	Amount (g)
	Component	
	Polydimethylsiloxane 100% end capped with 66.4% β ethyltrimethoxy tetramethyldisiloxane	163.47
	Precipitated Calcium Carbonate	118.53
	Ground Calcium Carbonate	9.75
	Methyltrimethoxysilane	4.83
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	2.25
	Tetra-n-butoxy titanate	0.84
	3-Mercaptopropyltrimethoxysilane	0.33

Sample 24	Speedmixer Component	Amount (g)
	Polydimethylsiloxane 100% end capped with 76.6% β ethyltrimethoxy tetramethyldisiloxane	163.47
	Precipitated Calcium Carbonate	118.53
	Ground Calcium Carbonate	9.75
	Methyltrimethoxysilane	4.83
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	2.25
	Tetra-n-butoxy titanate	0.84
	3-Mercaptopropyltrimethoxysilane	0.33

Sample 25	Speedmixer Component	Amount (g)
	Polydimethylsiloxane 100% end capped with 86.8% β ethyltrimethoxy tetramethyldisiloxane	163.47
	Precipitated Calcium Carbonate	118.53
	Ground Calcium Carbonate	9.75
	Methyltrimethoxysilane	4.83
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	2.25
	Tetra-n-butoxy titanate	0.84
	3-Mercaptopropyltrimethoxysilane	0.33

Sample 26	Speedmixer Component	Amount (g)
	Polydimethylsiloxane 100% end capped with 96.4% β ethyltrimethoxy tetramethyldisiloxane	163.47
	Precipitated Calcium Carbonate	118.53
	Ground Calcium Carbonate	9.75
	Methyltrimethoxysilane	4.83
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	2.25
	Tetra-n-butoxy titanate	0.84
	3-Mercaptopropyltrimethoxysilane	0.33

Sample 27	Speedmixer Component	Amount (g)
	Polydimethylsiloxane 100% end capped with 65% β Pr-T EHM	163.47
	Precipitated Calcium Carbonate	118.53
	Ground Calcium Carbonate	9.75
	Methyltrimethoxysilane	4.83
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	2.25
	Tetra-n-butoxy titanate	0.84
	3-Mercaptopropyltrimethoxysilane	0.33

Sample 28	Speedmixer Component	Amount (g)
	Polydimethylsiloxane 100% end capped with 95% β Pr-T EHM	163.47
	Precipitated Calcium Carbonate	118.53
	Ground Calcium Carbonate	9.75
	Methyltrimethoxysilane	4.83
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	2.25
	Tetra-n-butoxy titanate	0.84
	3-Mercaptopropyltrimethoxysilane	0.33

Sample 29	Speedmixer Component	Amount (g)
	Polydimethylsiloxane 100% end capped with 66.4% β ethyltrimethoxy tetramethylsiloxane	171.9
	Precipitated Calcium Carbonate	108.99
	Ground Calcium Carbonate	62.1
	Methyltrimethoxysilane	7.62
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	2.76
	Tetra-n-butoxy titanate	1.26
	3-Mercaptopropyltrimethoxysilane	0.87
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	0.39

Sample 30	Speedmixer	Amount (g)
	Component	
	Polydimethylsiloxane 100% end capped with 76.6% β ethyltrimethoxy tetramethyldisiloxane	171.9
	Precipitated Calcium Carbonate	108.99
	Ground Calcium Carbonate	62.1
	Methyltrimethoxysilane	7.62
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	2.76
	Tetra-n-butoxy titanate	1.26
	3-Mercaptopropyltrimethoxysilane	0.87
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	0.39

Sample 31	Speedmixer	Amount (g)
	Component	
	Polydimethylsiloxane 100% end capped with 86.8% β ethyltrimethoxy tetramethyldisiloxane	171.9
	Precipitated Calcium Carbonate	108.99
	Ground Calcium Carbonate	62.1
	Methyltrimethoxysilane	7.62
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	2.76
	Tetra-n-butoxy titanate	1.26
	3-Mercaptopropyltrimethoxysilane	0.87
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	0.39

Sample 32	Speedmixer	Amount (g)
	Component	
	Polydimethylsiloxane 100% end capped with 96.4% β ethyltrimethoxy tetramethyldisiloxane	171.9
	Precipitated Calcium Carbonate	108.99
	Ground Calcium Carbonate	62.1
	Methyltrimethoxysilane	7.62
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	2.76
	Tetra-n-butoxy titanate	1.26
	3-Mercaptopropyltrimethoxysilane	0.87
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	0.39

Sample 33	Speedmixer	Amount (g)
	Component	
	Polydimethylsiloxane 100% end capped with 65% β Pr-T EHM	171.9
	Precipitated Calcium Carbonate	108.99
	Ground Calcium Carbonate	62.1
	Methyltrimethoxysilane	7.62
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	2.76
	Tetra-n-butoxy titanate	1.26
	3-Mercaptopropyltrimethoxysilane	0.87
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	0.39

Sample 34	Speedmixer	Amount (g)
	Component	
	Polydimethylsiloxane 100% end capped with 95% β Pr-T EHM	171.9
	Precipitated Calcium Carbonate	108.99
	Ground Calcium Carbonate	62.1
	Methyltrimethoxysilane	7.62
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	2.76
	Tetra-n-butoxy titanate	1.26
	3-Mercaptopropyltrimethoxysilane	0.87
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	0.39

Sample 35	Speedmixer	Amount (g)
	Component	
	Polydimethylsiloxane 100% end capped with 66.4% β ethyltrimethoxy tetramethyldisiloxane	158.22
	Precipitated Calcium Carbonate	131.22
	Methyltrimethoxysilane	7.26
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	3.3

Sample 36	Speedmixer	Amount (g)
	Component	
	Polydimethylsiloxane 100% end capped with 76.6% β ethyltrimethoxy tetramethyldisiloxane	158.22
	Precipitated Calcium Carbonate	131.22
	Methyltrimethoxysilane	7.26
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	3.3

Sample 37	Speedmixer	Amount (g)
	Component	
	Polydimethylsiloxane 100% end capped with 86.8% β ethyltrimethoxy tetramethyldisiloxane	158.22
	Precipitated Calcium Carbonate	131.22
	Methyltrimethoxysilane	7.26
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	3.3

Sample 38	Speedmixer	Amount (g)
	Component	
	Polydimethylsiloxane 100% end capped with 96.4% β ethyltrimethoxy tetramethyldisiloxane	158.22
	Precipitated Calcium Carbonate	131.22
	Methyltrimethoxysilane	7.26
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	3.3

Sample 39	Speedmixer	Amount (g)
	Component	
	Polydimethylsiloxane 100% end capped with 65% β Pr-T EHM	158.22
	Precipitated Calcium Carbonate	131.22
	Methyltrimethoxysilane	7.26
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	3.3

Sample 40	Speedmixer Component	Amount (g)
	Polydimethylsiloxane 100% end capped with 95% β Pr-T EHM	158.22
	Precipitated Calcium Carbonate	131.22
	Methyltrimethoxysilane	7.26
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	3.3

Sample 41	Speedmixer Component	Amount (g)
	Polydimethylsiloxane 100% end capped with 66.4% β ethyltrimethoxy tetramethyldisiloxane	208.04
	Precipitated Calcium Carbonate	126.88
	Methyltrimethoxysilane	10.15
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	4.66
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	0.28

Sample 42	Speedmixer Component	Amount (g)
	Polydimethylsiloxane 100% end capped with 76.6% β ethyltrimethoxy tetramethyldisiloxane	208.04
	Precipitated Calcium Carbonate	126.88
	Methyltrimethoxysilane	10.15
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	4.66
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	0.28

Sample 43	Speedmixer Component	Amount (g)
	Polydimethylsiloxane 100% end capped with 86.8% β ethyltrimethoxy tetramethyldisiloxane	208.04
	Precipitated Calcium Carbonate	126.88
	Methyltrimethoxysilane	10.15
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	4.66
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	0.28

Sample	Speedmixer	Amount (g)
	Component	
44	Polydimethylsiloxane 100% end capped with 96.4% β ethyltrimethoxy tetramethyldisiloxane	208.04
	Precipitated Calcium Carbonate	126.88
	Methyltrimethoxysilane	10.15
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	4.66
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	0.28

Sample	Speedmixer	Amount (g)
	Component	
45	Polydimethylsiloxane 100% end capped with 65% β Pr-T EHM	208.04
	Precipitated Calcium Carbonate	126.88
	Methyltrimethoxysilane	10.15
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	4.66
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	0.28

Sample	Speedmixer	Amount (g)
	Component	
46	Polydimethylsiloxane 100% end capped with 95% β Pr-T EHM	208.04
	Precipitated Calcium Carbonate	126.88
	Methyltrimethoxysilane	10.15
	Slurry 80% Titanium Ethyl Acetoacetate 20% Methyltrimethoxysilane	4.66
	N-(3-(Trimethoxysilyl)propyl)ethylenediamine	0.28

Industrial Applicability

[0108] The examples and comparative examples above show that when a polyorganosiloxane is endblocked with an alkoxy-functional organohydrogensiloxane oligomer prepared by the method described herein and having > 90 mol% of linear divalent hydrocarbon linking groups, and the resulting endblocked polyorganosiloxane is formulated into a condensation reaction curable composition, the composition cures faster than a comparative composition containing a polyorganosiloxane endblocked with an alkoxy-functional organohydrogensiloxane oligomer having a lower amount of linear

divalent hydrocarbyl linking groups and a higher amount of branched divalent hydrocarbon linking groups.

Claims:

1. A method for preparing an alkoxy-functional organohydrogensiloxane oligomer, where the method comprises:

1) reacting starting materials comprising:

(A) a polyorganohydrogensiloxane oligomer of unit formula:

$(HR^1_2SiO_{1/2})^e(R^1_3SiO_{1/2})^f(HR^1SiO_{2/2})^g(R^1_2SiO_{2/2})^h(R^1SiO_{3/2})^i(HSiO_{3/2})^j(SiO_{4/2})^k$
where subscripts e, f, g, h, i, j, and k have values such that $5 \geq e \geq 0$, $5 \geq f \geq 0$, $10 \geq g \geq 0$, $5 \geq h \geq 0$, subscript i is 0 or 1, $5 \geq j \geq 0$, subscript k is 0 or 1, with the proviso that a quantity $(e + g + j) \geq 2$, and a quantity $(e + f + g + h + i + j + k) \leq 50$; and each R^1 is independently a monovalent hydrocarbon group of 1 to 18 carbon or a monovalent halogenated hydrocarbon group of 1 to 18 carbon atoms;

(B) an aliphatically unsaturated alkoxy silane of formula:

$$R^2-Si\begin{array}{c} R^1 \\ | \\ c \end{array}-OR^3)^{(3-c)}$$
, where each R^2 is independently an aliphatically unsaturated monovalent hydrocarbon group of 2 to 18 carbon atoms, each R^3 is independently a monovalent hydrocarbon group of 1 to 18 carbon atoms, subscript c is 0 or 1; and

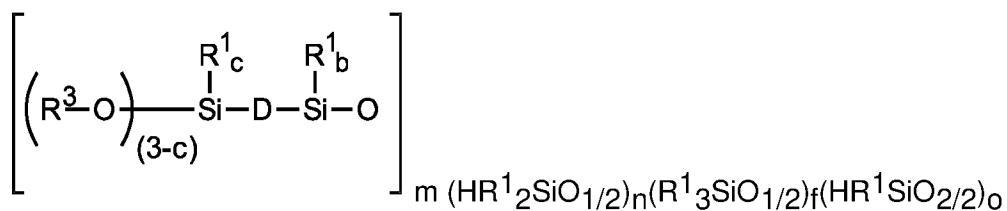
(C) a rhodium diphosphine chelate, thereby preparing a reaction product comprising the alkoxy-functional organohydrogensiloxane oligomer; and
optionally 2) isolating the alkoxy-functional organohydrogensiloxane oligomer prepared in step 1).

2. The method of claim 1, where (C) the rhodium diphosphine chelate has a formula selected from (C1) and (C2), where

(C1) is $[(R^4(R^5_2P)_2)RhR^6]_2$, where each R^4 is independently a divalent hydrocarbon group, each R^5 is independently a monovalent hydrocarbon group, and each R^6 is a negatively charged ligand; and

(C2) is $[(R^4(R^5_2P)_2)Rh(X)]R^7$, where R^4 , and R^5 , are as described above, and R^7 is an anion, and X is a donor ligand.

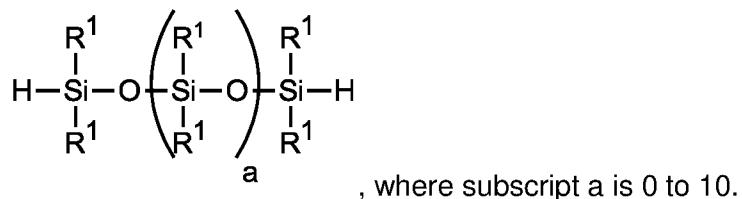
3. The method of claim 1 or claim 2, where the alkoxy-functional organohydrogensiloxane oligomer has unit formula:



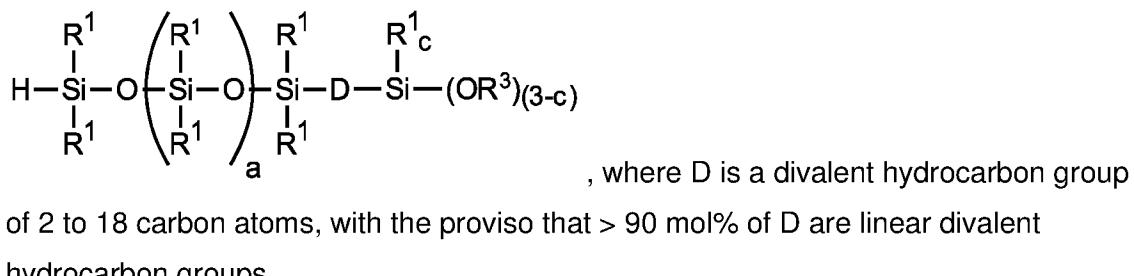
$(\text{R}^1_2\text{SiO}_{2/2})_h(\text{R}^1\text{SiO}_{3/2})_i(\text{HSiO}_{3/2})_p(\text{SiO}_{4/2})_k$, where

R^1 , R^3 , and subscripts c, f, h, i, and k are as described above, subscript b is 0 to 2, $m > 0$, and a quantity $(m + n + o + p) = (e + g + j)$, and each D is independently a divalent hydrocarbon group of 2 to 18 carbon atoms, with the proviso that > 90 mol% of all D groups produced in step 1) are linear.

4. The method of claim 1 or claim 2, where (A) the polyorganohydrogensiloxane oligomer has formula:



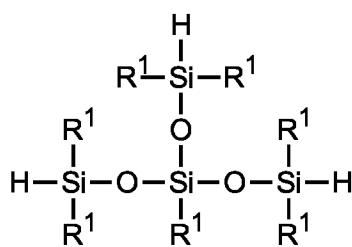
5. The method of claim 4, where the alkoxy-functional organohydrogensiloxane oligomer has formula:



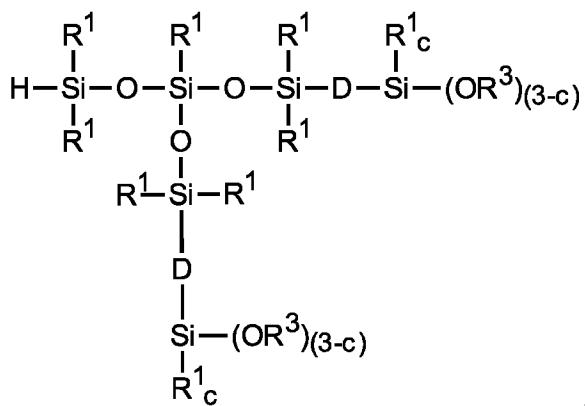
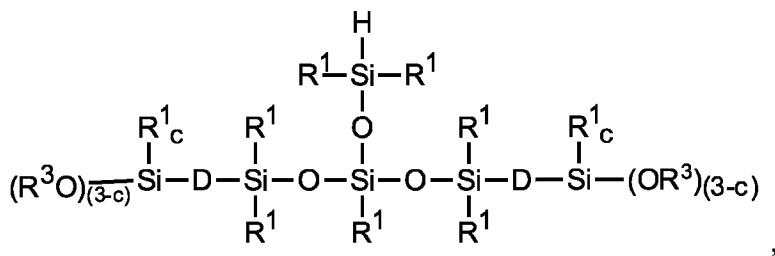
6. The method of claim 1 or claim 2, where (A) the polyorganohydrogensiloxane oligomer has unit formula:

$(\text{HR}^1_2\text{SiO}_{1/2})_3(\text{R}^1_2\text{SiO}_{2/2})_q(\text{R}^1\text{SiO}_{3/2})$, where subscript q is 0 to 3.

7. The method of claim 6, where (A) the polyorganohydrogensiloxane oligomer has formula:



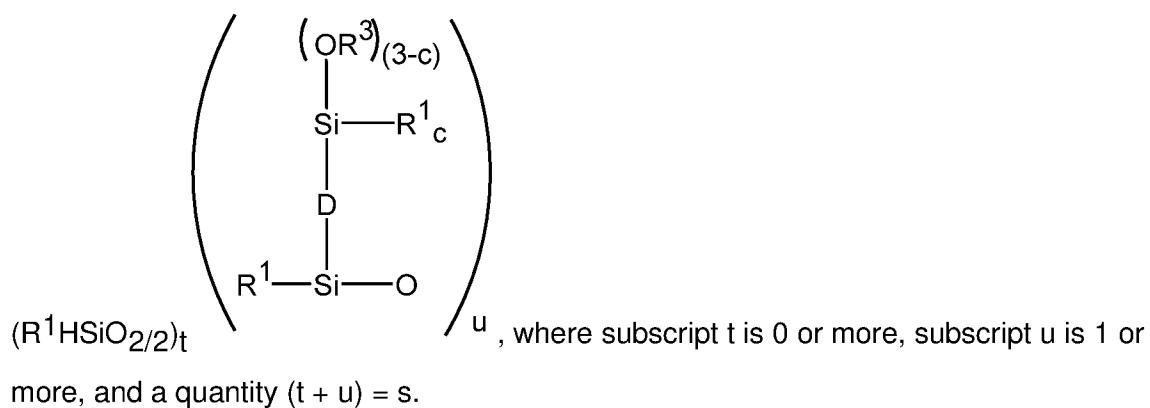
8. The method of claim 7, where the alkoxy-functional organohydrogensiloxane oligomer has formulae comprising:



or both, where each D is independently a divalent hydrocarbon group of 2 to 18 carbon atoms, with the proviso that > 90 mol% of D are linear divalent hydrocarbon groups.

9. The method of claim 1 or claim 2, where the organohydrogensiloxane oligomer is a cyclic organohydrogensiloxane oligomer of unit formula: $(\text{R}^1\text{HSiO}_{2/2})_s$, where subscript s is at least 3.

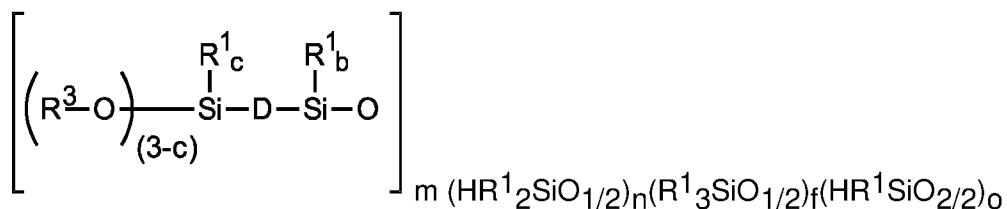
10. The method of claim 9, where the alkoxy-functional organohydrogensiloxane oligomer has unit formula:



11. A method for preparing a poly-alkoxy functional polyorganosiloxane, where the method comprises:

(1) reacting starting materials comprising:

(a) an alkoxy-functional organohydrogensiloxane oligomer of unit formula:

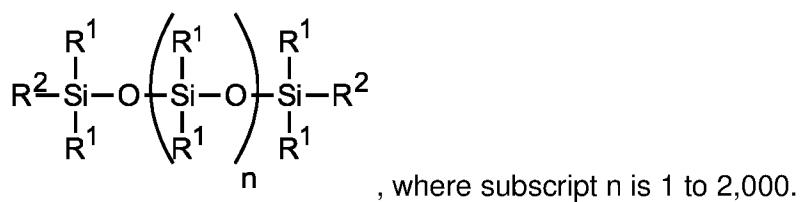


$(R^1_2SiO_{2/2})_h (R^1SiO_{3/2})_i (HSiO_{3/2})_p (SiO_{4/2})_k$, where subscripts b, c, m, n, f, o, h, i, p, and k have values such that subscript b is 0 to 2, subscript c is 0 or 1, $5 \geq m > 0$, $5 \geq n \geq 0$, $5 \geq f \geq 0$, $10 \geq o \geq 0$, $5 \geq h \geq 0$, subscript i is 0 or 1, $5 \geq p \geq 0$, subscript k is 0 or 1, with the proviso that a quantity $(m + n + o + p) \geq 2$, a quantity $(m + n + f + o + h + i + p + k) \leq 50$, each R^1 is independently a monovalent hydrocarbon group of 1 to 18 carbon atoms or a monovalent halogenated hydrocarbon group of 1 to 18 carbon atoms, each R^3 is independently a monovalent hydrocarbon group of 1 to 6 carbon atoms, and each D is independently a divalent hydrocarbon group of 2 to 18 carbon atoms, with the proviso that at least 90% of all D groups are linear;

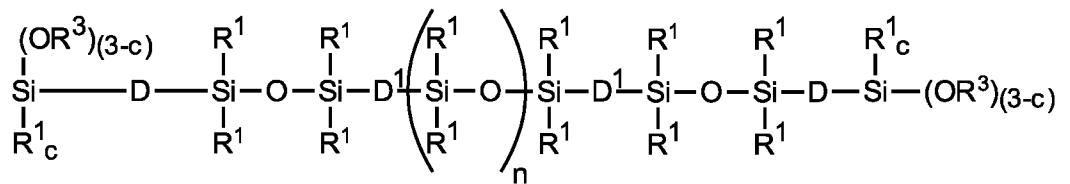
(b) a polyorganosiloxane having, per molecule, an average of at least two aliphatically unsaturated monovalent hydrocarbon groups; and

(c) a hydrosilylation reaction catalyst.

12. The method of claim 11, where starting material (b) is a polydiorganosiloxane of formula:

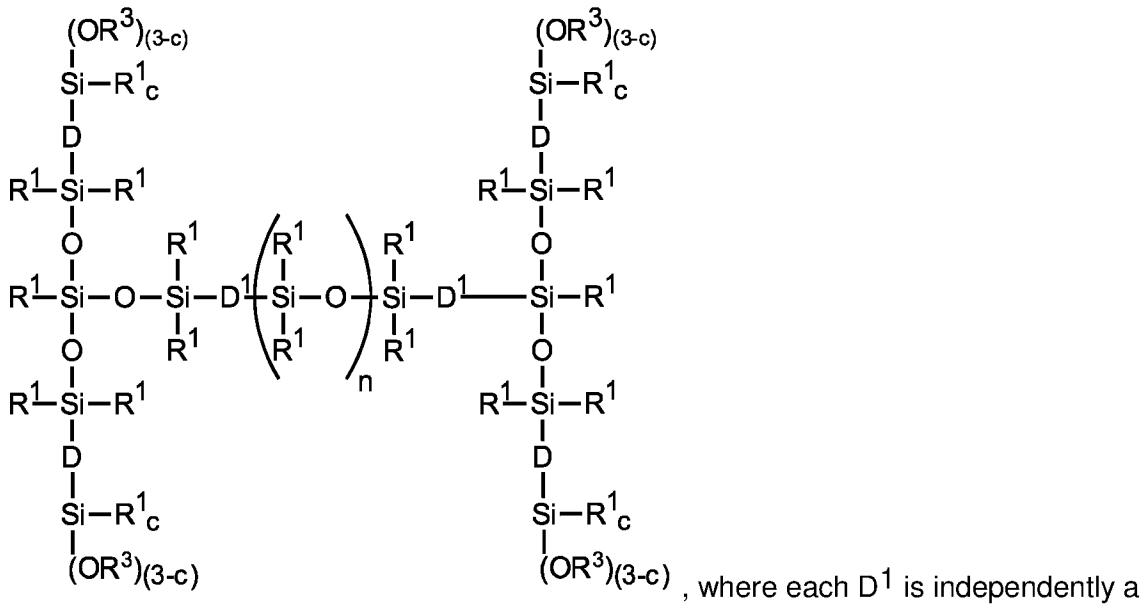


13. The method of claim 11 or claim 12, where the poly-alkoxy functional polyorganosiloxane has formula:



where each D¹ is independently a divalent hydrocarbon group.

14. The method of claim 11 or claim 12, where the poly-alkoxy functional polyorganosiloxane has formula:



divalent hydrocarbon group.

15. A method for making a condensation reaction curable composition comprising mixing starting materials comprising:

(i) the poly-alkoxy functional polyorganosiloxane prepared by the method any one of claims 11 to 14, and

(ii) a condensation reaction catalyst.

16. The method of claim 15, where the condensation reaction catalyst comprises a titanate catalyst.

17. The method of claim 15 or claim 16, where the composition further comprises one or more additional starting materials, where the one or more additional starting materials are selected from the group consisting of (iii) a filler; (iv) a filler treating (v) a crosslinker; (vi) an adhesion promoter, (vii) a drying agent; (viii) an extender, a plasticizer, or a combination thereof; (ix) a biocide; (x) a flame retardant; (xi) a chain lengthener; (xii) an endblocker; (xiii) a nonreactive binder; (xiv) an anti-aging additive; (xv) a water release agent; (xvi) a pigment; (xvii) a rheological additive; (xviii) a vehicle (such as a solvent and/or a diluent); (xix) a tackifying agent; (xx) a corrosion inhibitor; and a combination of two or more of (iii), (iv), (v), (vi), (vii), (viii), (ix), (x), (xi), (xii), (xiii), (xiv), (xv), (xvi), (xvii), (xviii), (xix), and (xx).

18. A condensation reaction curable composition comprising:

(1) a poly-alkoxy functional polyorganosiloxane prepared by a method comprising
 (i) reacting of starting materials comprising
 (a) an alkoxy-functional organohydrogensiloxane oligomer of unit formula:



$(R^1_2SiO_{2/2})_h(R^1SiO_{3/2})_i(HSiO_{3/2})_p(SiO_{4/2})_k$, where subscript b is 0 to 2, subscript c is 0 or 1, $5 \geq m > 0$, $5 \geq n \geq 0$, $5 \geq f \geq 0$, $10 \geq o \geq 0$, $5 \geq h \geq 0$, subscript i is 0 or 1, $5 \geq p \geq 0$, subscript k is 0 or 1, with the proviso that a quantity $(m + n + o + p) \geq 2$, and a quantity $(m + n + f + o + h + i + p + k) \leq 50$, each R^1 is independently a monovalent hydrocarbon group of 1 to 18 carbon atoms or a monovalent halogenated hydrocarbon group of 1 to 18 carbon atoms, each R^3 is independently a monovalent hydrocarbon group of 1 to 6 carbon atoms, and each D is independently a divalent hydrocarbon group of 2 to 18 carbon atoms with the proviso that > 90% of all D groups in the (a) alkoxy-functional organohydrogensiloxane oligomer are linear;

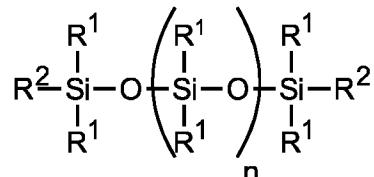
(b) a polyorganosiloxane having, per molecule, an average of at least two aliphatically unsaturated monovalent hydrocarbon groups; and

(c) a hydrosilylation reaction catalyst; and

optionally (ii) isolating the poly-alkoxy functional polyorganosiloxane; and

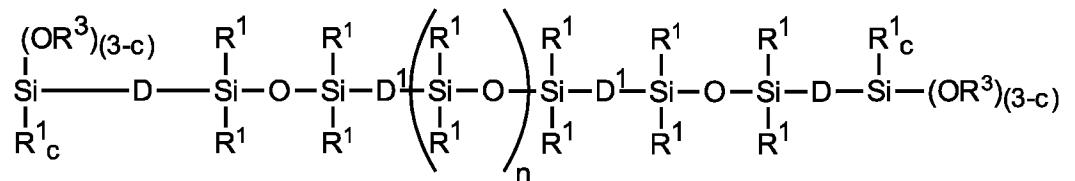
(2) a condensation reaction catalyst.

19. The composition of claim 18, where starting material (b) is a polydiorganosiloxane of formula:



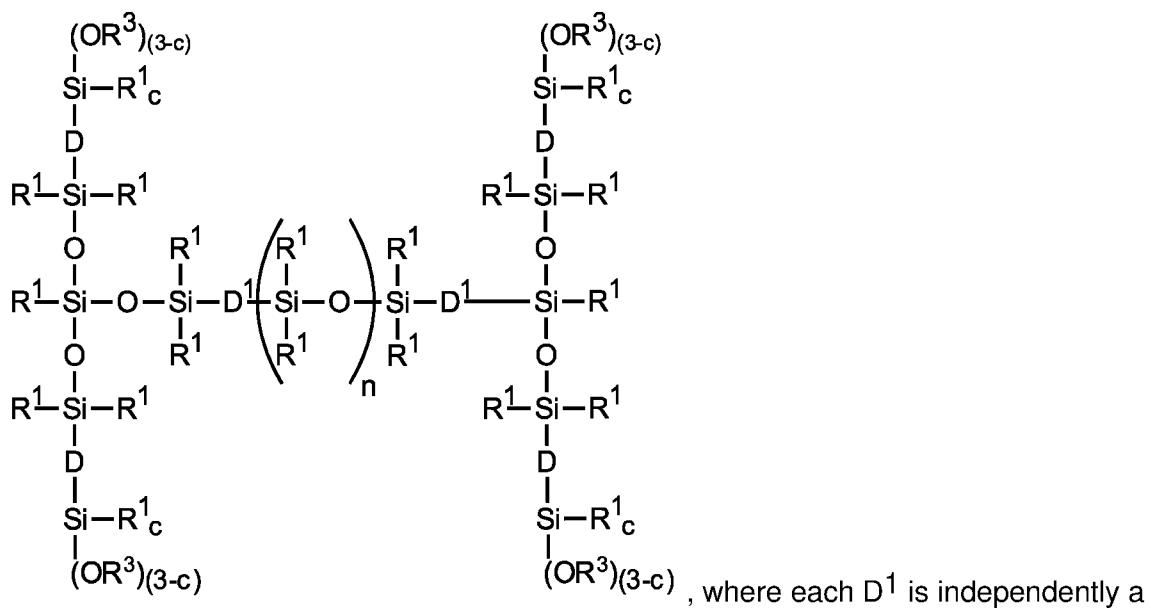
, where subscript n is 1 to 2,000 and each R² is independently an aliphatically unsaturated monovalent hydrocarbon group.

20. The composition of claim 18 or claim 19, where the poly-alkoxy functional polyorganosiloxane has formula:



where each D¹ is independently a divalent hydrocarbon group.

21. The composition of claim 18 or claim 19, where the poly-alkoxy functional polyorganosiloxane has formula:



22. The composition of any one of claims 18 to 21, where the condensation reaction catalyst comprises a titanate catalyst.

23. The composition of any one of claims 18 to 22, where the composition further comprises one or more additional starting materials, where the one or more additional starting materials are selected from the group consisting of (iii) a filler; (iv) a filler treating agent (v) a crosslinker; (vi) an adhesion promoter, (vii) a drying agent; (viii) an extender, a plasticizer, or a combination thereof; (ix) a biocide; (x) a flame retardant; (xi) a chain lengthener; (xii) an endblocker; (xiii) a nonreactive binder; (xiv) an anti-aging additive; (xv) a water release agent; (xvi) a pigment; (xvii) a rheological additive; (xviii) a vehicle (such as a solvent and/or a diluent); (xix) a tackifying agent; (xx) a corrosion inhibitor; and a combination of two or of (iii), (iv), (v), (vi), (vii), (viii), (ix), (x), (xi), (xii), (xiii), (xiv), (xv), (xvi), (xvii), (xviii), (xix), and (xx).

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/039377

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08G77/08 C08G77/04 C08G77/12 C08G77/18 C08L83/04
 ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G 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	US 6 235 832 B1 (DENG QIN [US] ET AL) 22 May 2001 (2001-05-22) "preparation of polymer 3", "polymers 1 and 3"; columns 9-14; example 2 ----- A US 2007/290202 A1 (MATSUMOTO NOBUAKI [JP] ET AL) 20 December 2007 (2007-12-20) paragraph [0066]; example 1 ----- -/-	11-23 1-10

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
 "E" earlier application or patent but published on or after the international filing date
 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
 "O" document referring to an oral disclosure, use, exhibition or other means
 "P" document published prior to the international filing date but later than the priority date claimed

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 September 2018	21/09/2018
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 Dalet, Pierre

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/039377

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GANICZ T ET AL: "The effectiveness of rhodium(I), (II) and (III) complexes as catalysts in hydrosilylation of model olefin and polyether with triethoxysilane and poly(dimethylsiloxane-co-methylsiloxane)", APPLIED CATALYSIS A: GEN, ELSEVIER, AMSTERDAM, NL, vol. 259, no. 1, 8 March 2004 (2004-03-08), pages 49-55, XP004490490, ISSN: 0926-860X, DOI: 10.1016/J.APCATA.2003.09.009 abstract; tables 1-2 -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2018/039377

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
US 6235832	B1	22-05-2001	AU	2201300 A	12-07-2000
			EP	1141132 A1	10-10-2001
			JP	2002533518 A	08-10-2002
			US	6235832 B1	22-05-2001
			WO	0037565 A1	29-06-2000
<hr/>					
US 2007290202	A1	20-12-2007	CN	101089003 A	19-12-2007
			EP	1867652 A1	19-12-2007
			JP	2007332104 A	27-12-2007
			KR	20070120044 A	21-12-2007
			TW	200815461 A	01-04-2008
			US	2007290202 A1	20-12-2007
<hr/>					