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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
30 January 2014 (30.01.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/018814 A1

(51) International Patent Classification:
C09J 183/04 (2006.01) *C08K 9/10* (2006.01)
B01J 37/02 (2006.01)

(21) International Application Number:
PCT/US2013/052155

(22) International Filing Date:
26 July 2013 (26.07.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/676,445 27 July 2012 (27.07.2012) US

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

(72) Inventors: **GOKHALE, Abhijit**; 9663 Waterford Place, Apartment 103, Loveland, OH 45140 (US). **LOXLEY, Andrew**; 36 Water Street #310, Vancouver, BC V6B 1A4 (CA). **RHODES, Susan**; 3793 Old Pine Trail, Midland, MI 48642 (US).

(74) Agent: **PURCHASE, Claude, F.**; Dow Corning Corporation, Patent Department - Mail CO1232, 2200 West Salzburg Road, Midland, MI 48686-0994 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

WO 2014/018814 A1

(54) Title: SELF-ADHERING CURABLE SILICONE ADHESIVE COMPOSITIONS AND PROCESS FOR MAKING THEREOF

(57) Abstract: A self-adhering curable silicone adhesive composition comprising: (A) an alkenyl substituted organopolysiloxane containing on average at least 0.1 alkenyl groups per molecule; (B) an organohydrogenpolysiloxane containing on average at least 2 silicon-bonded hydrogen atoms per molecule in an amount that the molar ratio of the total number of the silicon-bonded hydrogen atoms of component (B) to the total quantity of all alkenyl radicals of component (A) is less than 1.3:1; (C) a hydrosilylation catalyst; (D) an adhesion promoter; and (E) an adhesion catalyst in the form of microscopic particles comprising: (a) a thermally activated semi-crystalline polymer, and (b) at least one organometallic condensation catalyst having a metal M wherein the organometallic condensation catalyst is either admixed or encapsulated with the thermally activated semi-crystalline polymer. A process for making the adhesion catalyst (E).

SELF-ADHERING CURABLE SILICONE ADHESIVE COMPOSITIONS AND PROCESS FOR MAKING THEREOF

[0001] Disclosed herein are self-adhering curable silicone adhesive compositions and a process for making self-adhering curable silicone adhesive compositions, and products formed by curing the self-adhering curable silicone compositions. More particularly, this invention relates to hydrosilylation-curable compositions that provide low temperature adhesion, while maintaining good shelf-stability.

[0002] One-part heat curing, hydrosilylation-curable silicone adhesive compositions have the general problem that adhesion develops at temperatures much higher than their curing temperatures. This effect can cause problems in fabricating joint designs with integrity, as manufacturers are unable to determine adhesion properties until after parts have been fabricated. Thus, it is desirable to provide compositions that cure and provide adhesion at similar temperatures. This invention provides compositions that cure and provide adhesion at similar temperatures.

[00033] In recent years, organometallic compounds (e.g. metal chelates) have been used to reduce the temperature required to obtain adhesion (as well as provide improved adhesion to many engineering plastics. However, antagonistic interactions between the organometallic compounds and silicon hydride groups in organohydrogenpolysiloxanes affect their curability, limit their shelf-stability and cause reduced thermal stability. The compositions of this invention are free of antagonistic interactions between the organometallic compounds and silicon hydride groups of the organohydrogenpolysiloxanes.

[00044] Thus, there is a need for a simple approach for introducing organometallic compounds into hydrosilylation-curable adhesive compositions. The approach within this invention provides long term curability, shelf-stability, and thermal stability.

BRIEF SUMMARY OF THE INVENTION

[00055] The present invention relates to a self-adhering curable silicone adhesive composition comprising:

(A) an alkenyl substituted organopolysiloxane containing on average at least 0.1 silicon-bonded alkenyl groups per molecule;

(B) an organohydrogenpolysiloxane containing on average at least 1.5 silicon-bonded hydrogen atoms per molecule in an amount that the molar ratio of the total number of the silicon-bonded hydrogen atoms of component (B) to the total quantity of all alkenyl radicals of component (A) is less than 1.3:1;

(C) a hydrosilylation catalyst;

(D) an adhesion promoter; and

(E) an adhesion catalyst in the form of microscopic particles comprising:

(a) a thermally activated semi-crystalline polymer, and

(b) at least one organometallic condensation catalyst having a metal M wherein the organometallic condensation catalyst is either admixed or encapsulated with the thermally activated semi-crystalline polymer. The composition may be called “Aspect 1” herein.

[00066] The present invention also relates to a process for making the adhesion catalyst (E), the process comprising forming the adhesion catalyst by a single layer process or a double layer process.

DETAILED DESCRIPTION OF THE INVENTION

[00077] All amounts, ratios, and percentages are by weight unless otherwise indicated. The following is a list of definitions as used in this application.

[00088] The terms "a" and "an" each mean one or more.

[000909] The term "crystalline" refers to a polymer that possesses a first order phase transition characteristic of a crystalline melting point (T_m) as determined by differential scanning calorimetry (DSC) or equivalent technique.

[00100] The term "amorphous" refers to a polymer that possesses a first order phase transition characteristic of a glass transition (T_g) and lacks a crystalline melting point as determined by differential scanning calorimetry (DSC) or equivalent technique.

[00111] The term "semi-crystalline" refers to a polymer that possesses both crystalline and amorphous properties, as defined above.

[00122] The term "release temperature" refers to the temperature at which microcapsules melt and the encapsulate adhesion catalyst can diffuse into the composition.

[00133] The term "thermally activated semi-crystalline polymer" refers to a polymeric composition that contains microscopic particles that are thermally triggered to release the active component inside.

[00144] The abbreviation "M" means a siloxane unit of formula $R_3SiO_{1/2}$, where each R independently represents a monovalent atom or group.

[00155] The abbreviation "D" means a siloxane unit of formula $R_2SiO_{2/2}$, where each R independently represents a monovalent atom or group.

[00166] The abbreviation "T" means a siloxane unit of formula $RSiO_{3/2}$, where R represents a monovalent atom or group.

[00177] The abbreviation "Q" means a siloxane unit of formula $SiO_{4/2}$.

[00188] The abbreviation "Me" represents a methyl group.

[001919] The abbreviation "Vi" represents a vinyl group.

[00200] Component (A), the alkenyl substituted organopolysiloxane, is a polydiorganosiloxane having an average per molecule of at least two aliphatically unsaturated organic groups and at least one aromatic group. Component (A) can be a single polydiorganosiloxane or a combination comprising two or more polydiorganosiloxanes that differ in at least one of the following properties: structure, viscosity, average molecular weight, siloxane units, and sequence. The viscosity of component (A) is not critical; however, viscosity may range from 10 to 1,000,000 mPa·s at 25 ºC, alternatively 100 to 50,000 mPa·s, to improve handling properties of the cured silicone resin prepared from the silicone composition. The amount of component (A) in the composition may range from 10 to 40, alternatively 15 to 30, parts by weight based on the total weight of the composition.

[00211] The aliphatically unsaturated organic groups in component (A) may be alkenyl exemplified by, but not limited to, vinyl, allyl, butenyl, pentenyl, and hexenyl, alternatively vinyl. The aliphatically unsaturated organic groups may be alkynyl groups exemplified by, but not limited to, ethynyl, propynyl, and butynyl. The aliphatically unsaturated organic groups in component (A) may be located at terminal, pendant, or both terminal and pendant positions. The aromatic group or groups in component (A) may be located at terminal, pendant, or both terminal and pendant positions. The aromatic group is exemplified by, but not limited to, ethylbenzyl, naphthyl, phenyl, tolyl, xylyl, benzyl, styryl, 1-phenylethyl, and 2-phenylethyl, alternatively phenyl. Component (A) contains an average of at least one aromatic group per molecule. However, component (A) may contain more than 40 mol%, alternatively more than 45 mol% aromatic groups.

[00222] The remaining silicon-bonded organic groups in component (A), if any, may be monovalent substituted and unsubstituted hydrocarbon groups free of aromatics and free aliphatic unsaturation. Monovalent unsubstituted hydrocarbon groups are exemplified by, but not limited to alkyl groups such as methyl, ethyl, propyl, pentyl, octyl, undecyl, and octadecyl and cycloalkyl groups such as cyclohexyl. Monovalent substituted hydrocarbon groups are exemplified by, but not limited to halogenated alkyl groups such as chloromethyl, 3-chloropropyl, and 3,3,3-trifluoropropyl, 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.

[00233] Component (A) may have general formula (I): $R^1{}_3SiO\text{-}(R^2{}_2SiO)_a\text{-}SiR^1{}_3$, where each R^1 and each R^2 are independently selected from the group consisting of aliphatically unsaturated organic groups, aromatic groups, and monovalent substituted and unsubstituted hydrocarbon groups described above, and subscript a is an integer having a value sufficient to provide component (A) with a viscosity ranging from 10 to 1,000,000 mPa·s at 25 ºC, with

the proviso that on average at least two of R^1 and/or R^2 are unsaturated organic groups and at least one of R^1 and/or R^2 is an aromatic group. Alternatively, at least two of R^1 are unsaturated organic groups, at least one of R^2 is an aromatic group, and subscript a has a value ranging from 5 to 1,000. Alternatively, formula (I) is an α,ω-dialkenyl-functional polydiorganosiloxane.

[00244] Component (B), the organohydrogenpolysiloxane, is an organohydrogenpolysiloxane having an average of at least 2 silicon-bonded hydrogen atoms per molecule. Component (B) can be a homopolymer, copolymer, or polymer blend. Component (B) can have a linear, branched, cyclic, or resinous structure. The silicon-bonded hydrogen atoms in the component (B) can be located
at terminal, pendant, or at both terminal and pendant positions.

[00255] Component (B) can comprise siloxane units including, but not limited to, $HR^6_2SiO_{1/2}$, $R^6_3SiO_{1/2}$, $HR^6SiO_{2/2}$, $R^6_2SiO_{2/2}$, $R^6SiO_{3/2}$, and $SiO_{4/2}$ units. In the preceding formulae, each R^6 is independently selected from hydrocarbyl groups free of aliphatic unsaturation.

[00266] Component (B) may comprise a compound of the formula

$$R^7_3SiO(R^7_2SiO)_e(R^7HSiO)_fSiR^7_3,$$

$$R^8_2HSiO(R^8_2SiO)_g(R^8HSiO)_hSiR^8_2H, \text{ or}$$

combinations thereof.

[00277] Subscript e has an average value of 0 to 2000, and subscript f has an average value of 2 to 2000. Each R^7 is independently a hydrocarbyl group free of aliphatic unsaturation. Suitable hydrocarbyl groups free of aliphatic unsaturation include alkyl groups such as methyl, ethyl, propyl, and butyl; aromatic groups such as phenyl, tolyl, and xylyl.

[00288] Subscript g has an average value of 0 to 2000, and subscript h has an average value of 0 to 2000. Each R^8 is independently a hydrocarbyl group free of aliphatic unsaturation. Suitable hydrocarbyl groups free of aliphatic unsaturation include alkyl groups such as methyl, ethyl, propyl, and butyl; aromatic groups such as phenyl, tolyl, and xylyl.

[002929] Component (B) is exemplified by

i) dimethylhydrogensiloxy-terminated polydimethylsiloxane,

ii) dimethylhydrogensiloxy-terminated poly(dimethylsiloxane/methylhydrogensiloxane),

iii) dimethylhydrogensiloxy-terminated polymethylhydrogensiloxane,

iv) trimethylsiloxy-terminated poly(dimethylsiloxane/methylhydrogensiloxane),

v) trimethylsiloxy-terminated polymethylhydrogensiloxane,

vi) a resin consisting essentially of $H(CH_3)_2SiO_{1/2}$ units and $SiO_{4/2}$ units, and

vii) combinations thereof.

[00300] Component (B) can be a combination of two or more organohydrogenpolysiloxanes that differ in at least one of the following properties: structure, average molecular weight, viscosity, and siloxane units.

[00311] The molar ratio of silicon-bonded hydrogen atoms in component (B) to aliphatically unsaturated groups in component (A) (SiH_B/Vi_A) is less than 1.3:1, alternatively the ratio may be about 1:1 or less than 1:1. In still other embodiments, the ratio is less than 0.9:1, 0.8:1, 0.7:1, 0.6:1 or 0.5 to 10:1.

[00322] Component (C), the hydrosilylation catalyst, is a hydrosilylation catalyst used for promoting the hydrosilylation reaction between Components (A) and (B). Component (C) is added to the composition in an amount of 0.1 to 1000 ppm of platinum group metal, alternatively 1 to 500 ppm, alternatively 2 to 200, alternatively 5 to 150 ppm, based on the weight of the composition. Suitable hydrosilylation catalysts are known in the art and commercially available. Component (C) may comprise a transition group metal selected from platinum, rhodium, ruthenium, palladium, osmium or iridium metal or organometallic compound thereof, or a combination thereof. Component (C) is exemplified by compounds such as chloroplatinic acid, chloroplatinic acid hexahydrate, platinum dichloride, and complexes of said compounds with low molecular weight organopolysiloxanes, supported platinum compounds, 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. Examples of supported platinum compounds include carbon supported platinum and alumina supported platinum.

[00333] Component (C) is present in the silicone composition in amounts of from 0.01 to 1000 parts per million (ppm), from 0.1 to 1000 ppm, from 0.01 to 500 ppm, from 0.1 to 500 ppm, from 0.5 to 100 ppm, or from 1 to 25 ppm, based on the total weight of (A), (B), and (C).

[00344] Component (D) is an adhesion promoter. Component (D) is added to the composition in an amount of 0.01 to 50 weight parts based on the weight of the composition.

[00355] Component (D) may comprise an alkoxysilane, a combination of an alkoxysilane and a hydroxyl-functional polyorganosiloxane, or a combination thereof. The alkoxysilane can be unsaturated or epoxy-functional. Suitable epoxy-functional compounds are known in the art and commercially available. Component (D) may comprise an unsaturated or epoxy-functional alkoxysilane. For example, the functional alkoxysilane can have the formula $R^9_iSi(OR^{10})_{(4-i)}$, wherein subscript i is 1, 2, or 3, alternatively subscript i is 1.

[00366] Each R^9 is independently a monovalent organic group with the proviso that at least one R^9 is an unsaturated organic group or an epoxy-functional organic group. Epoxy-functional organic groups for R^9 are exemplified by 3-glycidoxypropyl and (epoxycyclohexyl)ethyl. Unsaturated organic groups for R^9 are exemplified by 3-methacryloyloxypropyl, 3-acryloyloxypropyl, and unsaturated monovalent hydrocarbon groups such as vinyl, allyl, hexenyl, undecylenyl.

[00377] Each R^{10} is independently an unsubstituted, saturated hydrocarbon group of at least 1 carbon atom. R^{10} may have up to 4 carbon atoms, alternatively up to 2 carbon atoms. R^{10} is exemplified by methyl, ethyl, propyl, and butyl.

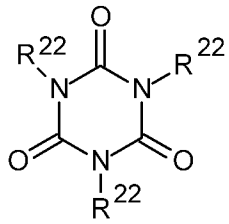
[00388] Examples of suitable epoxy-functional alkoxysilanes include 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropyltriethoxysilane, (epoxycyclohexyl)ethyldimethoxysilane, (epoxycyclohexyl)ethyldiethoxysilane and combinations thereof. Examples of suitable unsaturated alkoxysilanes include vinyltrimethoxysilane, allyltrimethoxysilane, allyltriethoxysilane, hexenyltrimethoxysilane, undecylenyltrimethoxysilane, 3-methacryloyloxypropyl trimethoxysilane, 3-methacryloyloxypropyl triethoxysilane, 3-acryloyloxypropyl trimethoxysilane, 3-acryloyloxypropyl triethoxysilane, and combinations thereof.

[003939] Component (D) may comprise an epoxy-functional siloxane such as a reaction product of a hydroxy-terminated polyorganosiloxane with an epoxy-functional alkoxysilane, as described above, or a physical blend of the hydroxy-terminated polyorganosiloxane with the epoxy-functional alkoxysilane. Component (D) may comprise a combination of an epoxy-functional alkoxysilane and an epoxy-functional siloxane. For example, component (D) 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. When used as a physical blend rather than as a reaction product, these components may be stored separately in multiple-part kits.

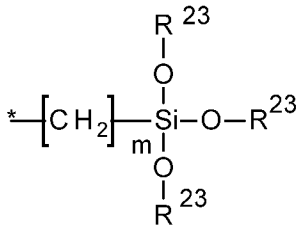
[00400] Suitable adhesive promoters include organosilicon compounds such as organosilanes and organopolysiloxanes having silicon atom-bonded alkoxy groups. Examples of the organosilicon compounds include alkoxysilanes such as: tetramethoxysilane, tetraethoxysilane, dimethyldimethoxysilane, methylphenyldimethoxysilane, methylphenyldiethoxysilane, phenyltrimethoxysilane, methyltrimethoxysilane, methyltriethoxysilane, vinyltrimethoxysilane, allyltrimethoxysilane,

allyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, and 3-methacryloxypropyltrimethoxysilane as well as siloxane compounds of linear chain or cyclic structure (i.e., organosiloxane oligomers) having about 4 to about 30 silicon atoms in one embodiment, or about 4 to about 20 silicon atoms in another embodiment and comprising a molecule at least two, or three functional groups selected from among silicon atom-bonded hydrogen atoms (SiH groups), silicon atom-bonded alkenyl groups (e.g., Si--CH.dbd.CH.sub.2 groups), alkoxysilyl groups (e.g., trialkoxysilyl groups such as trimethoxysilyl), and epoxy groups (e.g., glycidoxypropyl and 3,4-epoxycyclohexylethyl).

[00411] In one embodiment, organoxysilyl-modified isocyanurate compounds having the below general formula and/or hydrolytic condensates thereof (i.e., organosiloxane-modified isocyanurate compounds) are used as the adhesive promoter.



wherein R^{22} is each independently a silicon atom-comprising organic group (or organoxysilylalkyl group) having the formula:

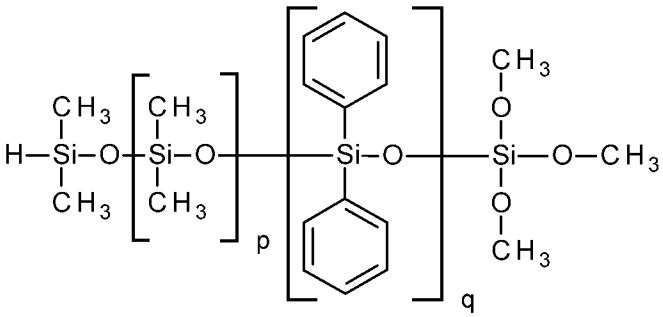


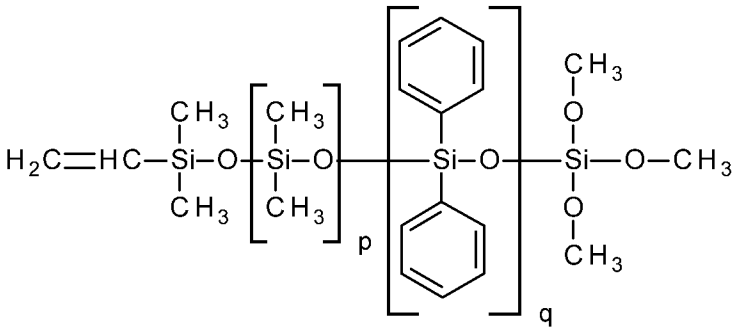
or a monovalent hydrocarbon group comprising an aliphatic unsaturated bond, at least one R^{22} is a silicon atom-organic group of formula (4), R^{23} is each independently hydrogen or a monovalent hydrocarbon group of 1 to 6 carbon atoms, and subscript m is an integer of 1 to 6, alternatively 1 to 4.

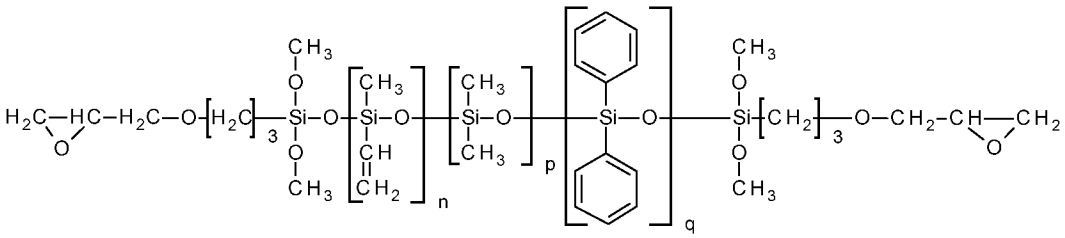
[00422] Examples of the monovalent hydrocarbon group comprising an aliphatic unsaturated bond, represented by R^{22}, include alkenyl groups of 2 to 8 carbon atoms in one embodiment, or 2 to 6 carbon atoms in another embodiment, such as vinyl, allyl, propenyl, isopropenyl, butenyl, isobutenyl, pentenyl, hexenyl, and cyclohexenyl. The monovalent hydrocarbon groups represented by R^{23} include those of 1 to 8 carbon atoms in one embodiment, or 1 to 6 carbon atoms in another embodiment, for example, alkyl groups such

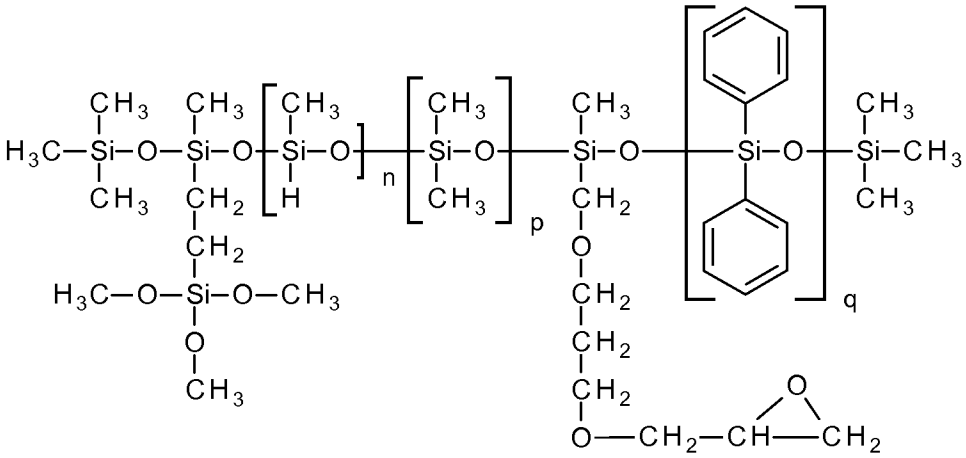
as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, and hexyl, cycloalkyl groups such as cyclohexyl, alkenyl groups such as vinyl, allyl, propenyl and isopropenyl, and aryl groups such as phenyl.

[00433] Illustrative examples of the adhesive promoter are provided below:

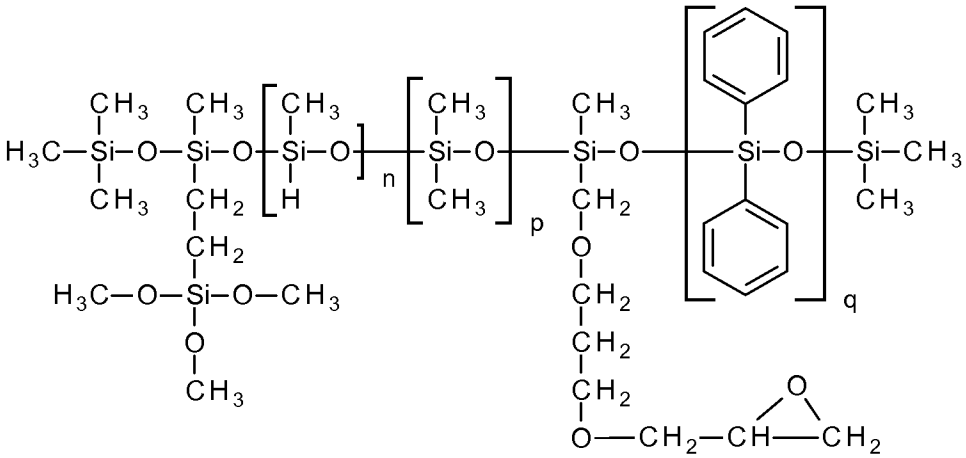


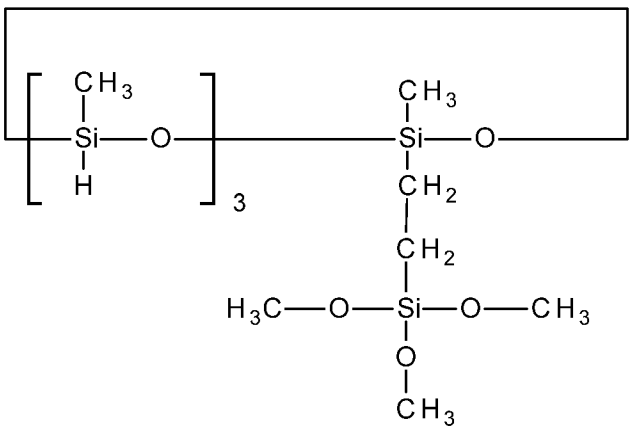


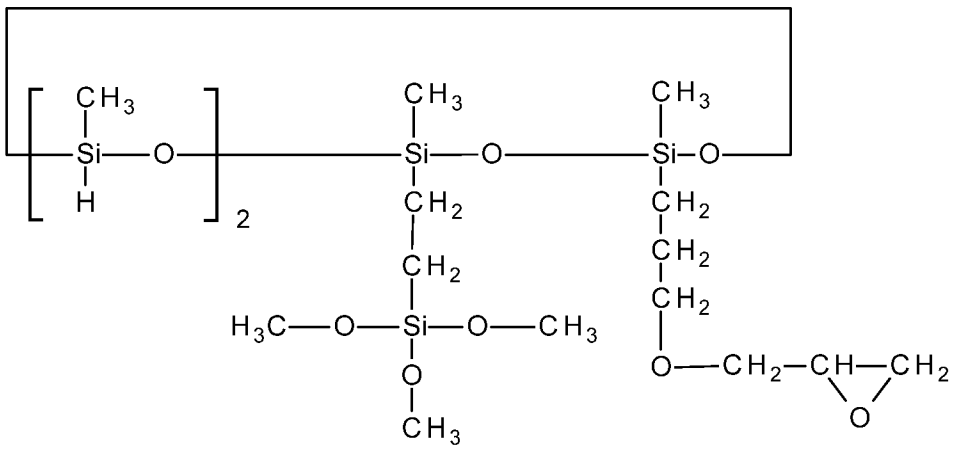


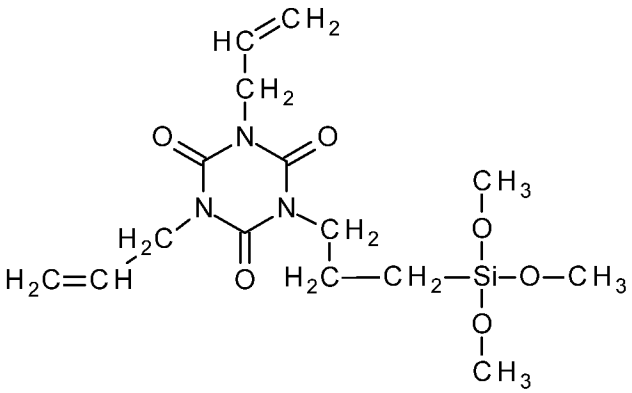


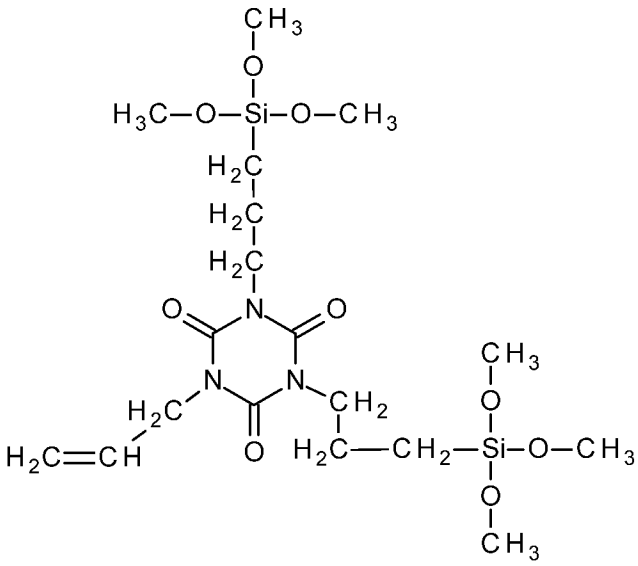
[00444] In the above examples, subscripts n and p are integers of at least 1, subscript q is 0 or greater, in various embodiments satisfying p+q=2 to 50, alternatively p+q=2 to 10, n+p+q=4 to 20, alternatively n+p+q=2 to 50.

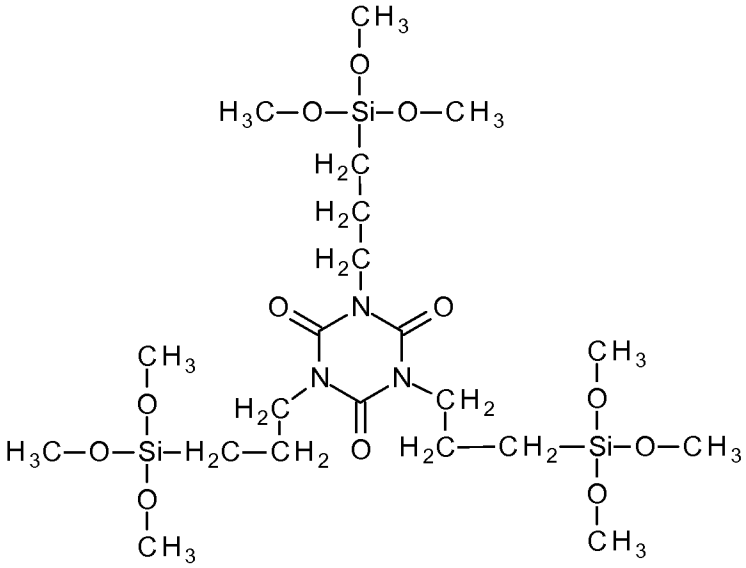












[00455] Of the organosilicon compounds, those organosilicon compounds having silicon atom-bonded alkoxy groups and silicon atom-bonded alkenyl groups or silicon atom-bonded hydrogen atoms (i.e., SiH groups) in a molecule may be preferred because the cured compositions may be more adhesive.

[00466] Component (D) is present in the silicone adhesive composition at from 0.1 to 10 parts by weight (pbw), alternatively at from 0.5 to 7.5 pbw, and alternatively at from 0.75 to 5 pbw per 100 pbw of (A).

[00477] The adhesion catalyst Component (E) exerts a catalytic function in the presence of Component D. That is, the adhesion catalyst may have a catalytic effect on the adhesion promoter.

[00488] In practicing this invention, components (A) and (B) react with each other in the presence of component (C). This reaction product plus the other components of (D) adhesion promoter, optional component (F) filler, and optional component (G) inhibitor need to adhere to a substrate in order for the invention to function as a silicone adhesive composition. The (A) to (E) composition is cured to a substrate, however, its temperature of adhesion is much higher than its cure temperature. Because of this disparity in temperatures, a manufacturer is unable to determine adhesion properties until after the parts have already been fabricated. By the addition of an adhesive catalyst (E), the temperature of adhesion is lowered to that of the cure temperature.

[004949] The adhesion catalyst is in the form of microscopic particles having a mean particle size of from 0.01 to 100 microns, alternatively from 0.01 to 50 microns. The adhesion

catalyst (E) can be formed by a single layer process or a double layer process. Further, the adhesion catalyst (E) has a release temperature of from 35°C to 125°C.

[00500] Single Layer Process. The single layer process comprises

melting a thermally activated semi-crystalline polymer (E)(a),

adding an organometallic condensation catalyst (E)(b) to the melted (E)(a),

mixing (E)(a) and (E)(b) to obtain a homogeneous mixture,

cooling the homogeneous mixture,

adding the cooled homogeneous mixture to a hot aqueous solution to form a hot aqueous mixture,

emulsifying the hot aqueous mixture,

cooling the hot emulsified aqueous mixture, and

removing water from the cooled emulsified aqueous mixture to yield a dry powder.

[00511] Double Layer Process. The double layer process comprises

melting a thermally activated semi-crystalline polymer (E)(a),

preparing a dispersion comprising an organometallic condensation catalyst and solvent and combining it with a solution comprising an amorphous polymer and solvent to form a mixture, and removing the solvent to form an encapsulated organometallic composition,

mixing the encapsulated organometallic composition with the molten thermally activated semi-crystalline polymer (E)(a) to obtain a homogeneous mixture,

cooling the homogeneous mixture,

adding the cooled homogeneous mixture to a hot aqueous solution to form a hot aqueous mixture,

emulsifying the hot aqueous mixture,

cooling the hot emulsified aqueous mixture, and

removing water from the cooled emulsified aqueous mixture to yield a dry powder.

[00522] Both of the above procedures utilize (E)(a) a thermally activated semi-crystalline polymer, and (E)(b) at least one organometallic condensation catalyst.

[00533] The thermally activated semi-crystalline polymer (E)(a) is selected from polyolefin waxes and natural paraffin waxes. The polyolefin waxes include synthetic paraffin waxes. Polyolefin waxes are prepared from homopolymers of ethylene or of propylene or copolymers of propylene with ethylene or copolymers of ethylene with propylene or with one or more alpha-olefins. The alpha olefins used are linear or branched olefins having 3-18 carbon atoms, alternatively from 3-6 carbon atoms. Examples thereof are propene, 1-butene, 1-hexene, 1-octene or 1-octadecene, and also styrene. Copolymers of ethylene with

propene or 1-butene are preferred. The ethylene content of the copolymers is from 70 to 99.9% by weight, preferably from 80 to 99% by weight.

[00544] Preferred examples of the natural wax include, but are not limited to, a natural wax selected from the group consisting of carnauba wax, candelilla wax, beeswax, spermaceti wax, privet wax, and montan wax.

[00555] The organometallic condensation catalyst (E)(b) is at least one organometallic compound having a general formula

$$M\,X_k\,(OR^{12})_{l-k},$$

where M is selected from Ti, Al, Zr, Sn, Cu, Ce, Co, Cr, Hf, Mo, Pd, Pt, V, and Fe, each X is independently selected from carboxylate ligands, organosulfonate ligands, organophosphate ligands, β-ketonate ligands, β-diketonate ligands, β-ketoester ligands, β-hydroxyacids, α-hydroxyacids, salicylate ligands, fluoro-substituted ligands, and chloride ligands, subscript l is the oxidation state of M, subscript k is a value from 0 to the value of subscript l, each R^{12} is independently hydrogen or a hydrocarbyl group selected from monovalent alkyl group having from 1 to 6 carbon atoms, aryl group having from 6 to 8 carbon atoms, or siloxane group having a formula $-(SiO)_mR^{14}$, where subscript m is a value from 1 to 8, and R^{14} is an independently selected hydrogen atom or monovalent alkyl group having from 1 to 6 carbon atoms.

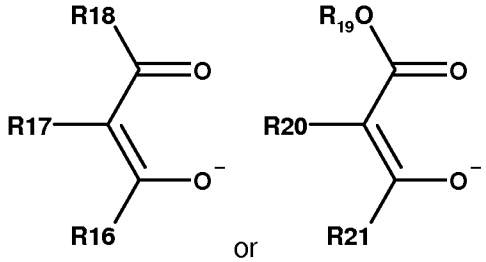
[00566] Examples of the alkyl groups of R^{12} include methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, and hexyl. Examples of the aryl groups of R^{12} include phenyl and benzyl.

[00577] Examples of the alkyl groups having from 1 to 6 carbon atoms of R^{14} are as described above for R^{12}. Subscript m is a value from 1 to 8, alternatively 1 to 4.

[00588] Alternatively, R^{14} is an independently selected hydrogen atom or monovalent alkyl group having from 1 to 6 carbon atoms, alternatively methyl, ethyl, n-propyl, isopropyl, n-butyl and t-butyl, alternatively methyl and ethyl.

[005959] X is independently selected from carboxylate ligands, organosulfonate ligands, organophosphate ligands, β-ketonate ligands, β-diketonate ligands, β-ketoester ligands, β-hydroxyacids, α-hydroxyacids, salicylate ligands, fluoro-substituted ligands, and chloride ligands, alternatively carboxylate ligands, β-diketonate ligands and β-ketoester ligands. The carboxylate ligands useful for X have a formula $R^{15}COO^-$ where R^{15} is selected from hydrogen, alkyl groups, alkenyl groups, and aryl groups. Examples of useful alkyl groups for R^{15} include alkyl groups having from 1 to 18 carbon atoms, alternatively 1 to 8 carbon atoms. Examples of useful alkenyl groups for R^{15} include alkenyl groups having from 2 to 18

carbon atoms, alternatively 2 to 8 carbon atoms such as vinyl, 2-propenyl, allyl, hexenyl, and octenyl. Alternatively R^{15} is methyl, 2-propenyl, allyl, and phenyl. Non-limiting examples of β-diketonate and β-diketoester ligands useful for X respectively, can have the following structures:



wherein R^{16}, R^{18}, R^{19} and R^{21} are selected from alkyl, alkenyl and aryl groups. Examples of useful alkyl groups for R^{16}, R^{18}, R^{19} and R^{21} include alkyl groups having from 1 to 18 carbon atoms, alternatively 1 to 10 carbon atoms such as methyl, ethyl, ethyltrifluoro, t-butyl, hexafluoropropyl, and undecylenyl. Examples of useful aryl groups for R^{16}, R^{18}, R^{19} and R^{21} include aryl groups having from 6 to 18 carbon atoms, alternatively 6 to 8 carbon atoms such as phenyl and tolyl. Examples of useful alkenyl groups for R^{16}, R^{18}, R^{19}, and R^{21} include alkenyl groups having from 2 to 18 carbon atoms, alternatively 2 to 8 carbon atoms such as allyl, hexenyl, and octenyl. R^{17} and R^{20} are hydrogen or alkyl, alkenyl, and aryl groups. Examples of useful alkyl groups for R^{17} and R^{20} include alkyl groups having from 1 to 12 carbon atoms, alternatively 1 to 8 carbon atoms such as methyl and ethyl. Examples of useful alkenyl groups for R^{17} and R^{20} include alkenyl groups having from 2 to 18 carbon atoms, alternatively 2 to 8 carbon atoms such as vinyl, allyl, hexenyl, and octenyl. Examples of useful aryl groups for R^{17} and R^{20} include aryl groups having from 6 to 18 carbon atoms, alternatively 6 to 8 carbon atoms such as phenyl and tolyl. R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, and R^{21} are each independently selected and can be the same or different.

[00600] Subscript l is the oxidation state of M, ranging from 1 to 4. Alternatively, subscript l ranges from 2 to 4.

[00611] Subscript k is a value from 0 to the value of subscript l, alternatively 0 to 2, alternatively 0.

[00622] Examples of the organometallic compounds useful in this invention include cerium acetylacetonate, chromium acetylacetonate, cobalt acetylacetonate, hafnium (trifluoro acetylacetonate), molybdenum (IV) dioxide acetylacetonate, palladium acetylacetonate, vanadyl acetylacetonate, titanium tetrapropoxides, titanium tetrabutoxides, zirconium tetrapropoxides, and zirconium tetrabutoxides, aluminum tripropoxides, aluminum

tributoxides, aluminum phenoxide, copper (II) ethoxide, copper (II) methoxyethoxyethoxide, iron (III) ethoxide, di-n-butyldi-n-butoxytin, di-n-butyldimethoxytin, tetra-t-butoxytin, tri-n-butylethoxytin, titanium ethoxide, titanium 2-ethylhexoxide, titanium methoxide, titanium methoxypropoxide, titanium n-nonyloxide, zirconium ethoxide, zirconium 2-ethylhexoxide, zirconium 2-methyl-2-butoxide, and zirconium 2-methoxymethyl-2-propoxide, aluminum s-butoxide bis(ethylacetoacetate), aluminum di-s-butoxide ethylacetoacetate, aluminum diisopropoxide ethylacetoacetate, aluminum 9-octdecenylacetoacetate diisopropoxide, titanium allylacetoacetate triisopropoxide, titanium bis(triethanolamine) diisopropoxide, titanium chloride triisopropoxide, titanium dichloride diethoxide, titanium diisopropoxy bis(2,4-pentanedionate), titanium diisopropoxide bis(tetramethylheptanedionate), titanium diisopropoxide bis(ethylacetoacetate), titanium methacrylate triisopropoxide, titanium methacryloxyethylacetoacetate triisopropoxide, titanium trimethacrylate methoxyethoxyethoxide, titanium tris(dioctylphosphato)isopropoxide, titanium tris(dodecylbenzenesulfonate)isopropoxide, titanium tetrakisacetoacetate, zirconium (bis-2,2'-(alloxymethyl)-butoxide)tris(dioctylphosphate), zirconium diisopropoxide bis(2,2,6,6-tetramethyl-3,5-heptanedionate), zirconium dimethacrylate dibutoxide, zirconium methacryloxyethylacetoacetate tri-n-propoxide, and zirconium tetrakisacetoacetate.

[00633] Many of the organometallic compounds are generally available from Gelest (Morrisville, PA USA) or Dorf Ketal (Stafford, TX USA).

[00644] The amorphous polymer has a T_g of less than 140°C. Suitable amorphous polymers include, e.g., polystyrenes, polycarbonates, polyacrylates, polymethacrylates, elastomers, such as styrenic block copolymers, e.g., styrene-isoprene-styrene (SIS), styrene-ethylene/butylene-styrene block copolymers (SEBS), polybutadiene, polyisoprene, polychloroprene, random and block copolymers of styrene and dienes (e.g., styrene-butadiene rubber (SBR)), ethylene-propylene-diene monomer rubber, natural rubber, ethylene propylene rubber, polyethylene-terephthalate (PET). Other examples of amorphous polymers include, e.g., polystyrene-polyethylene copolymers, polyvinylcyclohexane, polyvinyl chloride, thermoplastic polyurethanes, aromatic epoxies, amorphous polyesters, amorphous polyamides, acrylonitrile-butadiene-styrene (ABS) copolymers, polyphenylene oxide alloys, high impact polystyrene, polystyrene copolymers, polymethylmethacrylate (PMMA), fluorinated elastomers, polydimethyl siloxane, amorphous fluoropolymers, amorphous polyolefins, polyphenylene oxide, polyphenylene oxide--polystyrene alloys, copolymers containing at least one amorphous component, and mixtures thereof.

[00655] Component (E) is present at from 0.5 to 5 and alternatively at from 1 to 3 parts by weight per 100 parts by weight of component (A).

[00666] Preparation of the Adhesion Catalyst (E). The adhesion catalyst (E) is prepared by a single layer process or a double layer process. The single layer process comprises the steps of:

melting a thermally activated semi-crystalline polymer (E)(a) described above,

adding an organometallic condensation catalyst (E)(b) described above to the melted (E)(a),

mixing (E)(a) and (E)(b) to obtain a homogeneous mixture,

cooling the homogeneous mixture,

adding the cooled homogeneous mixture to a hot aqueous solution to form a hot aqueous mixture,

emulsifying the hot aqueous mixture,

cooling the hot emulsified aqueous mixture, and

removing water from the cooled emulsified aqueous mixture to yield a dry powder.

The double layer process procedure comprises the steps of:

melting a thermally activated semi-crystalline polymer (E)(a),

preparing a dispersion comprising an organometallic condensation catalyst and solvent and combining it with a solution comprising an amorphous polymer and solvent to form a mixture, and removing the solvent to form an encapsulated organometallic composition,

mixing the encapsulated organometallic composition with the molten thermally activated semi-crystalline polymer (E)(a) to obtain a homogeneous mixture,

cooling the homogeneous mixture,

adding the cooled homogeneous mixture to a hot aqueous solution to form a hot aqueous mixture,

emulsifying the hot aqueous mixture,

cooling the hot emulsified aqueous mixture, and

removing water from the cooled emulsified aqueous mixture to yield a dry powder.

[00677] The above described processes employ an aqueous melt-emulsify-chill (MEC) process. In the MEC process, the thermally active semi-crystalline polymer (E)(a) is heated from between 40℃ up to 200℃ such that the thermally active semi-crystalline polymer (E)(a) becomes molten. The organometallic condensation catalyst (E)(b) is then introduced into the thermally active semi-crystalline polymer (E)(a) by one of two processes. In the first process, the organometallic condensation catalyst (E)(b) is added neat to the thermally active semi-crystalline polymer (E)(a) and mixed until a homogenous mixture is obtained. In the second process, the organometallic condensation catalyst (E)(b) is coated with an

amorphous polymer and then added to the thermally active semi-crystalline polymer (E)(a) and mixed until a homogenous mixture is obtained. Coating of the organometallic condensation catalyst (E)(b) with an amorphous polymer can be performed by spray drying from a suitable solvent to obtain uniformly coated catalyst particles. In either method, the homogeneous mixture of the first process or of the second process is cooled to between 5°C and 80°C.

[00688] In the second process, the amorphous polymer has a T_g of less than 140°C. Suitable amorphous polymers include, e.g., polystyrenes, polycarbonates, polyacrylates, polymethacrylates, elastomers, such as styrenic block copolymers, e.g., styrene-isoprene-styrene (SIS), styrene-ethylene/butylene-styrene block copolymers (SEBS), polybutadiene, polyisoprene, polychloroprene, random and block copolymers of styrene and dienes (e.g., styrene-butadiene rubber (SBR)), ethylene-propylene-diene monomer rubber, natural rubber, ethylene propylene rubber, polyethylene-terephthalate (PET). Other examples of amorphous polymers include, e.g., polystyrene-polyethylene copolymers, polyvinylcyclohexane, polyvinyl chloride, thermoplastic polyurethanes, aromatic epoxies, amorphous polyesters, amorphous polyamides, acrylonitrile-butadiene-styrene (ABS) copolymers, polyphenylene oxide alloys, high impact polystyrene, polystyrene copolymers, polymethylmethacrylate (PMMA), fluorinated elastomers, polydimethyl siloxane, amorphous fluoropolymers, amorphous polyolefins, polyphenylene oxide, polyphenylene oxide--polystyrene alloys, copolymers containing at least one amorphous component, and mixtures thereof.

[006969] The amorphous polymer is combined with a solvent to form a solution. Added to this solution is a dispersion of the organometallic condensation catalyst (E)(b) and solvent. Suitable solvents are those which can be easily removed when the solution of amorphous polymer and solvent and organometallic condensation catalyst (E)(b) dispersion and solvent are subjected to spray drying for solvent removal. An encapsulated organometallic composition is formed upon solvent removal. Suitable solvents are for example, low molecular weight ketones such as acetone, methyl ethyl ketone, methyl n-propyl ketone, methyl iso-propyl ketone, and methyl n-butyl ketone; and low molecular weight ethers, either symmetrical or nonsymmetrical for example, such as diethyl ether and methyl ethyl ether.

[00700] The cooled homogeneous mixture, by either process, is then added to a hot aqueous surfactant solution having a temperature of up to the boiling point of the solution to obtain a hot mixture. The surfactant may be cationic (based on quaternary ammonium cations), anionic (based on sulfate, sulfonate or carboxylate anions), nonionic or amphoteric. Examples of surfactants are, but are not limited to, sodium dodecyl sulfate (SDS) and other

alkyl sulfate salts, sodium laureth sulfate, also known as sodium lauryl ether sulfate (SLES), alkyl benzene sulfonate, soaps, fatty acid salts, cetyl trimethylammonium bromide (CTAB), cetyl trimethylammonium chloride (CTAC) and other alkyltrimethylammonium salts, cetylpyridinium chloride (CPC), polyethoxylated tallow amine (POEA), benzalkonium chloride (BAC), benzethonium chloride (BZT), zwitterionic (amphoteric), dodecyl betaine, dodecyl dimethylamine oxide, cocamidopropyl betaine, coco ampho glycinate, nonionic alkyl poly(ethylene oxide), copolymers of poly(ethylene oxide) and poly(propylene oxide) (commercially called Poloxamers, Pluronics or Poloxamines), alkyl polyglucosides, including: octyl glucoside, decyl maltoside, fatty alcohols, cetyl alcohol, oleyl alcohol, cocamide MEA, cocamide DEA, sorbitol ester or fatty acids, or any combination thereof. The surfactant is present in the aqueous solution at from 0.25 to 3% by weight.

[00711] The hot mixture, by either process, is then emulsified by mechanical stirring and then cooled to below 45°C. Water is then removed from the cooled emulsified mixture to obtain (E) as a powder. Methods for water removal can be selected from lyophilization, spray drying, spray cooling, and filtration. In the first process the final particles comprise a catalyst with a single coating layer, whereas in the second process the final particles comprise a catalyst with two distinct coating layers.

[00722] Optional Components. One or more optional components may be added to this composition in addition to components (A) – (E). Suitable optional components include (F), a filler, (G), an inhibitor, (H), a void reducing agent, (I), a pigment, (J), a rheology modifier, (K), a spacer, and combinations thereof.

[00733] (F) The Filler. Optional component (F) is a reinforcing and extending inorganic filler. Examples of the aforementioned inorganic fillers (F) are the following: glass fiber, mineral fiber, alumina fiber, ceramic fiber that contains alumina and silica as components, boron fiber, zirconia fiber, silicon carbide fiber, metal fiber, or other fibrous filler; fused silica, crystalline silica, precipitated silica, fumed silica, baked silica, zinc oxide, baked clay, carbon black, glass beads, alumina, talc, calcium carbonate, clay, aluminum hydroxide, magnesium hydroxide, barium sulfate, titanium dioxide, aluminum nitride, boron nitride, silicon carbide, aluminum oxide, magnesium oxide, titanium oxide, beryllium oxide, kaolin, mica, zirconium, or other powdered fillers. These fillers can be used in combinations of two or more. Alternatively the filler (F) is a spherical silica with an average particle size in the range of 0.1 to 40 μm.

[00744] In another embodiment, the filler is a thermally conductive filler that is used for imparting conductivity to the composition of the invention. This may be, e.g., an aluminum powder, copper powder, nickel powder, or another metal powder; an alumina powder,

magnesium oxide powder, beryllium oxide powder, chromium oxide powder, titanium oxide powder, or a similar metal oxide powder; boron nitride powder, aluminum nitride powder, or similar nitride powder; boron carbide powder, titanium carbide powder, silicon carbide powder, or similar metal carbide powder; metal oxide powder used for imparting conductivity to surfaces by coating them with a metal-containing substance; or mixtures of two or more of the above. The particles of the thermally conductive filler may have spherical, round, needle-like, disk-like, rod-like, or irregular shape. When it is required that the composition or a cross-linked body of the composition possess electrical, insulating properties, it is preferable to use metal oxide-type powder, metal nitride-type powder, or a metal carbonate-type powder, especially alumina powder. There are no special restrictions with regard to an average particle size of the thermally conductive filler, but it is recommended that the average size of the particles be within the range of 0.1 to 100 microns, and preferably 0.1 to 50 microns. When alumina powder is used as the thermally conductive filler, it is recommended that the thermally conductive filler be a mixture of a spherical or round shaped alumina powder having an average particle size within the range of 5 to 50 microns and a spherical or irregularly shaped alumina powder having an average particle size within the range of 0.1 to 5 microns. Moreover, it is recommended that in the mixture of constitutes the former constitutes 30 to 90% by weight, and the latter constitutes 10 to 70% by weight.

[00755] Component (F) is present at from 10 to 200 and alternatively at from 75 to 150 parts by weight per 100 parts by weight of component (A).

[00766] (G) The Inhibitor. The self-adhering curable silicone adhesive composition of the present invention may also optionally comprise an inhibitor (G). Component (G) can be any material that is known to be, or can be, used to inhibit the catalytic activity of component (C). As used herein, the term inhibitor means a material that retards the activity of a catalyst at room temperature, but does not interfere with the properties of the catalyst at elevated temperatures. Examples of suitable inhibitors include ethylenically or aromatically unsaturated amides, acetylenic compounds, silylated acetylenic compounds, ethylenically unsaturated isocyanates, olefinic siloxanes, unsaturated hydrocarbon monoesters and diesters, conjugated ene-ynes, hydroperoxides, nitriles, and diaziridines.

[00777] Typical inhibitors include acetylenic alcohols exemplified by 1-ethynyl-1-cyclohexanol, 2-methyl-3-butyn-2-ol, 2-phenyl-3-butyn-2-ol, 2-ethynyl-isopropanol, 2-ethynyl-butane-2-ol, and 3,5-dimethyl-1-hexyn-3-ol, silylated acetylenic alcohols exemplified by trimethyl(3,5-dimethyl-1-hexyn-3-oxy)silane, dimethyl-bis-(3-methyl-1-butyn-oxy)silane, methylvinylbis(3-methyl-1-butyn-3-oxy)silane, and ((1,1-dimethyl-2-propynyl)oxy)trimethylsilane, unsaturated carboxylic esters exemplified by diallyl maleate,

dimethyl maleate, diethyl fumarate, diallyl fumarate, and bis-2-methoxy-1-methylethylmaleate, mono-octylmaleate, mono-isooctylmaleate, mono-allyl maleate, mono-methyl maleate, mono-ethyl fumarate, mono-allyl fumarate, and 2-methoxy-1-methylethylmaleate; conjugated ene-ynes exemplified by 2-isobutyl-1-butene-3-yne, 3,5-dimethyl-3-hexene-1-yne, 3-methyl-3-pentene-1-yne, 3-methyl-3-hexene-1-yne, 1-ethynylcyclohexene, 3-ethyl-3-butene-1-yne, and 3-phenyl-3-butene-1-yne, vinylcyclosiloxanes such as 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, and a mixture of a conjugated ene-yne as described above and a vinylcyclosiloxane as described above. Typically the inhibitors are diallyl maleate, bis-2-methoxy-1-methylethylmaleate, 1-ethynyl-1-cyclohexanol, and 3,5-dimethyl-1-hexyn-3-ol.

[00788] Component (G) is present at from 0.5 to 5 and alternatively at from 1 to 3 parts by weight per 100 parts by weight of component (A).

[007979] (H) The Void Reducing Agent. Component (H) is a void reducing agent. Component (H) is added to the composition in an amount sufficient to reduce voids. Suitable void reducing agents are known in the art and commercially available, see for example, EP 0 850 997 A2 and U.S. Patents 4,273,902 and 5,684,060. Suitable void reducing agents can comprise zeolites, anhydrous aluminum sulfate, molecular sieves (preferably with a pore diameter of 10 Å or less), kieselguhr, silica gel, activated carbon, palladium compounds such as palladium metal, palladium metal supported on a substrate exemplified by carbon or alumina, and organopalladium compounds.

[00800] (I) The Pigment. Component (I) is a pigment. The amount of component (I) added to the composition depends on the type of pigment selected. Component (I) may be added to the composition in an amount of 0.001 % to 30 % based on the weight of the composition. Pigments are known in the art and commercially available. Suitable pigments include carbon blacks, such as LB-1011C carbon black from Williams, chromium oxide pigments, such as Harcros G-6099, titanium dioxides such as those available from DuPont, and UV-active dyes such as (thiophenediyl)bis(t-butylbenzoxazole) which is commercially available under the name UVITEX OB from Ciba Specialty Chemicals.

[00811] (J) The Rheology Modifier. Component (J) is a rheology modifier. Rheology modifiers can be added to change the thixotropic properties of the composition. Component (J) is exemplified by flow control additives; reactive diluents; anti-settling agents; alpha-olefins; hydroxyl-terminated silicone-organic copolymers, including but not limited to hydroxyl-terminated polypropyleneoxide-dimethylsiloxane copolymers; and combinations thereof.

[00822] (K) The Spacer. Component (K) is a spacer. Spacers can comprise organic particles, inorganic particles, or a combination thereof. Spacers can be thermally conductive, electrically conductive, or both. Spacers can have a particle size of 25 micrometers to 250 micrometers. Spacers can comprise monodisperse beads. The amount of component (K) depends on various factors including the distribution of particles, pressure to be applied during placement of the composition, temperature of placement, and others. The composition can contain up to 15%, alternatively up to 5% of component (K).

[00833] Other Optional Components. Other optional components may be added in addition to, or instead of, all or a portion of those described above, provided the optional component does not prevent the composition from curing to form a silicone product having improved adhesion and chemical resistance, as described above. Examples of other optional components include, but are not limited to, acid acceptors; anti-oxidants; stabilizers such as magnesium oxide, calcium hydroxide, metal salt additives such as those disclosed in EP 0 950 685 A1, heat stabilizers, and ultra-violet (UV) stabilizers; flame retardants; silylating agents, such as 4-(trimethylsilyloxy)-3-penten-2-one and N-(t-butyl dimethylsilyl)-N-methyltrifluoroacetamide; desiccants, such as zeolites, anhydrous aluminum sulfate, molecular sieves (preferably with a pore diameter of 10 Å or less), kieselguhr, silica gel, and activated carbon; and blowing agents, such as water, methanol, ethanol, iso-propyl alcohol, benzyl alcohol,1,4 butanediol, 1,5 pentanediol, 1,7 heptanediol, and silanols.

Following are representative examples for the formation of adhesion catalyst (G).

[00844] Example 1 – Single Layer Process. Added to a mixing vessel were 50 parts of a thermally active semi-crystalline polymer (E)(a) identified as Polywax 655, commercially available from Baker Petrolite and having a molecular weight of 655. The semi-crystalline polymer was heated until molten. Added to the molten polymer was 50 parts of an organometallic condensation catalyst (E)(b) identified as ground zirconium trisacetylacetonate (GZAA). The contents were mixed by hand to obtain a homogenous mixture, which was then cooled. A hot aqueous surfactant solution of 890 parts water and 10 parts cetyl trimethylammonium chloride were prepared and the cooled mixture was added to the hot surfactant solution and mixed until the homogenous mixture melted. An emulsion was formed using a Silverson rotor stator mixer at 5000 revolutions per minute (rpm) for 10 minutes. The emulsion was then cooled to room temperature while stirring with an overhead mixer. A dry powder was obtained by lyophilization.

[00855] Example 2 – Double Layer Process. In this example, an organometallic condensation catalyst (E)(b) was coated with an amorphous polymer using a spray dry process. An amorphous polymer of polymethylmethacrylate (PMMA) at 0.6 wt/vol% was

dissolved in acetone. Added to the acetone solution was an organometallic condensation catalyst (E)(b) identified as ground zirconium trisacetylacetonate at 2.4 wt/vol%. The contents were mixed and spray dried to yield a PMMA coated GZAA. Heated until molten was 40 parts of a thermally active semi-crystalline polymer (E)(a) identified as synthetic paraffin 80. Added to the molten (E)(a) was 40 parts of the PMMA coated GZAA. The contents were mixed by hand to obtain a homogenous mixture, which was then cooled. A hot aqueous surfactant solution of 890 parts water and 10 parts cetyl trimethylammonium chloride were prepared and the cooled mixture was added to the hot surfactant solution and mixed until the homogenous mixture melted. An emulsion was formed using a Silverson rotor stator mixer at 5000 revolutions per minute (rpm) for 10 minutes. The emulsion was then cooled to room temperature while stirring with an overhead mixer. A dry powder was obtained by lyophilization.

[00866] The following examples 3 and 4 are illustrative of this invention in that they contain components (A) through (E).

[00877] Example 3. Added to a mixing vessel were 100 parts of an organopolysiloxane resin consisting essentially of $CH_2=CH(CH_3)_2SiO_{1/2}$ units, $(CH_3)_3SiO_{1/2}$ units, and $SiO_{4/2}$ units, wherein the mole ratio of $CH_2=CH(CH_3)_2SiO_{1/2}$ units and $(CH_3)_3SiO_{1/2}$ units combined to $SiO_{4/2}$ units is 0.7, and the resin has weight-average molecular weight of 22,000, a polydispersity of 5, and contains 1.8% by weight (5.5 mole%) of vinyl groups, as component (A), 6.8 parts of a trimethylsiloxy-terminated poly(dimethylsiloxane/methylhydrogensiloxane) having an average of 3 dimethylsiloxane units and 5 methylhydrogensiloxane units per molecule and containing 0.8% of silicon-bonded hydrogen atoms as component (B), 0.3 parts of a mixture of 1% of a platinum(IV) complex of 1,1-diethenyl-1,1,3,3-tetramethyldisiloxane, 92% of dimethylvinylsiloxy-terminated polydimethylsiloxane having a viscosity of 0.45 Pa·s at 25°C, and 7% of tetramethyldivinyldisiloxane as component (C), 2.5 parts of a mixture of 46% 3-glycidoxypropyltrimethoxysilane, 40% hydroxy-terminated methylvinylsiloxane, 7% cyclic methylvinylsiloxane, 6% of a reaction product of hydroxy terminated methylvinyl siloxane, with 3-glycidoxypropyltrimethoxysilane, and 1% methanol as component (D), wherein the mixture has a viscosity of 15 cSt at 25 ºC, 60 parts of hexamethyldisilazane-treated silica having a BET surface area of between 200 and 250 meters squared per gram (m^2/g), pH of 4.5 to 6.5, and moisture content not exceeding 0.6 % measured gravimetrically at 105°C, sold under the name of Cab-O-Sil TS-530 by Cabot Corporation as component (F), 0.35 parts of bis-2-methoxy-1-methylethylmaleate as component (G), and 0.86 parts of component E as the product of Example 1. The contents were mixed using a dispersion mixer.

[00888] Example 4. The procedure of Example 3 is repeated expect that 0.86 parts of component E as the product of Example 1 (single layer process) is replaced with 0.86 parts of component E as the product of Example 2 (double layer process).

[008989] A control example is also prepared using the above weights for Examples 3 and 4 less component (E).

[00900] The compositions of Examples 3 and 4 and the control example were individually applied onto panels of polybutylene terephthalate (Ticona Celanex ® 3300D PBT) and then de-aired for 5 min to remove bubbles that might have been introduced during the application process. An 18 gauge copper wire was placed in the adhesive composition at each end of the panel. A 3 mil piece of aluminum foil was then placed on top of the sample. The samples were placed onto a thermal gradient hot plate and allowed to cure for one hour. Samples were allowed to cool to room temperature. For each sample, the aluminum foil was then peeled back using a 90° peel adhesion test methodology. The temperature of adhesive cure (T_C) and the temperature of adhesion to the substrate (T_A, as demonstrated by a cohesive failure mode) were determined by calculation, based upon the displacement measured during the peel test and the linearity equation from the thermal gradient applied.

[00911] Further, the compositions were aged for 6 months at 5℃ and then re-tested according to the method just described.

[00922] Table 1 below shows the T_C℃ and T_A℃ at both the initial preparation of the panel samples and after a 6 month ageing period.

Table 1

Composition	Initial T_C℃	Initial T_A℃	Aged T_C℃	Aged T_A℃
Control	97	144	81	149
Example 3	98	98	No cure	No cure
Example 4	98	98	81	84

[00933] Embodiments of the invention also include the following numbered aspects:

2. The composition of aspect 1, wherein component (A) comprises an alkenyl substituted organopolysiloxane of the formulae

$$R^1{}_3SiO(R^1{}_2SiO)_a(R^1R^2SiO)_bSiR^1{}_3,$$

$$R^3{}_2R^4SiO(R^3{}_2SiO)_c(R^3R^4SiO)_dSiR^3{}_2R^4,$$

or combinations thereof;

wherein subscript a has an average value of 0 to 2000, subscript b has an average value of at least 0.1 to 2000, each R^1 is independently a hydrocarbyl group, each R^2 is independently an unsaturated monovalent organic group, subscript c has an average value

of at least 0.1 to 2000, and subscript d has an average value of 0 to 2000, each R^3 is independently a hydrocarbyl group, each R^4 is independently an unsaturated monovalent group.

3. The composition of any one of the preceding aspects wherein component (A) comprises an MQ resin selected from $R^5_3SiO_{1/2}$ units and $SiO_{4/2}$ units, a TD resin selected from $R^5SiO_{3/2}$ units and $R^5_2SiO_{2/2}$ units, an MT resin selected from $R^5_3SiO_{1/2}$ units and $R^5SiO_{3/2}$ units, an MTD resin selected from $R^5_3SiO_{1/2}$ units, $R^5SiO_{3/2}$ units, and $R^5_2SiO_{2/2}$ units, or combinations thereof,

wherein each R^5 is a monovalent organic group of 1 to 20 carbon atoms, and the resin contains an average of 3 to 30 mole percent of unsaturated organic groups.

4. The composition of any one of the preceding aspects wherein component (B) comprises siloxane units selected from $HR^6_2SiO_{1/2}$, $R^6_3SiO_{1/2}$, $HR^6SiO_{2/2}$, $R^6_2SiO_{2/2}$, $R^6SiO_{3/2}$, $SiO_{4/2}$, or combinations thereof; where each R^6 is independently selected from monovalent organic groups free of aliphatic unsaturation.

5. The composition of any one of the preceding aspects wherein component (B) comprises an organohydrogenpolysiloxane compound of the formulae:

$$R^7_3SiO(R^7_2SiO)_e(R^7HSiO)_fSiR^7_3,$$

$$R^8_2HSiO(R^8_2SiO)_g(R^8HSiO)_hSiR^8_2H,$$

or combinations thereof,

wherein subscript e has an average value of 0 to 2000, subscript f has an average value of 2 to 2000, each R^7 is independently a monovalent organic group free of aliphatic unsaturation, subscript g has an average value of 0 to 2000, subscript h has an average value of 0 to 2000, and each R^8 is independently a monovalent organic group free of aliphatic unsaturation.

6. The composition of any one of the preceding aspects, wherein the hydrosilylation catalyst (C) comprises a platinum metal, a rhodium metal, or an organometallic compound.

7. The composition of any one of the preceding aspects wherein component (D) is selected from an unsaturated alkoxysilane, an epoxy-functional alkoxysilane, an epoxy-functional siloxane, or a combination thereof.

8. The composition of any one of the preceding aspects wherein component (D) comprises an alkoxysilane of the formula $R^9_iSi(OR^{10})_{(4-i)}$,

wherein subscript i is 1, 2, or 3, each R^9 is independently a monovalent organic group, with the proviso that at least one R^9 is an unsaturated organic group or an epoxy-functional group, and each R^{10} is independently an unsubstituted, saturated hydrocarbon group of at least 1 carbon atom.

9. The composition of any one of the preceding aspects, where component (D) is selected from 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropyltriethoxysilane, (epoxycyclohexyl)ethyldimethoxysilane, (epoxycyclohexyl)ethyldiethoxysilane, vinyltrimethoxysilane, allyltrimethoxysilane, allyltriethoxysilane, hexenyltrimethoxysilane, undecylenyltrimethoxysilane, 3-methacryloyloxypropyl trimethoxysilane, 3-methacryloyloxypropyl triethoxysilane, 3-acryloyloxypropyl trimethoxysilane, 3-acryloyloxypropyl triethoxysilane, and combinations thereof.

10. The composition of any one of the preceding aspects, where component (D) is selected from a reaction product of a hydroxy-terminated polyorganosiloxane with an epoxy-functional alkoxysilane or an unsaturated alkoxysilane, a physical blend of a hydroxy-terminated polyorganosiloxane with an epoxy-functional alkoxysilane or an unsaturated alkoxysilane, and combinations thereof.

11. The composition of any one of the preceding aspects, wherein the thermally activated semi-crystalline polymer (E)(a) is selected from synthetic polyolefin waxes, natural paraffin waxes, and synthetic paraffin waxes.

12. The composition of any one of the preceding aspects, wherein the thermally activated semi-crystalline polymer (E)(a) is selected from synthetic polyethylene waxes and synthetic paraffin waxes.

13. The composition of any one of the preceding aspects, wherein the organometallic condensation catalyst (E)(b), is represented by the formula

$$MX_k(OR^{12})_{l-k}$$

where M is selected from Ti, Al, Zr, Sn, Cu, Ce, Co, Cr, Hf, Mo, Pd, Pt, V, and Fe, each X is independently selected from carboxylate ligands, organosulfonate ligands, organophosphate ligands, β-ketonate ligands, β-diketonate ligands, β-ketoester ligands, β-hydroxy acids, α-hydroxy acids, salicylate ligands, fluoro-substituted ligands, and chloride ligands, subscript l is the oxidation state of M, subscript k is from 0 to the value of subscript l, each R^{11} is independently an alkyl group having from 1 to 18 carbon atoms, each R^{12} is independently selected from a monovalent alkyl group having from 1 to 6 carbon atoms, an aryl group, and a polyether group of the formula

$$(R^{13}O)_mR^{14}$$

wherein subscript m is from 1 to 4, each R^{13} is independently selected from a divalent alkylene group having from 2 to 6 carbon atoms, and R^{14} is selected from a hydrogen atom or a monovalent alkyl group having from 1 to 6 carbon atoms.

14. The composition of any one of the preceding aspects, wherein the organometallic condensation catalyst (E)(b) has a ligand selected from a monodentate, bidentate, tridentate, and poldentate, and combinations thereof.

15. The composition of any one of the preceding aspects, wherein the organometallic compound (E)(b) in component (E) is within the range of 1 to 75 wt.%.

16. The composition of any one of the preceding aspects, wherein component (E) has a mean particle size of from 0.01 to 100 microns.

17. The composition of any one of the preceding aspects, wherein component (E)(a) has a mean particle size of less than 50 microns.

18. The composition of any one of the preceding aspects, wherein component (E) has a release temperature of from 35°C to 125°C.

19. A process for making the adhesion catalyst (E) of any one of the preceding aspects comprising,

forming the adhesion catalyst by a single layer process or a double layer process.

20. The process of aspect 19 wherein the adhesion catalyst (E) is formed by a single layer process comprising,

melting a thermally activated semi-crystalline polymer (E)(a),

adding an organometallic condensation catalyst (E)(b) to the melted (E)(a),

mixing (E)(a) and (E)(b) to obtain a homogeneous mixture,

cooling the homogeneous mixture,

adding the cooled homogeneous mixture to a hot aqueous solution to form a hot aqueous mixture,

emulsifying the hot aqueous mixture,

cooling the hot emulsified aqueous mixture, and

removing water from the cooled emulsified aqueous mixture to yield a dry powder.

21. The process of aspect 19 wherein the adhesion catalyst (E) is formed by a double layer process comprising,

melting a thermally activated semi-crystalline polymer (E)(a),

preparing a dispersion comprising an organometallic condensation catalyst (E)(b) and solvent and combining it with a solution comprising an amorphous polymer and solvent to form a mixture, and removing the solvent to form an encapsulated organometallic composition,

mixing the encapsulated organometallic composition with the molten thermally activated semi-crystalline polymer (E)(a) to obtain a homogeneous mixture,

cooling the homogeneous mixture,

adding the cooled homogeneous mixture to a hot aqueous solution to form a hot aqueous mixture,

emulsifying the hot aqueous mixture,

cooling the hot emulsified aqueous mixture, and

removing water from the cooled emulsified aqueous mixture to yield a dry powder.

22. The process of aspect 21, wherein the amorphous polymer is selected from polyacrylates, polymethacrylates, polystyrenes, polycarbonates, and mixtures thereof.

23. The process of aspect 21, wherein the amorphous polymer has a glass transition temperature, Tg, of less than 140°C.

24. The process of aspects 20 or 21, wherein the hot aqueous solution contains from 0.25 to 3.0 wt% of a surfactant and wherein the hot aqueous solution has a temperature of up to the boiling point of the solution.

25. The process of aspects 20 or 21, wherein water removal is selected from lyophilization, spray drying, spray cooling, and filtration.

[00944] While the invention has been explained in relation to its preferred embodiments and aspcts, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the description. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

What is claimed is:

1. A self-adhering curable silicone adhesive composition comprising:

(A) an alkenyl substituted organopolysiloxane containing on average at least 0.1 alkenyl groups per molecule;

(B) an organohydrogenpolysiloxane containing on average at least 1.5 silicon-bonded hydrogen atoms per molecule in an amount that the molar ratio of the total number of the silicon-bonded hydrogen atoms of component (B) to the total quantity of all alkenyl radicals of component (A) is less than 1.3:1;

(C) a hydrosilylation catalyst;

(D) an adhesion promoter; and

(E) an adhesion catalyst in the form of microscopic particles comprising:

(a) a thermally activated semi-crystalline polymer, and

(b) at least one organometallic condensation catalyst having a metal M wherein the organometallic condensation catalyst is either admixed or encapsulated with the thermally activated semi-crystalline polymer.

2. The composition of claim 1, wherein component (A) comprises an alkenyl substituted organopolysiloxane of the formulae

$$R^1{}_3SiO(R^1{}_2SiO)_a(R^1R^2SiO)_bSiR^1{}_3,$$

$$R^3{}_2R^4SiO(R^3{}_2SiO)_c(R^3R^4SiO)_dSiR^3{}_2R^4,$$

or combinations thereof;

wherein subscript a has an average value of 0 to 2000, subscript b has an average value of at least 0.1 to 2000, each R^1 is independently a hydrocarbyl group, each R^2 is independently an unsaturated monovalent organic group, subscript c has an average value of at least 0.1 to 2000, and subscript d has an average value of 0 to 2000, each R^3 is independently a hydrocarbyl group, each R^4 is independently an unsaturated monovalent group; or

wherein component (A) comprises an MQ resin selected from $R^5{}_3SiO_{1/2}$ units and $SiO_{4/2}$ units, a TD resin selected from $R^5SiO_{3/2}$ units and $R^5{}_2SiO_{2/2}$ units, an MT resin selected from $R^5{}_3SiO_{1/2}$ units and $R^5SiO_{3/2}$ units, an MTD resin selected from $R^5{}_3SiO_{1/2}$ units, $R^5SiO_{3/2}$ units, and $R^5{}_2SiO_{2/2}$ units, or combinations thereof, wherein each R^5 is a monovalent organic group of 1 to 20 carbon atoms, and the resin contains an average of 3 to 30 mole percent of unsaturated organic groups.

3. The composition of any one of the preceding claims wherein component (B) comprises siloxane units selected from $HR^6_2SiO_{1/2}$, $R^6_3SiO_{1/2}$, $HR^6SiO_{2/2}$, $R^6_2SiO_{2/2}$, $R^6SiO_{3/2}$, $SiO_{4/2}$, or combinations thereof; where each R^6 is independently selected from monovalent organic groups free of aliphatic unsaturation; or

wherein component (B) comprises an organohydrogenpolysiloxane compound of the formulae:

$$R^7_3SiO(R^7_2SiO)_e(R^7HSiO)_fSiR^7_3,$$

$$R^8_2HSiO(R^8_2SiO)_g(R^8HSiO)_hSiR^8_2H,$$

or combinations thereof,

wherein subscript e has an average value of 0 to 2000, subscript f has an average value of 2 to 2000, each R^7 is independently a monovalent organic group free of aliphatic unsaturation, subscript g has an average value of 0 to 2000, subscript h has an average value of 0 to 2000, and each R^8 is independently a monovalent organic group free of aliphatic unsaturation.

4. The composition of any one of the preceding claims wherein component (D) is selected from an unsaturated alkoxysilane, an epoxy-functional alkoxysilane, an epoxy-functional siloxane, or a combination thereof; or

wherein component (D) comprises an alkoxysilane of the formula $R^9_iSi(OR^{10})_{(4-i)}$, wherein subscript i is 1, 2, or 3, each R^9 is independently a monovalent organic group, with the proviso that at least one R^9 is an unsaturated organic group or an epoxy-functional group, and each R^{10} is independently an unsubstituted, saturated hydrocarbon group of at least 1 carbon atom; or

where component (D) is selected from 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropyltriethoxysilane, (epoxycyclohexyl)ethyldimethoxysilane, (epoxycyclohexyl)ethyldiethoxysilane, vinyltrimethoxysilane, allyltrimethoxysilane, allyltriethoxysilane, hexenyltrimethoxysilane, undecylenyltrimethoxysilane, 3-methacryloyloxypropyl trimethoxysilane, 3-methacryloyloxypropyl triethoxysilane, 3-acryloyloxypropyl trimethoxysilane, 3-acryloyloxypropyl triethoxysilane, and combinations thereof; or

where component (D) is selected from a reaction product of a hydroxy-terminated polyorganosiloxane with an epoxy-functional alkoxysilane or an unsaturated alkoxysilane, a

physical blend of a hydroxy-terminated polyorganosiloxane with an epoxy-functional alkoxysilane or an unsaturated alkoxysilane, and combinations thereof.

5. The composition of any one of the preceding claims, wherein the thermally activated semi-crystalline polymer (E)(a) is selected from synthetic polyolefin waxes, natural paraffin waxes, and synthetic paraffin waxes; or

wherein the thermally activated semi-crystalline polymer (E)(a) is selected from synthetic polyethylene waxes and synthetic paraffin waxes; or

wherein the organometallic condensation catalyst (E)(b), is represented by the formula

$$MX_k(OR^{12})_{l-k}$$

where M is selected from Ti, Al, Zr, Sn, Cu, Ce, Co, Cr, Hf, Mo, Pd, Pt, V, and Fe, each X is independently selected from carboxylate ligands, organosulfonate ligands, organophosphate ligands, β-ketonate ligands, β-diketonate ligands, β-ketoester ligands, β-hydroxy acids, α-hydroxy acids, salicylate ligands, fluoro-substituted ligands, and chloride ligands, subscript l is the oxidation state of M, subscript k is from 0 to the value of subscript l, each R^{11} is independently an alkyl group having from 1 to 18 carbon atoms, each R^{12} is independently selected from a monovalent alkyl group having from 1 to 6 carbon atoms, an aryl group, and a polyether group of the formula

$$(R^{13}O)_mR^{14}$$

wherein subscript m is from 1 to 4, each R^{13} is independently selected from a divalent alkylene group having from 2 to 6 carbon atoms, and R^{14} is selected from a hydrogen atom or a monovalent alkyl group having from 1 to 6 carbon atoms; or

wherein the organometallic condensation catalyst (E)(b) has a ligand selected from a monodentate, bidentate, tridentate, and poldentate, and combinations thereof; or

wherein the organometallic compound (E)(b) in component (E) is within the range of 1 to 75 wt.%; or

wherein component (E) has a mean particle size of from 0.01 to 100 microns; or

wherein component (E)(a) has a mean particle size of less than 50 microns; or

wherein component (E) has a release temperature of from 35°C to 125°C.

6. A process for making the adhesion catalyst (E) described in any one of the preceding claims, the process comprising,

forming the adhesion catalyst by a single layer process or a double layer process.

7. The process of claim 6 wherein the adhesion catalyst (E) is formed by a single layer process comprising,

melting a thermally activated semi-crystalline polymer (E)(a),

adding an organometallic condensation catalyst (E)(b) to the melted (E)(a),

mixing (E)(a) and (E)(b) to obtain a homogeneous mixture,

cooling the homogeneous mixture,

adding the cooled homogeneous mixture to a hot aqueous solution to form a hot aqueous mixture,

emulsifying the hot aqueous mixture,

cooling the hot emulsified aqueous mixture, and

removing water from the cooled emulsified aqueous mixture to yield a dry powder; or

wherein the adhesion catalyst (E) is formed by a double layer process comprising,

melting a thermally activated semi-crystalline polymer (E)(a),

preparing a dispersion comprising an organometallic condensation catalyst (E)(b) and solvent and combining it with a solution comprising an amorphous polymer and solvent to form a mixture, and removing the solvent to form an encapsulated organometallic composition,

mixing the encapsulated organometallic composition with the molten thermally activated semi-crystalline polymer (E)(a) to obtain a homogeneous mixture,

cooling the homogeneous mixture,

adding the cooled homogeneous mixture to a hot aqueous solution to form a hot aqueous mixture,

emulsifying the hot aqueous mixture,

cooling the hot emulsified aqueous mixture, and

removing water from the cooled emulsified aqueous mixture to yield a dry powder.

8. The process of claim 7 wherein the amorphous polymer is selected from polyacrylates, polymethacrylates, polystyrenes, polycarbonates, and mixtures thereof; or

wherein the amorphous polymer has a glass transition temperature, Tg, of less than 140°C.

9. The process of claim 7 or 8, wherein the hot aqueous solution contains from 0.25 to 3.0 wt% of a surfactant and wherein the hot aqueous solution has a temperature of up to the boiling point of the solution.

10. The process of claim 7 or 8, wherein water removal is selected from lyophilization, spray drying, spray cooling, and filtration.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/052155

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09J183/04 B01J37/02 C08K9/10
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09J B01J C08G C08K

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.
Y	WO 2005/123839 A1 (DOW CORNING TORAY CO LTD [JP]; NAKATA TOSHIKI [JP]; ONISHI MASAYUKI [J) 29 December 2005 (2005-12-29) Practical example 1; paragraphs [0001], [0009] - [0025]	1-10
Y	US 4 766 176 A (LEE CHI-LONG [US] ET AL) 23 August 1988 (1988-08-23) columns 5,8-9	1-10
Y	US 6 040 361 A (FUJIKI HIRONAO [JP] ET AL) 21 March 2000 (2000-03-21) columns 6-7 column 5	1-10
Y	WO 99/55454 A1 (DOW CHEMICAL CO [US]; LANDEC CORP [US]) 4 November 1999 (1999-11-04) pages 1, 5-8	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
9 October 2013	16/10/2013

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Dalet, Pierre

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2013/052155

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2005123839 A1	29-12-2005	AT 458790 T	15-03-2010
		CN 1969015 A	23-05-2007
		EP 1776420 A1	25-04-2007
		JP 4733933 B2	27-07-2011
		JP 2006002093 A	05-01-2006
		KR 20070020075 A	16-02-2007
		US 2008262157 A1	23-10-2008
		WO 2005123839 A1	29-12-2005
US 4766176 A	23-08-1988	AU 603469 B2	15-11-1990
		AU 1914388 A	27-01-1989
		BR 8803632 A	08-02-1989
		CA 1306572 C	18-08-1992
		DE 3886607 D1	10-02-1994
		DE 3886607 T2	30-06-1994
		EP 0300643 A2	25-01-1989
		ES 2007268 A6	01-06-1989
		JP H0639569 B2	25-05-1994
		JP S6445468 A	17-02-1989
		US 4766176 A	23-08-1988
US 6040361 A	21-03-2000	DE 69804573 D1	08-05-2002
		DE 69804573 T2	21-11-2002
		EP 0918067 A2	26-05-1999
		US 6040361 A	21-03-2000
WO 9955454 A1	04-11-1999	AT 259257 T	15-02-2004
		AU 3666799 A	16-11-1999
		BR 9910337 A	09-01-2001
		CA 2330472 A1	04-11-1999
		CN 1298321 A	06-06-2001
		DE 69914739 D1	18-03-2004
		DE 69914739 T2	30-09-2004
		EP 1077763 A1	28-02-2001
		ES 2212552 T3	16-07-2004
		JP 2002513045 A	08-05-2002
		JP 2011072999 A	14-04-2011
		US 6224793 B1	01-05-2001
		WO 9955454 A1	04-11-1999