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(54) **POLYORGANOHYDROGENSILOXANE
COMPOSITION INCLUDING A LEWIS
ACIDIC MONOCATIONIC PHOSPHONIUM
SALT**

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(57) **ABSTRACT**

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A composition contains a phosphonium catalyst and a poly-
organohydrogensiloxane. The composition is shelf stable at
C room temperature and cures when heated. The composi-
tion and method are useful for preparing polyorganosiloxane
products such as coatings, adhesives, elastomers, and
foams.

**POLYORGANOHYDROGENSILOXANE
COMPOSITION INCLUDING A LEWIS
ACIDIC MONOCATIONIC PHOSPHONIUM
SALT**

[0001] This application claims the benefit of U.S. Provisional Patent Application Ser. No. 63/352,315 filed on 15 Jun. 2022 under 35 U.S.C. § 119 (e). U.S. Provisional Patent Application Ser. No. 63/352,315 is hereby incorporated by reference.

TECHNICAL FIELD

[0002] A curable polyorganosiloxane composition and methods for the preparation and cure thereof is provided. More particularly, the curable polyorganosiloxane composition includes a monocationic Lewis acidic phosphonium salt (catalyst) and a polyorganohydrogensiloxane.

INTRODUCTION

[0003] Silyl hydride (Si—H) and siloxane linkages (Si—O—Si) have been found to undergo a rearrangement reaction in the presence of a strong Lewis acid where a silicon from the siloxane linkage becomes bound to the hydrogen of the silyl hydride while the silicon of the silyl hydride becomes bound to the oxygen of the siloxane linkage. The silyl hydride and siloxane linkage that participate in the rearrangement reaction can be on the same molecule or can be on different molecules. This rearrangement reaction tends to be rapid in the presence of a strong Lewis acid. Such a reaction can be useful for rapidly curing systems containing Si—H and siloxane linkages without requiring water or moisture. However, it requires a two-part system for storage where the Lewis acid catalyst is kept away from a combination of the silyl hydride and siloxane linkage until such time as curing is desired. It is desirable to be able to provide a shelf-stable one-component system that utilizes the rearrangement reaction that is shelf stable at room temperature, but that can be triggered with heating to cure.

SUMMARY

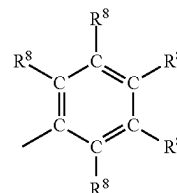
[0004] A curable polyorganohydrogensiloxane composition (composition) comprises (A) a phosphonium catalyst and (B) a polyorganohydrogensiloxane. Methods for preparing and curing the composition are provided.

DETAILED DESCRIPTION

[0005] The composition introduced above comprises (A) the phosphonium catalyst and (B) the polyorganohydrogensiloxane. The phosphonium catalyst comprises (i) a tetravalent monocation of phosphorus and (ii) a non-coordinating anion.

Starting Material (A) Phosphonium Catalyst

[0006] Starting material (A) used herein is the phosphonium catalyst, which comprises (i) the tetravalent monocation of phosphorus and (ii) the non-coordinating anion. The tetravalent monocation of phosphorus is a Lewis acidic phosphorus cation of formula (i-1): $[PR^1_3R^2]^+$, where each R^1 is an independently selected halogenated aryl group, and each R^2 is independently selected from the group consisting of a halogen atom and an electron withdrawing group.



[0007] The halogenated aryl group R^1 may have formula: R, where each R^8 is independently selected from H, X, and a group of formula $-CX_3$, where each X is an independently selected halogen; with the proviso that at least one R^8 is not H. Each X may be independently selected from chlorine (Cl) or fluorine (F). Alternatively, each X may be F. Alternatively, each R^8 may be independently selected from the group consisting of H, Cl, F, and a group of formula $-CF_3$, with the proviso that at least one R^8 is Cl, F, or $-CF_3$.

[0008] The halogen atom for R^2 may be selected from the group consisting of bromine (Br), Cl, and F; alternatively Cl and F. Alternatively, the halogen atom for R^2 may be F. The electron withdrawing group for R^2 may comprise, bonded to P, an atom with an electronegativity ≥ 2.5 , such as carbon (C) or oxygen (O). Alternatively, the electron withdrawing group may have formula $-CX'_3$, where X' is a halogen atom selected from Br, Cl, or F; alternatively Cl or F; and alternatively F. Alternatively, the electron withdrawing group for R^2 may have formula $-CF_3$. Alternatively, the electron withdrawing group for R^2 may have formula $-OR^9$, where R^9 is alkyl or aryl. Suitable alkyl groups for R^9 may be linear, branched, cyclic, or combinations of two or more thereof. The alkyl groups are exemplified by methyl, ethyl, propyl (including n-propyl and/or isopropyl), butyl (including n-butyl, tert-butyl, sec-butyl, and/or isobutyl), pentyl, hexyl, heptyl, octyl, decyl, dodecyl, undecyl, and octadecyl (and branched isomers having 5 to 18 carbon atoms), and the alkyl groups are further exemplified by cycloalkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl. Suitable aryl groups for R^9 may be monocyclic or polycyclic and may have pendant hydrocarbon groups. For example, the aryl groups for R^9 include phenyl, tolyl, xylyl, and naphthyl and further include aralkyl groups such as benzyl, 1-phenylethyl and 2-phenylethyl. Alternatively, the aryl group for R^9 may be monocyclic, such as phenyl, tolyl, or benzyl; alternatively the aryl group for R^9 may be phenyl.

[0009] Alternatively, in formula (i-1), each R^1 may be a fluorinated aryl group. Alternatively, in formula (i-1), R^2 may be F. Alternatively, (i) the tetravalent monocation of phosphorus may have formula: $[P(C_6F_5)_3F]^+$.

[0010] In (A) the phosphonium catalyst, (ii) the anion is a non-coordinating anion. The non-coordinating anion may have a charge that is delocalized over the surface of the anion, rather than localized at a specific atom. Suitable non-coordinating anions include trifluoromethane sulfonate (triflate) of formula $[CF_3SO_3]^-$ and an anion of formula $[BR^3_4]^-$, where each R^3 is independently selected from the group consisting of a monovalent hydrocarbon group and a monovalent halogenated hydrocarbon group. The monovalent hydrocarbon group may be an alkyl group or an aryl group. The monovalent halogenated hydrocarbon group may

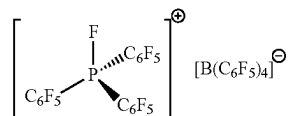
be an alkyl group or an aryl group where one or more hydrogen atoms has been replaced with F, Cl, or Br.

[0011] Suitable alkyl groups for R^3 may be linear, branched, cyclic, or combinations of two or more thereof. The alkyl groups for R^3 are exemplified by methyl, ethyl, propyl (including n-propyl and/or isopropyl), butyl (including n-butyl, tert-butyl, sec-butyl, and/or isobutyl); pentyl, hexyl, heptyl, octyl, decyl, dodecyl, undecyl, and octadecyl (and branched isomers having 5 to 18 carbon atoms), and the alkyl groups are further exemplified by cycloalkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl. Suitable halogenated alkyl groups include chlorinated alkyl groups such as chloromethyl and chloropropyl groups; fluorinated alkyl groups such as fluoromethyl, difluoromethyl, trifluoromethyl, 2-fluoropropyl, 3,3,3-trifluoropropyl, 4,4,4-trifluorobutyl, 4,4,4,3,3-pentafluorobutyl, 5,5,5,4,4,3,3-heptafluoropentyl, 6,6,6,5,5,4,4,3,3-nonafluorohexyl, and 8,8,8,7,7-pentafluorooctyl; chlorinated cycloalkyl groups such as 2,2-dichlorocyclopropyl, 2,3-dichlorocyclopentyl; and fluorinated cycloalkyl groups such as 2,2-difluorocyclopropyl, 2,3-difluorocyclobutyl, 3,4-difluorocyclohexyl, and 3,4-difluoro-5-methylcycloheptyl.

[0012] Suitable aryl groups for R^3 may be monocyclic or polycyclic and may have pendant hydrocarbyl groups. For example, the aryl groups for R^3 include phenyl, tolyl, xyl, and naphthyl and further include aralkyl groups such as benzyl, 1-phenylethyl and 2-phenylethyl. Alternatively, the aryl group for R^3 may be monocyclic, such as phenyl, tolyl, or benzyl; alternatively the aryl group for R^3 may be phenyl. The halogenated aryl group for R^3 may be as described above for R^1 .

[0013] Alternatively, the non-coordinating anion may be fully saturated and have no free valence electron to engage in a covalent or dative bond with the phosphonium. The fully saturated anion may have formula $[BR^3_4]^-$, where each R^3 is independently selected from the group consisting of a monovalent hydrocarbon group and a monovalent halogenated hydrocarbon group, as described above. Alternatively, each R^3 may be a halogenated aryl group. Alternatively, the anion may have formula $B(C_6F_5)_4$.

[0014] Alternatively, (A) the catalyst may have formula:



[0015] Starting material (A) may be prepared by methods known in the art, such as those disclosed in Science 2013, 341, 1374-1377 by varying appropriate starting materials. Starting material (A) used herein may be any one of the catalysts described above, or a combination of two or more of the catalysts described above.

[0016] The composition described herein contains a sufficient amount of (A) the catalyst to cure the composition. The exact amount of (A) the catalyst depends on various factors including the selection of (B) the polyorganohydrogensiloxane, and whether (C) the (non-functional) polyorganosiloxane is present. However, the composition may contain enough catalyst to provide a concentration of tetravalent monocation of phosphorus that may be at least 1 ppm, alternatively at least 2 ppm, alternatively at least 5

ppm; while at the same time the amount may be up to 1,000 ppm, alternatively up to 500 ppm, alternatively up to 100 ppm, and alternatively up to 50 ppm; each based on combined weights of starting materials (A) and (B) (and, when present (C)). Alternatively, the amount of (A) the phosphonium catalyst may be 1 ppm to 1,000 ppm, alternatively 2 ppm to 500 ppm, alternatively 5 ppm to 100 ppm, and alternatively 10 ppm based on weight of (B) the polyorganohydrogensiloxane, and when present, (C) the (non-functional) polyorganosiloxane in the composition.

Starting Material (B) Polyorganohydrogensiloxane

[0017] The composition described herein further comprises (B) a polyorganohydrogensiloxane. The polyorganohydrogensiloxane comprises both Si—H and Si—O—Si moieties. Therefore, the composition comprising (A) the phosphonium catalyst and (B) the polyorganohydrogensiloxane may cure to form a gel when heated, without additional components. Without wishing to be bound by theory, it is thought that (A) the phosphonium catalyst catalyzes rearrangement reaction of Si—H and Si—O—Si moieties both within the (B) polyorganohydrogensiloxane to cure the composition.

[0018] The polyorganohydrogensiloxane has at least one Si—H moiety per molecule. Alternatively, the polyorganohydrogensiloxane may have more than one Si—H moiety per molecule, such as 2 Si—H moieties per molecule or 3 Si—H moieties per molecule, or even more.

[0019] The polyorganohydrogensiloxane may comprise two or more siloxane units selected from the group consisting of $HR^4_2SiO_{1/2}$, $R^4_3SiO_{1/2}$, $HR^4SiO_{2/2}$, $R^4_2SiO_{2/2}$, $R^4SiO_{3/2}$, $HSiO_{3/2}$ and $SiO_{4/2}$ units; wherein each R^4 is an independently selected monovalent hydrocarbon group, which is free of aliphatic unsaturation; with the proviso that at least one unit, per molecule, contains an Si—H moiety (i.e., at least one of $HR^4_2SiO_{1/2}$, $HR^4SiO_{2/2}$, and $HSiO_{3/2}$ is present in the polyorganohydrogensiloxane). The monovalent hydrocarbon group, which is free of aliphatic unsaturation, may be an alkyl group or an aryl group, as described above for R^3 . Alternatively, each R^4 may be an independently selected alkyl group. Alternatively, each R^4 may be independently selected from the group consisting of methyl and phenyl. Alternatively, each R^4 may be methyl.

[0020] Alternatively, (B) the polyorganohydrogensiloxane may be linear or cyclic. For example, (B) the polyorganohydrogensiloxane may be a linear polydiorganohydrogensiloxane comprising unit formula (B-1): $(HR^4_2SiO_{1/2})_g(R^4_3SiO_{1/2})_h(R^4_2SiO_{2/2})_i(HR^4SiO_{2/2})_j$, where R^4 is as described above, and subscripts g, h, i, and j have values such that $g \geq 0$, $h \geq 0$, a quantity $(g+h)=2$, $i \geq 0$, $j \geq 0$, and a quantity $(g+j) \geq 1$, and a quantity $(i+j)$ is 0 to 2,000. The quantity $(i+j)$ may be 2,000 or less, alternatively 1,000 or less, alternatively 750 or less, alternatively 500 or less, alternatively 250 or less, alternatively 100 or less, and alternatively 50 or less; while at the same time, the quantity $(i+j)$ may be 0 or more, alternatively 1 or more, alternatively 2 or more, alternatively 3 or more, alternatively 4 or more, alternatively 5 or more, alternatively 10 or more, alternatively 15 or more, and alternatively 20 or more. Alternatively $(i+j)$ may be 0 to 1,000; alternatively 1 to 500; alternatively 2 to 250, and alternatively 3 to 100. Alternatively $(i+j)$ may be 1 to 100. Alternatively, $(i+j)$ may be 2 to 50. Alternatively, $(i+j)$ may be 5 to 25. Alternatively, when $g=0$ and $h=2$, $j \geq 1$ (alternatively ≥ 2). Alternatively, g may be

1, and h may be 1. Alternatively, g may be 2 and h may be 0. Alternatively, i may be 0 to 5, alternatively 1 to 4, alternatively 2 to 4, and alternatively 3 to 3.5. Alternatively, i may be 5 to 25. Alternatively, j may be 1 to 10, alternatively 2 to 9, alternatively 3 to 8, alternatively 4 to 7, and alternatively 5 to 6. Alternatively, when $g > 0$, then j may be 0.

[0021] Suitable linear polydiorganohydrogensiloxanes for use herein are exemplified by:

[0022] (i) α,ω -dimethylhydrogensiloxy-terminated poly(dimethylsiloxane/methylhydrogensiloxane),

[0023] (ii) α,ω -dimethylhydrogensiloxy-terminated polymethylhydrogensiloxane,

[0024] (iii) α,ω -trimethylsiloxy-terminated poly(dimethylsiloxane/methylhydrogensiloxane),

[0025] (iv) α,ω -trimethylsiloxy-terminated polymethylhydrogensiloxane, and

[0026] (v) α -dimethylhydrogensiloxy- ω -trimethylsiloxy-terminated poly(dimethylsiloxane/methylhydrogensiloxane),

[0027] (vi) α -dimethylhydrogensiloxy- ω -trimethylsiloxy-terminated polymethylhydrogensiloxane,

[0028] (vii) a combination of two or more thereof.

[0029] Alternatively, the polyorganohydrogensiloxane may be cyclic. The cyclic polydiorganohydrogensiloxane may comprise unit formula (B-2): $(R^4)_2SiO_{2/2}u(R^4HSiO_{2/2})v$, where R^4 is as described above, subscript u is 0 or more, subscript v is 1 or more, a quantity (u+v) is 3 to 15. Alternatively u may be 0. Alternatively, u may be 0 or more, alternatively 1 or more, alternatively 2 or more, alternatively 3 or more; while at the same time u may be up to 6, alternatively up to 5, and alternatively up to 4. Alternatively, u may be 0 to 6, alternatively 0 to 4, alternatively 0 to 2, and alternatively 1 to 6. Alternatively, v may be 1 or more, alternatively 2 or more, alternatively 3 or more, and alternatively 4 or more; while at the same time, v may be 12 or less, alternatively 10 or less, alternatively 8 or less, alternatively 6 or less, and alternatively 5 or less. Alternatively, v may have an average value of 4. Alternatively, v may be 1 to 12, alternatively 2 to 10, alternatively 3 to 8, alternatively 3 to 6, and alternatively 3 to 5. In unit formula (B-2), each R^4 may be methyl. Examples of cyclic polyorganohydrogensiloxanes include (i) trimethylcyclotrisiloxane, (ii) tetramethylcyclotetrasiloxane, (iii) pentamethylcyclopentasiloxane, (iv) hexamethylcyclohexasiloxane, and (v) combinations of two or more thereof.

[0030] Suitable polyorganohydrogensiloxanes are known in the art and are commercially available. For example, DOWSIL™ 6-3570 Polymer, DOWSIL™ SH 1107 Fluids and XIAMETER™ MHX-1107 Fluids are available from The Dow Chemical Company of Midland, Michigan, USA. Polydiorganohydrogensiloxanes such as HMS-992 (trimethylsilyl terminated polymethylhydrogensiloxane), HMS-HM271 (hydride-terminated methylhydrogensiloxane—dimethylsiloxane copolymer), and HMS-031 (trimethylsiloxy-terminated methylhydrogensiloxane dimethylsiloxane copolymer) are available from Gelest, Inc. of Morrisville, Pennsylvania, USA. Other polydiorganohydrogensiloxanes available from Gelest include HMS-H271, HMS-071, HMS-993; HMS-301 and HMS-301 R, HMS-991, HMS-993, HMS-082, HMS-151, HMS-013, HMS-053, HAM-301 (which is octyl functional), and HPM-502 (which is phenyl functional). Methods of preparing linear and branched polyorganohydrogensiloxanes suitable for use herein, such as hydrolysis and

condensation of organohalosilanes, are well known in the art, as exemplified in U.S. Pat. No. 3,957,713 to Jeram et al.; U.S. Pat. No. 4,329,273 to Hardman, et al.; U.S. Pat. No. 4,370,358 to Hayes, et al.; U.S. Pat. No. 4,707,531 to Shirahata; U.S. Pat. No. 5,310,843 to Morita; and U.S. Pat. No. 2,823,218 to Speier, et al., which discloses organohydrogensiloxane oligomers and linear polymers as well as cyclic polymethylhydrogensiloxanes.

[0031] The amount of (B) the polyorganohydrogensiloxane in the composition depends on various factors including the Si—H content of the polyorganosiloxane (which may be determined using quantitative infra-red analysis in accordance with ASTM E168), and any optional, additional starting materials are present. However, the amount of polyorganohydrogensiloxane may be 1 wt % or more, alternatively 5 wt % or more, alternatively 10 wt % or more, alternatively 20 wt % or more, alternatively 30 wt % or more, alternatively 40 wt % or more, alternatively 50 wt % or more, alternatively 60 wt % or more, alternatively 70 wt % or more, alternatively 80 wt % or more, alternatively 90 wt % or more, alternatively 95 wt % or more, and alternatively 99 wt % or more, while at the same time the amount of polyorganohydrogensiloxane may be <100 wt %, alternatively 99.9 wt % or less, alternatively 99.5 wt % or less, alternatively 99.1 wt % or less, alternatively 95 wt % or less, alternatively 90 wt % or less, alternatively 85 wt % or less, alternatively 80 wt % or less; each based on combined weight of starting materials (A), (B), and (C) in the composition. Alternatively, the amount of polyorganohydrogensiloxane may be 1 wt % to <100 wt %, alternatively 5 wt % to <100 wt %, alternatively 10 wt % to 99.9 wt %, on the same basis.

[0032] Alternatively, in addition to (B) the polyorganohydrogensiloxane, the composition may further comprise (C) a polyorganosiloxane that is free of Si—H moieties that may serve as a source of Si—O—Si moieties in the curing reaction for the composition.

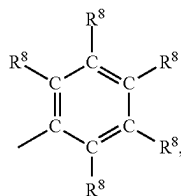
Starting Material (C) Polyorganosiloxane

[0033] Starting material (C) is an optional polyorganosiloxane that is free of Si—H moieties. The polyorganosiloxane comprises two or more siloxane units selected from $R^4_3SiO_{1/2}$, $R^4_2SiO_{2/2}$, $R^4SiO_{3/2}$, and $SiO_{4/2}$ units; wherein each R^4 is an independently selected monovalent hydrocarbon group, which is free of aliphatic unsaturation. The monovalent hydrocarbon group, which is free of aliphatic unsaturation, may be an alkyl group or an aryl group.

[0034] Suitable alkyl groups for R^4 may be linear, branched, cyclic, or combinations of two or more thereof. The alkyl groups are exemplified by methyl, ethyl, propyl (including n-propyl and/or isopropyl), butyl (including n-butyl, tert-butyl, sec-butyl, and/or isobutyl), pentyl, hexyl, heptyl, octyl, decyl, dodecyl, undecyl, and octadecyl (and branched isomers having 5 to 18 carbon atoms), and the alkyl groups are further exemplified by cycloalkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl. Suitable halogenated alkyl groups include chlorinated alkyl groups such as chloromethyl and chloropropyl groups; fluorinated alkyl groups such as fluoromethyl, difluoromethyl, trifluoromethyl, 2-fluoropropyl, 3,3,3-trifluoropropyl, 4,4,4-trifluorobutyl, 4,4,4,3,3-pentafluorobutyl, 5,5,5,4,4,3,3-heptafluoropentyl, 6,6,6,5,5,4,4,3,3-nonafluorohexyl, and 8,8,8,7,7-pentafluorooctyl; chlorinated cycloalkyl groups such as 2,2-dichlorocyclopropyl, 2,3-dichlorocyclopentyl;

and fluorinated cycloalkyl groups such as 2,2-difluorocyclopropyl, 2,3-difluorocyclobutyl, 3,4-difluorocyclohexyl, and 3,4-difluoro-5-methylcycloheptyl.

[0035] Suitable aryl groups for R^4 may be monocyclic or polycyclic and may have pendant hydrocarbyl groups. For example, the aryl groups for R^3 include phenyl, tolyl, xylyl, and naphthyl and further include aralkyl groups such as benzyl, 1-phenylethyl and 2-phenylethyl. Alternatively, the aryl group for R^4 may be monocyclic, such as phenyl, tolyl, or benzyl; alternatively the aryl group for R^4 may be phenyl. The halogenated aryl group for R^4 may have formula:



where each R^8 is independently selected from H, X, and a group of formula $-CX_3$, where each X is an independently selected halogen; with the proviso that at least one R^8 is not H. Each X may be independently selected from Cl or F. Alternatively, each X may be F. Alternatively, each R^8 may be independently selected from the group consisting of H, Cl, F, and a group of formula $-CF_3$, with the proviso that at least one R^8 is Cl, F, or $-CF_3$. Alternatively, each R^4 may be an independently selected alkyl group. Alternatively, each R^4 may be independently selected from the group consisting of methyl and phenyl. Alternatively, each R^4 may be methyl.

[0036] Starting material (C) the polyorganosiloxane may be a polydiorganosiloxane, which may be linear or cyclic. For example, starting material (C) may be a linear polydiorganosiloxane comprising unit formula (C-1): $(R^4_2SiO_{1/2})_x$, where R^4 is as described above, and $1,000 \geq x \geq 1$. Alternatively, subscript x may be at least 1, alternatively at least 2, alternatively at least 3, alternatively at least 5, alternatively at least 10, alternatively at least 25; while at the same time subscript x may be up to 1,000, alternatively up to 500, alternatively up to 250, alternatively up to 100, and alternatively up to 50. Alternatively, subscript x may have a value such that $500 \geq x \geq 1$, alternatively $250 \geq x \geq 2$, alternatively $100 \geq x \geq 5$, alternatively $50 \geq x \geq 10$, and alternatively $50 \geq x \geq 25$.

[0037] Suitable linear polydiorganosiloxanes for use herein are exemplified by:

[0038] (i) α,ω -trimethylsiloxy-terminated polydimethylsiloxane,

[0039] (ii) α,ω -dimethylphenylsiloxy-terminated poly(dimethylsiloxane/methylphenylsiloxane),

[0040] (iii) α,ω -dimethylphenylsiloxy-terminated polymethylphenylsiloxane,

[0041] (iv) α,ω -trimethylsiloxy-terminated poly(dimethylsiloxane/methylphenylsiloxane),

[0042] (v) α,ω -trimethylsiloxy-terminated polymethylphenylsiloxane, and

[0043] (vi) a combination of two or more thereof.

[0044] Polydiorganosiloxanes are known in the art and are commercially available. For example, DOWSIL™ 200 Fluids, DOWSIL™ OS Fluids, and XIAMETER™ PMX-200

Silicone Fluids are commercially available from The Dow Chemical Company of Midland, Michigan, USA.

[0045] Alternatively, (C) the polyorganosiloxane may be a cyclic polydiorganosiloxane comprising unit formula (C-2): $(R^4_2SiO_{2/2})_y$, where R^4 is as described above, and $15 \geq y \geq 3$. Alternatively, subscript y may be at least 3, alternatively at least 4, alternatively at least 5, and alternatively at least 6; while at the same time, subscript y may be up to 15, alternatively up to 12, alternatively up to 10, alternatively up to 8, and alternatively up to 6. Alternatively, subscript y may have a value such that $12 \geq y \geq 3$, alternatively $10 \geq y \geq 3$, alternatively $8 \geq y \geq 3$, alternatively $6 \geq y \geq 3$, and alternatively $6 \geq y \geq 4$.

[0046] Examples of cyclic polydiorganosiloxanes include hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, and a combination of two or more thereof. These cyclic polydiorganosiloxanes are commercially available, e.g., from Sigma-Aldrich, Inc. of St. Louis, Missouri, USA.

[0047] Starting material (C) is optional. However, when present, the amount of starting material (C) depends on various factors including the type of polyorganohydrogen-siloxane selected for starting material (B) and its Si—H content. The amount of (C) the polyorganosiloxane may be 0 to <99 wt % based on combined weight of starting materials (A), (B), and (C) in the composition.

Starting Material (D) Solvent

[0048] Starting material (D) is an optional solvent, which may be used to facilitate combination of starting materials (A) and (B), and, when present (C), in the composition and method described herein. Solvents used herein are those that help fluidize the starting materials, but essentially do not react with any of these starting materials. Solvent may be selected based on solubility of the starting materials and volatility of the solvent. The solubility refers to the solvent being sufficient to dissolve and/or disperse the starting materials. Volatility refers to vapor pressure of the solvent. For example, starting material (A), the phosphonium catalyst, may be dissolved in a solvent before combining starting material (A) with starting material (B) (and when present (C)). Alternatively, starting material (B) may be dissolved in a solvent before combining with starting material (A) (and (C), when present) when starting material (B) is a viscous fluid, such as a gum, or a solid at RT, such as a resin. Alternatively, starting material (C) may be dissolved in a solvent before combining with starting materials (A) and (B), e.g., when starting material (C) is a solid at RT, such as a resin or a gum. The solvent may be used in any amount, which will be selected by one of skill in the art, depending on various factors, such as the selection of starting materials (A) and (B) (and when present (C)) and their solubilities.

[0049] Suitable solvents may be hydrocarbons. Suitable hydrocarbons include aromatic hydrocarbons such as benzene, toluene, or xylene; and/or aliphatic hydrocarbons such as heptane, hexane, or octane. Alternatively, the solvent may be a halogenated hydrocarbon such as chloroform, 1,1,1-trichloroethane or methylene chloride. One solvent, or a combination comprising two or more solvents, may be used herein.

[0050] The amount of solvent can depend on various factors including the type of solvent selected and the amounts and types of other starting materials selected. However, the amount of solvent may be 0.1 wt % or more, alternatively 2 wt % or more, while at the same time the amount of solvent may be up to 99 wt %, alternatively up to 50 wt %, based on combined weights of starting materials (A), (B), and (C). Alternatively, the amount of (D) the solvent may be 0.1 wt % to 99 wt %, alternatively 2 wt % to 50 wt %, based on combined weights of (A) the catalyst, (B) the polyorganohydrogensiloxane, and (C) the polyorganosiloxane compound in the composition.

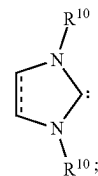
[0051] The composition can consist of (A) the phosphonium catalyst and (B) the polyorganohydrogensiloxane (and when present, (C) the polyorganosiloxane and/or (D) the solvent). Alternatively, the composition described herein may optionally further comprise an additional component. An optional additional component may be present at a concentration of 50 wt % or less, 40 wt % or less, 30 wt % or less, 20 wt % or less, 10 wt % or less, 5 wt % or less, or even one wt % or less based on composition weight. Alternatively, an optional additional component may be present at a concentration of 0 to 50 wt %, alternatively 0 to 40 wt %, alternatively 0 to 30 wt %, alternatively 0 to 20 wt %, alternatively 0 to 10 wt %, alternatively 0 to 5 wt %, and alternatively 1 wt % to 30 wt %.

Optional Additional Components

[0052] Examples of possible optional components include one or a combination of more than one component selected from a group consisting of pigments such as carbon black or titanium dioxide, fillers such as metal oxides including SiO_2 (e.g., at a concentration of 50 wt % or less based on composition weight), moisture scavengers, fluorescent brighteners, stabilizers (such as antioxidants and ultraviolet stabilizers), and corrosion inhibitors. The composition alternatively can be free of any one or any combination of more than one such additional components. In addition, the composition can contain one wt % or less, alternatively 0.5 wt % or less water relative to composition weight. Alternatively, the composition may be free of water.

[0053] The composition described herein may be free of transition metals. "Free of transition metals" means that the composition contains none, or a non-detectable amount, or an amount insufficient to gel the composition at room temperature after 24 hours, of a metal in Groups 4-12 of the IUPAC Periodic Table of the Elements dated 1 Dec. 2018. Without wishing to be bound by theory, it is thought that transition metals may catalyze reaction of Si—H and Si—O moieties, at an undesirably low temperature (e.g., $<65^\circ\text{C}$).

[0054] The composition described herein may be free of Lewis base. "Free of Lewis base" means that the composition contains none or an insufficient amount of a compound or ionic species, that can donate an electron pair to (A) the phosphonium catalyst, to prevent the composition from sufficiently curing to form a gel within 20 minutes when heated at 65°C . For example, the composition may be free of a Lewis base selected from a group consisting of the following bases: PR^{10}_3 , $\text{P}(\text{NR}^{10}_2)_3$, NR^{10}_3 , $\text{N}(\text{SiR}^{10}_3)_x\text{R}^{10}_{3-x}$, $\text{R}^{10}\text{C}(\text{NR}^{10})\text{N}$, $\text{P}(\text{N}=\text{R}^{10})\text{R}^{10}_3$, guanidines ($\text{C}(\text{NR}^{10})_3$), amidines ($\text{R}^{10}\text{C}(\text{NR}^{10})\text{NR}^{10}_2$), phosphazenes,



where R^{10} is in each occurrence independently selected from a group consisting of hydrogen, alkyl, substituted alkyl, aryl and substituted aryl.

Method

[0055] The composition described above may be a one part composition. The one part composition contains starting materials (A) and (B) in the same part. The composition may be prepared in a method, which comprises step: i) combining starting materials comprising (A) the phosphonium catalyst, (B) the polyorganohydrogensiloxane, and when present (C) the polyorganosiloxane, (D) the solvent, and/or the optional additional component, described above, thereby forming a mixture. Starting material (D) the solvent may be used to facilitate combining starting materials (A) and (B), and when present (C). For example, one or more of starting materials (A) and (B), and when present (C), may be dissolved in the solvent before being mixed with the other starting materials. Alternatively, the starting materials may consist essentially of starting materials (A) and (B) (and optionally (C) and/or (D)), described above. Alternatively, the starting materials may consist of starting materials (A) and (B) (and optionally (C) and/or (D)), described above.

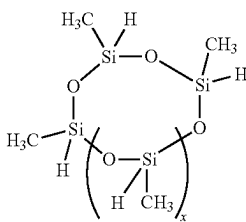
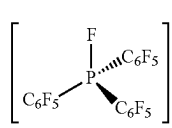

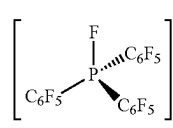

[0056] Combining the starting materials to form the mixture and prepare the polyorganohydrogensiloxane composition is performed under conditions that will not cure (e.g., not significantly react the Si—H moieties from (B) the polyorganohydrogensiloxane and the Si—O—Si moieties (from (B) the polyorganohydrogensiloxane and/or (C) the polyorganosiloxane). These conditions may comprise mixing, e.g., by any convenient means. Mixing may be performed using conventional mixing equipment, such as an agitated batch kettle. Alternatively, when the polyorganosiloxane selected for starting material (C) and/or the polyorganohydrogensiloxane selected for starting material (B) is viscous or solid (e.g., gum or resin), mixing under shear may be performed, e.g., with an extruder. The composition may be formed, e.g., by mixing starting materials comprising (A) and (B) described above. Starting materials (A) and (B) may be combined at RT or less. Alternatively, the temperature for combining starting materials (A) and (B) (and (C) and/or (D), when present) may be 5°C to 30°C . Starting materials (A) and (B), (and (C) and/or (D), when present) may be combined concurrently. Alternatively, starting materials (A) and (B) (and (D), when present) may be combined to form a mixture, and thereafter the mixture may be combined with starting material (C) (and additional (D), when present), e.g., by adding starting material (C) (or a solvent solution thereof) to said mixture, e.g., by metering over a period of time or by adding in one or more aliquots.

Curing the Composition

[0057] A method for curing the composition comprises:

as limiting the scope of the invention set forth in the claims. Starting materials used in these examples are shown in Table 1.

TABLE 1

Starting Materials			
Ingredient Type	Product Name	Chemical Description, Chemical formula, or Structure	Source
Reagent 1	D^H_x	Cyclic polymethylhydrogensiloxane with density 0.98 g/ml, and formula  where subscript x is 1 to 3	The Dow Chemical Company
Catalyst 1	$[P(C_6F_5)_3F]^+[B(C_6F_5)_4]^-$	 	Prepared at The Dow Chemical Company according to Science 2013, 341, 1374-1377.
Catalyst 2	$[P(C_6F_5)_3F]^+F^-$	 	Prepared at The Dow Chemical Company according to Science 2013, 341, 1374-1377.
FAB (comparative catalyst)	$(C_6F_5)_3B$	tris(pentafluorophenyl)borane	Sigma-Aldrich
Solvent	Dichloromethane	CH_2Cl_2	Sigma-Aldrich
Et_3N	Triethylamine	$N(CH_2CH_3)_3$	Sigma-Aldrich

[0058] 1) providing the composition, as described above, and

[0059] 2) heating the composition to a temperature sufficient to catalyze reaction of silicon bonded hydrogen atoms in (B) the polyorganohydrogensiloxane. For example, the temperature in step 2) may be $\geq 65^\circ C$. Alternatively, the temperature may be $> 30^\circ C$., but the time for reaction may be longer at lower temperatures than at higher temperatures. The method for curing the composition may optionally further comprise an additional step. For example, the method may further comprise an additional step after step 1) and before step 2), wherein the additional step comprises placing the composition in a mold or applying the composition on a substrate.

EXAMPLES

[0060] These examples are provided to illustrate the invention to one skilled in the art and are not to be construed

Reference Example 1—General Conditions

[0061] The reactions were carried out in an N_2 -filled glovebox using solvents that were dried over 4 Å molecular sieves. Except as specified in Table 1, all starting materials were obtained from commercial sources and used as received.

[0062] Catalyst Stock Solutions were prepared as follows:

[0063] $[(C_6F_5)_3PF][B(C_6F_5)_4]$ stock solution A: $[(C_6F_5)_3PF][B(C_6F_5)_4]$ (2.2 mg) was dissolved in CH_2Cl_2 (5 mL) to afford $[(C_6F_5)_3PF][B(C_6F_5)_4]$ stock solution A (0.44 mg/mL).

[0064] $[(C_6F_5)_3PF][F]$ stock solution A': $IP(C_6F_5)_3F^+F^-$ (6.6 mg) was dissolved in CH_2Cl_2 (15 mL) to afford $[P(C_6F_5)_3F^+]F^-$ stock solution A' (0.44 mg/mL).

[0065] $[(C_6F_5)_3PF][B(C_6F_5)_4]+NEt_3$ stock solution A: Et_3N was added in a 1:1 molar ratio with Catalyst 1. The Et_3N stock solution (49.9 μL Et_3N in 1 mL CH_2Cl_2) was added first to the reaction mixture, followed by the catalyst stock solution A (0.44 mg/mL).

[0066] FAB stock solution A: FAB (2.6 mg) was dissolved in CH_2Cl_2 (5.8 mL) to afford FAB stock solution A (0.44 mg/mL).

Reference Example 2—Working Examples
Reaction Setup & Progress Using Catalyst 1 at r.t

[0067] $\text{D}^{\text{H}}_{\text{x}}$ (1 mL, 0.98 g) was added to a 30 mL vial containing a magnetic stir bar. To this vial was added 0.2 mL of $[(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$ stock solution A (0.088 mg of $[(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$). The solution was stirred at room temperature. The reaction was monitored at different time intervals to see if a gel had formed. Gel formation was indicative of crosslinking (curing). No effort was made to remove the cured material from the vial. The results are shown below in Table 2.

Reference Example 3—Comparative Example
Reaction Setup & Progress

[0068] Reference Example 2 was repeated, except 0.2 mL of FAB stock solution A (0.088 mg of FAB) was used. The results are shown below in Table 2.

Reference Example 4—Comparative Example
Reaction Setup & Progress

[0069] Reference Example 2 was repeated, except 0.2 mL of $[(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$ stock solution A (0.088 mg of $[(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$ +0.2 mL of NEt_3 stock solution (1:1 molar ratio with Catalyst 1)) was used. The results are shown below in Table 2.

Reference Example 6—Working Examples
Reaction Setup & Progress Using Catalyst 1 at 65° C.

[0071] $\text{D}^{\text{H}}_{\text{x}}$ (1 mL, 0.98 g) was added to a 30 mL vial containing a magnetic stir bar. To this vial was added 0.5 mL of $[(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$ stock solution A (0.22 mg of $[(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$). The reaction was monitored at different time intervals to see if a gel had formed. The solution was held at room temperature. And thereafter, the solution was stirred at 65° C. via a pre-heated aluminum block. Gel formation was indicative of crosslinking (curing). No effort was made to remove the cured material from the vial. The results are shown below in Table 2.

Reference Example 7—Comparative Example
Reaction Setup & Progress

[0072] Reference Example 6 was repeated, except 0.5 mL of $[(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$ stock solution A (0.22 mg of $[(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$ +0.5 mL of NEt_3 stock solution (1:1 molar ratio with catalyst 1)) was used. The results are shown below in Table 2.

Reference Example 8—Comparative Example
Reaction Setup & Progress

[0073] Reference Example 6 was repeated, except 0.5 mL of $[(\text{C}_6\text{F}_5)_3\text{PF}][\text{F}]$ stock solution A (0.22 mg of $[(\text{C}_6\text{F}_5)_3\text{PF}][\text{F}]$) was used. The results are shown below in Table 2.

TABLE 2

Curing of $\text{D}^{\text{H}}_{\text{x}}$ using FAB (comparative) vs. catalyst 1 (inventive) and catalyst 2 (comparative).					
Example	Stock solution conc.	Amount of stock added	$\text{D}^{\text{H}}_{\text{x}}$ (mL)	CAT loading vs. $\text{D}^{\text{H}}_{\text{x}}$ (ppm)	Observations
Ref. Ex. 2 (Inventive) Catalyst 1	0.44 mg/mL (CH_2Cl_2)	0.2 mL (0.088 mg of 1)	1	90	No gel after 24 h at r.t. Gel at r.t. after >24 h ¹
Ref. Ex. 3 (Comparative) FAB	0.44 mg/mL (CH_2Cl_2)	0.2 mL (0.088 mg of FAB)	1	90	Gel at r.t. after 20 min
Ref. Ex. 4 (Comparative) Catalyst 1 + Et_3N	0.44 mg/mL (CH_2Cl_2)	0.2 mL (0.088 mg of 1)	1	90	No gel at r.t. >24 h
Ref. Ex. 5 (Comparative) Catalyst 2	0.44 mg/mL (CH_2Cl_2)	0.2 mL (0.088 mg of 2)	1	90	No gel at r.t. >24 h
Ref. Ex. 6 (Inventive) Catalyst 1	0.44 mg/mL (CH_2Cl_2)	0.5 mL (0.22 mg of 1)	1	224	No gel at r.t. after 1 h Gel at 65° C. after 20 min
Ref. Ex. 7 (Comparative) Catalyst 1 + Et_3N	0.44 mg/mL (CH_2Cl_2)	0.5 mL (0.22 mg of 1)	1	224	No gel at r.t. 1 h and no gel at 65° C. 20 min
Ref. Ex. 8 (Comparative) Catalyst 2	0.44 mg/mL (CH_2Cl_2)	0.5 mL (0.22 mg of 2)	1	224	No gel at r.t. 1 h and no gel at 65° C. 20 min

¹There was no gel after 24 h at r.t. Subsequently, the solution sat over a 4 day holiday weekend when no one was present, and a gel was observed to have formed when observations resumed.

Reference Example 5—Comparative Example
Reaction Setup & Progress

[0070] Reference Example 2 was repeated, except 0.2 mL of $[(\text{C}_6\text{F}_5)_3\text{PF}][\text{F}]$ stock solution A (0.088 mg of $[(\text{C}_6\text{F}_5)_3\text{PF}][\text{F}]$) was used. The results are shown below in Table 2.

[0074] The data in Table 2 for Reference Examples 2 and 6 show that the phosphonium catalyst comprising a tetravalent monocation of phosphorus and a non-coordinating anion can be used to prepare a one part composition that is stable (not gelling) for at least 1 day at r.t., but that cures in

20 minutes at elevated temperature of 65° C. Reference Examples 4 and 7 showed that the presence of a Lewis base (triethyl amine) prevented curing under the conditions tested. Reference Examples 5 and 8 show that catalyst 2, which included a strongly coordinating anion, did not cure the composition when tested at 65° C. Reference Example 3 shows the rapid cure at room temperature when FAB was used instead of the catalyst described herein.

INDUSTRIAL APPLICABILITY

[0075] The composition described above is shelf stable, which means that the composition does not gel at RT in 1 hour or less, alternatively 5 hours or less, alternatively 24 hours or less, alternatively 48 hours or less, and alternatively 36 hours or less. The composition and method described herein are useful for preparing and curing silicone compositions that cure to form products such as coatings, adhesives, elastomers, and foams. The inventors surprisingly found that the catalyst described herein will cure the polyorganosiloxane composition. Furthermore, the inventors surprisingly found that there is no need for a Lewis base and/or a bridging molecule to stabilize the catalyst described herein. In contrast, the presence of a Lewis base such as triethylamine, can render the present composition incurable under the conditions tested in the examples above. The composition and method of this invention provide a polyorganohydrogensiloxane composition that is shelf stable at RT and that is curable with heating to mild temperatures.

Definitions and Usage of Terms

[0076] Abbreviations used in the specification have the definitions in Table 3, below.

TABLE 3

Abbreviations	
Abbreviation	Definition
ASTM	ASTM International
° C.	degrees Celsius
g	grams
GPC	gel permeation chromatography
h	hours
Me	methyl
mg	milligrams
min	minutes
mL	milliliters
mmol	millimoles
Ph	phenyl
ppm	parts per million
RT or r.t.	room temperature of 23° C. ± 2° C.
s	seconds
wt	weight

[0077] All amounts, ratios, and percentages are by weight unless otherwise indicated. The amounts of all starting materials in a composition total 100% by weight. The SUMMARY and ABSTRACT are hereby incorporated by reference. The articles ‘a’, ‘an’, and ‘the’ each refer to one or more, unless otherwise indicated by the context of specification. The singular includes the plural unless otherwise indicated.

[0078] The term “comprising” and derivatives thereof, such as “comprise” and “comprises” are used herein in their broadest sense to mean and encompass the notions of “including,” “include,” “consist(ing) essentially of,” and

“consist(ing) of.” The use of “for example,” “e.g.,” “such as,” and “including” to list illustrative examples does not limit to only the listed examples. Thus, “for example” or “such as” means “for example, but not limited to” or “such as, but not limited to” and encompasses other similar or equivalent examples.

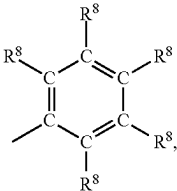
[0079] Generally, as used herein a hyphen “-” or dash “-” in a range of values is “to” or “through”; a “>” is “above” or “greater-than”; a “≥” is “at least” or “greater-than or equal to”; a “<” is “below” or “less-than”; and a “≤” is “at most” or “less-than or equal to.”

Embodiments of the Invention

[0080] In a first embodiment, a composition comprises a mixture of:

[0081] 1 ppm to 1,000 ppm by weight, based on combined weights of starting materials (A) and (B) of (A) a phosphonium catalyst comprising

[0082] (i) a tetravalent monocation of phosphorus of formula [PR¹₃R²]⁺, where each R¹ is an independently selected halogenated aryl group of formula



where each R⁸ is selected from Cl, F, or —CF₃, and each R² is independently selected from Br, Cl, F, and —CF₃, and

[0083] (ii) a non-coordinating anion of formula [BR³₄]⁻, where each R³ is independently selected from the group consisting of a monovalent hydrocarbon group and a monovalent halogenated hydrocarbon group;

[0084] 1 weight % to <100 weight % based on combined weights of starting materials (A), (B), and (C), of (B) a polydiorganohydrogensiloxane selected from the group consisting of

[0085] a linear polydiorganohydrogensiloxane comprising unit formula (B-1): (HR⁴₂SiO_{1/2})_g(R⁴₃SiO_{1/2})_i(R⁴₂SiO_{2/2})_h(HR⁴SiO_{2/2})_j, where each R⁴ is an independently selected monovalent hydrocarbon group, which is free of aliphatic unsaturation, and subscripts g, h, i, and j have values such that g≥0, h≥0, a quantity (g+h)=2, i≥0, j≥0, and a quantity (g+j)≥1, and a quantity (i+j) is 0 to 2,000;

[0086] a cyclic polydiorganohydrogensiloxane comprising unit formula (B-2): (R⁴₂SiO_{2/2})_u(R⁴HSiO_{2/2})_v, where R⁴ is as described above, subscript u is 0 or more, subscript v is 1 or more, a quantity (u+v) is 3 to 15; and

(B-3) a combination of both (B-1) and (B-2).

[0087] In a second embodiment, in the composition of the first embodiment, (A) the phosphonium catalyst has formula [(C₆F₅)₃PF]⁺[B(C₆F₅)₄]⁻.

[0088] In a third embodiment, in the composition of the first embodiment or the second embodiment, (B) the polyorganohydrogensiloxane is selected from the group consisting of:

[0089] (i) α,ω -dimethylhydrogensiloxy-terminated poly(dimethylsiloxane/methylhydrogensiloxane),

[0090] (ii) α,ω -dimethylhydrogensiloxy-terminated polymethylhydrogensiloxane,

[0091] (iii) α,ω -trimethylsiloxy-terminated poly(dimethylsiloxane/methylhydrogensiloxane),

[0092] (iv) α,ω -trimethylsiloxy-terminated polymethylhydrogensiloxane, and

[0093] (v) α -dimethylhydrogensiloxy- ω -trimethylsiloxy-terminated poly(dimethylsiloxane/methylhydrogensiloxane),

[0094] (vi) α -dimethylhydrogensiloxy- ω -trimethylsiloxy-terminated polymethylhydrogensiloxane,

[0095] (vii) a combination of two or more thereof.

[0096] In a fourth embodiment, in the composition of any one of the first to third embodiments, (C) the polyorganosiloxane is selected from the group consisting of: α,ω -trimethylsiloxy-terminated polydimethylsiloxane, α,ω -dimethylphenylsiloxy-terminated poly(dimethylsiloxane/methylphenylsiloxane), α,ω -dimethylphenylsiloxy-terminated polymethylphenylsiloxane, α,ω -trimethylsiloxy-terminated poly(dimethylsiloxane/methylphenylsiloxane), α,ω -trimethylsiloxy-terminated polymethylphenylsiloxane, hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, and a combination of two or more thereof.

[0097] In a fifth embodiment, in the composition of any one of the first to fourth embodiments, the composition further comprises 1 weight % to 99 weight %, based on total weight of the composition, of (D) a solvent.

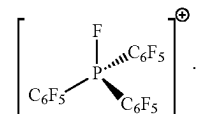
[0098] In a sixth embodiment, the composition of any one of the first to fifth embodiments is used for preparing a product selected from the group consisting of a coating, an adhesive, an elastomer, and a foam.

[0099] In a seventh embodiment, where the composition of any one of the first to fifth embodiments is a cure system, and a method comprises i) adding the composition to a polyorganosiloxane formulation and ii) curing the polyorganosiloxane formulation to form a product selected from the group consisting of a coating, an adhesive, an elastomer, and a foam.

1. A composition comprising a mixture of (A) a phosphonium catalyst comprising (i) a tetravalent monocation of phosphorus and (ii) a non-coordinating anion of formula $[\text{BR}^3_4]^+$ where each R^3 is independently selected from the group consisting of a monovalent hydrocarbon group and a monovalent halogenated hydrocarbon group; and (B) a polyorganohydrogensiloxane; wherein the composition is free of Lewis base.

2. The composition of claim 1, where (i) the tetravalent monocation of phosphorus is a Lewis acidic phosphorus cation of formula $[\text{PR}^1_3\text{R}^2]^+$, where each R^2 is independently selected from the group consisting of X^1 , $-\text{CX}'_3$, and $-\text{OR}^9$, where each X^1 is independently selected from the group consisting of Br, Cl, and F, and R^9 is an alkyl group or an aryl group; and each R^1 is an independently selected halogenated aryl group.

3. The composition of claim 2, where (i) the tetravalent monocation of phosphorus has formula

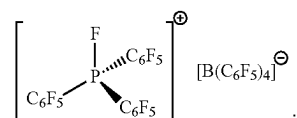


4. The composition of any one of claim 1 to 3, where (ii) the non-coordinating anion has formula $[\text{BR}^3_4]^-$ where each R^3 a halogenated aryl group.

8.-15. (canceled)

16. The composition of claim 4, wherein (ii) the anion has formula $\text{B}(\text{C}_6\text{F}_5)_4^-$.

17. The composition of claim 1, wherein (A) the phosphonium catalyst has formula:



18. The composition of claim 1, where (B) the polyorganohydrogensiloxane comprises two or more siloxane units selected from the group consisting of $\text{HR}^4_2\text{SiO}_{1/2}$, $\text{R}^4_3\text{SiO}_{1/2}$, $\text{HR}^4\text{SiO}_{2/2}$, $\text{R}^4_2\text{SiO}_{2/2}$, $\text{R}^4\text{SiO}_{3/2}$, $\text{HSiO}_{3/2}$ and $\text{SiO}_{4/2}$ units; wherein each R^4 is an independently selected monovalent hydrocarbon group, which is free of aliphatic unsaturation.

19. The composition of claim 18, where (B) the polyorganohydrogensiloxane is selected from the group consisting of:

(B-1) a linear polydiorganohydrogensiloxane comprising unit formula $(\text{HR}^4_2\text{SiO}_{1/2})_g(\text{R}^4_3\text{SiO}_{1/2})_h(\text{R}^4_2\text{SiO}_{2/2})_i(\text{HR}^4\text{SiO}_{2/2})_j$, where R^4 is as described above, and subscripts g, h, i, and j have values such that $g \geq 0$, $h \geq 0$, a quantity $(g+h)=2$, $i \geq 0$, $j \geq 0$, and a quantity $(g+j) \geq 1$, and a quantity $(i+j)$ is 0 to 1,000;

(B-2) a cyclic polydiorganohydrogensiloxane comprising unit formula $(\text{R}^4_2\text{SiO}_{2/2})_u(\text{R}^4\text{HSiO}_{2/2})_v$, where subscript u is 0 or more, subscript v is 1 or more, a quantity $(u+v)$ is 3 to 15, and each R is an independently selected monovalent hydrocarbon group; and

(B-3) a combination of both (B-1) and (B-2).

20. The composition of claim 1, further comprising (C) a polyorganosiloxane, wherein (C) the polyorganosiloxane comprises two or more siloxane units selected from $\text{R}^4_3\text{SiO}_{1/2}$, $\text{R}^4_2\text{SiO}_{2/2}$, $\text{R}^4\text{SiO}_{3/2}$, and $\text{SiO}_{4/2}$ units; wherein each R^4 is an independently selected monovalent hydrocarbon group, which is free of aliphatic unsaturation.

21. The composition of claim 20, where (C) the polyorganosiloxane is selected from the group consisting of

(C-1) a linear polydiorganosiloxane comprising unit formula: $(\text{R}^4_3\text{SiO}_{1/2})_2(\text{R}^4_2\text{SiO}_{2/2})_x$, where R^4 is as described above, and $1,000 \geq x \geq 1$;

(C-2) a cyclic polydiorganosiloxane comprising unit formula: $(\text{R}^4_2\text{SiO}_{2/2})_y$, where R^4 is as described above, and $15 \geq y \geq 3$; and

(C-3) a combination of both (C-1) and (C-2).

22. The composition of claim **1**, where an amount of (A) the phosphonium catalyst is 1 ppm to 1,000 ppm, based on weight of (B) the polyorganohydrogensiloxane, and when present, (C) the polyorganosiloxane.

23. The composition of claim **1**, further comprising (D) a solvent.

24. The composition of claim **1**, further comprising one or a combination of more than one component selected from a group consisting of pigments, fillers, moisture scavengers, fluorescent brighteners, stabilizers, and corrosion inhibitors.

25. The composition of claim **1**, where the composition is free of transition metals.

26. A method comprising the steps of:

- 1) providing a composition according to claim **1**, and
 - 2) heating the composition to a temperature sufficient to catalyze reaction of silicon bonded hydrogen atoms in (B) the polyorganohydrogensiloxane; and
- optionally placing the composition in a mold or applying the composition on a substrate after step 1) and before step 2).

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