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(71) Demandeur/Applicant:
MOMENTIVE PERFORMANCE MATERIALS INC., US

(72) Inventeurs/Inventors:
PATEL, MIHIRKUMAR MAHESHBAI, IN;
MOHAMMAD, AMJAD BASHA, IN;
DINKAR, SUMI, IN;
DHANABALAN, ANANTHARAMAN, IN

(74) Agent: BRION RAFFOUL

(54) Titre : COMPOSITION D'ORGANOPOLYSILOXANE DURCISSABLE A L'HUMIDITE
(54) Title: MOISTURE CURABLE ORGANOPOLYSILOXANE COMPOSITION

(57) Abrégé/Abstract:

The present invention provides curable compositions comprising non-tin metal catalysts that accelerate the condensation curing of moisture-curable silicones/non-silicones. In particular, the present composition employs a catalyst system comprising an (alkyl)acrylic acid, a salt of an (alkyl)acrylic acid, or a mixture of two or more thereof. The (alkyl)acrylic acids or their salts exhibit catalytic activity comparable or superior to organotin such as dibutyltin dilaurate (DBTDL) and exhibit certain behavior in the presence of components such as adhesion promoters that allow for tuning or adjusting the cure characteristics of the present compositions and provide good adhesion and storage stability.

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(71) **Applicant**: **MOMENTIVE PERFORMANCE MATERIALS INC** [US/US]; 260 Hudson River Road, Waterford, NY 12188 (US).

(72) **Inventors**: **PATEL, Mihirkumar, Maheshbai**; B-501, Ittina Akkala, Rajpalya, Nr. Hoodi Circle, Whitefield Road, Bangalore 560048 (IN). **MOHAMMAD, Amjad, Basha**; Flat#219, Sri Sai Paradise, No. 179/2, Kothanur, Gottigere Main Road, Off. Kanakapura Main Road, Bangalore 560062 (IN). **DINKAR, Sumi**; P 302, Shriram Samruddi Apartments, Varthur Road, Bangalore 560066 (IN). **DHANABALAN, Anantharaman**; No. 7, 5th Cross, Vignan Nagar, Malleshpalaya Extension, New Thippasandra Post, Bangalore 560075 (IN).

(74) **Agent**: **SLABY, Scott, M.**; Mcdonald Hopkins LLP, 600 Superior Avenue, East, Suite 2100, Cleveland, OH 44114 (US).

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PCT PATENT APPLICATION

TITLE

MOISTURE CURABLE ORGANOPOLYSILOXANE COMPOSITION

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application No.: 61/641,438 entitled “Moisture Curable Organopolysiloxane Composition” filed on May 2, 2012, which is incorporated by reference herein in its entirety.

FIELD

[0002] The present invention relates to curable compositions comprising curable polymers having reactive terminal silyl groups and tin-free catalysts. In particular, the present invention provides curable compositions comprising an (alkyl)acrylic acid or a salt thereof as alternatives to organotin catalysts.

BACKGROUND

[0003] Polymers having reactive terminal silyl groups or compositions comprising such polymers can be hydrolyzed and condensed in the presence of water and metal catalysts. Suitable known catalysts for curable compositions include compounds employing metals such as Sn, Ti, Zn, or Ca. Organotin compounds such as, for example, dibutyltin dilaurate (DBTDL) are widely used as condensation cure catalysts to accelerate the moisture-assisted curing of a number of different polyorganosiloxanes and non-silicone polymers having reactive terminal silyl groups such as room temperature vulcanizing (RTV) formulations including RTV-1 and RTV-2 formulations. Environmental regulatory agencies and directives, however, have increased or are expected to increase restrictions on the use of organotin compounds in formulated products. For example, while formulations with greater than 0.5 wt. % dibutyltin presently require labeling as toxic with reproductive 1B classification, dibutyltin-containing formulations are proposed to be completely phased out in consumer applications during the next four to six years.

[0004] The use of alternative organotin compounds such as dioctyltin compounds and dimethyltin compounds can only be considered as a short-term remedial plan, as these organotin compounds may also be regulated in the future. It would be beneficial to identify non-tin metal catalysts that accelerate the condensation curing of moisture-curable silicones and non-silicones. Desirably, substitutes for organotin catalysts should exhibit properties similar to organotin compounds in terms of curing, storage, and appearance. Non-tin catalysts would also desirably initiate the condensation reaction of the selected polymers and complete this reaction upon the surface and may be in the bulk in a desired time schedule. There are therefore many proposals for the replacement of organometallic tin compounds with other metal-based compounds. These other metal-based compounds have specific advantages and disadvantages in view of replacing tin compounds perfectly. Therefore, there is still a need to address the limitations of possible metal compounds as suitable catalysts for condensation cure reactions. The physical properties of uncured and cured compositions also warrant examination, in particular to maintain the ability to adhere onto the surface of several substrates.

SUMMARY

[0005] The present invention provides tin-free, curable compositions comprising silyl-terminated polymers and a non-toxic condensation catalyst based on an (alkyl)acrylic acid or a salt thereof. In one aspect, the present invention provides tin-free curable compositions. In another aspect, the present invention provides a catalyst comprising an (alkyl)acrylic acid that is also a metal-free curable composition. In one embodiment, the catalyst can comprise a metal (alkyl)acrylate. In one embodiment, the catalyst comprises methacrylic acid and/or a metal methacrylate. Applicants have found that an (alkyl)acrylic acid can function as a curing catalyst in the absence of other catalytic materials. Additionally, the (alkyl)acrylic acid based catalyst materials work with a wide range of adhesion promoters and generally do not exhibit the poisoning effects that adhesion promoters may have on curable composition employing other metal-based catalyst complexes.

[0006] In one embodiment, the present invention provides a composition for forming a cured polymer composition comprising (A) a polymer having at least a reactive silyl group; (B) a crosslinker or chain extender; (C) a catalyst comprising an (alkyl)acrylic acid, a salt of an (alkyl)acrylic acid, or a mixture of two or more thereof; and (D) an optional adhesion promoter. In one embodiment, the composition further comprises (E) an optional filler component; and (F) an optional acidic compound. In one embodiment, the (alkyl)acrylic acid is methacrylic acid.

[0007] In one embodiment the catalyst comprises a salt of an (alkyl)acrylic acid, the salt of the (alkyl)acrylic acid comprising a cation chosen from a monovalent cation, a divalent cation, a trivalent cation, or a tetravalent cation. In one embodiment, the salt of the (alkyl)acrylic acid comprises a metal cation chosen from lithium, sodium, potassium, rubidium, cesium, beryllium, magnesium, calcium, strontium, barium, titanium, zirconium, hafnium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, silver, gold, zinc, scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, or a combination or two or more thereof. In one embodiment, the catalyst comprises zirconium(IV) methacrylate. In one embodiment, the composition comprises from about 0.01 to about 7 parts per weight catalyst (C) per 100 parts per weight of the polymer (A).

[0008] In one embodiment, the polymer (A) has the formula: $[R^1_aR^2_{3-a}Si–Z-]_n$-X-Z- $SiR^1_aR^2_{3-a}$. In another embodiment, X is chosen from a polyurethane; a polyester; a polyether; a polycarbonate; a polyolefin; a polyester ether; and a polyorganosiloxane having units of $R_3SiO_{1/2}$, R_2SiO, $RSiO_{3/2}$, and/or SiO_2, n is 0 to 100, a is 0 to 2, R and R^1 can be identical or different at the same silicon atom and chosen from C_1-C_{10} alkyl; C_1-C_{10} alkyl substituted with one or more of Cl, F, N, O, or S; a phenyl; C_7-C_{16} alkylaryl; C_7-C_{16} arylalkyl; C_2-C_{20}-polyalkylene ether; or a combination of two or more thereof. In yet another aspect, R^2 is chosen from OH, alkoxy, alkoxyalkyl, alkoxyaryl, oximoalkyl, oximoaryl, enoxyalkyl, enoxyaryl, aminoalkyl, aminoaryl, carboxyalkyl, carboxyaryl, amidoalkyl, amidoaryl, carbamatoalkyl, carbamatoaryl, or a combination of two or more thereof, and Z is a bond, a divalent unit selected from the group of a C_1-C_{14} alkylene, or O.

[0009] According to one embodiment, the crosslinker component (B) is chosen from tetraethylorthosilicate (TEOS), a polycondensate of TEOS, methyltrimethoxysilane (MTMS), vinyltrimethoxysilane, methylvinyldimethoxysilane, dimethyldimethoxysilane, dimethyldiethoxysilane, vinyltriethoxysilane, tetra-n-propylorthosilicate, tris(methylethylketoximo)vinylsilane, tris(methylethylketoximo)methylsilane, tris(acetamido)methylsilane, bis(acetamido)dimethylsilane, tris(*N*-methylacetamido)methylsilane, bis(*N*-methylacetamido)dimethylsilane, (*N*-methylacetamido)methyldialkoxysilane, tris(benzamido)methylsilane, tris(propenoxy)methylsilane, alkyldialkoxyamidosilanes, alkylalkoxybisamidosilanes, methylethoxybis(N-methylbenzamido)silane, methylethoxydibenzamidosilane, methyldimethoxy(ethylmethylketoximo)silane; bis(ethylmethylketoximo)methylmethoxysilane; (acetaldoximo)methyldimethoxysilane; (*N*-methylcarbamato)methyldimethoxysilane; (*N*-methylcarbamato) ethyldimethoxy silane; (isopropenoxy)methyldimethoxysilane; (isopropenoxy)trimethoxysilane;

tris(isopropenoxy)methylsilane; (but-2-en-2-oxy)methyldimethoxysilane; (1-phenylethenoxy)methyldimethoxysilane; 2-((1-carboethoxy)propenoxy) methyldimethoxysilane; bis(*N*-methylamino)methylmethoxysilane; (*N*-methylamino)vinyldimethoxysilane; tetrakis(*N*,*N*-diethylamino)silane; methyldimethoxy(*N*-methylamino)silane; methyltris(cyclohexylamino)silane; methyldimethoxy(*N*-ethylamino)silane; dimethylbis(*N*,*N*-dimethylamino)silane; methyldimethoxy(*N*-isopropylamino)silane dimethylbis(*N*,*N*-diethylamino)silane; ethyldimethoxy(*N*-ethylpropionamido)silane; methyldimethoxy(*N*-methylacetamido)silane; methyltris(*N*-methylacetamido)silane; ethyldimethoxy(*N*-methylacetamido)silane; methyltris(*N*-methylbenzamido)silane; methylmethoxybis(*N*-methylacetamido)silane; methyldimethoxy(ε-caprolactamo)silane; trimethoxy(*N*-methylacetamido)silane; methyldimethoxy(O-ethylacetimidato)silane; methyldimethoxy(O-propylacetimidato)silane; methyldimethoxy(*N*,*N*',*N*'-trimethylureido)silane; methyldimethoxy(*N*-allyl-*N*',*N*'-dimethylureido)silane; methyldimethoxy(*N*-phenyl-*N*',*N*'-dimethylureido)silane; methyldimethoxy(isocyanato)silane; dimethoxydiisocyanatosilane; methyldimethoxy-isothiocyanatosilane; methylmethoxydiisothiocyanatosilane; methyltriacetoxysilane; methylmethoxydiacetoxysilane; methylethoxydiacetoxysilane; methylisopropoxydiacetoxysilane; methyl(n-propoxy)diacetoxysilane; methyldimethoxyacetoxysilane; methyldiethoxyacetoxysilane; methyldiisopropoxyacetoxysilane; methyldi(n-propoxy)acetoxysilane; or a combination of two or more thereof.

[0010] According to one embodiment, the adhesion promoter component (D) is chosen from an (aminoalkyl)trialkoxysilane, an (aminoalkyl)alkyldialkoxysilane, a bis(trialkoxysilylalkyl)amine, a tris(trialkoxysilylalkyl)amine, a tris(trialkoxysilylalkyl)cyanuarate, a tris(trialkoxysilylalkyl)isocyanurate, an (epoxyalkyl)trialkoxysilane, an (epoxyalkylether)trialkoxysilane, or a combination of two or more thereof.

[0011] According to one embodiment, the component (F) is chosen from a phosphate ester of the formula: $(R^3O)PO(OH)_2$; a phosphite ester of the formula $(R^3O)P(OH)_2$; or a phosphonic acid of the formula: $R^3P(O)(OH)_2$. In another aspect, R^3 is a C_1-C_{18} alkyl, a C_2-C_{20} alkoxyalkyl, phenyl, a C_7-C_{12} alkylaryl, a C_2-C_4 polyalkylene oxide ester or its mixtures with diesters; a branched C_4-C_{14} alkyl carboxylic acid; or a combination of two or more thereof.

[0012] According to one embodiment, the composition comprises about 1 to about 10 wt. % of the crosslinker component (B) based on 100 wt.% of the polymer component (A).

[0013] According to one embodiment, the crosslinker component (B) is chosen from a silane or a siloxane, the silane or siloxane having two or more reactive groups that can undergo hydrolysis and/or condensation reaction with polymer (A) or on its own in the presence of water and component (F).

[0014] According to one embodiment, the polymer component (A) is chosen from a polyorganosiloxane comprising divalent units of the formula $[R_2SiO]$ in the backbone, wherein R is chosen from C_1-C_{10} alkyl; C_1-C_{10} alkyl substituted with one or more of Cl, F, N, O, or S; phenyl; C_7-C_{16} alkylaryl; C_7-C_{16} arylalkyl; C_2-C_{20} polyalkylene ether; or a combination of two or more thereof.

[0015] According to one embodiment, the catalyst (C) is present in an amount of from about 0.1 to about 7 wt. pt. per 100 wt. pt. of component (A).

[0016] According to one embodiment, the component (F) is present in an amount of from about 0.02 to about 7 wt. pt. per 100 wt. pt. of component (A).

[0017] According to one embodiment, the polymer component (A) has the formula: $R^2_{3-a}R^1_aSi\text{-}Z\text{-}[R_2SiO]_x\text{-}[R^1_2SiO]_y\text{-}Z\text{-}SiR^1_aR^2_{3-a}$ whereby x is 0 to 10000; y is 0 to 1000; a is 0 to 2; R is methyl. In another aspect, R^1 is chosen from a C_1-C_{10} alkyl; a C_1-C_{10} alkyl substituted with one or more of Cl, F, N, O, or S; a phenyl; a C_7-C_{16} alkylaryl; a C_7-C_{16} arylalkyl; a C_2-C_{20} polyalkylene ether; or a combination of two or more thereof, and other siloxane units may be present in amounts less than 10 mol.% preferably methyl, vinyl, phenyl. In yet another embodiment, R^2 is chosen from OH, a C_1-C_8 alkoxy, a C_2-C_{18} alkoxyalkyl, an oximoalkyl, an enoxyalkyl, an aminoalkyl, a carboxyalkyl, an amidoalkyl, an amidoaryl, a carbamatoalkyl, or a combination of two or more thereof, and Z is -O-, a bond, or $-C_2H_4-$.

[0018] According to one embodiment, the composition further comprises a solvent chosen from an alkylbenzene, a trialkylphosphate, a triarylphosphate, a phthalic acid ester, an arylsulfonic acid ester having a viscosity-density constant (VDC) of at least 0.86 that is miscible with a polyorganosiloxane and catalyst component (C), a polyorganosiloxane devoid of reactive groups and having a viscosity of less than 2000 mPa.s at 25 °C, or a combination of two or more thereof.

[0019] According to one embodiment, the composition is provided as a one-part composition.

[0020] According to one embodiment, the composition comprises 100 pt. wt. of component (A); 0.1 to about 10 pt. wt. of at least one crosslinker (B); 0.01 to about 7 pt. wt. of a catalyst (C); 0.1 to about 5 pt. wt. of an adhesion promoter (D); 0 to about 300 pt. wt. of component (E); 0 to about 7 pt. wt. of component (F) whereby this composition can be stored in the absence of humidity and is curable in the presence of humidity upon exposure to ambient air.

[0021] According to one embodiment, the composition is a two-part composition comprising: (i) a first portion comprising the polymer component (A), optionally the filler component (E), and optionally the acidic compound (F); and (ii) a second portion comprising the crosslinker (B), the catalyst component (C), the adhesion promoter (D), and optionally the acidic compound (F), whereby (i) and (ii) are stored separately until applied for curing by mixing of the components (i) and (ii).

[0022] According to one embodiment, portion (i) comprises 100 pt. wt. of component (A), and 0 to 70 pt. wt. of component (E); and portion (ii) comprises 0.1 to 10 pt. wt. of at least one crosslinker (B), 0.01 to 7 pt. wt. of a catalyst (C), 0 to 5 pt. wt. of an adhesion promoter (D), and 0 to 3 pt. wt. component (F). According to one embodiment, the composition comprises 100 pt. wt. of polymer component (A), 0.1 to about 10 pt. wt. of at least one crosslinker (B), 0.01 to about 7 pt. wt. of a catalyst comprising an (alkyl)acrylic acid, a salt of an (alkyl)acrylic acid, or a mixture of two or more thereof (C), 0.1 to about 5 pt. wt. of an amino-containing adhesion promoter (D), 0 to about 300 pt. wt. of a filler (E), 0 to about 7 pt. wt. of an acidic component (F), and 0.01 to about 8 pt. wt. of an auxiliary component (G), whereby this composition can be stored in the absence of humidity and is curable in the presence of humidity upon exposure to ambient air.

[0023] In another aspect, the present invention provides a method of providing a cured material comprising exposing the composition to ambient air.

[0024] According to one embodiment, a method of providing a cured material comprises combining the first portion and the second portion and curing the mixture.

[0025] According to one embodiment, the composition is stored in a sealed cartridge or flexible bag having outlet nozzles for extrusion and/or shaping of the uncured composition prior to cure.

[0026] In still another aspect, the present invention provides a cured polymer material formed from the composition.

[0027] According to one embodiment, the cured polymer material is in the form of an elastomeric or duromeric seal, an adhesive, a coating, an encapsulant, a shaped article, a mold, or an impression material.

[0028] The compositions are found to exhibit good storage stability and adhere to a variety of surfaces. In one embodiment, the curable compositions exhibit excellent adherence to thermoplastic surfaces, including polyacrylate and polymethylmethacrylate (PMMA) surfaces.

[0029] In one embodiment, the composition is a two-part composition comprising: (i) a first portion comprising the polymer component (A), optionally a filler component (E), and optionally an acidic compound (F); and (ii) a second portion comprising the crosslinker (B), the catalyst component (C), the adhesion promoter (D), and optionally the acidic compound (F), whereby (i) and (ii) are stored separately until applied for curing by mixing of the components (i) and (ii).

[0030] In one embodiment, the composition comprises 100 pt. wt. of component (A), and 0 to 70 pt. wt. of component (E); and portion (ii) comprises 0.1 to 10 pt. wt. of at least one crosslinker (B), 0.01 to 7 pt. wt. of a catalyst (C), 0 to 5 pt. wt. of an adhesion promoter (D), and 0 to 3 pt. wt. component (F).

[0031] According to one embodiment, the catalyst comprises a mixture of two or more (alkyl)acrylic acids, a mixture of at least one (alkyl)acrylic acid and at least one salt of an (alkyl)acrylic acid, a mixture of two or more salts of (alkyl)acrylic acids, or a combination thereof.

DETAILED DESCRIPTION

[0032] The present invention provides a curable composition employing a tin-free catalyst as a condensation catalyst. The catalyst comprises an (alkyl) acrylic acid or a salt thereof and exhibits similar or superior curing properties as compared to compositions employing organotin compounds, such as DBTDL, in terms of accelerating moisture-assisted condensation curing of silicones to result in cross-linked silicones that can be used as sealants and RTVs (Room-Temperature Vulcanized Rubber). The non-toxic nature of these compounds makes them more attractive and practical than organotin catalysts, given the forthcoming strict regulations on organotin catalysts.

[0033] In one embodiment, the present invention provides a curable composition comprising a polymer component (A) comprising a reactive terminal silyl group; a crosslinker component (B); a catalyst component (C) comprising an (alkyl)acrylic acid compound or a salt thereof; optionally an adhesion promoter component (D); an optional filler component (E); optionally an acidic compound (F), and optionally auxiliary components (G).

[0034] The polymer component (A) may be a liquid- or solid-based polymer having a reactive terminal silyl group. The polymer component (A) is not particularly limited and may be chosen from any cross-linkable polymer as may be desired for a particular purpose or intended use. Non-limiting examples of suitable polymers for the polymer component (A) include polyorganosiloxanes (A1) or organic polymers free of siloxane bonds (A2), wherein the polymers (A1) and (A2) comprise reactive terminal silyl groups. In one embodiment, the polymer component (A) may be present in an amount of from about 10 to about 90 wt. % of the curable composition. In one embodiment, the curable composition comprises about 100 pt. wt. of the polymer component (A).

[0035] As described above, the polymer component (A) may include a wide range of polyorganosiloxanes. In one embodiment, the polymer component may comprise one or more polysiloxanes and copolymers of formula (2):

$$[R^1_cR^2_{3-c}Si–Z–]_n–X–Z–SiR^1_cR^2_{3-c} \qquad (2)$$

R^1 may be chosen from linear or branched alkyl, linear or branched heteroalkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, linear or branched aralkyl, linear or branched heteroaralkyl, or a combination of two or more thereof. In one embodiment, R^1 may be chosen from C_1-C_{10} alkyl; C_1-C_{10} alkyl substituted with one or more of Cl, F, N, O, or S; phenyl; C_7-C_{16} alkylaryl; C_7-C_{16} arylalkyl; C_2-C_{20} polyalkylene ether; or a combination of two or more thereof. Exemplary preferred groups are methyl, trifluoropropyl, and/or phenyl groups.

[0036] R^2 may be a group reactive to protic agents such as water. Exemplary groups for R^2 include OH, alkoxy, alkoxyalkyl, alkenyloxy, alkyloximo, alkylcarboxy, arylcarboxy, alkylamido, arylamido, or a combination of two or more thereof. In one embodiment, R^2 is chosen from OH, C_1-C_8 alkoxy, C_2-C_{18} alkoxyalkyl, amino, alkenyloxy, alkyloximo, alkylamino, arylamino, alkylcarboxy, arylcarboxy, alkylamido, arylamido, alkylcarbamato, arylcarbamato, or a combination of two or more thereof.

[0037] Z may be a bond, a divalent linking unit selected from the group of O, hydrocarbons which can contain one or more O, S, or N atom, amide, urethane, ether, ester, urea units or a combination of two or more thereof. If the linking group Z is a hydrocarbon group, then Z is linked to the silicon atom over a silicon-carbon bond. In one embodiment, Z is chosen from a C_1-C_{14} alkylene.

[0038] X is chosen from a polyurethane; a polyester; a polyether; a polycarbonate; a polyolefin; a polyester ether; and a polyorganosiloxane having units of $R^1_3SiO_{1/2}$, R^1_2SiO, $R^1SiO_{3/2}$, and/or SiO_2, where R^1 is defined as above. X may be a divalent or multivalent polymer unit selected from the group of siloxy units linked over oxygen or hydrocarbon groups to the terminal silyl group comprising the reactive group R^2 as described above, polyether, alkylene, isoalkylene, polyester, or polyurethane units linked over hydrocarbon groups to the silicon atom comprising one or more reactive groups R^2 as described above. The hydrocarbon group X can contain one or more heteroatoms such as N, S, O, or P forming amides, esters, ethers, urethanes, esters, and/or ureas. In one embodiment, the average polymerization degree (P_n) of X should be more than 6, e.g. polyorganosiloxane units of $R^1_3SiO_{1/2}$, R^1_2SiO, $R^1SiO_{3/2}$, and/or SiO_2. In formula (2), n is 0 to 100; desirably 1, and c is 0 to 2, desirably 0 to 1.

[0039] Non-limiting examples of the components for unit X include polyoxyalkylene polymers such as polyoxyethylene, polyoxypropylene, polyoxybutylene, polyoxyethylene-polyoxypropylene copolymer, polyoxytetramethylene, or polyoxypropylene-polyoxybutylene copolymer; ethylene-propylene copolymer, polyisobutylene, polychloroprene, polyisoprene, polybutadiene, copolymer of isobutylene and isoprene, copolymers of isoprene or butadiene and acrylonitrile and/or styrene, or hydrocarbon polymers such as hydrogenated polyolefin polymers produced by hydrogenating these polyolefin polymers; polyester polymer manufactured by a condensation of dibasic acid such as adipic acid or phthalic acid and glycol, or ring-opening polymerization of lactones; polyacrylic acid ester produced by radical polymerization of a monomer such as C_2-C_8-alkyl acrylates, vinyl polymers, e.g., acrylic acid ester copolymer of acrylic acid ester such as ethyl acrylate or butyl acrylate and vinyl acetate, acrylonitrile, methyl methacrylate, acrylamide, or styrene; graft polymer produced by polymerizing the above organic polymer with a vinyl monomer; polycarbonates; polysulfide polymer; polyamide polymer such as Nylon 6 produced by ring-opening polymerization of ε-caprolactam, Nylon 6-6 produced by polycondensation of hexamethylenediamine and adipic acid, etc., Nylon 12 produced by ring-opening polymerization of ε-laurolactam, copolymeric polyamides, polyurethanes, or polyureas.

[0040] Particularly suitable polymers include, but are not limited to, polysiloxanes, polyoxyalkylenes, saturated hydrocarbon polymers such as polyisobutylene, hydrogenated polybutadiene and hydrogenated polyisoprene, or polyethylene, polypropylene, polyesters, polycarbonates, polyurethanes, polyurea polymers and the like. Furthermore, saturated hydrocarbon polymer, polyoxyalkylene polymer, and vinyl copolymer are particularly suitable due to their low glass transition temperature which provide a high flexibility at low temperatures, i.e., below 0 °C.

[0041] The reactive silyl groups in formula (2) can be introduced by employing silanes containing a functional group which has the ability to react by known methods with unsaturated hydrocarbons via hydrosilylation, or reaction of SiOH, aminoalkyl or -aryl, HOOC-alkyl or -aryl, HO-alkyl or -aryl, HS-alkyl or -aryl, Cl(O)C-alkyl or -aryl, epoxyalkyl or epoxycycloalkyl groups in the prepolymer to be linked to a reactive silyl group via condensation or ring-opening reactions. Examples of the main embodiments include the following: (i) siloxane prepolymers having a SiOH group that can undergo a condensation reaction with a silane $(LG)SiR^1{}_cR^2{}_{3-c}$ whereby a siloxy bond $\equiv Si\text{-}O\text{-}SiR^1{}_cR^2{}_{3-c}$ is formed while the addition product of the leaving group (LG) and hydrogen is released (LG-H); (ii) silanes having an unsaturated group that is capable of reacting via hydrosilylation or radical reaction with a SiH group or radically activated groups of a silane such as SiH or an unsaturated group; and (iii) silanes including organic or inorganic prepolymers having OH, SH, amino, epoxy, -COCl, -COOH groups, which can react complementarily with epoxy, isocyanato, OH, SH, cyanato, carboxylic halogenides, reactive alkylhalogenides, lactones, lactams, or amines, that is to link the reactive prepolymer with the organofunctional silanes to yield a silyl functional polymer.

[0042] Silanes suitable for method (i) include alkoxysilanes, especially tetraalkoxysilanes, di- and trialkoxysilanes, di- and triacetoxysilanes, di- and triketoximosilanes, di- and trialkenyloxysilanes, di- and tricarbonamidosilanes, wherein the remaining residues at the silicon atom of the silane are substituted or unsubstituted hydrocarbons. Other non-limiting silanes for method (i) include alkyltrialkoxysilanes, such as vinyltrimethoxysilane, methyltrimethoxysilane, propyltrimethoxysilane, aminoalkyltrimethoxysilane, ethyltriacetoxysilane, methyl- or propyltriacetoxysilane, methyltributanonoximosilane, methyltripropenyloxysilane, methyltribenzamidosilane, or methyltriacetamidosilane. Prepolymers suitable for reaction under method (i) are SiOH-terminated polyalkylsiloxanes, which can undergo a condensation reaction with a silane having hydrolyzable groups attached to the silicon atom. Exemplary SiOH-terminated polyalkyldisiloxanes include polydimethylsiloxanes.

[0043] Suitable silanes for method (ii) include alkoxysilanes, especially trialkoxysilanes ($HSi(OR)_3$) such as trimethoxysilane, triethoxysilane, methyldiethoxysilane, methyldimethoxysilane, and phenyldimethoxysilane. Hydrogenchlorosilanes are in principle possible but are less desirable due to the additional replacement of the halogen through an alkoxy, acetoxy group, etc. Other suitable silanes include organofunctional silanes having unsaturated groups which can be activated by radicals, such as vinyl, allyl, mercaptoalkyl, or acrylic groups. Non-limiting examples include vinyltrimethoxysilane, mercaptopropyltrimethoxysilane, and methacryloxypropyltrimethoxysilane. Prepolymers suitable for reaction under method (ii) include vinyl-terminated polyalkylsiloxanes, preferably polydimethylsiloxanes, hydrocarbons with unsaturated groups which can undergo hydrosilylation or can undergo radically induced grafting reactions with a corresponding organofunctional group of a silane comprising, for example, unsaturated hydrocarbon or a SiH group.

[0044] Another method for introducing silyl groups into hydrocarbon polymers can be the copolymerization of unsaturated hydrocarbon monomers with the unsaturated groups of silanes. The introduction of unsaturated groups into a hydrocarbon prepolymer may include, for example, the use of alkenyl halogenides as chain stopper after polymerization of the silicon free hydrocarbon moiety.

[0045] Desirable reaction products between the silanes and prepolymers include the following structures:

$$-SiR^1_2O-SiR^1_2-CH_2-CH_2-SiR^1_cR^2_{3-c}, \text{ or (hydrocarbon)}-[Z-SiR^1_cR^2_{3-c}]_n$$

[0046] Suitable silanes for method (iii) include, but are not limited to, alkoxysilanes, especially silanes having organofunctional groups to be reactive to -OH, -SH, amino, epoxy, -COCl, or –COOH.

[0047] In one embodiment, these silanes have an isocyanatoalkyl group such as gamma-isocyanatopropyltrimethoxysilane, gamma-isocyanatopropylmethyldimethoxysilane, gamma-isocyanatopropyltriethoxysilane, gamma-glycidoxypropylethyldimethoxysilane, gamma-glycidoxypropyltrimethoxysilane, gamma-glycidoxypropyltriethoxysilane, beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, beta-(3,4-epoxycyclohexyl)ethyltriethoxysilane, epoxylimonyltrimethoxysilane, *N*-(2-aminoethyl)-aminopropyltrimethoxysilane, gamma-aminopropyltriethoxysilane, gamma-aminopropyltrimethoxysilane, gamma-aminopropylmethyldimethoxysilane, gamma-aminopropylmethyldiethoxysilane, etc.

[0048] In one embodiment, it is desirable to select either blocked amines or isocyanates $(Z'-X)_n-Z'$ for carrying out first a complete mixing and then the following coupling reaction. Examples of blocking agents are disclosed in EP 0947531 and other blocking procedures that employ heterocyclic nitrogen compounds such as caprolactam or butanone oxime, or cyclic ketones referred to in U.S. Patent 6,827,875 both of which are incorporated herein by reference in their entirety..

[0049] Examples of suitable prepolymers for a reaction under method (iii) include, but are not limited to, polyalkylene oxides having OH groups, preferably with a high molecular weight (M_w, weight-average molecular weight > 6000 g/mol) and a polydispersity M_w/M_n of less than 1.6; urethanes having remaining NCO groups, such as NCO functionalized polyalkylene oxides, especially blocked isocyanates. Prepolymers selected from the group of hydrocarbons having –OH, -COOH, amino, epoxy groups, which can react complementarily with an epoxy, isocyanato, amino, carboxyhalogenide or halogenalkyl group of the corresponding silane having further reactive groups useful for the final cure.

[0050] Suitable isocyanates for the introduction of a NCO group into a polyether may include toluene diisocyanate, diphenylmethane diisocyanate, or xylene diisocyanate, or aliphatic polyisocyanate such as isophorone diisocyanate, or hexamethylene diisocyanate.

[0051] The polymerization degree of the unit X depends on the requirements of viscosity and mechanical properties of the cured product. If X is a polydimethylsiloxane unit, the average polymerization degree based on the number average molecular weight M_n is preferably 7 to 5000 siloxy units, preferably 200 to2000 units. In order to achieve a sufficient tensile strength of > 5 MPa, an average polymerization degree P_n of > 250 is suitable whereby the polydimethylsiloxanes have a viscosity of more than 300 mPa.s at 25 °C. If X is a hydrocarbon unit other than a polysiloxane unit, the viscosity with respect to the polymerization degree is much higher.

[0052] Examples of the method for synthesizing a polyoxyalkylene polymer include, but are not limited to, a polymerization method using an alkali catalyst such as KOH, a polymerization method using a metal-porphyrin complex catalyst such as a complex obtained by reacting an organoaluminum compound, a polymerization method using a composite metal cyanide complex catalyst disclosed, e.g., in U.S. Patent Nos. 3,427,256; 3,427,334; 3,278,457; 3,278,458; 3,278,459; 3,427,335; 6,696,383; and 6,919,293.

[0053] If the group X is selected from hydrocarbon polymers, then polymers or copolymers having isobutylene units are particularly desirable due to its physical properties such as excellent weatherability, excellent heat resistance, and low gas and moisture permeability.

[0054] Examples of the monomers include olefins having 4 to 12 carbon atoms, vinyl ether, aromatic vinyl compound, vinylsilanes, and allylsilanes. Examples of the copolymer component include 1-butene, 2-butene, 2-methyl-1-butene, 3-methyl-1-butene, pentene, 4-methyl-1-pentene, hexene, vinylcyclohexene, methyl vinyl ether, ethyl vinyl ether, isobutyl vinyl ether, styrene, alpha-methylstyrene, dimethylstyrene, beta-pinene, indene, and for example, but not limited to, vinyltrialkoxysilanes, e.g. vinyltrimethoxysilane, vinylmethyldichlorosilane, vinyldimethylmethoxysilane, divinyldichlorosilane, divinyldimethoxysilane, allyltrichlorosilane, allylmethyldichlorosilane, allyldimethylmethoxysilane, diallyldichlorosilane, diallyldimethoxysilane, gamma-methacryloyloxypropyltrimethoxysilane, and gamma-methacryloyloxypropylmethyldimethoxysilane.

[0055] Examples of suitable siloxane-free organic polymers include, but are not limited to, silylated polyurethane (SPUR), silylated polyester, silylated polyether, silylated polycarbonate, silylated polyolefins like polyethylene, polypropylene, silylated polyesterether and combinations of two or more thereof. The siloxane-free organic polymer may be present in an amount of from about 10 to about 90 wt. % of the composition or about 100 pt. wt.

[0056] In one embodiment, the polymer component (A) may be a silylated polyurethane (SPUR). Such moisture curable compounds are known in the art in general and can be obtained by various methods including (i) reacting an isocyanate-terminated polyurethane (PUR) prepolymer with a suitable silane, e.g., one possessing both hydrolyzable functionality at the silicon atom, such as, alkoxy, etc., and secondly active hydrogen-containing functionality such as mercaptan, primary or secondary amine, preferably the latter, etc., or by (ii) reacting a hydroxyl-terminated PUR (polyurethane) prepolymer with a suitable isocyanate-terminated silane, e.g., one possessing one to three alkoxy groups. The details of these reactions and those for preparing the isocyanate-terminated and hydroxyl-terminated PUR prepolymers employed therein can be found in, amongst others: U.S. Pat. Nos. 4,985,491; 5,919,888; 6,207,794; 6,303,731; 6,359,101; and 6,515,164, and published U.S. Patent Publication Nos. 2004/0122253 and US 2005/0020706 (isocyanate-terminated PUR prepolymers); U.S. Pat. Nos. 3,786,081 and 4,481,367 (hydroxyl-terminated PUR prepolymers); U.S. Pat. Nos. 3,627,722; 3,632,557; 3,971,751; 5,623,044; 5,852,137;

6,197,912; and 6,310,170 (moisture-curable SPUR (silane modified/terminated polyurethane) obtained from reaction of isocyanate-terminated PUR prepolymer and reactive silane, e.g., aminoalkoxysilane); and, U.S. Pat. Nos. 4,345,053; 4,625,012; 6,833,423; and published U.S. Patent Publication 2002/0198352 (moisture-curable SPUR obtained from reaction of hydroxyl-terminated PUR prepolymer and isocyanatosilane). The entire contents of the foregoing U.S. patent documents are incorporated by reference herein. Other examples of moisture-curable SPUR materials include those described in U.S. Pat. No. 7,569,653, the disclosure of which is incorporated by reference in its entirety.

[0057] In one embodiment, the polymer component (A) may be a polymer of formula (3):

$$R^2_{3-c}R^1_cSi\text{-}Z\text{-}[R_2SiO]_x\,[R^1_2SiO]_y\,\text{-}Z\text{-}SiR^1_cR^2_{3-c} \qquad (3)$$

where R^1, R^2, Z, and c are defined as above with respect to formula (3); R is C_1-C_6 alkyl (an exemplary alkyl being methyl); x is 0 to about 10,000, in one embodiment from 11 to about 2500; and y is 0 to about 10,000; preferably 0 to 500. In one embodiment, Z in a compound of formula (3) is a bond or a divalent C_1-C_{14} alkylene group, especially preferred is $-C_2H_4-$.

[0058] In one embodiment, the polymer component (A) may be a polyorganosiloxane of the formula (4):

$$R^2_{3-c-d}SiR^3_cR^4_d\text{-}[OSiR^3R^4]_x\text{-}[OSiR^3R^4]_y\text{-}OSiR^3_eR^4_fR^2_{3-e-f}\,(4)$$

R^3 and R^4 can be identical or different on the same silicon atom and are chosen from hydrogen; C_1-C_{10} alkyl; C_1-C_{10} heteroalkyl, C_3-C_{12} cycloalkyl; C_2-C_{30} heterocycloalkyl; C_6-C_{13} aryl; C_7-C_{30} alkylaryl; C_7-C_{30} arylalkyl; C_4-C_{12} heteroaryl; C_5-C_{30} heteroarylalkyl; C_5-C_{30} heteroalkylaryl; C_2-C_{100} polyalkylene ether; or a combination of two or more thereof. R^2, c, x, and y are as defined above; d is 0, 1, or 2; e is 0, 1, or 2; and f is 0, 1, or 2.

[0059] Non-limiting examples of suitable polysiloxane-containing polymers (A1) include, for example, silanol-stopped polydimethylsiloxane, silanol or alkoxy-stopped polyorganosiloxanes, e.g., methoxystopped polydimethylsiloxane, alkoxy-stopped polydimethylsiloxane-polydiphenylsiloxane copolymer, and silanol or alkoxy-stopped fluoroalkyl-substituted siloxanes such as poly(methyl 3,3,3-trifluoropropyl)siloxane and poly(methyl 3,3,3-trifluoropropyl)siloxane-polydimethyl siloxane copolymer. The polyorganosiloxane component (A1) may be present in an amount of about 10 to about 90 wt. % of the composition or 100 pt. wt. In one preferred embodiment, the polyorganosiloxane component has an average chain length in the range of about 10 to about 2500 siloxy units, and the viscosity is in the range of about 10 to about 500,000 mPa.s at 25 °C.

[0060] Alternatively, the composition may include silyl-terminated organic polymers (A2) that are free of siloxane units, and which undergo curing by a condensation reaction comparable to that of siloxane containing polymers (A1). Similar to the polyorganosiloxane polymer (A1), the organic polymers (A2) that are suitable as the polymer component (A) include a terminal silyl group. In one embodiment, the terminal silyl group may be of the formula (5):

$$-SiR^1_dR^2_{3-d} \qquad (5)$$

where R^1, R^2, and d are as defined above.

[0061] The polysiloxane composition may further include a crosslinker or a chain extender as component (B). In one embodiment, the crosslinker is of the formula (6):

$$R^1_dSiR^2_{4-d} \qquad (6)$$

wherein R^1, R^2, and d are as defined above. Alternatively, the crosslinker component may be a condensation product of formula (6) wherein one or more but not all R^2 groups are hydrolyzed and released in the presence of water and then intermediate silanols undergo a condensation reaction to give a Si-O-Si bond and water. The average polymerization degree can result in a compound having 2 to 10 Si units.

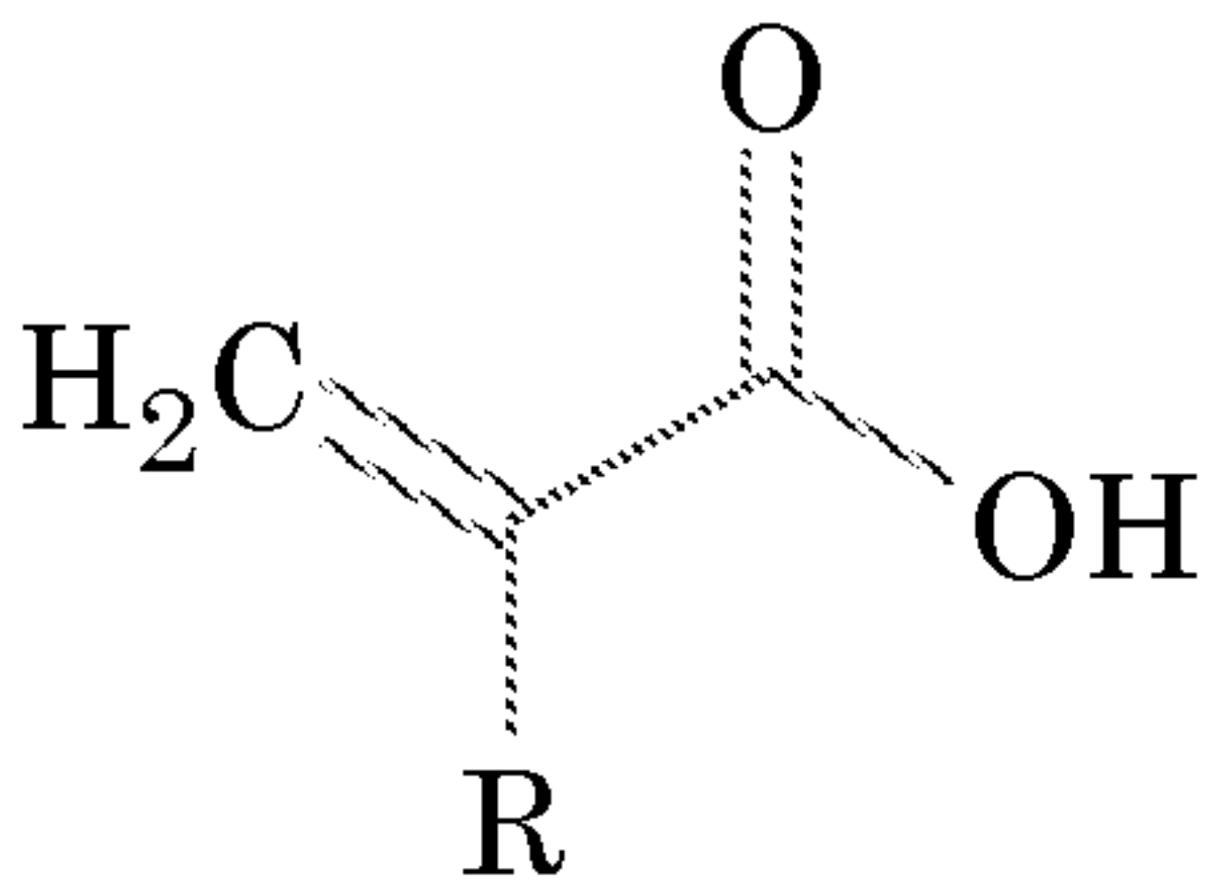
In one embodiment, the crosslinker is an alkoxysilane having a formula $R^3_d(R^1O)_{4-d}Si$, wherein R^1, R^3, and d are defined as above. In another embodiment, the crosslinker is an acetoxysilane having a formula $(R^3{}_d(R^1CO_2)_{4-d}Si$, wherein R^1, R^3, and d are defined as above. In still another embodiment, the crosslinker is an oximosilane having a formula $R^3{}_d(R^1R^4C{=}N{-}O)_{4-d}Si$, where R^1, R^3, R^4, and d are defined as above.

[0062] As used herein, the term crosslinker includes a compound including an additional reactive component having at least two hydrolysable groups and less than three silicon atoms per molecule not defined under (A). In one embodiment, the crosslinker or chain extender may be chosen from an alkoxysilane, an alkoxysiloxane, an oximosilane, an oximosiloxane, an enoxysilane, an enoxysiloxane, an aminosilane, an aminosiloxane, a carboxysilane, a carboxysiloxane, an alkylamidosilane, an alkylamidosiloxane, an arylamidosilane, an arylamidosiloxane, an alkoxyaminosilane, an alkylarylaminosiloxane, an alkoxycarbamatosilane, an alkoxycarbamatosiloxane, an imidatosilane, a ureidosilane, an isocyanatosilane, a isothiocyanatosilane, and combinations of two or more thereof. Examples of suitable cross-linkers include, but are not limited to, tetraethylorthosilicate (TEOS); methyltrimethoxysilane (MTMS); methyltriethoxysilane; vinyltrimethoxysilane; vinyltriethoxysilane; methylphenyldimethoxysilane; 3,3,3-trifluoropropyltrimethoxysilane; methyltriacetoxysilane; vinyltriacetoxysilane; ethyltriacetoxysilane; di-butoxydiacetoxysilane; phenyltripropionoxysilane; methyltris(methylethylketoximo)silane; vinyltris(methylethylketoximo)silane; 3,3,3-trifluoropropyltris(methylethylketoximo)silane; methyltris(isopropenoxy)silane; vinyltris(isopropenoxy)silane; ethylpolysilicate; dimethyltetraacetoxydisiloxane; tetra-n-propylorthosilicate; methyldimethoxy(ethylmethylketoximo)silane; methylmethoxybis(ethylmethylketoximo)silane; methyldimethoxy(acetaldoximo)silane; methyldimethoxy(*N*-methylcarbamato)silane; ethyldimethoxy(*N*-methylcarbamato)silane; methyldimethoxyisopropenoxysilane; trimethoxyisopropenoxysilane; methyltriisopropenoxysilane; methyldimethoxy(but-2-en-2-

oxy)silane; methyldimethoxy(1-phenylethenoxy)silane; methyldimethoxy-2-(1-carboethoxypropenoxy)silane; methylmethoxydi(*N*-methylamino)silane; vinyldimethoxy(methylamino)silane; tetra-*N*,*N*-diethylaminosilane; methyldimethoxy(methylamino)silane; methyltri(cyclohexylamino)silane; methyldimethoxy(ethylamino)silane; dimethyldi(*N*,*N*-dimethylamino)silane; methyldimethoxy(isopropylamino)silane; dimethyldi(*N*,*N*-diethylamino)silane; ethyldimethoxy(*N*-ethylpropionamido)silane; methyldimethoxy(*N*-methylacetamido)silane; methyltris(*N*-methylacetamido)silane; ethyldimethoxy(*N*-methylacetamido)silane; methyltris(*N*-methylbenzamido)silane; methylmethoxybis(*N*-methylacetamido)silane; methyldimethoxy(caprolactamo)silane; trimethoxy(*N*-methylacetamido)silane; methyldimethoxy(ethylacetimidato)silane; methyldimethoxy(propylacetimidato)silane; methyldimethoxy(*N*,*N'*,*N'*-trimethylureido)silane; methyldimethoxy(*N*-allyl-*N'*,*N'*-dimethylureido)silane; methyldimethoxy(*N*-phenyl-*N'*,*N'*-dimethylureido)silane; methyldimethoxyisocyanatosilane; dimethoxydiisocyanatosilane; methyldimethoxyisothiocyanatosilane; methylmethoxydiisothiocyanatosilane, or combinations of two or more thereof. In one embodiment, the crosslinker may be present in an amount from about 1 to about 10 wt. % of the composition or from about 0.1 to about 10 pt. wt. per 100 pt. wt. of the polymer component (A). In another embodiment, the crosslinker may be present in an amount from about 0.1 to about 5 pt. wt. per 100 pt. wt. of the polymer component (A). In still another embodiment, the crosslinker may be present in an amount from about 0.5 to about 3 pt. wt. per 100 pt. wt. of the polymer component (A). Here as elsewhere in the specification and claims, numerical values may be combined to form new or undisclosed ranges.

[0063] Additional alkoxysilanes in an amount greater than 0.1 wt.% of component (A) that are not consumed by the reaction between the prepolymer Z′-X-Z′ and which comprise additional functional groups selected from R^5 can also work as an adhesion promoter and are defined and counted under component (D).

[0064] The curable compositions further comprise catalyst (C) comprising a (alkyl)acrylic acid or a salt thereof. As used herein, an (alkyl)acrylic acid includes acrylic acids of the formula (7):



(7)

where R can be chosen from hydrogen or an alkyl group having 1 to 4 carbon atoms. In one embodiment, the (alkyl)acrylic acid is acrylic acid. In another embodiment, the (alkyl)acrylic acid is methacrylic acid.

[0065] In one embodiment, the catalyst component (C) comprises a salt of an (alkyl)acrylic acid. The salt of the (alkyl)acrylic acid may comprise any suitable metal cation. In one embodiment, the metal cation can be chosen from a monovalent, divalent, trivalent, or tetravalent cation. Suitable metal cations include, but are not limited to, alkali metals such as lithium, sodium, potassium, rubidium or cesium; alkali-earth metals such as beryllium, magnesium, calcium, strontium or barium; rare-earth metals such as scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium or the like; transition metals such as titanium, zirconium, hafnium, niobium, tantalum, molybdenum, tungsten, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, silver, gold, zinc, or the like.

[0066] In one embodiment the catalyst comprise a metal methacrylate chosen from Zr (IV) methacrylate, hafnium (IV) methacrylate or a combination thereof.

[0067] The catalyst composition (C) can comprise a mixture of (alkyl)acrylic acids and/or salts thereof, e.g., metal (alkyl)acrylates. In one embodiment, the catalyst composition comprises a mixture of two or more (alkyl)acrylic acids. In another embodiment, the catalyst composition comprises a mixture of at least one (alkyl)acrylic acid and at least one salt of an (alkyl)acrylic acid. In still another embodiment, the catalyst composition comprises a mixture of two or more salts of (alkyl)acrylic acids, e.g., a mixture of two or more metal (alkyl)acrylates.

[0068] The catalyst component (C) comprising the (alkyl)acrylic acid compound can be present in the curable composition in an amount of from about 0.01 to about 7 parts per weight per 100 parts per weight of the polymer (A); from about 0.05 to about 5 parts per weight per 100 parts per weight of the polymer (A); from about 0.1 to about 2 parts per weight per 100 parts per weight of the polymer (A); even from about 0.2 to about 1 parts per weight per 100 parts per weight of the polymer (A). Here as elsewhere in the specification and claims, numerical values may be combined to form new and non-disclosed ranges. Applicants have found that the curing rate, at least as measured by tack-free time (TFT), can be increased or decreased by increasing or decreasing the loading of the (alkyl)acrylic acid compounds.

[0069] The composition optionally includes an adhesion promoter component (D) that is different from component (A) or (B). In one embodiment, the adhesion promoter (D) may be an organofunctional silane comprising the group R^5, e.g., aminosilanes, and other silanes that are not identical to the silanes of component (B), or are present in an amount that exceeds the amount of silanes necessary for endcapping the polymer (A). The amount of non-reacted silane (B) or (D) in the reaction for making (A) can be defined in that after the endcapping reaction the free silanes are evaporated at a higher temperature up to 200 °C and vacuum up to 1 mbar to be more than 0.1 wt.% of (A).

[0070] While the (alkyl)acrylic acid catalysts can exhibit cure properties at least as good as tin catalysts, the adhesion promoters can be added to promote adhesion of the resulting cured material to a variety of substrates. It has been found that the (alkyl)acrylic acid catalyst materials can be utilized with a variety of adhesion promoters without loss in catalytic activity as has been found with some metal-based, non-tin catalysts. The combination of the adhesion promoter with the (alkyl)acrylic acid catalyst can provide a composition exhibiting improved curing characteristics compared to the (alkyl)acrylic acid compound alone. Thus, some selected amines can advantageously be added to fine tune the rate of the (alkyl)acrylic acid catalyzed condensation curing of silicone/non-silicone polymer containing reactive silyl groups, as desired.

[0071] In one embodiment, the composition comprises an adhesion promoter (D) comprising a group R^5 as described by the general formula (8):

$$R^5{}_gR^1{}_dSi(R^2)_{4-d-g} \qquad (8)$$

where R^5 is $E\text{-}(CR^3{}_2)_h\text{-}W\text{-}(CH_2)_h\text{-}$; R^1, R^2, and d are as described above; g is 1 or 2; d + g = 1 to 2; and h is 0 to 8, and may be identical or different.

Non-limiting examples of suitable compounds include:

$$E^1\text{-}(CR^3{}_2)_h\text{-}W\text{-}(CH_2)_h\text{-}SiR^1{}_d(R^2)_{3-d} \qquad \text{(8a) or (8d)}$$

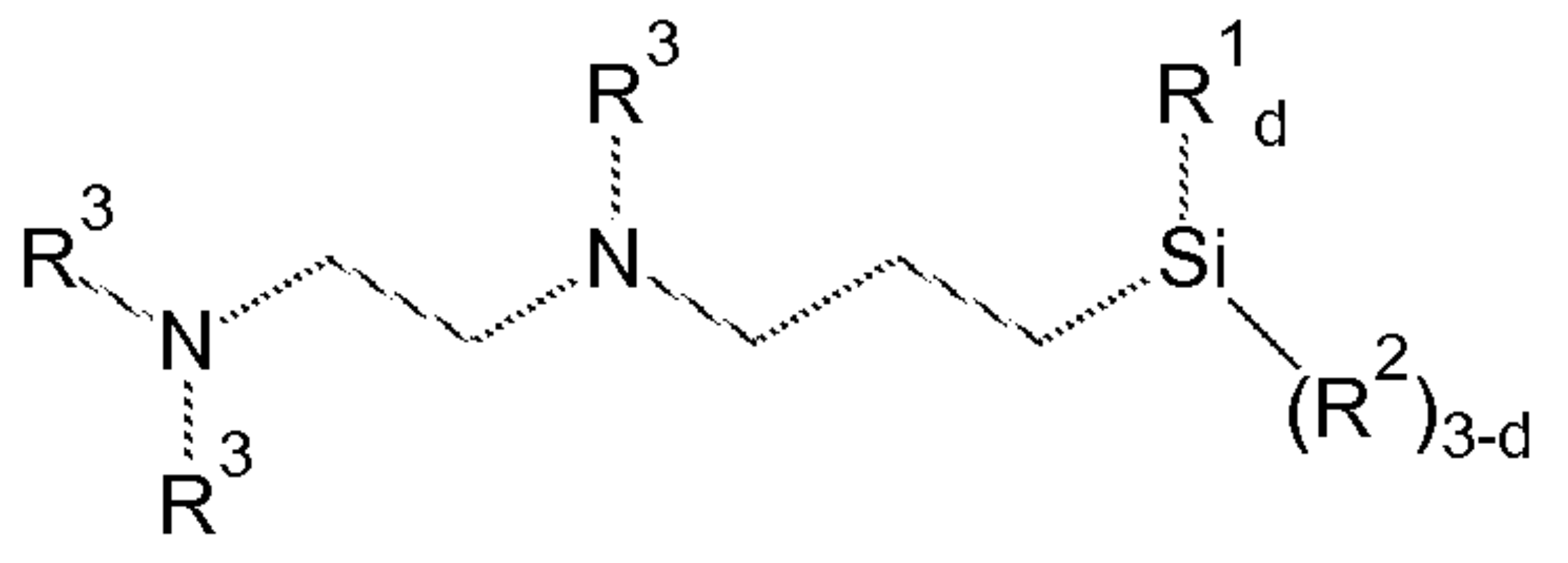
$$E^2\text{-}[(CR^3{}_2)_h\text{-}W\text{-}(CH_2)_h\text{-}SiR^1{}_d(R^2)_{3-d}]_j \qquad \text{(8b) or (8f)}$$

where j is 2 to 3.

[0072] The group E may be selected from either a group E^1 or E^2. E^1 may be selected from a monovalent group comprising amine, $-NH_2$, $-NHR$, $-(NHC_2H_5)_aNHR$, NHC_6H_5, halogen, pseudohalogen, unsaturated aliphatic group with up to 14 carbon atoms, epoxy-group-containing aliphatic group with up to 14 carbon atoms, cyanurate-containing group, and an isocyanurate-containing group.

[0073] E^2 may be selected from a group comprising a di- or multivalent group consisting of amine, polyamine, cyanurate–containing, and an isocyanurate–containing group, sulfide, sulfate, phosphate, phosphite, and a polyorganosiloxane group, which can contain R^5 and R^2 groups; W is selected from the group consisting of a single bond, a heteroatomic group selected from –COO–, –O–, epoxy, –S–, –CONH–, –HN–CO–NH– units; R^3 is as defined above, R^1 may be identical or different as defined above, R^2 is defined as above and may be identical or different.

[0074] Non-limiting examples of component (D) include:



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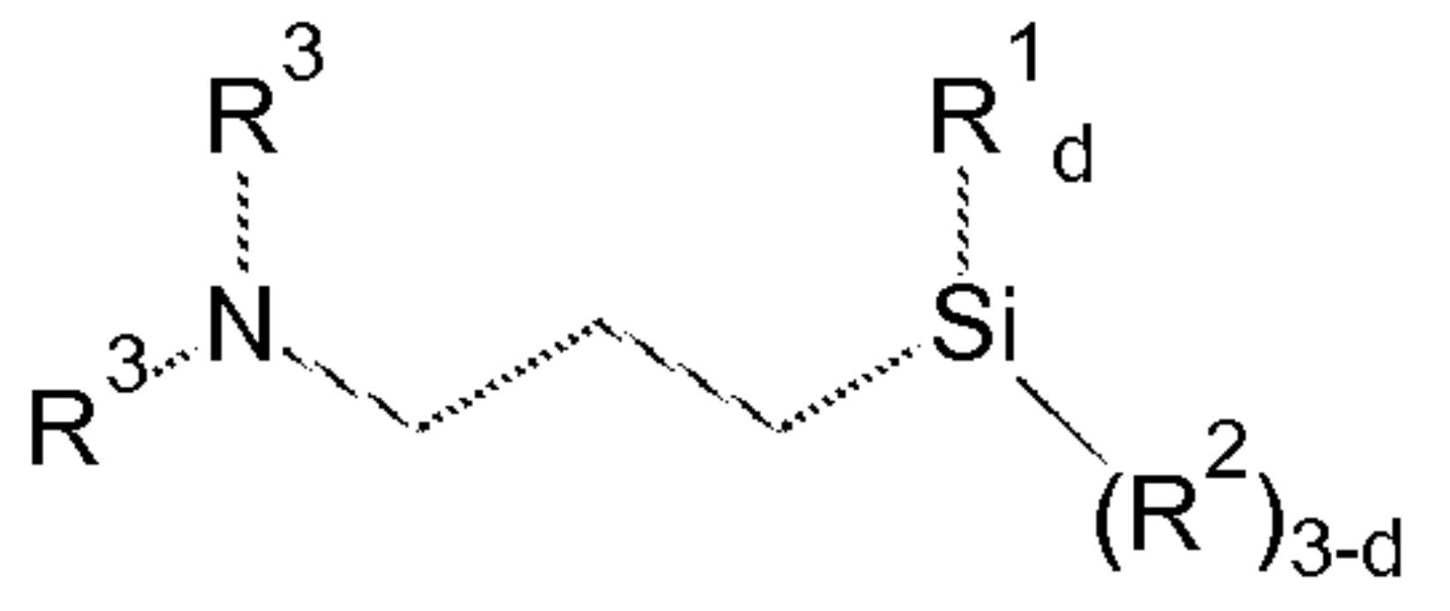

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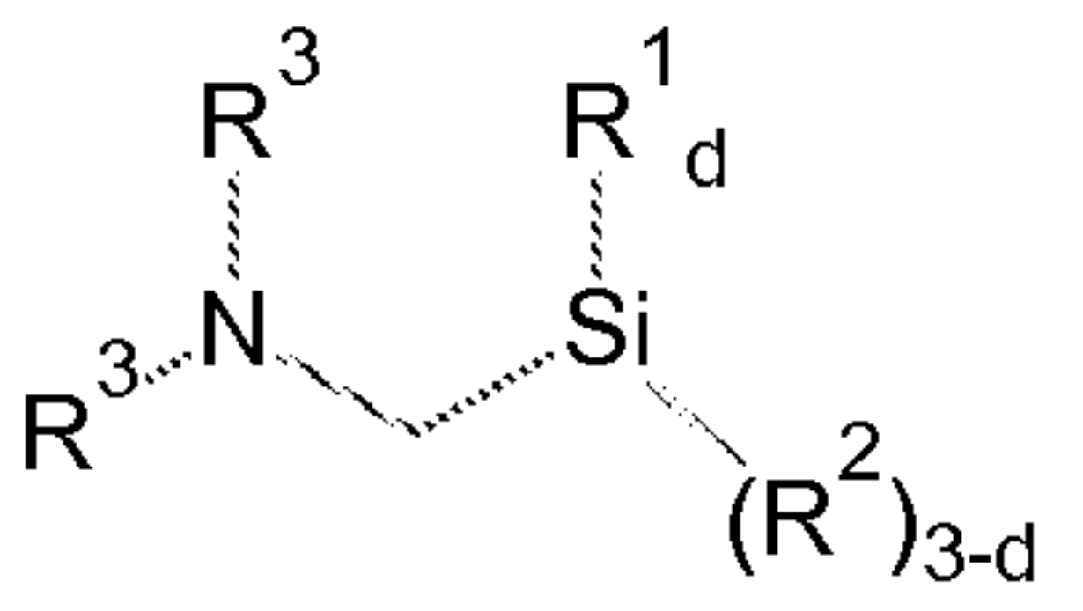

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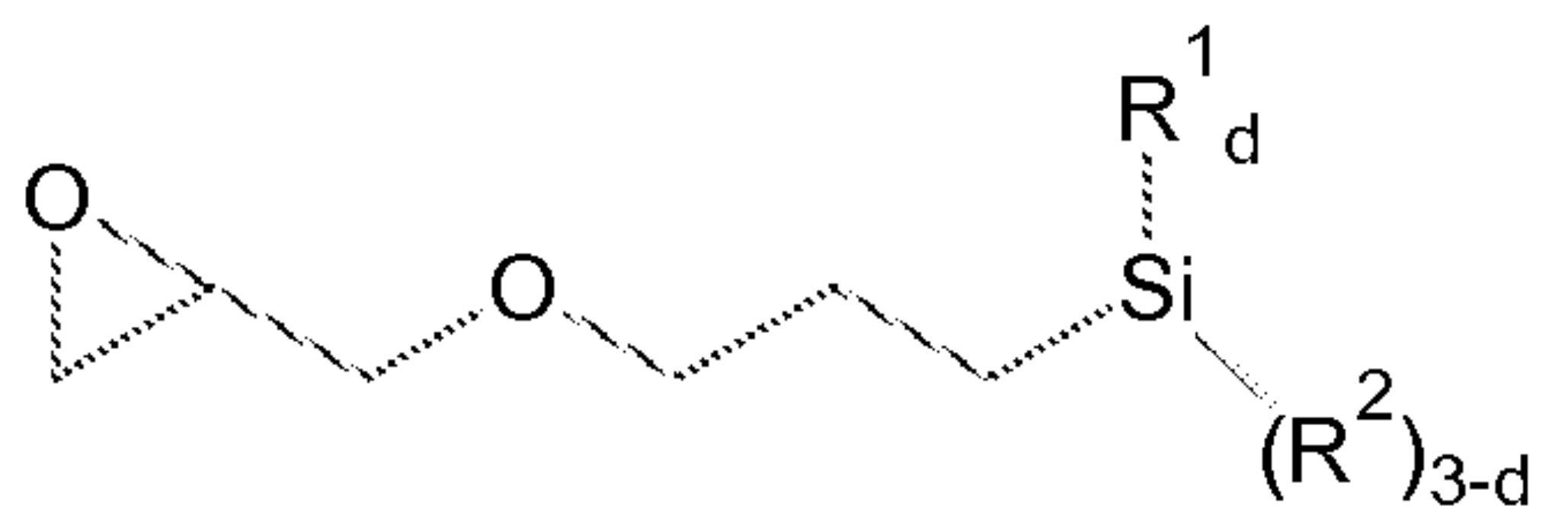

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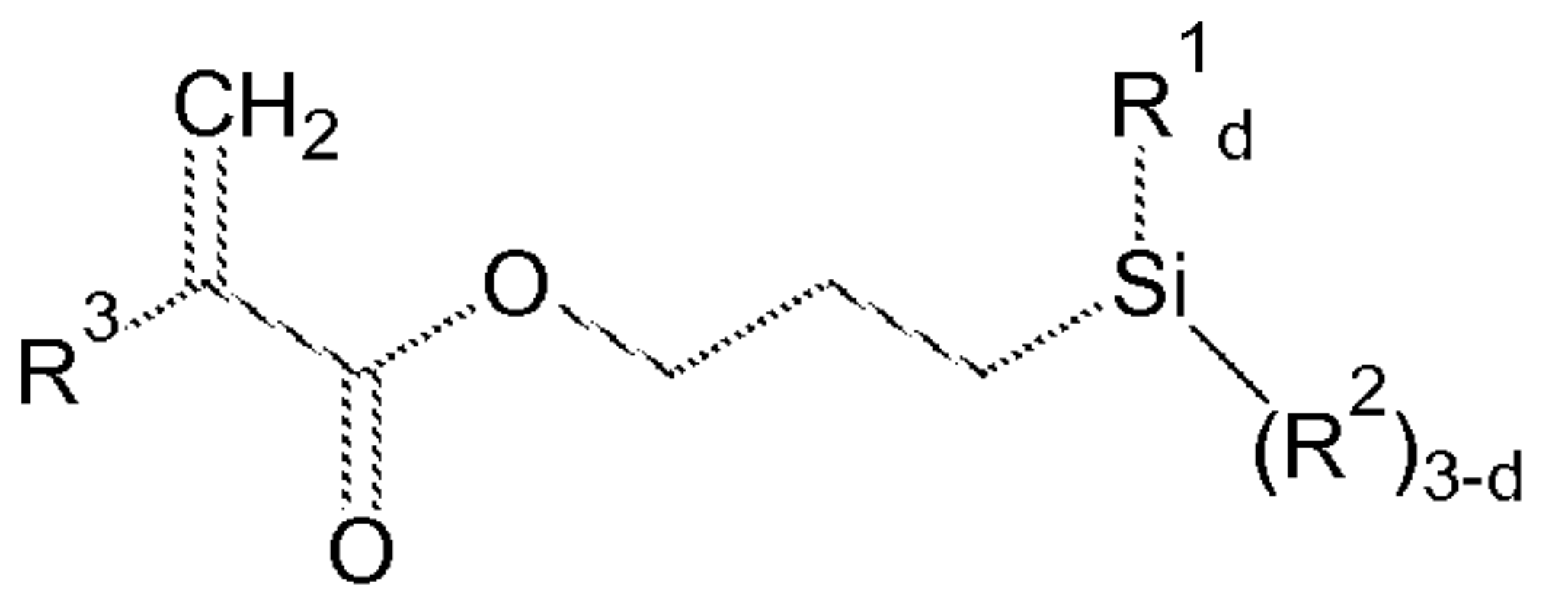

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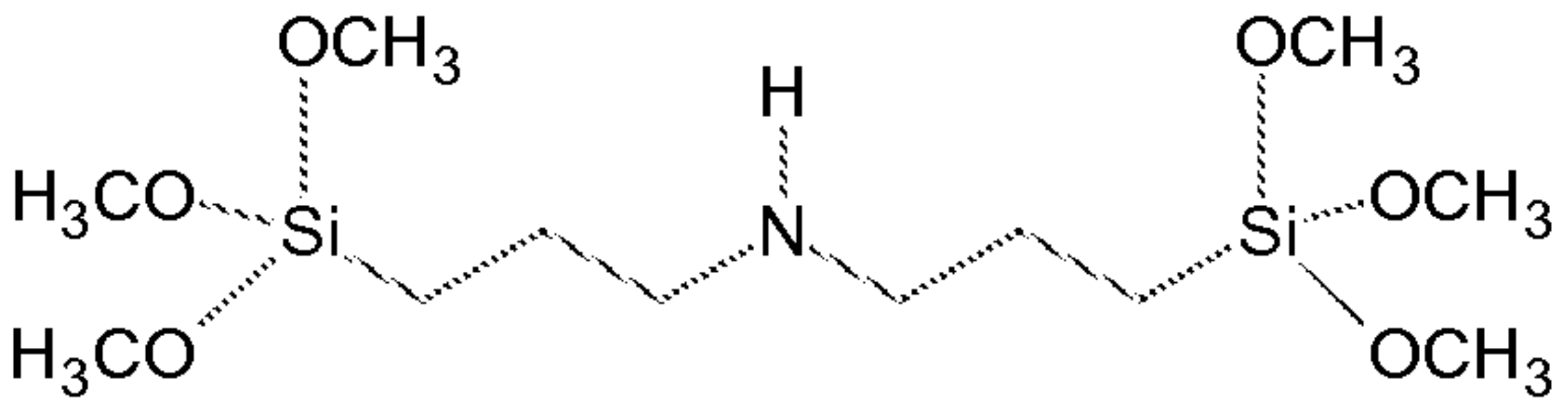

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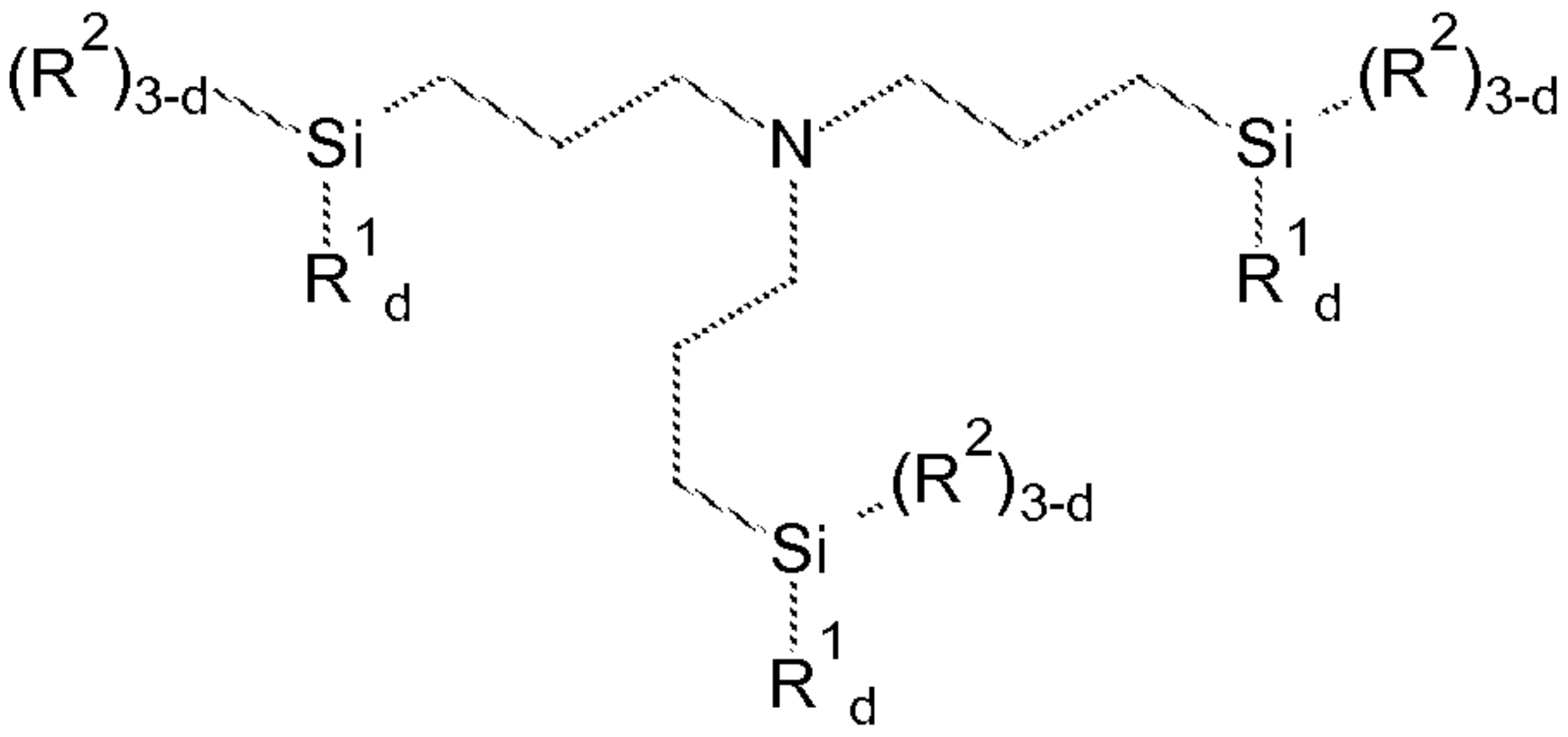

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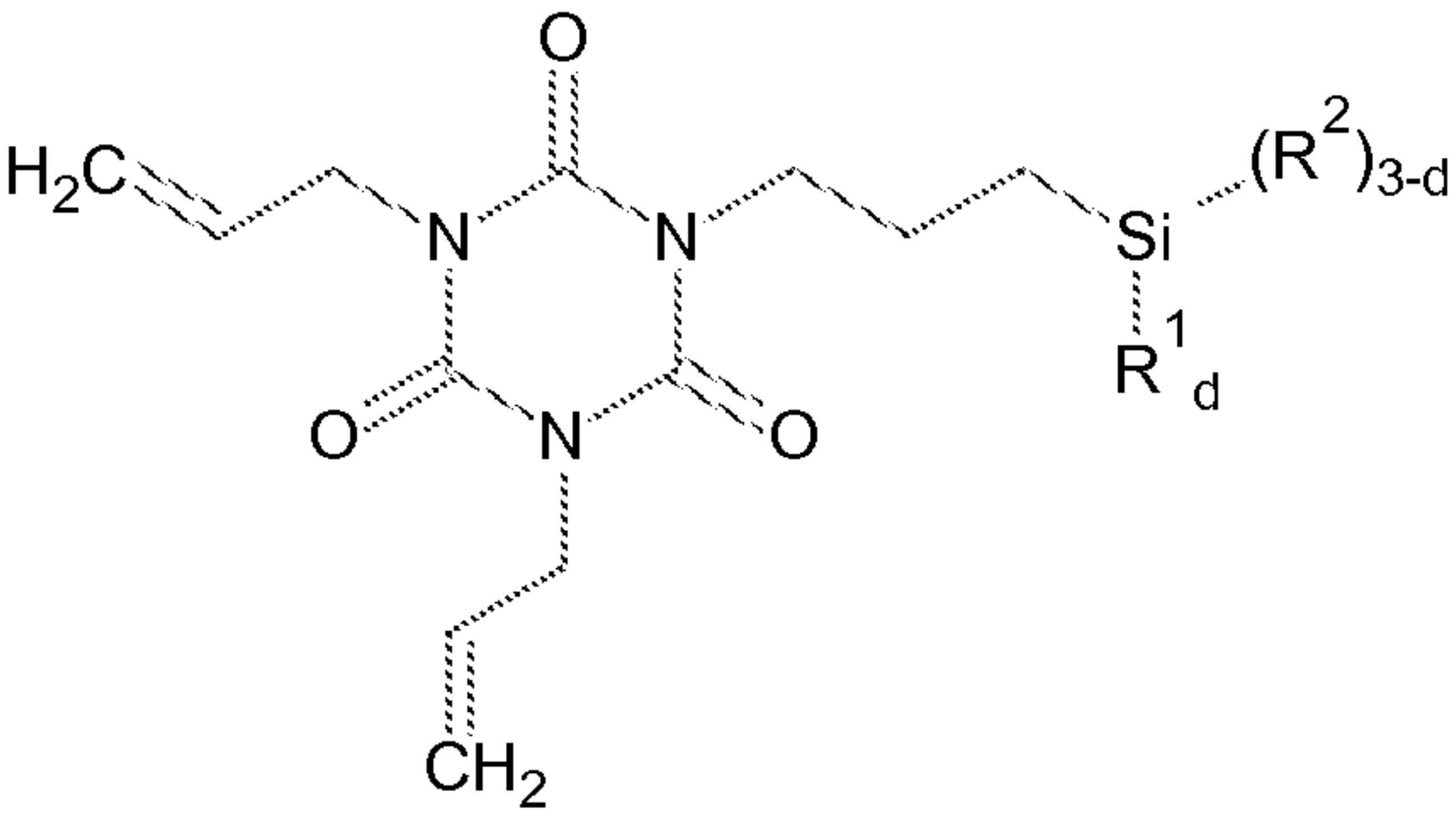

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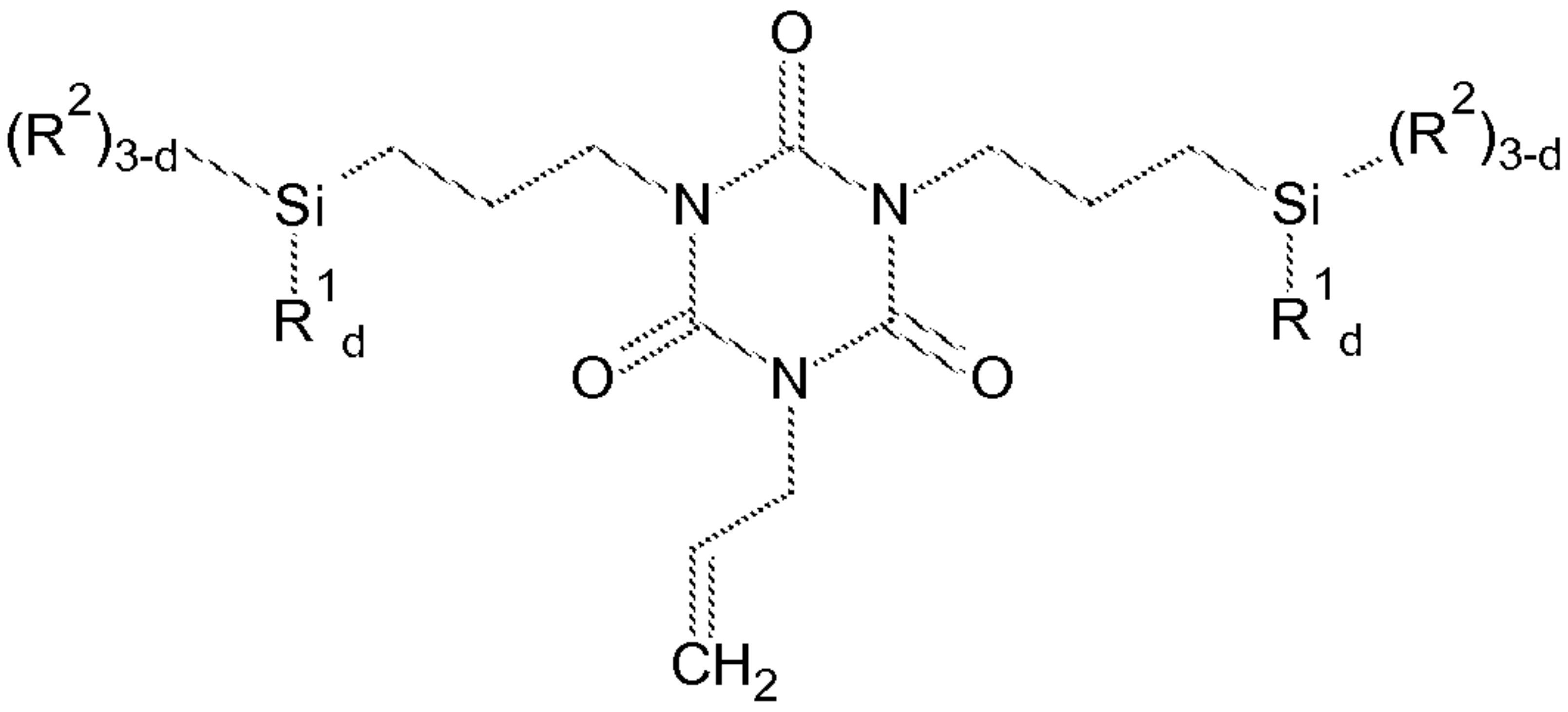

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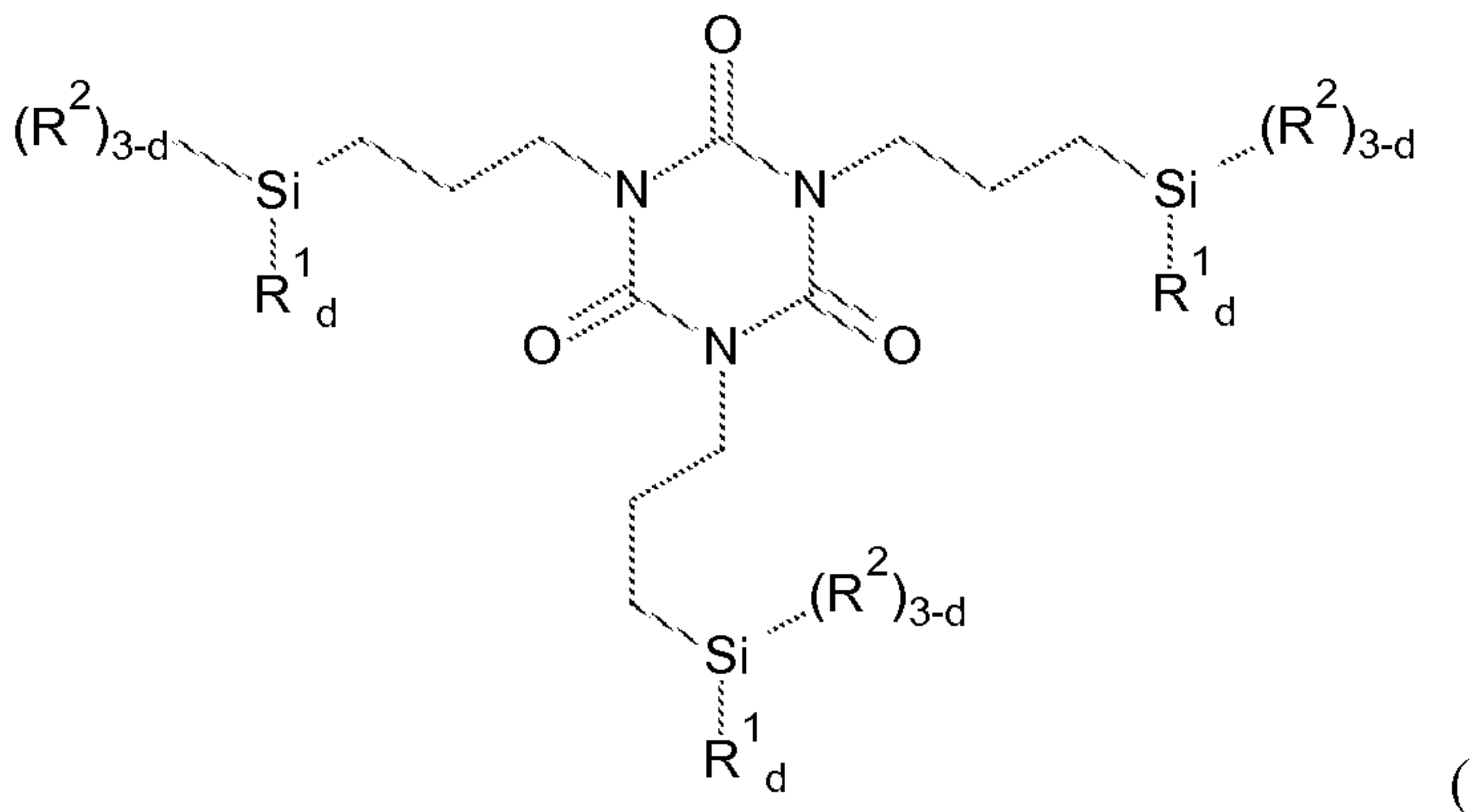
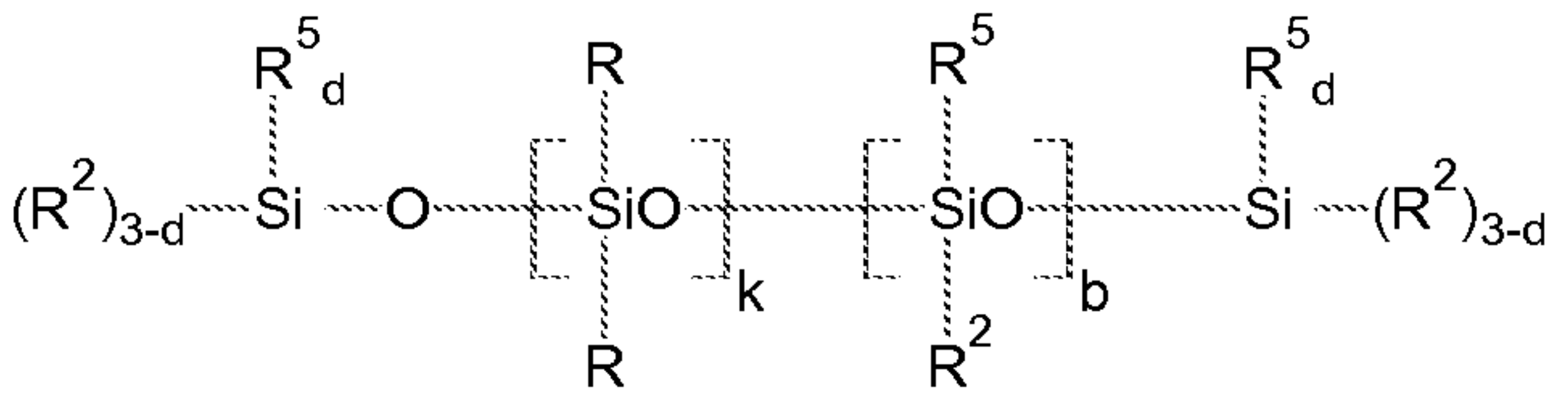


(8l)

wherein R^1, R^2, and d are as defined above. Examples of component (D) include compounds of the formulas (8a-8l). Furthermore the formula (8b) of compounds (D) shall comprise compounds of the formula (8m):

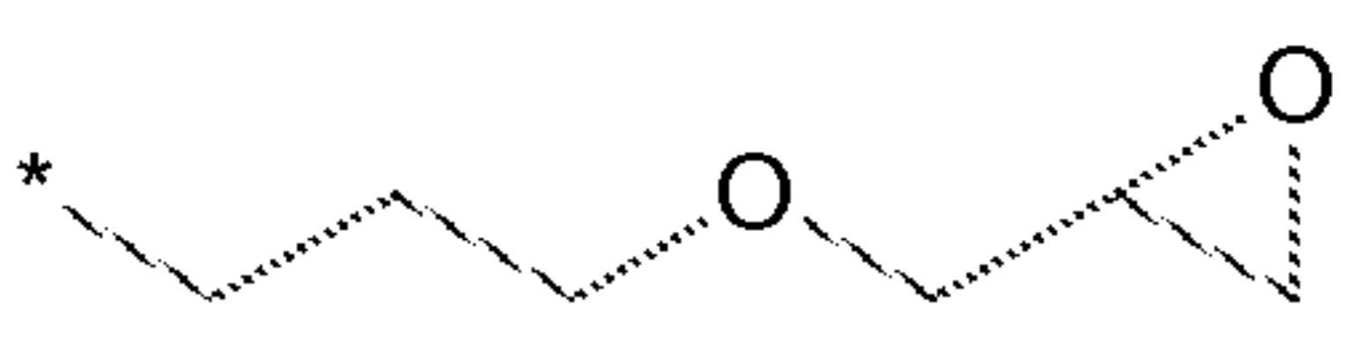


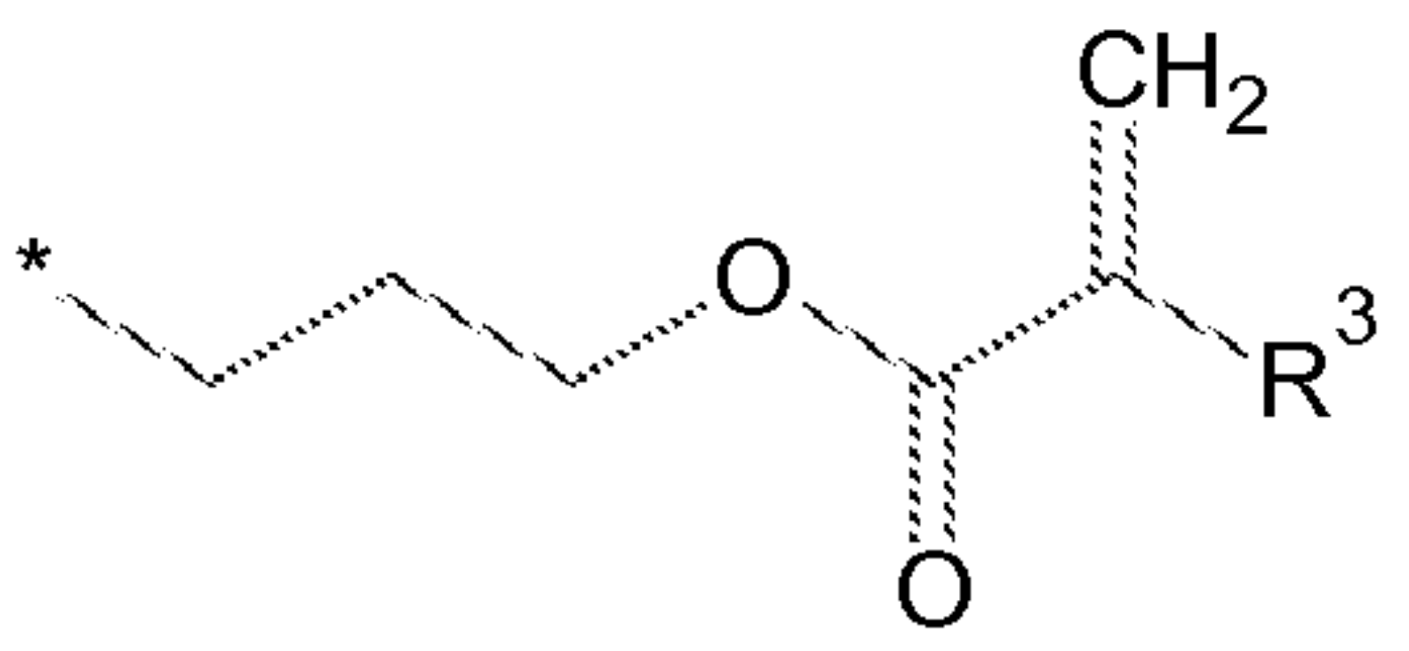
$$(R^2)_{3-d}\overset{R^5_d}{Si}-O-\left[\overset{R}{\underset{R}{Si}}O\right]_k-\left[\overset{R^5}{\underset{R^2}{Si}}O\right]_b-\overset{R^5_d}{Si}-(R^2)_{3-d}$$

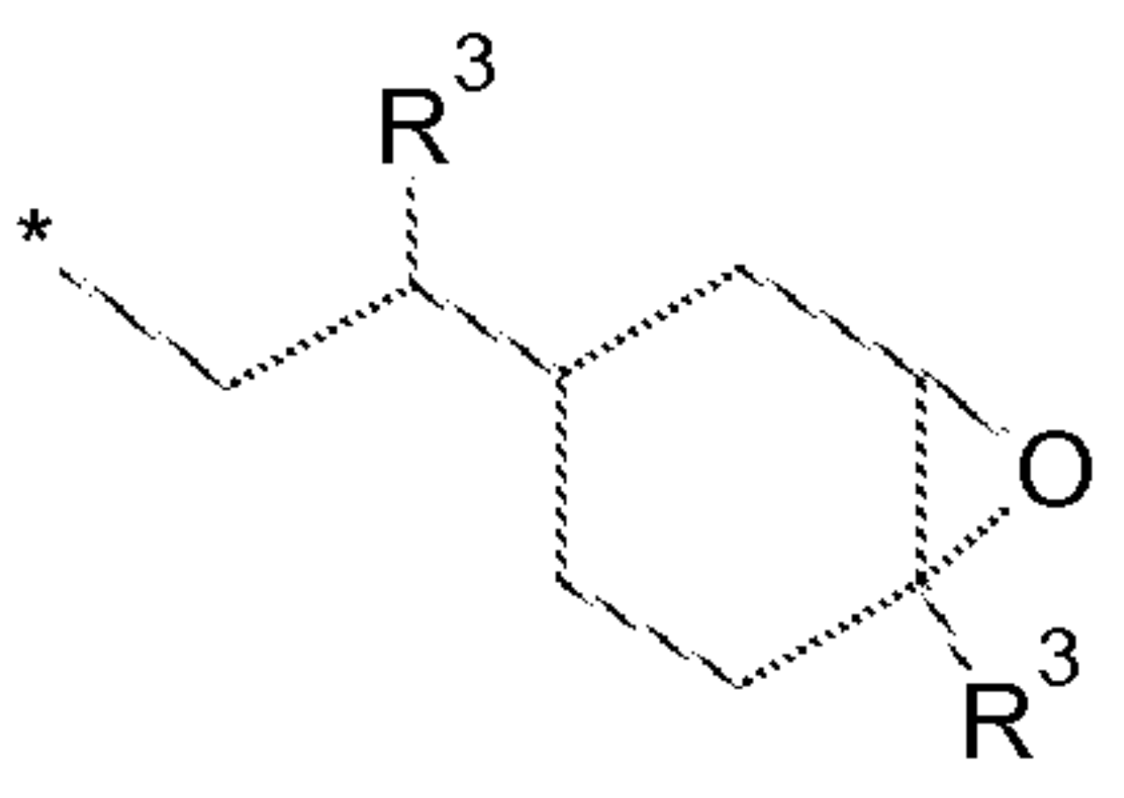
(8m)

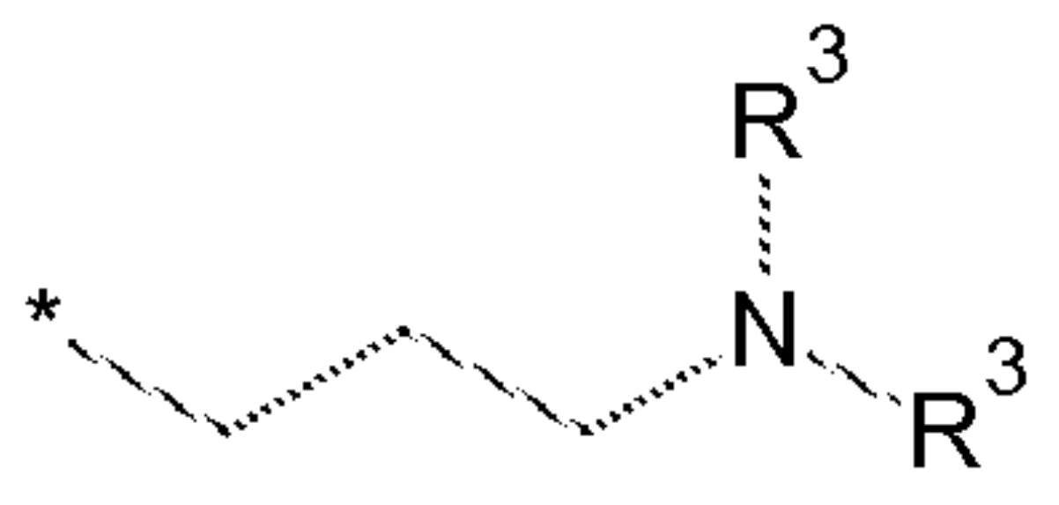
wherein: R, R^2, R^5, and d are as defined above; k is 0 to 6 (and in one embodiment desirably 0); b is as described above (in one embodiment desirably 0 to 5); and $1 + b \leq 10$. In one embodiment, R^5 is selected from:

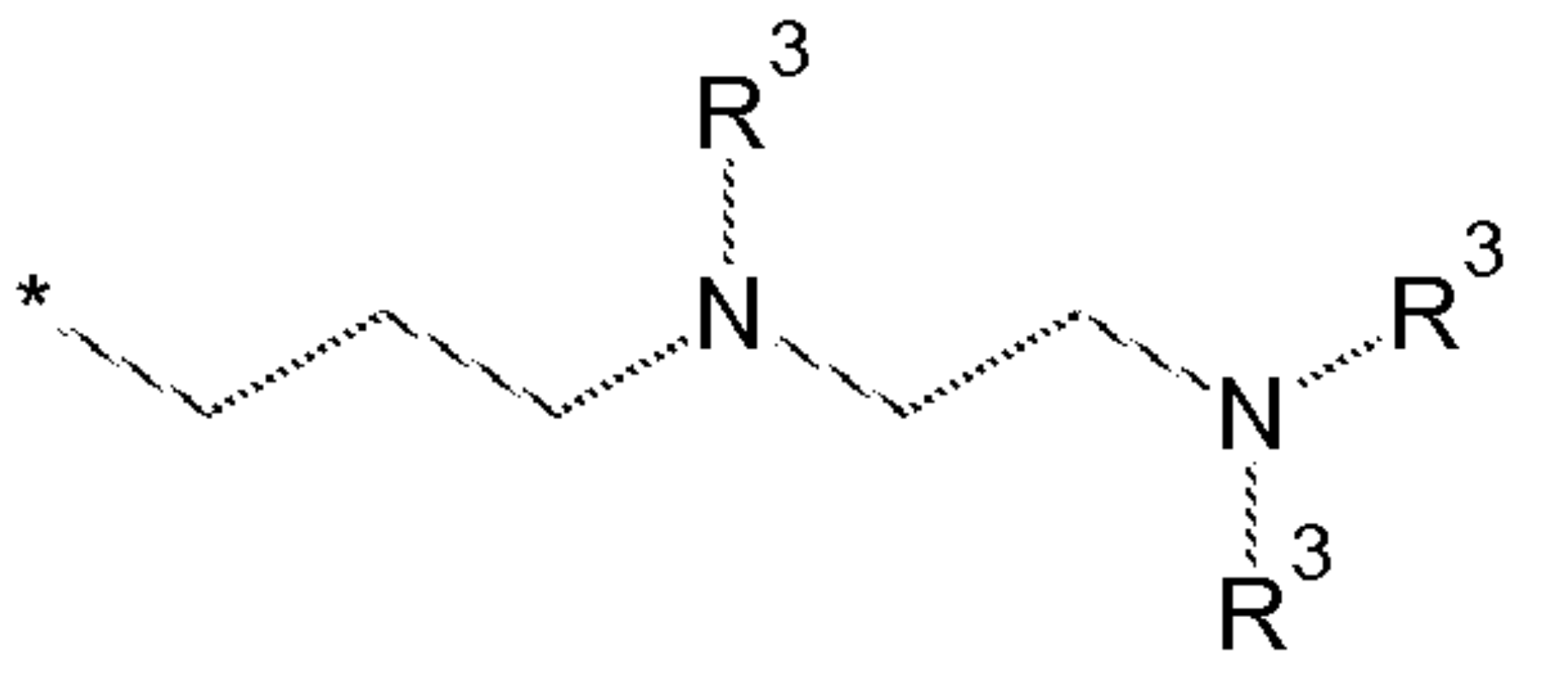
$$E^1\text{-}(CR^3{}_2)_h\text{-}W\text{-}(CH_2)_h\text{-}$$

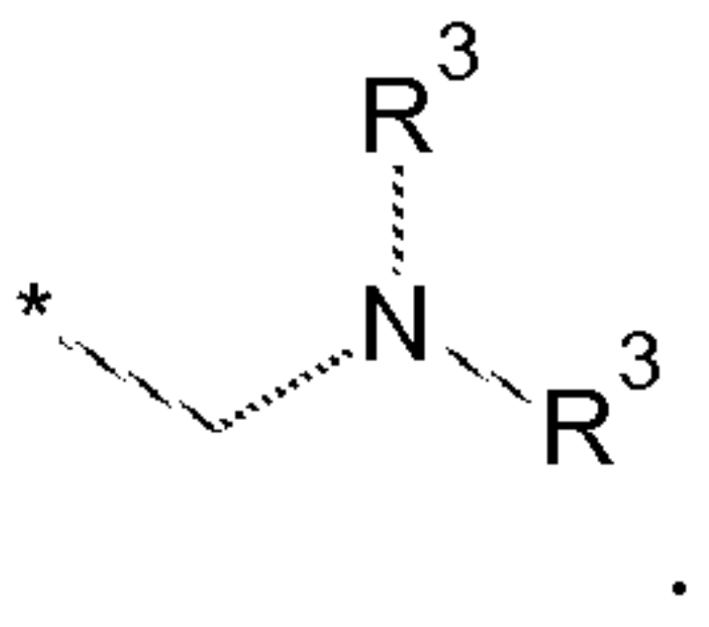












[0066] An exemplary group of adhesion promoters are selected from the group that consists of amino-group-containing silane coupling agents. The amino-group-containing silane adhesion promoter agent (D) is a compound having a group containing a silicon atom bonded to a hydrolyzable group (hereinafter referred to as a hydrolyzable group attached to the silicon atom) and an amino group. Specific examples thereof include the same silyl groups with hydrolyzable groups described above. Among these groups, the methoxy group and ethoxy group are particularly suitable. The number of the hydrolyzable groups may be 2 or more, and particularly suitable are compounds having 3 or more hydrolyzable groups.

[0067] Examples of other suitable adhesion promoter (D) include, but are not limited to *N*-(2-aminoethyl)aminopropyltrimethoxysilane, gamma-aminopropyltriethoxysilane, gamma-aminopropyltrimethoxysilane, bis(3-trimethoxysilypropyl)amine, *N*-phenyl-gamma-aminopropyltrimethoxysilane, triaminofunctionaltrimethoxysilane, gamma-aminopropylmethyldimethoxysilane, gamma-aminopropylmethyldiethoxysilane, methacryloxypropyltrimethoxysilane, methylaminopropyltrimethoxysilane, gamma-glycidoxypropylethyldimethoxysilane, gamma-glycidoxypropyltrimethoxysilane, gammaglycidoxyethyltrimethoxysilane, gamma-glycidoxypropylmethyldimethoxysilane, gamma-glycidoxypropylmethyldiethoxysilane, beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, beta-(3,4-epoxycyclohexyl)ethylmethyldimethoxysilane, beta-(3,4-epoxycyclohexyl)ethyltriethoxysilane, beta-(3,4-epoxycyclohexyl)ethylmethyldiethoxysilane, epoxylimonyltrimethoxysilane, isocyanatopropyltriethoxysilane, isocyanatopropyltrimethoxysilane, isocyanatopropylmethyldimethoxysilane, beta-cyanoethyltrimethoxysilane, gamma-acryloxypropyltrimethoxysilane, gamma-methacryloxypropylmethyldimethoxysilane, alpha, omega-bis(aminoalkyldiethoxysilyl)polydimethylsiloxanes (Pn =1-7), alpha, omega-bis(aminoalkyldiethoxysilyl)octamethyltetrasiloxane, 4-amino-3,3-dimethylbutyltrimethoxysilane, and *N*-ethyl-3-trimethoxysilyl-2-methylpropanamine, 3-(*N*,*N*-diethylaminopropyl) trimethoxysilane combinations of two or more thereof, and the like. Particularly suitable adhesion promoters include bis(alkyltrialkoxysilyl)amines and tris(alkyltrialkoxysilyl)amines including, but not limited to, bis(3-trimethoxysilylpropyl)amine and tris(3-trimethoxysilylpropyl)amine.

[0068] Also it is possible to use derivatives obtained by modifying them, for example, amino-modified silyl polymer, silylated amino polymer, unsaturated aminosilane complex, phenylamino long-chain alkyl silane and aminosilylated silicone. These amino-group-containing silane coupling agents may be used alone, or two or more kinds of them may be used in combination.

[0069] The adhesion promoter (D) may be present in an amount of from about 0.1 to about 5.0 pt. wt. based on 100 parts of the polymer component (A). In one embodiment, the adhesion promoter may be present in an amount of from about 0.15 to about 2.0 pt. wt. based on 100 parts of the polymer component (A). In another embodiment, the adhesion promoter may be present in an amount of from about 0.5 to about 1.5 pt. wt of the polymer component

(A). This defines the amount of (D) in composition of (A) wherein the content of free silanes coming from the endcapping of polymer (A) is smaller than 0.1 wt.%.

[0070] The present compositions may further include a filler component (E). The filler component(s) (E) may have different functions, such as to be used as reinforcing or semi-reinforcing filler, i.e., to achieve higher tensile strength after curing. The filler component may also have the ability to increase viscosity, establish pseudoplasticity/shear thinning, and demonstrate thixotropic behavior. Non-reinforcing fillers may act as volume extenders. The reinforcing fillers are characterized by having a specific surface area of more than 50 m^2/g related BET-surface, whereby the semi-reinforcing fillers have a specific surface area in the range of 10-50 m^2/g. So-called extending fillers have preferably a specific surface area of less than 10 m^2/g according to the BET-method and an average particle diameter below 100 μm. In one embodiment, the semi-reinforcing filler is calcium carbonate filler, silica filler, or a mixture thereof. Examples of suitable reinforcing fillers include, but are not limited to, fumed silicas or precipitated silicas, which can be partially or completely treated with organosilanes or siloxanes to make them less hydrophilic and decrease the water content or control the viscosity and storage stability of the composition. These fillers are named hydrophobic fillers. Tradenames are Aerosil®, HDK®, Cab-O-Sil® etc.

[0071] Examples of suitable extending fillers include, but are not limited to, ground silicas (Celite™), precipitated and colloidal calcium carbonates (which are optionally treated with compounds such as stearate or stearic acid); reinforcing silicas such as fumed silicas, precipitated silicas, silica gels and hydrophobized silicas and silica gels; crushed and ground quartz, cristobalite, alumina, aluminum hydroxide, titanium dioxide, zinc oxide, diatomaceous earth, iron oxide, carbon black, powdered thermoplastics such as acrylonitrile, polyethylene, polypropylene, polytetrafluoroethylene and graphite or clays such as kaolin, bentonite or montmorillonite (treated/untreated), and the like.

[0072] The type and amount of filler added depends upon the desired physical properties for the cured silicone/non-silicone composition. As such, the filler may be a single species or a mixture of two or more species. The extending fillers can be present from about 0 to about 300 pt. wt. of the composition related to 100 parts of component (A). The reinforcing fillers can be present from about 5 to about 60 pt. wt. of the composition related to 100 parts of component (A), preferably 5 to 30 pt. wt.

[0073] The inventive compositions optionally comprise an acidic compound (F), which, in conjunction with the adhesion promoter and (alkyl)acrylic acid catalyst, can accelerate curing (as compared to curing in the absence of such compounds). The component (F) may be present in an amount of from about 0.01 to about 5 wt. % of the composition. In another embodiment 0.01 to about 8 parts per weight (pt. wt.) per 100 pt. wt. of component (A) are used, more preferably 0.02 to 3 pt. wt. per 100 pt. wt. of component (A) and most preferably 0.02 to 1 pt. wt. per 100 pt. wt. of component (A) are used.

[0074] The acidic compounds (F) may be chosen from various phosphate esters, phosphonates, phosphites, phosphonites, sulfites, sulfates, pseudohalogenides, branched alkyl carboxylic acids, combinations of two or more thereof, and the like. Without being bound to any particular theory, the acidic compounds (F) may, in one embodiment, be useful as stabilizers in order to ensure a longer storage time when sealed in a cartridge before use in contact with ambient air. Especially alkoxy-terminated polysiloxanes can lose the ability to cure after storage in a cartridge and show decreased hardness under curing conditions. It may, therefore be useful to add compounds of the formula (8), which can extend storage time or ability to cure over months.

$$O{=}P(OR^6)_{3-c}(OH)_c \qquad (8)$$

whereby c is as defined above; and R^6 is selected from the group of linear or branched and optionally substituted C_1-C_{30} alkyl groups, linear or branched C_5-C_{14} cycloalkyl groups, C_6-

C_{14} aryl groups, C_6-C_{31} alkylaryl groups, linear or branched C_2-C_{30} alkenyl groups or linear or branched C_1-C_{30} alkoxyalkyl groups, C_4-C_{300} polyalkenylene oxide groups (polyethers), such as Marlophor® N5 acid, triorganylsilyl- and diorganyl (C_1-C_8)-alkoxysilyl groups. The phosphates can include also mixtures of primary and secondary esters. Non-limiting examples of suitable phosphonates include 1-hydroxyethane-(1,1-diphosphonic acid) (HEDP), aminotris(methylene phosphonic acid) (ATMP), diethylenetriaminepenta(methylene phosphonic acid) (DTPMP), 1,2-diaminoethane-tetra(methylene phosphonic acid) (EDTMP), and phosphonobutanetricarboxylic acid (PBTC).

[0075] In another embodiment, a compound of the formula $O{=}P(OR^7)_{3-g}(OH)_g$ may be added where g is 1 or 2, and R^7 is defined as R^6 or di- or mulitvalent hydrocarbons with one or more amino group.

[0076] Another type are phosphonic acid compounds of the formula $R^6P(O)(OH)_2$ such as alkyl phosphonic acids preferably hexyl or octyl phosphonic acid.

[0077] In one embodiment, the acidic compound may be chosen from a mono ester of phosphoric acid of the formula $(R^8O)PO(OH)_2$; a phosphonic acid of the formula $R^8P(O)(OH)_2$; or a monoester of phosphorous acid of the formula $(R^8O)P(OH)_2$ where R^8 is a C_1-C_{18} alkyl, a C_2-C_{20} alkoxyalkyl, phenyl, a C_7-C_{12} alkylaryl, a C_2-C_4 polyalkylene oxide ester or its mixtures with diesters, etc.

[0078] In another embodiment, the acidic compound is a branched C_4-C_{30} alkyl carboxylic acids, including C_5-C_{19} acids with an alpha tertiary carbon, or a combination of two or more thereof. Examples of such suitable compounds include, but are not limited to, Versatic™ Acid, lauric acid, and stearic acid. In one embodiment, the acidic compound may be a mixture comprising branched alkyl carboxylic acids. In one embodiment, the acidic compound is a mixture of mainly tertiary aliphatic C_{10} carboxylic acids.

[0079] Generally, the acidic component (F) is added in a molar ratio of less than or equal to 1 with respect to catalyst (C). In embodiments, the acidic component (F) is added in a molar ratio of (F):(C) of 1:15 to 1:1.

[0080] The curable composition may also include auxiliary substances (G) such as plastizers, pigments, stabilizers, anti-microbial agents, fungicides, biocides, and/or solvents. Preferred plastizers for reactive polyorganosiloxanes (A) are selected from the group of polyorganosiloxanes having chain lengths of 10 to 300 siloxy units. Preferred are trimethylsilyl terminated polydimethylsiloxanes having a viscosity of 100 to 1000 mPa.s at 25 °C. The choice of optional solvents (dispersion media or extenders) may have a role in assuring uniform dispersion of the catalyst, thereby altering curing speed. Such solvents include polar and non-polar solvents such as toluene, hexane, chloroform, methanol, ethanol, isopropyl alcohol, acetone, methylethyl ketone, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), *N*-methylpyrrolidinone (NMP), and propylene carbonate. Water can be an additional component (G) to accelerate fast curing 2-part compositions RTV-2, whereby the water can be in one part of the 2 compositions. Particularly suitable non-polar solvents include, but are not limited to, toluene, hexane, and the like if the solvents should evaporate after cure and application. In another embodiment, the solvents include high-boiling hydrocarbons such as alkylbenzenes, phtalic acid esters, arylsulfonic acid esters, trialkyl- or triarylphosphate esters, which have a low vapor pressure and can extend the volume providing lower costs. Examples cited by reference may be those of U.S. 6,599,633; U.S. 4,312,801. The solvent can be present in an amount of from about 20 to about 99 wt. % of the catalyst composition.

[0081] Applicants have found that present catalysts can provide a curable composition that yields a cured polymer exhibiting a tack-free time, hardness, and/or adhesion comparable to compositions made using tin catalysts.

[0082] In one embodiment, a composition in accordance with the present invention comprises: 100 pt. wt. polymer component (A); about 0.1 to about 10 pt. wt. crosslinker component (B); and about 0.01 to about 7 pt. wt. catalyst component (C). In one embodiment, the composition further comprises from about 0.1 to about 5 pt. wt., in one embodiment 0.15 to 1 pt. wt., of an adhesion promoter component (D); about 0 to about 300 pt. wt. filler component (E); about 0.01 to about 7 pt. wt. of acidic compound (F); optionally 0 to about 15 pt. wt. component (G), where the pt. wt. of components (B) – (G) are each based on 100 parts of the polymer component (A). In one embodiment, the composition comprises the component (F) in an amount of from about 0.01 to about 1 pt. wt. per 100 pt. wt. of component (A). In still another embodiment, the composition comprises the catalyst (C) in an amount of from about 0.1 to about 0.8 wt. pt. per 100 wt. pt of component (A).

[0083] It will be appreciated that the curable compositions may be provided as either a one-part composition or a two-part composition. A one-part composition refers to a composition comprising a mixture of the various components described above. A two-part composition may comprise a first portion and a second portion that are separately stored and subsequently mixed together just prior to application for curing. In one embodiment, a two-part composition comprises a first portion (P1) comprising a polymer component (A) and a crosslinker component (B), and a second portion (P2) comprising the catalyst component (C) comprising an (alkyl)acrylic acid, a salt of an (alkyl)acrylic acid, or a mixture of two or more thereof. The first and second portions may include other components (F) and/or (G) as may be desired for a particular purpose or intended use. For example, in one embodiment, the first portion (P1) may optionally comprise an adhesion promoter (D) and/or a filler (E), and the second portion (P2) may optionally comprise auxiliary substances (G), a cure rate modifying component (F), and water (G).

[0084] In one embodiment, a two-part composition comprises (i) a first portion comprising the polymer component (A), optionally the filler component (E), and optionally the acidic compound (F); and (ii) a second portion comprising the crosslinker (B), the catalyst component (C), the adhesive promoter (D), and the acidic compound (F), where portions (i) and (ii) are stored separately until applied for curing by mixing of the components (i) and (ii).

[0085] An exemplary two-part composition comprises: a first portion (i) comprising 100 pt. wt. of component (A), and 0 to 70 pt. wt. of component (E); and a second portion (ii) comprising 0.1 to 5 pt. wt. of at least one crosslinker (B); 0.01 to 4 pt. wt. of a catalyst (C); 0.1 to 2 pt. wt. of an adhesion promoter (D); and 0.02 to 1 pt. wt. component (F).

[0086] The curable compositions may be used in a wide range of applications including as materials for sealing, mold making, glazing, proto-typing; as adhesives; as coatings in sanitary rooms; as joint seal between different materials, e.g., sealants between ceramic or mineral surfaces and thermoplastics; as paper release; as impregnation materials; and the like. A curable composition in accordance with the present invention comprising a catalyst comprising an (alkyl)acrylic acid, a salt of an (alkyl)acrylic acid, or a mixture of two or more thereof may be suitable for a wide variety of applications such as, for example, a general purpose and industrial sealant, potting compound, caulk, adhesive or coating for construction use, insulated glass, structural glazing, where glass sheets are fixed and sealed in metal frame; caulks, adhesives for metal plates, car bodies, vehicles, electronic devices, and the like. Furthermore, the present composition may be used either as a one-part RTV-1 or as a two-part RTV-2 formulation that can adhere onto broad variety of metal, mineral, ceramic, rubber, or plastic surfaces.

[0087] Curable compositions comprising a catalyst comprising an (alkyl)acrylic acid, a salt of an (alkyl)acrylic acid, or a mixture of two or more thereof may be further understood with reference to the following Examples.

EXAMPLES

[0088] To a mixture of 1 g of ethylpolysilicate (EPS), 0.5 g adhesion promoter, and catalyst (0.4 g), 99.66 g of a mixture of silanol-stopped PDMS, silica filler and low molecular weight PDMS is added and mixed using a Hauschild mixer for 1.5 min. The mixed formulation is poured into a Teflon mold (length x breadth x depth ~ 10 cm x 10 cm x 1 cm) and placed inside a fume hood. The surface curing (TFT) and bulk curing are monitored as a function of time (maximum of 7 days).

[0089] The surface cure is denoted by tack free time (TFT). In a typical TFT measurement, a stainless steel (SS) weight (weighing ~10 g) is placed on the surface of the formulation spread on the Teflon mold to infer the tackiness of the surface as whether any material is adhered to the surface of the SS weight or not. TFT is defined as the time taken for getting a non-tacky surface. Bulk curing is the time taken for complete curing of formulation throughout the thickness (i.e. Top to bottom) and it is monitored as a function of time (visual inspection).

[0090] For aging studies, the pre-mixed mixture containing ethylpolysilicate (EPS), adhesion promoter, catalyst, and cure accelerator or storage stabilizer are kept in an oven for (1) 4 hours at 50 °C, or (2) 5 days at 70 °C, after which time the mixture is removed from the oven and allow to cool to room temperature. The mixture is then mixed with a mixture of silanol-stopped PDMS, silica filler and low molecular weight PDMS using a Hauschild mixer for 1.5 min. The mixed formulation is poured into a Teflon mold (length x breadth x depth ~ 10 cm x 10 cm x 1 cm) and placed inside a fume hood. The surface curing (TFT) and bulk curing are monitored as a function of time (maximum of 7 days) and °Shore A hardness in order to determine to what extent the compositions maintain performance after storage under accelerated conditions. The increased temperature for the storage test is indicative of the long-term storage stability of the composition at room temperature (25 °C 50 % relative humidity).

[0091] Table 1 and 2 illustrate the TFT and bulk cure properties of compositions employing methacrylic acid or Zr(IV) methacrylate as a catalyst along with different cross-linkers and adhesion promoters, in comparison to DBTDL.

Table 1

Formulation	Comp Ex-1	Comp Ex-2	Working Ex-1	Working Ex-2	Working Ex-3	Working Ex-4	Working Ex-5	Working Ex-6	Working Ex-7
Component A									
OH-end capped PDMS (Viscosity ~4 Pa.S)	52.8	52.8	52.8	52.8	52.8	52.8	52.8	52.8	52.8
OH-end capped PDMS (Viscosity 3500cPs))	20	20	20	20	20	20	20	20	20
Treated fumed silica	26.4	26.4	26.4	26.4	26.4	26.4	26.4	26.4	26.4
Component-B									
Ethyl polysilicate (EPS)	1		1	1	1	1			
Methyltrimethoxy silane (MTMS)		3					3	3	3
Bis-[γ-(trimethoxysilyl) propyl amine	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Dibutyltin dilaurate (DBTDL)	0.1	0.1							
Zirconium methacrylate (Zr-Me)			0.05	0.1	0.2	0.4	0.1	0.2	0.4
Cure Characteristic									
Tack-free time (min) - immediately after mixing comp-A & B	11	11	18	6	2	2	11	5	2
Bulk cure time (hours) - immediately after mixing comp-A & B	6	6	9	6	1	1	6	1	1

Table 2

Formulation	Comp Ex-1	Comp Ex-2	Working Ex-8	Working Ex-9	Working Ex-10	Working Ex-11	Working Ex-12	Working Ex-13
Component A								
OH-end capped PDMS (Viscosity ~4 Pa.S)	52.8	52.8	52.8	52.8	52.8	52.8	52.8	52.8
OH-end capped PDMS (Viscosity 3500cPs))	20	20	20	20	20	20	20	20
Treated fumed silica	26.4	26.4	26.4	26.4	26.4	26.4	26.4	26.4
Component-B								
Ethyl polysilicate (EPS)	1							
Methyltrimethoxy silane (MTMS)		3						
Bis-[γ-(trimethoxysilyl) propyl amine	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Dibutyltin dilaurate (DBTDL)	0.1	0.1						
Methacrylic Acid			0.1	0.2	0.4	0.1	0.2	0.4
Cure Characteristic								
Tack-free time (min) - immediately after mixing comp-A & B	11	11	4	2	1	4	1	1
Bulk cure time (hours) - immediately after mixing comp-A & B	6	6	6	1	1	6	1	1

[0092] As shown in Tables 1 and 2, the present catalysts exhibit cure properties similar to or better than DBTDL and that the cure properties can be controlled or tuned by adjusting the catalyst concentration.

[0093] Embodiments of the invention have been described above and modifications and alterations may occur to others upon the reading and understanding of this specification. The claims as follows are intended to include all modifications and alterations insofar as they come within the scope of the claims or the equivalent thereof.

CLAIMS

We claim:

1. A composition for forming a cured polymer composition comprising:

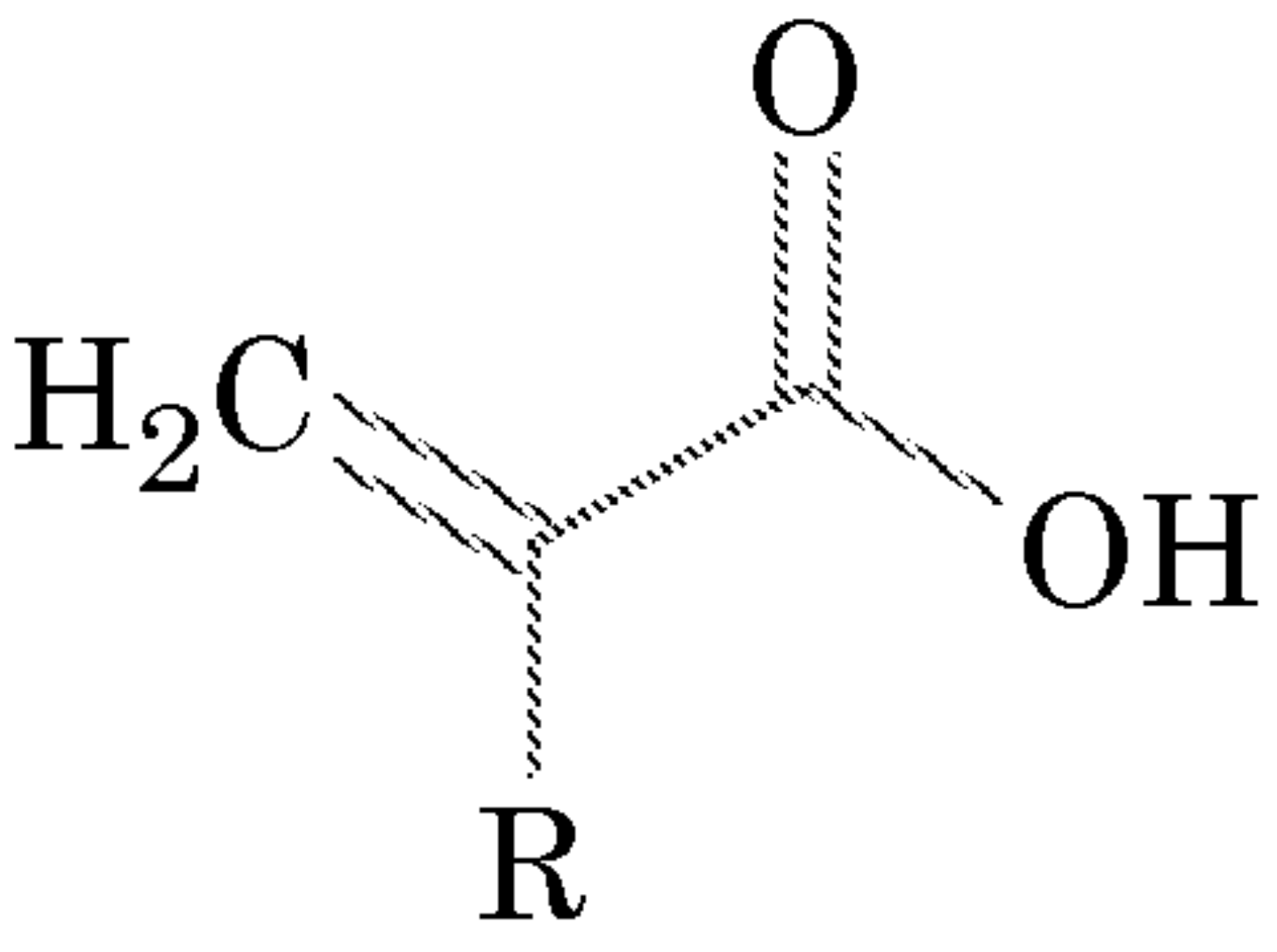
(A) a polymer having at least a reactive silyl group;

(B) a cross-linker or chain extender;

(C) a catalyst comprising an (alkyl)acrylic acid, a salt of an (alkyl)acrylic acid, or a mixture of two or more thereof; and

(D) an optional adhesion promoter.

2. The composition of claim 1, wherein the (alkyl)acrylic acid is of the formula:



where R is hydrogen or an alkyl group having 1 to 4 carbon atoms.

3. The composition of claims 1 or 2, wherein the (alkyl)acrylic acid is methacrylic acid.

4. The composition of any of claims 1-3, wherein the catalyst comprises a salt of an (alkyl)acrylic acid, the salt of the (alkyl)acrylic acid comprising a cation chosen from a monovalent cation, a divalent cation, a trivalent cation, or a tetravalent cation.

5. The composition of any of claims 1-4, wherein the salt of the (alkyl)acrylic acid comprises a metal cation chosen from lithium, sodium, potassium, rubidium, cesium, beryllium,

magnesium, calcium, strontium, barium, titanium, zirconium, hafnium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, silver, gold, zinc, scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, or a combination or two or more thereof.

6. The composition of claim 1, wherein the catalyst comprises zirconium(IV) methacrylate.

7. The composition of any of claims 1-6 comprising from about 0.01 to about 7 parts per weight catalyst (C) per 100 parts per weight of the polymer (A).

8. The polymer composition of any of claims 1-7, wherein the polymer (A) has the formula (2)

$$[R^1_aR^2_{3-a}\,Si-Z-]_n-X-Z-SiR^1_aR^2_{3-a} \quad (2)$$

where X is chosen from a polyurethane; a polyester; a polyether; a polycarbonate; a polyolefin; a polyester ether; and a polyorganosiloxane having units of $R_3SiO_{1/2}$, R_2SiO, $RSiO_{3/2}$, and/or SiO_2,

n is 0 to 100,

a is 0 to 2,

R and R^1 can be identical or different at the same Si-atom and chosen from a C_1-C_{10} alkyl; a C_1-C_{10} alkyl substituted with one or more of Cl, F, N, O or S; a phenyl; a C_7-C_{16} alkylaryl; a C_7-C_{16} arylalkyl; a C_2-C_4 polyalkylene ether; or a combination of two or more thereof,

R^2 is chosen from OH, C_1-C_8 alkoxy, C_2-C_{18} alkoxyalkyl, oximoalkyl, enoxyalkyl, aminoalkyl, carboxyalkyl, amidoalkyl, amidoaryl, carbamatoalkyl, or a combination of two or more thereof, and

Z is a bond, a divalent unit selected from the group of a C_1-C_8 alkylene, or O.

9. The composition of any of claims 1-8, wherein the crosslinker component (B) is chosen from tetraethylorthosilicate (TEOS); methyltrimethoxysilane (MTMS); methyltriethoxysilane; vinyltrimethoxysilane; vinyltriethoxysilane; methylphenyldimethoxysilane; 3,3,3-trifluoropropyltrimethoxysilane; methyltriacetoxysilane; vinyltriacetoxysilane; ethyltriacetoxysilane; di-butoxydiacetoxysilane; phenyltripropionoxysilane; methyltris(methylethylketoximo)silane; vinyltris(methylethylketoximo)silane; 3,3,3-trifluoropropyltris(methylethylketoximo)silane; methyltris(isopropenoxy)silane; vinyltris(isopropenoxy)silane; ethylpolysilicate; dimethyltetraacetoxydisiloxane; tetra-n-propylorthosilicate; methyldimethoxy(ethylmethylketoximo)silane; methylmethoxybis(ethylmethylketoximo)silane; methyldimethoxy(acetaldoximo)silane; methyldimethoxy(*N*-methylcarbamato)silane; ethyldimethoxy(*N*-methylcarbamato)silane; methyldimethoxyisopropenoxysilane; trimethoxyisopropenoxysilane; methyltriisopropenoxysilane; methyldimethoxy(but-2-en-2-oxy)silane; methyldimethoxy(1-phenylethenoxy)silane; methyldimethoxy-2-(1-carboethoxypropenoxy)silane; methylmethoxydi(*N*-methylamino)silane; vinyldimethoxy(methylamino)silane; tetra-*N*,*N*-diethylaminosilane; methyldimethoxy(methylamino)silane; methyltri(cyclohexylamino)silane; methyldimethoxy(ethylamino)silane; dimethyldi(*N*,*N*-dimethylamino)silane; methyldimethoxy(isopropylamino)silane; dimethyldi(*N*,*N*-diethylamino)silane; ethyldimethoxy(*N*-ethylpropionamido)silane; methyldimethoxy(*N*-methylacetamido)silane;

methyltris(*N*-methylacetamido)silane; ethyldimethoxy(*N*-methylacetamido)silane; methyltris(*N*-methylbenzamido)silane; methylmethoxybis(*N*-methylacetamido)silane; methyldimethoxy(caprolactamo)silane; trimethoxy(*N*-methylacetamido)silane; methyldimethoxy(ethylacetimidato)silane; methyldimethoxy(propylacetimidato)silane; methyldimethoxy(*N*,*N'*,*N'*-trimethylureido)silane; methyldimethoxy(*N*-allyl-*N'*,*N'*-dimethylureido)silane; methyldimethoxy(*N*-phenyl-*N'*,*N'*-dimethylureido)silane; methyldimethoxyisocyanatosilane; dimethoxydiisocyanatosilane; methyldimethoxyisothiocyanatosilane; methylmethoxydiisothiocyanatosilane, or a combination of two or more thereof.

10. The composition of any of claims 1-9, wherein the adhesion promoter component (D) is chosen from an (aminoalkyl)trialkoxysilane, an (aminoalkyl)alkyldialkoxysilane, a bis(trialkoxysilylalkyl)amine, a tris(trialkoxysilylalkyl)amine, a tris(trialkoxysilylalkyl)cyanurate, and a tris(trialkoxysilylalkyl)isocyanurate, an (epoxyalkyl)alkyldialkoxysilane, an (epoxyalkyl)trialkoxysilane, an (epoxyalkylether)trialkoxysilane , or a combination of two or more thereof.

11. The polymer composition of any of claims 1-10, wherein the polymer component (A) has the formula (4):

$$R^2_{3-a}R^1_aSi\text{-}Z\text{-}[R_2SiO]_x\,[R^1_2SiO]_y\text{-}Z\text{-}SiR^1_a\,R^2_{3-a} \qquad (4)$$

whereby

x is 0 to 10000;

y is 0 to 1000;

a is 0 to 2;

R is methyl;

R^1 is chosen from a C_1-C_{10} alkyl; a C_1-C_{10} alkyl substituted with one or more of Cl, F, N, O, or S; a phenyl; a C_7-C_{16} alkylaryl; a C_7-C_{16} arylalkyl; a C_2-C_4 polyalkylene ether; or a combination of two or more thereof, and other siloxane units may be present in amounts less than 10 mol.%;

R^2 is chosen from OH, a C_1-C_8 alkoxy, a C_2-C_{18} alkoxyalkyl, an oximoalkyl, an oximoaryl, an enoxyalkyl, an enoxyaryl, an aminoalkyl, an aminoaryl, a carboxyalkyl, a carboxyaryl, an amidoalkyl, an amidoaryl, a carbamatoalkyl, a carbamatoaryl, or a combination of two or more thereof; and

Z is -O-, a bond, or $-C_2H_4$-.

12. The composition of any of claims 1-8, wherein the composition is provided as a one part composition.

13. The composition of any of claims 1-11, wherein the composition is provided as a two part composition comprising a first portion (P1) and a second portion (P2).

14. The composition of any of claims 1-13 comprising:

100 pt. wt. of polymer component (A),

0.1 to about 10 pt. wt. of at least one crosslinker (B),

0.01 to about 7 pt. wt. of a catalyst comprising an (alkyl)acrylic acid, a salt of an (alkyl)acrylic acid, or a mixture of two or more thereof (C), 0.1 to about 5 pt. wt. of an amino-containing adhesion promoter (D),

0 to about 300 pt. wt. of a filler (E),

0 to about 7 pt. wt. of an acidic component (F), and

0.01 to about 8 pt. wt. of an auxiliary component (G),

whereby this composition can be stored in the absence of humidity and is curable in the presence of humidity upon exposure to ambient air.

15. A method of providing a cured material comprising exposing the composition of any of claims 1-14 to ambient air.

16. A method of providing a cured material comprising combining the first portion and the second portion of claim 13 and curing the mixture.

17. A cured polymer formed from the composition or method of any of claims 1-16.

18. The cured polymer of claim 17 in the form of an elastomeric seal, duromeric seal, an adhesive, a coating, an encapsulant, a shaped article, a mold, or an impression material.

19. The composition of claim 1, wherein the composition a two-part composition comprising:

(i) a first portion comprising the polymer component (A), optionally a filler component (E), and optionally an acidic compound (F); and

(ii) a second portion comprising the crosslinker (B), the catalyst component (C), the adhesion promoter (D), and optionally the acidic compound (F), whereby (i) and (ii) are stored separately until applied for curing by mixing of the components (i) and (ii).

20. The composition of claim 19, wherein portion (i) comprises 100 pt. wt. of component (A), and 0 to 70 pt. wt. of component (E); and portion (ii) comprises 0.1 to 10 pt. wt. of at least one crosslinker (B), 0.01 to 7 pt. wt. of a catalyst (C), 0 to 5 pt. wt. of an adhesion promoter (D), and 0 to 3 pt. wt. component (F).

21. The composition of claim 1, wherein the catalyst comprises a mixture of two or more (alkyl)acrylic acids, a mixture of at least one (alkyl)acrylic acid and at least one salt of an (alkyl)acrylic acid, a mixture of two or more salts of (alkyl)acrylic acids, or a combination thereof.