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(54) Title: SILOXANE COMPOSITIONS INCLUDING METAL-OXIDE NANOPARTICLES SUITABLE FOR FORMING ENCAPSULANTS

(57) **Abstract**: A composition includes an organopolysiloxane component (A) having at least one aryl group and having an average of at least two alkenyl groups per molecule. The composition further includes an organohydrogensiloxane component (B) having at least one of an alkyl group and an aryl group and an average of at least two silicon-bonded hydrogen atoms per molecule. Components (A) and (B) each independently have a number average molecular weight less than or equal to 1500. The composition yet further includes a catalytic amount of a hydrosilylation catalyst component (C), and metal-oxide nanoparticles (D) other than titanium dioxide (TiO_2) nanoparticles. The composition has a molar ratio of alkyl groups to aryl groups ranging from 1:0.25 to 1:3.0. A product of the present invention is the reaction product of the composition, which may be used to make a light emitting diode.

SILOXANE COMPOSITIONS INCLUDING METAL-OXIDE NANOPARTICLES SUITABLE FOR FORMING ENCAPSULANTS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application Serial No. 61/420,921, filed on December 8, 2010, which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present invention generally relates to a siloxane composition suitable for forming encapsulants and, more specifically, to a composition comprising an organopolysiloxane component, an organohydrogensiloxane component, a hydrosilylation catalyst component, and metal-oxide nanoparticles other than titanium dioxide nanoparticles, and to a product formed therefrom.

DESCRIPTION OF THE RELATED ART

[0003] Light emitting diodes (LEDs) are well known in the art, and generally comprise one or more diodes (that emit light when activated) that are encapsulated, i.e., encased, in an encapsulant. LED designs utilizing either flip chip or wire bonded chips are connected to the diode to provide power to the diode. When bonding wires are present, a portion of the bonding wires is at least partially encapsulated along with the diode. When LEDs are activated and emitting light, a rapid rise in temperature occurs, subjecting the encapsulant to thermal shock. Accordingly, when the LED is turned on and off repeatedly, the encapsulant is exposed to temperature cycles. In addition to normal use, LEDs are also exposed to environmental changes in temperature and humidity, as well as subject to physical shocks. Therefore, encapsulation is required for optimal performance.

[0004] Epoxy resins are generally used as encapsulants for LEDs. However, since many epoxy resins have a high modulus, i.e., a high elastic modulus, the portion of the bonding wires of the LED that are encapsulated proximal the diode are subjected to stress from expansion and contraction of the encapsulant, and may break as a result of temperature cycling. Further, cracks may develop within the encapsulant itself. Epoxy resins also tend to yellow over time, which reduces LED brightness and changes color of the light emitted from the LED. This yellowing problem is particularly problematic for white and blue colored LEDs. Yellowing of the epoxy resin is believed to result from decomposition of the encapsulant induced by the aforementioned temperature cycles of the LED and/or absorption of UV-light emitted by the LED.

[0005] Since siloxane compositions employing silicone resins and copolymers exhibit comparatively superior heat resistance, moisture resistance and retention of transparency relative to epoxy resins, in recent years, LEDs that use siloxane compositions to form encapsulants, primarily blue LEDs and white LEDs, have become more prevalent. Previously disclosed siloxane compositions generally have a relatively high viscosity, which makes dispense methodologies for encapsulating the LEDs difficult and therefore more expensive, as well as detrimentally affecting phosphor settling rates and increasing bubble entrapment. Many of the aforementioned encapsulants also have refractive indices and optical transparencies which make them undesirable for use in LEDs. Many of the aforementioned encapsulants are also too soft, i.e., the aforementioned encapsulants have low Shore A or Shore 00 hardness values, which make them undesirable for some LED applications.

[0006] Accordingly, there remains an opportunity to provide an improved composition. There also remains an opportunity to provide an improved product relative to the prior art.

SUMMARY OF THE INVENTION

[0007] The present invention provides a composition. The composition comprises an organopolysiloxane component (A) having at least one aryl group and having an average of at least two alkenyl groups per molecule. The organopolysiloxane component (A) has a number average molecular weight less than or equal to 1500. The composition further comprises an organohydrogensiloxane component (B) having at least one of an alkyl group and an aryl group. The organohydrogensiloxane component (B) has an average of at least two silicon-bonded hydrogen atoms per molecule, and has a number average molecular weight less than or equal to 1500. The composition yet further comprises a catalytic amount of a hydrosilylation catalyst component (C), and metal-oxide nanoparticles (D) other than titanium dioxide nanoparticles. The composition has a molar ratio of alkyl groups to aryl groups ranging from 1:0.25 to 1:3.0.

[0008] The composition can be cured to form a product, such as lenses or encapsulants for making various devices, such as, but not limited to, light emitting diodes.

DETAILED DESCRIPTION OF THE INVENTION

[0009] A composition comprises an organopolysiloxane component (A), an organohydrogensiloxane component (B), a hydrosilylation catalyst component (C), and metal-oxide nanoparticles (D) other than titanium dioxide (TiO_2) nanoparticles. The composition may be reacted, i.e., cured, to form a product, which is described in further detail below. The product is especially suitable for use as an encapsulant. For example, the composition can be applied on a substrate, e.g. a diode, to form a light emitting diode (LED), which is described in further detail below. The product may also be used for other purposes, such as for lenses, photonic devices, etc.

[0010] The organopolysiloxane component (A), hereinafter component (A), generally comprises at least one of a disiloxane, a trisiloxane, a tetrasiloxane, a pentasiloxane, and a hexasiloxane. In other words, component (A) may include any one of the disiloxane, the trisiloxane, the tetrasiloxane, the pentasiloxane, or the hexasiloxane, or combinations of the disiloxane, the trisiloxane, the tetrasiloxane, the pentasiloxane, and/or the hexasiloxane, all of which is described in further detail below.

[0011] Component (A) typically has at least one aryl group, and more typically at least one aryl group and at least one alkyl group. In other words, component (A) has an aryl group, or a combination of alkyl and aryl groups. Suitable aryl groups for purposes of the present invention include, but are not limited to, phenyl and naphthyl groups; alkaryl groups, such as tolyl and xylyl groups; and aralkyl groups, such as benzyl and phenethyl groups. It is to be appreciated that component (A) may include any combination of two or more of the aforementioned aryl groups. Typically, component (A) has at least one phenyl group, alternatively at least two phenyl groups. Component (A) may include one or more aryl groups different than the phenyl groups, such as the aryl groups described and exemplified above. Suitable alkyl groups for purposes of the present invention include, but are not limited to, methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, pentyl, 1-methylbutyl, 1-ethylpropyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl, hexyl, heptyl, octyl, nonyl, and decyl groups. Other suitable alkyl groups for purposes of the present invention include cycloalkyl groups, such as cyclopentyl, cyclohexyl, and methylcyclohexyl groups. Typically, component (A) includes at least one methyl group, alternatively at least two methyl groups, alternatively at least four methyl groups, alternatively at least six methyl groups. It is to be appreciated that component (A) may include any combination of the aforementioned alkyl groups and/or aryl groups. In addition, if component (A) includes two or more alkyl groups, the alkyl groups may be the same as or different than each other, likewise if component (A) includes two or more aryl groups.

[0012] Component (A) has an average of at least two alkenyl groups per molecule, alternatively at least three alkenyl groups per molecule. The alkenyl groups typically have from two to ten carbon atoms, more typically from two to six carbon atoms, most typically from two to four carbon atoms. In one embodiment, the alkenyl groups have two carbon atoms. Suitable alkenyl groups, for purposes of the present invention, include, but are not limited to, vinyl, allyl, butenyl, hexenyl, and octenyl groups. In certain embodiments, component (A) includes at least two vinyl groups per molecule, alternatively at least three vinyl groups per molecule. It is to be appreciated that component (A) may include any combination of the aforementioned alkenyl groups. In addition, component (A) can include alkenyl groups that are the same as or different than each other.

[0013] In certain embodiments, component (A) comprises the disiloxane having the formula:

$$\text{(I)} \qquad R^1R^2R^3SiOSiR^1R^2R^3$$

wherein each R^1, R^2, and R^3 independently comprises an alkyl group, an aryl group, or an alkenyl group. Suitable alkyl, aryl, and alkenyl groups are as described and exemplified above.

[0014] In certain embodiments, the disiloxane has the formula:

$$\text{(i)} \qquad \text{ViPhMeSiOSiViPhMe}$$

wherein Vi is a vinyl group, Ph is a phenyl group, and Me is a methyl group. In these embodiments, the disiloxane of formula (i) imparts the composition with excellent homogeneity and with low viscosity and imparts the product with high modulus and an increased refractive index due to the phenyl groups, which is described in further detail below. It is believed that the presence of phenyl groups in these types of compounds results in higher boiling points with lower volatility, while maintaining low viscosity of the composition. It is to be appreciated that component (A) may include a combination of two or more different organopolysiloxanes (A) having formulas (I) and/or (i).

[0015] In certain embodiments, the organopolysiloxane (A) comprises at least one of the trisiloxane and the tetrasiloxane, each of the trisiloxane and the tetrasiloxane independently having the formula:

$$\text{(II)} \qquad (R^1R^3{}_2SiO)_{4\text{-}a}SiR^4{}_a$$

wherein each R^1, R^3, and R^4 independently comprises an alkyl group, an aryl group, or an alkenyl group, and subscript a is 0 for the tetrasiloxane or 1 for the trisiloxane. Suitable alkyl, aryl, and alkenyl groups are as described and exemplified above.

[0016] In certain embodiments, each of the trisiloxane and the tetrasiloxane independently have the formula:

$$\text{(ii)} \qquad (ViR^3{}_2SiO)_{4\text{-}a}SiR^4{}_a$$

wherein Vi is a vinyl group, each R^3 and R^4 independently comprises a phenyl group or a methyl group, and subscript a is 0 for the tetrasiloxane or 1 for the trisiloxane. In these embodiments, the trisiloxane and/or the tetrasiloxane of formula (ii) imparts the composition with excellent homogeneity and low viscosity and imparts the product with high modulus and a refractive index which can be tailored depending upon whether R^4 is a methyl or phenyl group, as described in further detail below. It is to be appreciated that component (A) may include a combination of two or more different organopolysiloxanes (A) having formulas (II) and/or (ii). In addition, component (A) may include a combination of two or more different organopolysiloxanes (A) having formulas (I), (i), (II), and/or (ii).

[0017] In certain embodiments, the organopolysiloxane (A) comprises at least one of the pentasiloxane and the hexasiloxane, each of the pentasiloxane and the hexasiloxane independently having the formula:

$$\text{(III)} \quad (R^1R^3_2SiO)_{6\text{-}a}SiR^4_a$$

wherein each R^1, R^3, and R^4 independently comprises an alkyl group, an aryl group, or an alkenyl group, and subscript a is 0 for the hexasiloxane or 1 for the pentasiloxane. Suitable alkyl, aryl, and alkenyl groups are as described and exemplified above.

[0018] In certain embodiments, each of the pentasiloxane and the hexasiloxane independently have the formula:

$$\text{(iii)} \quad (ViR^3_2SiO)_{6\text{-}a}SiR^4_a$$

wherein Vi is a vinyl group, each R^3 and R^4 independently comprises a phenyl group or a methyl group, and subscript a is 0 for the hexasiloxane or 1 for the pentasiloxane. In these embodiments, the pentasiloxane and/or the hexasiloxane of formula (iii) imparts the composition with excellent homogeneity and low viscosity and imparts the product with high modulus and a refractive index which can be tailored depending upon whether R^4 is a methyl or phenyl group, as described in further detail below. It is to be appreciated that component (A) may include a combination of two or more different organopolysiloxanes (A) having formulas (III) and/or (iii). In addition, component (A) may include a combination of two or more different organopolysiloxanes (A) having formulas (I), (i), (II), (ii), (III), and/or (iii).

[0019] Methods of preparing component (A) as described above and represented by formulas (I), (i), (II), (ii), (III), and (iii) are understood by those skilled in the silicone art. Component (A) as described and exemplified above, and other specific examples of suitable organopolysiloxanes (A) for purposes of the present invention, such as $(ViSiMe)_2OSiPh_2$, vinyldimethylsiloxy-group terminated phenylsilsesquioxanes, 1,3–dimethyl-1,3-diphenyl-1,3-divinyldisiloxane, 1,5-divinyl-3-(dimethylvinylsiloxy)-1,1,5,5-tetramethyl-3-phenyltrisiloxane, 1,5-divinyl-3-(dimethylvinylsiloxy)-1,1,5,5-tetramethyl-3-methyltrisiloxane, 1,1,3,3-tetramethyl-1,3-divinyldisiloxane, tetrakis(vinyldimethylsiloxy)silane, tetrakis(vinyldiphenylsiloxy)silane, and tetrakis(vinylmethylphenylsiloxy)silane, 1,1,5,5-tetramethyl-1,5-divinyl-3-diphenyltrisiloxane, 1,1,7,7-tetramethyl-1,7-divinyl-3,5-diphenyltetrasiloxane, 1,1,9,9-tetramethyl-1,9-divinyl-3,5,7-triphenylpentasiloxane, 1,1,11,11-tetramethyl-1,11-divinyl-3,5,7,9-tetraphenylhexasiloxane, and additional penta and hexasiloxanes with methylphenyl and/or diphenyl siloxanes, are available from Gelest of Morrisville, PA.

[0020] Component (A) has a number average molecular weight no greater than 1500, alternatively a number average molecular weight no greater than 1000, alternatively a number average molecular weight no greater than 800. Generally, decreasing the number average molecular weight of the organopolysiloxane (A) correlates to lower viscosity, which facilitates easier dispense.

[0021] In certain embodiments, such as when component (A) is of the formula (I) or (i) as described above, component (A) is typically present in an amount ranging from 30 to 65, more typically from 35 to 45, most typically from 38 to 44, parts by weight, based on 100 parts by weight of the composition. In other embodiments, such as when component (A) is of the formula (II) or (ii) as described above, component (A) is typically present in an amount ranging from 20 to 60, more typically from 25 to 45, most typically from 20 to 40, parts by weight, based on 100 parts by weight of the composition. It is to be appreciated that component (A), and therefore the composition, may include any combination of two or more of the aforementioned organopolysiloxanes (A).

[0022] The organohydrogensiloxane component (B), hereinafter component (B), has at least one of an alkyl group and an aryl group. In other words, component (B) has an alkyl group, or an aryl group, or a combination of alkyl and aryl groups. Suitable alkyl and aryl groups for component (B) are as described and exemplified above with description of component (A). In certain embodiments, component (B) has at least one phenyl group. In these embodiments, component (B) may include one or more aryl groups different than phenyl groups. Component (B) has an average of at least two silicon-bonded hydrogen atoms per molecule, alternatively at least three silicon-bonded hydrogen atoms per molecule.

[0023] In certain embodiments, component (B) comprises a silicone resin having the formula:

$$\text{(IV)} \qquad (R^6R^7_2SiO_{1/2})_y(R^5SiO_{3/2})_x$$

wherein each R^5 and R^6 independently comprises an alkyl group, an aryl group, an alkenyl group, or a hydrogen atom, each R^7 independently comprises an alkyl group, an aryl group, or an alkenyl group, subscript x ranges from 0.2 to 0.6, more typically from 0.35 to 0.45, most typically 0.4, and $x + y = 1$. Suitable alkyl, aryl, and alkenyl groups for formula (IV) are as described and exemplified above with the organopolysiloxane (A).

[0024] In certain embodiments, the silicone resin has the formula:

$$\text{(iv)} \qquad (HR^7_2SiO_{1/2})_y(R^5SiO_{3/2})_x$$

wherein each R^5 and R^7 independently comprises a phenyl group or a methyl group, subscript x ranges from 0.2 to 0.6, more typically from 0.35 to 0.45, most typically 0.4, and $x + y = 1$. In these embodiments, the organohydrogensiloxane (B) of formula (iv) imparts the composition with excellent homogeneity and low viscosity, and imparts the product with high modulus and an increased refractive index, which is described in further detail below. It is to be appreciated that component (B) may include a combination of two or more different organohydrogensiloxanes (B) having formulas (IV) and/or (iv).

[0025] In certain embodiments, component (B) comprises a siloxane having the formula:

$$\text{(V)} \qquad (R^6R^7_2SiO)(R^5_2SiO)_z(SiR^6R^7_2)$$

wherein each R^5 and R^6 independently comprises an alkyl group, an aryl group, an alkenyl group, or a hydrogen atom, each R^7 independently comprises an alkyl group, an aryl group, or an alkenyl group, and subscript $z \geq 1$, more typically $5 \geq z \geq 1$, most typically $2.5 \geq z \geq 1$. Suitable alkyl, aryl, and alkenyl groups for formula (V) are as described and exemplified above with description of the organopolysiloxane (A).

[0026] In certain embodiments, the siloxane has the formula:

$$\text{(v)} \qquad (HR^7_2SiO)(R^5_2SiO)_z(SiHR^7_2)$$

wherein each R^5 and R^7 independently comprises a phenyl group or a methyl group, and $5 \geq z \geq 1$, more typically $2.5 \geq z \geq 1$, most typically subscript $z = 2.5$, alternatively subscript $z = 1$. In these embodiments, the organohydrogensiloxane (B) of formula (v) imparts the composition with excellent homogeneity and low viscosity and imparts the product with high modulus and an increased refractive index, which is described in further detail below. It is to be appreciated that component (B) may include a combination of two or more different organohydrogensiloxanes (B) having formulas (V) and/or (v). In addition, component (B) may include a combination of two or more different organohydrogensiloxanes (B) having formulas (IV), (iv), (V), and/or (v).

[0027] Methods of preparing component (B) as described above and represented by formulas

(IV), (iv), (V), and (v), are understood by those skilled in the silicone art. Component (B) as described and exemplified above and other specific examples of suitable organohydrogensiloxanes (B) for purposes of the present invention, such as bis(dimethylsilyl)phenylene, 1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane, 1,3–dimethyl-1,3-diphenyl-1,3-dihydrodisiloxane, 1,5-dihydro-3-(dimethylhydrosiloxy)-1,1,5,5-tetramethyl-3-phenyltrisiloxane, 1,5-dihydro-3-(dimethylhydrosiloxy)-1,1,5,5-tetramethyl-3-methyltrisiloxane, 1,1,3,3-tetramethyl-1,3-dihydrodisiloxane, tetrakis(hydrodimethylsiloxy)silane, tetrakis(hydrodiphenylsiloxy)silane, tetrakis(hydromethylphenylsiloxy)silane, 1,9-dihydro-1,1,9,9-tetramethyl-3,5,7-triphenylpentasiloxane, and 1,11-dihydro-1,1,11,11-tetramethyl-3,5,7,9-tetraphenylhexasiloxane, are commercially available from Dow Corning Corporation of Midland, MI.

[0028] Component (B) has a number average molecular weight no greater than 1500, alternatively a number average molecular weight no greater than 1000, alternatively a number average molecular weight no greater than 900. In one embodiment, component (B) is of the general formula $M^{H}_{0.4}T^{Ph}_{0.6}$ and has a number average molecular weight of ~820. Generally, decreasing the number average molecular weight of the organohydrogensiloxane (B) correlates to lower viscosity, enabling easier dispense.

[0029] In certain embodiments, such as when component (B) is of the formula (IV) or (iv) as described above, component (B) is typically present in an amount ranging from 10 to 80, more typically from 25 to 70, most typically from 30 to 60, parts by weight, each based on 100 parts by weight of the composition. In other embodiments, such as when component (B) is of the formula (V) or (v) as described above, component (B) is typically present in an amount ranging from 10 to 80, more typically from 25 to 70, most typically from 30 to 60, parts by weight, based on 100 parts by weight of the composition. It is to be appreciated that component (B), and therefore the composition, may include any combination of two or more of the aforementioned organohydrogensiloxanes (B).

[0030] In certain embodiments, as alluded to above, the component (B) comprises the silicone resin and the siloxane. Both the silicone resin and siloxane are as described and exemplified above. In one embodiment, component (B) comprises the silicone resin of formula (IV) and the siloxane of formula (V). In a further embodiment, component (B) comprises the silicone resin of formula (iv) and the siloxane of formula (v). In these embodiments, the silicone resin and the siloxane may be present in the composition in various weight ratios relative to one another. If both the silicone resin and the siloxane are present in the composition, the silicone resin and siloxane are typically present in the composition in a weight ratio (silicone resin:siloxane) ranging from 1:0.5 to 1:6.0. In one embodiment, the silicone resin and the siloxane are present in the composition in a weight ratio ranging from 1:0.5 to 1:1.5. In another embodiment, the silicone resin and the siloxane are present in the composition in a weight ratio ranging from 1:1.5 to 1:2. In yet another embodiment, the silicone resin and the siloxane are present in the composition in a weight ratio ranging from 1:2.5 to 1:3.5. In yet another embodiment, the silicone resin and the siloxane are present in the composition in a weight ratio ranging from 1:3.5 to 1:6.0. In these embodiments, increasing the amount of the silicone resin relative to the amount of the siloxane present in the composition generally imparts the product with increased modulus.

[0031] In certain embodiments, the composition (prior to fully curing) has a surface energy ranging from 19 to 33, more typically from 23 to 31, most typically from 28 to 30, dynes/cm. These embodiments are especially useful when the composition is used as a matrix for incorporation of the metal-oxide nanoparticles (D), and, optionally, other materials, such as particles and/or optical active agents, e.g. phosphors, all of which are described in further detail below. If such materials are incorporated, it is believed that matching a surface energy of the material to that of the composition provides for increased homogeneity of the composition and the materials incorporated therein.

[0032] In certain embodiments, the composition has a molar ratio of alkyl groups to aryl groups ranging from 1:0.25 to 1:3.0, more typically from 1:0.5 to 1:2.5, most typically from 1:1 to 1:2. The refractive index of the product may be increased or decreased by increasing or decreasing the number of aryl groups, e.g. phenyl groups, present in the composition, respectively.

[0033] The hydrosilylation catalyst component (C), hereinafter component (C), can include any one of the well-known hydrosilylation catalysts comprising a group VIII transition metal, typically a platinum group metal, e.g. platinum, rhodium, ruthenium, palladium, osmium, and iridium, and/or a compound containing a platinum group metal. In one embodiment, the platinum group metal is platinum, based on its high activity in hydrosilylation reactions. Specific examples of suitable hydrosilylation catalysts (C), for purposes of the present invention, include complexes of chloroplatinic acid, platinum dichloride, and certain vinyl-containing organosiloxanes disclosed by Willing in U.S. Patent No. 3,419,593, which is hereby incorporated by reference. A catalyst of this type is the reaction product of chloroplatinic acid and 1,3-diethenyl-1,1,3,3-tetramethyldisiloxane. Other suitable hydrosilylation catalysts (C), for purposes of the present invention, are described in EP 0 347 895 B and U.S. Patent Nos. 3,159,601; 3,220,972; 3,296,291; 3,516,946; 3,814,730; 3,989,668; 4,784,879; 5,036,117; and 5,175,325.

[0034] Component (C) can also include a microencapsulated platinum group metal-containing catalyst comprising a platinum group metal encapsulated in a thermoplastic resin. Microencapsulated hydrosilylation catalysts and methods of preparing them are well known in the catalytic art, as exemplified in U.S. Patent No. 4,766,176 and the references cited therein, and U.S. Patent No. 5,017,654.

[0035] Component (C) can also include a platinum di(acetylacetonate) photo-activated hydrosilylation catalyst. The photo-activated hydrosilylation catalyst can be any hydrosilylation catalyst capable of catalyzing the hydrosilylation reaction of components (A) and (B) upon exposure to radiation having a wavelength ranging from 150 to 800 nm. The photo-activated hydrosilylation catalyst can be any of the well-known hydrosilylation catalysts comprising a platinum group metal or a compound containing a platinum group metal. The platinum group metals include platinum, rhodium, ruthenium, palladium, osmium, and iridium. In one embodiment, the platinum group metal is platinum, based on its high activity in hydrosilylation reactions.

[0036] Specific examples of suitable photo-activated hydrosilylation catalysts, for purposes of the present invention, include, but are not limited to, platinum(II) β-diketonate complexes such as platinum(II) bis(2,4-pentanedioate), platinum(II) bis(2,4-hexanedioate), platinum(II) bis(2,4-heptanedioate), platinum(II) bis(1-phenyl-1,3-butanedioate, platinum(II) bis(1,3-diphenyl-1,3-propanedioate), platinum(II) bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedioate); (η-cyclopentadienyl)trialkylplatinum complexes, such as (Cp)trimethylplatinum, (Cp)ethyldimethylplatinum, (Cp)triethylplatinum, (chloro-Cp)trimethylplatinum, and (trimethylsilyl-Cp)trimethylplatinum, where Cp represents cyclopentadienyl; triazene oxide-transition metal complexes, such as $Pt[C_6H_5NNNOCH_3]_4$, $Pt[p\text{-}CN\text{-}C_6H_4NNNOC_6H_{11}]_4$, $Pt[p\text{-}H_3COC_6H_4NNNOC_6H_{11}]_4$, $Pt[p\text{-}CH_3(CH_2)_x\text{-}C_6H_4NNNOCH_3]_4$, 1,5-cyclooctadiene.$Pt[p\text{-}CN\text{-}C_6H_4NNNOC_6H_{11}]_2$, 1,5-cyclooctadiene.$Pt[p\text{-}CH_3O\text{-}C_6H_4NNNOCH_3]_2$, $[(C_6H_5)_3P]_3Rh[p\text{-}CN\text{-}C_6H_4NNNOC_6H_{11}]$, and $Pd[p\text{-}CH_3(CH_2)_x\text{—}C_6H_4NNNOCH_3]_2$, where x is 1, 3, 5, 11, or 17; (η-diolefin)(σ-aryl)platinum complexes, such as (η^4-1,5-cyclooctadienyl)diphenylplatinum, η^4-1,3,5,7-cyclooctatetraenyl)diphenylplatinum, (η^4-2,5-norboradienyl)diphenylplatinum, (η^4-1,5-

cyclooctadienyl)bis-(4-dimethylaminophenyl)platinum, (η^4-1,5-cyclooctadienyl)bis-(4-acetylphenyl)platinum, and (η^4-1,5-cyclooctadienyl)bis-(4-trifluormethylphenyl)platinum. In certain embodiments, the photo-activated hydrosilylation catalyst is a Pt(II) β-diketonate complex, more typically platinum(II) bis(2,4-pentanedioate).

[0037] Methods of preparing photo-activated hydrosilylation catalysts are well known in the catalytic art. For example, methods of preparing platinum(II) β-diketonates are reported by Guo et al. (Chemistry of Materials, 1998, 10, 531-536); methods of preparing (η-cyclopentadienyl)-trialkylplatinum complexes are disclosed in U.S. Patent No. 4,510,094; methods of preparing triazene oxide-transition metal complexes are disclosed in U.S. Patent No. 5,496,961; and methods of preparing (η-diolefin)(σ-aryl)platinum complexes are disclosed in U.S. Patent No. 4,530,879.

[0038] Component (C) is typically present in a catalytic amount, i.e., in an amount sufficient to catalyze the hydrosilylation reaction of the organopolysiloxane (A) and the organohydrogensiloxane (B). For example, the hydrosilylation catalyst (C) is typically present in an amount to provide from 2 to 10, more typically from 6 to 8, most typically 6, ppm of the group VIII transition metal, based on 100 parts by weight of the composition. Generally, the rate of reaction is slower below 2 ppm, and is vulnerable to inhibition of the catalyst and using more than 10 ppm can result in yellowing upon thermal aging of the hydrosilylation reaction product of the organopolysiloxane (A) and the organohydrogensiloxane (B), i.e., the product, which is described in further detail below. It is to be appreciated that component (C) may include any combination of two or more of the aforementioned hydrosilylation catalysts (C).

[0039] The composition of the present invention can also include additional siloxanes and/or silanes, other than those described and exemplified herein for use as components (A) and (B). If employed, such additional siloxanes and silanes can be used for increasing compatibilization of the metal-oxide nanoparticles (D) within the composition. Examples of such additional components include octadecyltrimethoxysilane and $T^{Ph}_{0.40}T_{0.45}D^{Ph}_{0.05}D^{Ph2}_{0.10}$ having a molecular weight of ~2,500. Typically, the composition of the present invention is free of polydimethylsiloxane (PDMS). It is believed that employing PDMS, which lacks phenyl groups, imparts the composition, and therefore, products formed therefrom, with undesirable properties, such as reduced transparency (e.g. milkiness) and non-homogeneity.

[0040] The composition may further comprise an additive selected from the group of optically active agents, e.g. phosphors; cure modifiers, e.g. catalyst-inhibitors; and combinations thereof.

A specific example of a suitable cure inhibitor, for purposes of the present invention, is phenylbutynol (PBO). It is to be appreciated that the composition may include other additives known in the silicone art, some of which are further described below. For example, the composition may further comprise at least one of a co-crosslinker, an adhesion promoter, a filler, a treating agent, a rheology modifier, and combinations thereof. It is to be appreciated that the composition may include any combination of two or more of the aforementioned additives.

[0041] If included, any type of phosphor known in the art may be used. The phosphors are optionally included in the composition, and therefore the product, to adjust color emitted from the LED. The phosphors are generally any compound/material that exhibits phosphorescence. The phosphor material may be selected from the group of inorganic particles, organic particles, organic molecules, and combinations thereof. The aforementioned phosphor materials may be in the form of conventional bulk-particle powders, e.g. powders having an average diameter ranging from 1 to 25 um, and/or nanoparticle powders.

[0042] Suitable inorganic particles as the phosphor material, for purposes of the present invention, include, but are not limited to, doped garnets such as YAG:Ce and (Y,Gd)AG:Ce; aluminates such as $Sr_2Al_{14}O_{25}$:Eu, and BAM:Eu; silicates such as SrBaSiO:Eu; sulfides such as ZnS:Ag, CaS:Eu, and $SrGa_2S_4$:Eu; oxy-sulfides; oxy-nitrides; phosphates; borates; and tungstates such as $CaWO_4$. Other suitable inorganic particles, for purposes of the present invention, include quantum dot phosphors made of semiconductor nanoparticles including, but not limited to Ge, CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe, PbS, PbSe, PbTe, InN, InP, InAs, AIN, AIP, AlAs, GaN, GaP, GaAs and combinations thereof. Generally, a surface of each quantum dot phosphor will be at least partially coated with an organic molecule to prevent agglomeration and increase compatibility. In certain embodiments, the phosphor, e.g. quantum dot phosphor, is made up of several layers of different materials in a core-shell construction. Suitable organic molecules for coating the surface of the quantum dot phosphor include, but are not limited to, absorbing dies and fluorescent dyes, such as those described in U.S. Patent No. 6,600,175. Other suitable phosphors for purposes of the present invention are described in International Publication No. WO 2006/0600141 to Taskar et al., International Publication No. WO 2005/027576 to Taskar et al., U.S. Patent No. 6,734,465 to Taskar et al., and U.S. Patent No. 7,259,400 to Taskar at al., the disclosures of which pertaining to conventional and inventive phosphors are incorporated herein by reference in their entirety.

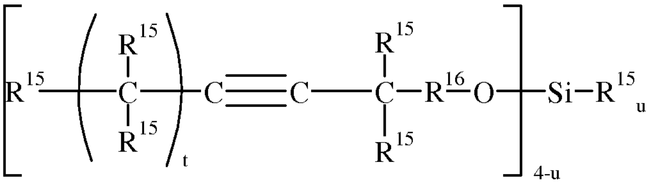
[0043] If employed, the amount of optically active agent used depends on various factors including the optically active agent selected and the end use application. If included, the optically active agent, e.g. phosphors, are typically present in an amount ranging from 0.01 to 25, more typically from 1 to 15, most typically from 5 to 10, parts by weight, each based on 100 parts by weight of the composition. The amount of optically active agent can be adjusted, for example, according to a thickness of a layer of the product containing the optically active agent and a desired color of emitted light. Other suitable optically active agents include photonic crystals and carbon nanotubes. It is to be appreciated that the composition may include any combination of two or more of the aforementioned optically active agents.

[0044] If included, any type of cure modifier known in the silicone art may be used. The cure modifier is optionally included in the composition to allow curing of the composition to be controlled after components (A), (B), and (C), are mixed together, which is described further below. The cure modifier is especially useful in the composition during formation of the product on the substrate, such as when making the LED. The cure modifier allows sufficient working time to be able to apply the composition onto the substrate prior to gelling and, ultimately, curing of the product.

[0045] The cure modifier can be added to extend the shelf life and/or the working time of the composition. The cure modifier can also be added to raise the curing temperature of the composition. Suitable cure modifiers are known in the silicone art and are commercially available. The cure modifier is exemplified by acetylenic alcohols, cycloalkenylsiloxanes, eneyne compounds, triazoles phosphines; mercaptans, hydrazines, amines, fumarates, maleates, and combinations thereof. Examples of acetylenic alcohols are disclosed, for example, in EP 0 764 703 A2 and U.S. Patent No. 5,449,802 and include methyl butynol, ethynyl cyclohexanol, dimethyl hexynol, 1-butyn-3-ol, 1-propyn-3-ol, 2-methyl-3-butyn-2-ol, 3-methyl-1-butyn-3-ol, 3-methyl-1-pentyn-3-ol, 3-phenyl-1-butyn-3-ol, 4-ethyl-1-octyn-3-ol, 3,5-diemthyl-1-hexyn-3-ol, and 1-ethynyl-1-cyclohexanol, and combinations thereof. Examples of cycloalkenylsiloxanes include methylvinylcyclosiloxanes exemplified by 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetrahexenylcyclotetrasiloxane, and combinations thereof. Examples of eneyne compounds include 3-methyl-3-penten-1-yne, 3,5-dimethyl-3-hexen-1-yne, and combinations thereof. Examples of triazoles include benzotriazole. Examples of phosphines include triphenylphosphine. Examples of amines include tetramethyl ethylenediamine. Examples of fumarates include dialkyl fumarates, dialkenyl fumarates, dialkoxyalkyl fumarates, and combinations thereof. Suitable cure modifiers are disclosed by, for example, U.S. Patent Nos. 3,445,420; 3,989,667; 4,584,361; and 5,036,117.

[0046] Alternatively, the cure modifier may comprise a silylated acetylenic inhibitor. Without being bound or limited to any particular theory, it is believed that adding a silylated acetylenic inhibitor reduces yellowing of the product prepared from the composition as compared to a product prepared from a hydrosilylation curable composition that does not contain an inhibitor or that contains an acetylenic alcohol.

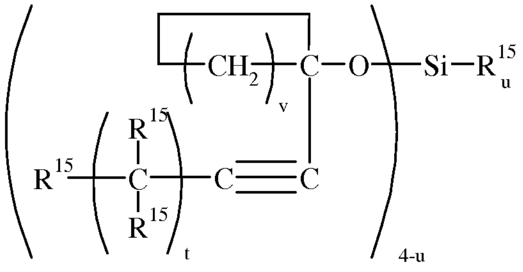
[0047] Suitable silylated acetylenic inhibitors may have the general formula (V):



$$\left[R^{15}\left(\underset{R^{15}}{\overset{R^{15}}{C}}\right)_t C\equiv C-\underset{R^{15}}{\overset{R^{15}}{C}}-R^{16}-O\right]_{4-u}Si-R^{15}_u$$

,

the general formula (VI):



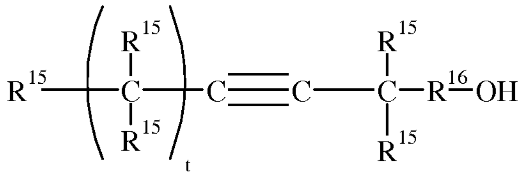
,

or a combination thereof; wherein each R^{15} is independently a hydrogen atom or a monovalent organic group, R^{16} is a covalent bond or a divalent hydrocarbon group, subscript u is 0, 1, 2, or 3, subscript t is 0 to 10, and subscript v is 4 to 12. Alternatively u is 1 or 3. Alternatively, in general formula (V) subscript u is 3. Alternatively, in general formula (VI) subscript u is 1, alternatively subscript t is 0, alternatively subscript v is 5, 6, or 7, and alternatively subscript v is 6. Examples of monovalent organic groups for R^{15} include an aliphatically unsaturated organic group, an aromatic group, or a monovalent substituted or unsubstituted hydrocarbon group free of aromatics and free aliphatic unsaturation, as described and exemplified above.

[0048] Suitable silylated acetylenic inhibitors are exemplified by (3-methyl-1-butyn-3-oxy)trimethylsilane, ((1,1-dimethyl-2-propynyl)oxy)trimethylsilane, bis(3-methyl-1-butyn-3-oxy)dimethylsilane, bis(3-methyl-1-butyn-3-oxy)silanemethylvinylsilane, bis((1,1-dimethyl-2-propynyl)oxy)dimethylsilane, methyl(tris(1,1-dimethyl-2-propynyloxy))silane, methyl(tris(3-methyl-1-butyn-3-oxy))silane, (3-methyl-1-butyn-3-oxy)dimethylphenylsilane, (3-methyl-1-

butyn-3-oxy)dimethylhexenylsilane, (3-methyl-1-butyn-3-oxy)triethylsilane, bis(3-methyl-1-butyn-3-oxy)methyltrifluoropropylsilane, (3,5-dimethyl-1-hexyn-3-oxy)trimethylsilane, (3-phenyl-1-butyn-3-oxy)diphenylmethylsilane, (3-phenyl-1-butyn-3-oxy)dimethylphenylsilane, (3-phenyl-1-butyn-3-oxy)dimethylvinylsilane, (3-phenyl-1-butyn-3-oxy)dimethylhexenylsilane, (cyclohexyl-1-ethyn-1-oxy)dimethylhexenylsilane, (cyclohexyl-1-ethyn-1-oxy)dimethylvinylsilane, (cyclohexyl-1-ethyn-1-oxy)diphenylmethylsilane, (cyclohexyl-1-ethyn-1-oxy)trimethylsilane, and combinations thereof. Alternatively, the silylated acetylenic inhibitor may comprise methyl(tris(1,1-dimethyl-2-propynyloxy))silane, ((1,1-dimethyl-2-propynyl)oxy)trimethylsilane, and combinations thereof.

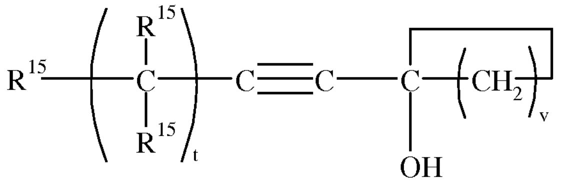
[0049] Silylated acetylenic inhibitors may be prepared by methods known in the art for silylating an alcohol such as reacting a chlorosilane of formula $R^{15}_uSiCl_{4-u}$ with an acetylenic alcohol of the general formula (VII):



$$R^{15}-\left(\begin{array}{c}R^{15}\\|\\C\\|\\R^{15}\end{array}\right)_t-C\equiv C-\begin{array}{c}R^{15}\\|\\C\\|\\R^{15}\end{array}-R^{16}-OH$$

,

or the general formula (VIII):



in the presence of an acid receptor˙

[0050] In the general formulas (VII) and (VIII), each of the R^{15}, R^{16}, and subscripts u, t, and v, are as described above. Examples of silylated acetylenic inhibitors and methods for their preparation are disclosed, for example, in EP 0 764 703 A2 and U.S. Patent No. 5,449,802.

[0051] Other suitable cure modifiers, for purposes of the present invention, include, but are not limited to, methyl-butynol, 3-methyl-3-penten-1-yne, 3,5-dimethyl-3-hexen-1-yne, 3,5-dimethyl-1-hexyn-3-ol, 1-ethynyl-1-cyclohexanol, 2-phenyl-3-butyn-2-ol, vinylcyclosiloxanes, and triphenylphosphine. Other suitable cure modifiers include acetylenic alcohols such as those described in U.S. Patent Nos. 3,989,666 and 3,445,420; unsaturated carboxylic esters such as those described in U.S. Patent Nos. 4,504,645; 4,256,870; 4,347,346; and 4,774,111; and certain olefinic siloxanes such as those described in U.S. Patent Nos. 3,933,880; 3,989,666; and

3,989,667. One specific example of a suitable cure modifier, for purposes of the present invention, is 3,5-dimethyl-1-hexyn-3-ol, commercially available from Air Products and Chemicals Inc, of Allentown, PA, under the trade name Surfynol® 61.

[0052] If employed, the amount of the cure modifier added to the composition will depend on the particular cure modifier used, and the makeup and amounts of components (C), (A), and (B). If included, the cure modifier is typically present in an amount ranging from 1.0 to 10000, more typically from 25 to 500, most typically from 50 to 100, ppm, each based on 100 parts by weight of the composition. It is to be appreciated that various amounts may be used, depending on strength of the cure modifier. It is to be appreciated that the composition may include any combination of two of more of the aforementioned cure modifiers.

[0053] If employed, the co-crosslinker may be added to the composition in an amount ranging from 0.01 to 50, alternatively ranging from 0.01 to 25, alternatively ranging from 1 to 5, parts by weight, all based on 100 parts by weight of the composition. The co-crosslinker may comprise a hydrogensilyl functional polyorganosiloxane having an average compositional formula given as $H_cR^8_dSiO_{(4-c-d)/2}$, wherein each R^8 is independently a methyl group or a phenyl group, with at least 30 mol% of R^8 being phenyl groups, subscripts a and b are positive numbers, and $c + d = 1$ to 2.2 and $c / (c + d) = 0.001$ to 0.05.

[0054] If employed, the adhesion promoter may be added to the composition in an amount ranging from 0.01 to 50, alternatively ranging from 0.01 to 10, alternatively ranging from 0.01 to 5, parts by weight, all based on 100 parts by weight of the composition. The adhesion promoter may comprise (a) an alkoxysilane, (b) a combination of an alkoxysilane and a hydroxy-functional polyorganosiloxane, or (c) a combination thereof, or a combination of component (a), (b) or (c) with a transition metal chelate. Alternatively, the adhesion promoter may comprise an unsaturated or epoxy-functional compound. Suitable epoxy-functional compounds are known in the silicone art and are commercially available; see e.g. U.S. Patent Nos. 4,087,585; 5,194,649; 5,248,715; and 5,744,507 (col. 4-5). The adhesion promoter may comprise an unsaturated or epoxy-functional alkoxysilane. For example, the unsaturated or epoxy-functional alkoxysilane can have the formula $R^9_eSi(OR^{10})_{(4-e)}$, wherein subscript e is 1, 2, or 3, alternatively subscript e is 1. 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. Each R^{10} is independently an unsubstituted, saturated hydrocarbon group of 1 to 4 carbon atoms, alternatively 1 to 2 carbon atoms. R^{10} is exemplified by methyl, ethyl, propyl, and butyl.

[0055] 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.

[0056] The adhesion promoter 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. The adhesion promoter may comprise a combination of an epoxy-functional alkoxysilane and an epoxy-functional siloxane. For example, the adhesion promoter is exemplified by a mixture of 3-glycidoxypropyltrimethoxysilane and a reaction product of hydroxy-terminated methylvinylsiloxane with 3-glycidoxypropyltrimethoxysilane, or a mixture of 3-glycidoxypropyltrimethoxysilane and a hydroxy-terminated methylvinylsiloxane, or a mixture of 3-glycidoxypropyltrimethoxysilane and a hydroxy-terminated methyvinyl/dimethylsiloxane copolymer, or a mixture of 3-glycidoxypropyltrimethoxysilane and a hydroxy-terminated methylvinyl/methylphenylsiloxane copolymer. When used as a physical blend rather than as a reaction product, these components may be stored separately in multiple-part kits.

[0057] If employed, suitable transition metal chelates include titanates, aluminum chelates such as aluminum acetylacetonate, and combinations thereof. Transition metal chelates and methods for their preparation are known in the art, see e.g. U.S. Patent No. 5,248,715; EP 0 493 791 A1; and EP 0 497 349 B1.

[0058] If employed, the amount of filler added to the composition depends on the type of filler selected and the resulting optical transparency. Filler may be added to the composition in an amount ranging from 0.1% to 50%, alternatively ranging from 0.1% to 25%, both based on the weight of the composition. Suitable fillers include reinforcing fillers, such as silica. Suitable reinforcing fillers are known in the art and are commercially available, such as a fumed silica sold under the name CAB-O-SIL by Cabot Corporation of Massachusetts.

[0059] Conductive fillers, i.e., fillers that are thermally conductive, electrically conductive, or both thermally and electrically conductive, may also be used as the filler. Suitable conductive fillers include metal particles, metal-oxide particles, and combinations thereof. Suitable thermally conductive fillers are exemplified by aluminum nitride; aluminum oxide; barium titanate; beryllium oxide; boron nitride; diamond; graphite; magnesium oxide; metal particulate such as copper, gold, nickel, or silver; silicon carbide; tungsten carbide; zinc oxide, and combinations thereof.

[0060] Conductive fillers are known in the art and are commercially available; see e.g. U.S. Patent No. 6,169,142 (col. 4, lines 7-33). For example, CB-A20S and Al-43-Me are aluminum oxide fillers of differing particle sizes, which are commercially available from Showa-Denko; and AA-04, AA-2, and AA18 are aluminum oxide fillers, which are commercially available from Sumitomo Chemical Company. Silver filler is commercially available from Metalor Technologies U.S.A. Corp. of Attleboro, Massachusetts, U.S.A. Boron nitride filler is commercially available from Advanced Ceramics Corporation, Cleveland, Ohio, U.S.A.

[0061] The shape of the filler particles is not specifically restricted; however, rounded or spherical particles may prevent viscosity increase to an undesirable level upon high loading of the filler in the composition. A combination of fillers having differing particle sizes and different particle size distributions may be used. For example, it may be desirable to combine a first filler having a larger average particle size with a second filler having a smaller average particle size in a proportion meeting the closest packing theory distribution curve. This may improve packing efficiency and may reduce viscosity.

[0062] All or a portion of the filler may comprise spacers. Spacers can comprise organic particles such as polystyrene, inorganic particles such as glass, or combinations thereof. Spacers can be thermally conductive, electrically conductive, or both thermally and electrically conductive. Spacers can have a particle size of 25 micrometers to 250 micrometers. Spacers can comprise monodisperse beads. The amount of spacer depends on various factors including, for example, the distribution of particles, pressure to be applied during placement of the composition, and temperature of placement.

[0063] The filler may optionally be surface treated with the treating agent. Treating agents and treating methods are known in the art; see e.g. U.S. Patent No. 6,169,142 (col. 4, line 42 to col. 5, line 2). The filler may be treated with the treating agent prior to combining the filler with the other components of the composition, or the filler may be treated *in situ*.

[0064] The treating agent can be an alkoxysilane having the formula: $R^{11}{}_fSi(OR^{12})_{(4-f)}$, wherein subscript f is 1, 2, or 3; alternatively subscript f is 3. Each R^{11} is independently a substituted or unsubstituted monovalent hydrocarbon group of 1 to 50 carbon atoms. R^{11} is exemplified by alkyl groups such as hexyl, octyl, dodecyl, tetradecyl, hexadecyl, and octadecyl; and aromatic groups such as benzyl, phenyl and phenylethyl. R^{11} can be saturated or unsaturated, branched or unbranched, and unsubstituted. R^{11} can be saturated, unbranched, and unsubstituted. Each R^{12} is independently an unsubstituted, saturated hydrocarbon group of 1 to 4 carbon atoms, alternatively 1 to 2 carbon atoms. The treating agent is exemplified by hexyltrimethoxysilane, octyltriethoxysilane, decyltrimethoxysilane, dodecyltrimethyoxysilane, tetradecyltrimethoxysilane, phenyltrimethoxysilane, phenylethyltrimethoxysilane, octadecyltrimethoxysilane, octadecyltriethoxysilane, and combinations thereof.

[0065] Alkoxy-functional oligosiloxanes can also be used as treating agents. Alkoxy-functional oligosiloxanes and methods for their preparation are known in the silicone art, see e.g. EP 1 101 167 A2. For example, suitable alkoxy-functional oligosiloxanes include those of the formula $(R^{13}O)_gSi(OSiR^{14}{}_2R^{15})_{4-g}$, wherein subscript g is 1, 2, or 3, alternatively subscript g is 3. Each R^{13} can independently be an alkyl group. Each R^{14} can be independently selected from saturated and unsaturated monovalent hydrocarbon groups of 1 to 10 carbon atoms. Each R^{15} can be a saturated or unsaturated monovalent hydrocarbon group having at least 11 carbon atoms.

[0066] If employed, metal fillers can be treated with alkylthiols such as octadecyl mercaptan and others, and fatty acids such as oleic acid, stearic acid, titanates, titanate coupling agents, and combinations thereof. Treating agents for alumina or passivated aluminum nitride may include alkoxysilyl functional alkylmethyl polysiloxanes, e.g. partial hydrolysis condensate of $R^{16}{}_hR^{17}{}_iSi(OR^{18})_{(4-h-i)}$, or cohydrolysis condensates or mixtures, similar materials where the hydrolyzable group would be silazane, acyloxy or oximo. In all of these, a group tethered to Si, such as R^{16} in the formula above, is a long chain unsaturated monovalent hydrocarbon or monovalent aromatic-functional hydrocarbon. Each R^{17} is independently a monovalent hydrocarbon group, and each R^{18} is independently a monovalent hydrocarbon group of 1 to 4 carbon atoms. In the formula above, subscript h is 1, 2, or 3 and subscript i is 0, 1, or 2, with the proviso that h + i is 1, 2, or 3. One skilled in the silicone art can optimize a specific treatment to aid dispersion of the filler without undue experimentation.

[0067] The rheology modifiers can be added to change the thixotropic properties of the composition. The rheology modifier is exemplified by flow control additives; reactive diluents; anti-settling agents; alpha-olefins; non-reactive phenyl silsesquioxanes; hydroxyl terminated methylphenyl siloxane homopolymers; hydroxyl-terminated silicone-organic copolymers, including, but not limited to, hydroxyl-terminated polypropyleneoxide-dimethylsiloxane copolymers; and combinations thereof.

[0068] Other optional components may be added in addition to, or instead of, all or a portion of those additive components described above, provided the optional components do not prevent the composition from curing to form the product. Examples of other optional additives 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 Angstroms or less), kieselguhr, silica gel, and activated carbon; optical diffusants; colloidal silica; and blowing agents, such as water, methanol, ethanol, iso-propyl alcohol, benzyl alcohol, 1,4 butanediol, 1,5 pentanediol, 1,7 heptanediol, and silanols. It is to be appreciated that the composition may include any combination of two or more of the aforementioned additive components.

[0069] The composition may be used alone, or may be used for incorporation of other materials, i.e., the composition may be used as a matrix for incorporation of other materials, such as the particles and/or the phosphors as described above. In certain embodiments, the composition further comprises at least one of metal-oxide particles and semiconductor particles. The metal-oxide particles and/or semiconductor particles can optionally be included in the composition to further increase a refractive index of the product, which is described in further detail below. Suitable metal-oxide particles and semiconductor particles are generally those that are substantially transparent over the emission bandwidth of the LED. “Substantially transparent” refers to the metal-oxide particles and/or semiconductor particles that are not capable of absorbing light emitted from the LED, i.e., the optical band-gap of the metal-oxide particles and/or semiconductor particles is greater than the photon energy of light emitted from the LED.

[0070] Suitable metal-oxide nanoparticles for purposes of the present invention include, but are not limited to, Al_2O_3, ZrO_2, V_2O_5, ZnO, SnO_2, or mixtures thereof. In one embodiment, the metal-oxide nanoparticles are ZrO_2. In other embodiments, the metal-oxide nanoparticles are the modified nanoparticles disclosed in U.S. Patent Application No. 61/420,925 filed concurrently with the subject application, the disclosure of which is incorporated by reference in its entirety. Suitable semiconductor particles for purposes of the present invention include, but are not limited to, ZnS, CdS, GaN, and mixtures thereof. In certain embodiments, the particles can include species that have a core of one material on which is deposited a material of another type.

[0071] The metal-oxide nanoparticles (D) other than titanium dioxide (TiO_2) nanoparticles are included in the composition to adjust a refractive index of the composition and, specifically, to raise the refractive index of the composition after curing, e.g. to raise the refractive index of the product, which is described in further detail below. Individually, the metal-oxide nanoparticles (D) have a higher refractive index than the composition as a whole. By other than, it is meant that the composition of the present invention is completely free of TiO_2 nanoparticles. It is to be appreciated that TiO_2 particles can be present in the compositions, so long as the TiO_2 particles are smaller of greater in size than nanoparticles. However, TiO_2 particles, regardless of size, are typically not employed in the composition of the present invention. By raising the refractive index of the composition, the refractive index can be more closely matched to the refractive index of the phosphors, when the phosphors are included in the composition. Typically, the metal-oxide nanoparticles (D) comprise zirconium dioxide (ZrO_2), which is also referred to in the art as zirconia. Suitable types of zirconia, including zirconia dispersions, are commercially available from Sumitomo Osaka Cement Co., Ltd., such as NZD-8J61, NZD-3001A, and ZRST-106. Other suitable metal-oxide nanoparticles (D) include those described and exemplified above, such as Al_2O_3. Without being bound or limited by any particular theory, it is believed that ZrO_2 has little to no photo catalytic effect, which imparts stability to the composition after curing, especially under strong light conditions. Further, it is believed that TiO_2 nanoparticles act as a UV light barrier, while ZrO_2 nanoparticles are generally UV light transparent, such that the use of ZrO_2 particles imparts the composition with excellent light transmitting properties when cured.

[0072] The metal-oxide nanoparticles (D) range in size less than 1 micron and greater than 1 nanometer, typically ranging from 1 to 300 nanometers, more typically from 1 to 50 nanometers, most typically from 20 to 40 nanometers, alternatively no greater than 10 nanometers. The aforementioned particle sizes are average particle sizes, wherein the particle size is based upon the longest dimension of the particles, which is a diameter for spherical particles.

[0073] In one embodiment, a mean particle size of the metal-oxide nanoparticles (D) is generally from 3 to 40 nanometers. In certain embodiments, the metal-oxide nanoparticles (D) have an average primary particle size less than 35, more typically less than 30, most typically less than 25, nanometers. The average particle size of the metal-oxide nanoparticles (D) is generally less than a wavelength of light emitted by the substrate of the LED, if employed. As such, the metal-oxide nanoparticles (D) do not scatter light emitted by the substrate, e.g. the diode, of the LED. The nanoparticles (D) may be in free flowing powder form, more typically the nanoparticles (D) are in a solvent (or slurry) dispersion. A solvent of the solvent dispersion may be any solvent known in the art. If employed, the solvent selected will depend on various factors including the surface treatment of the nanoparticles (D). Typically, the solvent will be selected such that the polarity of the solvent may be the same as or close to the polarity of the surface treatment of the nanoparticles (D). For example, nanoparticles (D) with a nonpolar surface treatment may be dispersed in a hydrocarbon solvent, such as toluene. Alternatively, nanoparticles (D) with a polar surface treatment may be dispersed in a more polar solvent, such as water. If dispersions are employed, the solvent can be removed from or left within the composition of the present invention.

[0074] In certain embodiments, the metal-oxide nanoparticles (D) are coated with a filler treating agent. Suitable filler treating agents, for purposes of the present invention, include the treating agent (or agents) as described and exemplified above. The filler treating agent typically comprises an alkoxysilane. In certain embodiments, the alkoxysilane is selected from the group of octyltrimethoxysilane, allyltrimethoxysilane, methacryloxypropyltrimethoxysilane, and combinations thereof. Suitable alkoxysilanes, for purposes of the present invention, are commercially available from Gelest, Inc. of Morrisville, PA. The filler treating agent is useful for increasing or decreasing clarity of the composition and the product.

[0075] In one embodiment, the metal-oxide nanoparticles (D) have an outer shell-coating between the metal-oxide nanoparticle (D) and the filler treating agent coating. It is to be appreciated that the metal-oxide nanoparticles (D) may also have the outer shell-coating even if the filler treating agent is not employed. If employed, the outer shell-coating typically comprises a material having a bandgap larger than a bandgap of the metal-oxide nanoparticle (D). The material having a larger bandgap is generally an oxide. In certain embodiments, the oxide is aluminum oxide.

[0076] The metal-oxide nanoparticles (D) are typically present in an amount ranging from 60 to 75, more typically from 60 to 70, most typically from 65 to 70, parts by weight, each based on 100 parts by weight of the composition. It is to be appreciated that the composition may include any combination of two or more types and/grades of the aforementioned metal-oxide nanoparticles. It is also to be appreciated that the composition may include any combination of the other aforementioned particles in addition to the metal-oxide nanoparticles (D), as described and exemplified above.

[0077] The composition typically has a molar ratio of SiH groups to alkenyl groups ranging from 0.80 to 1.5, more typically from 1.0 to 1.5, most typically from 1.0 to 1.1. It is generally understood by those skilled in the silicone art that cross-linking occurs when the sum of the average number of alkenyl groups per molecule of component (A) and the average number of silicon-bonded hydrogen atoms per molecule of component (B) is greater than four.

[0078] Components (A), (B), (C), and (D), and optionally, one or more of the additives and/or the other metal-oxide particles and/or semiconductor particles, can be combined in any order. Typically, components (A) and (B) are combined before the introduction of components (C) and (D).

[0079] The composition may be supplied to consumers for use by various means, such as in large-sized tanks, drums and containers or small-sized kits, packets, and containers. The composition may be supplied in a one-part, a two-part, or a multi-part system. Typically, any of the components having alkenyl groups, e.g. component (A), are kept separate from any of the components having SiH groups, e.g. component (B), to prevent premature reaction of the composition. Additional components such as components (C) and (D), and optionally, one of more of the additives and/or the other metal-oxide particles and/or semiconductor particles, may be combined with either of the previous described components (A) and (B), or kept separate therefrom. In one example of a two-part system, a first part comprises components (A) and (C), and a second part comprises components (A) and (B) and the cure modifier. In this example, component (D) could be included in the first part, the second part, or split between both parts. Alternatively, a three part system including the first and second parts described above could be made, wherein component (D) is in a third part. Preferably, all the siloxane components except the catalyst could be mixed with component (D) to make a first part, and the catalyst would be in a second part.

[0080] As described above, the product comprises the reaction product of components (A) and (B) in the presence of components (C) and (D), and optionally, one or more of the additives and/or the other metal-oxide particles and/or semiconductor particles. The product typically has the molar ratio of alkyl groups to phenyl groups as described above with the composition. The product typically has the viscosities as described with the composition, prior to reacting.

[0081] After cure, the product typically has a refractive index ranging from 1.40 to 1.70, more typically from 1.43 to 1.60, yet more typically from 1.43 to 1.56, and most typically from 1.50 to 1.56, measured at 632.8 nm wavelength. The refractive index can be determined using a prism-coupler. This method uses advanced optical wave guiding techniques to accurately measure refractive index at specific wavelengths. The product typically has an optical transparency at 0.1 mm thickness of at least 85%, more typically at least 90%, most typically least 95%, transmission of light of 632.8 nm wavelength. The optical transparency can be determined using a UV-spectrophotometer, using methods known to those skilled in the silicone art.

[0082] The more closely the surface energies of the composition match that of the metal-oxide nanoparticles, the better the optical clarity of the product. For example, if the difference in the surface energies of the composition and the particles becomes too great, the product will tend to become milky/opaque, which is undesirable for many photonic applications, such as for lenses and LEDs.

[0083] The product typically has a modulus of at least $9.0\text{x}10^5$, more typically from $9.0\text{x}10^5$ to $5.0\text{x}10^7$, dyn/cm^2, as measured in a controlled strain, parallel plate, oscillating rheometer. In certain embodiments, the product has a modulus ranging from $9.0\text{x}10^5$ to $5.0\text{x}10^6$ dyn/cm^2. In other embodiments, the product has a modulus ranging from $5.0\ \text{x}10^6$ to $1.0\text{x}10^7$ dyn/cm^2. In further embodiments, the product has a modulus ranging from $1.0\text{x}10^7$ to $5.0\text{x}10^7$ dyn/cm^2.

[0084] The product typically has a Shore A hardness greater than 50, more typically a Shore D hardness ranging from 5 to 40, yet more typically a Shore D hardness ranging from 10 to 30, most typically a Shore D hardness ranging from 10 to 25. Hardness of the product can be determined according to ASTM D-2240.

[0085] The reaction to form the product from the composition can be carried out in any standard reactor suitable for hydrosilylation reactions known to those skilled in the silicone art. Suitable reactors for purposes of the present invention include, but are not limited to, glass reactors and Teflon®-lined glass reactors. Preferably, the reactor is equipped with a means of agitation, such as stirring or other means of imparting shear mixing.

[0086] The reaction of the composition to form the product is typically carried out at a temperature ranging from 0°C to 200°C, more typically from room temperature (~23 ± 2°C) to 150°C, most typically from 80°C to 150°C. The reaction time depends on several factors, such as the amounts and makeup of components (A) and (B), stirring, and the temperature. The time of reaction is typically from 1/2 hour (30 minutes) to 24 hours at a temperature ranging from room temperature (~23 ± 2°C) to 150°C. In one embodiment, the time of reaction is two hours at 125°C. In another embodiment, the time of reaction is 1/2 hour (30 minutes) at 150°C. It is to be appreciated, that the mixed composition is typically applied to the substrate using various known methods, after which the reaction is carried out as set forth above. Encapsulation or coating techniques for LEDs are well known to the art. Such techniques include casting, dispensing, molding, and the like. For example, after the LED is encapsulated in the composition, typically performed in a mold, the composition is reacted, i.e., cured, at temperature ranges and times as described and exemplified above. It is to be appreciated that the composition may be cured in one or more stages, e.g. by two or more heating stages, to form the product.

[0087] As described above, the compositions and the products formed therefrom are useful for encapsulating LEDs, which can be any type of LED known in the art. LEDs are well known in the art; see e.g. E. FRED SCHUBERT, LIGHT-EMITTING DIODES (2d ed. 2006). The product of the present invention is typically used as an encapsulant for a LED. LEDs include the diode, i.e., the substrate, which emits light, whether visible, ultraviolet, or infrared. The diode can be an individual component or a chip made, for example, by semiconductor wafer processing procedures. The component or the chip can include electrical contacts suitable for application of power to energize the diode. Individual layers and other functional elements of the component or the chip are typically formed on the wafer scale, the finished wafer finally being diced into individual piece parts to yield a multiplicity of the diodes.

[0088] The compositions and the products described herein are useful for making a wide variety of LEDs, including, but not limited to, monochrome and phosphor-LEDs (in which blue or UV light is converted to another color via the phosphor). The LEDs may be packaged in a variety of configurations, including, but not limited to, LEDs surface mounted in ceramic or polymeric packages, which may or may not have a reflecting cup; LEDs mounted on circuit boards; LEDs mounted on plastic electronic substrates; etc.

[0089] LED emission light can be any light that an LED source can emit and can range from the UV to the visible portions of the electromagnetic spectrum depending on the composition and structure of semiconductor layers. The compositions and the products described herein are useful in surface mount and side mount LED packages where the encapsulant, i.e., the product, is cured in a reflector cup. The compositions and the products are also useful with LED designs containing a top wire bond. Additionally, the compositions and the products can be useful for making surface mount LEDs where there is no reflector cup and can be useful for making arrays of surface mounted LEDs attached to a variety of different substrates.

[0090] The products described herein are resistant to physical, thermal and photo-degradation (resistant to yellowing) and thus are particularly useful for white light sources, e.g. white LEDs. White light sources that utilize LEDs in their construction generally have two basic configurations. In one, referred to herein as direct emissive LEDs, white light is generated by direct emission of different colored LEDs. Examples include a combination of a red LED, a green LED, and a blue LED, and a combination of a blue LED and a yellow LED. In the other basic configuration, referred to herein as LED-excited phosphor-based light sources, a single LED generates light in a narrow range of wavelengths, which impinges upon and excites the phosphor (or phosphors) to produce visible light. As previously described, the phosphor can comprise a mixture or combination of distinct phosphor materials. The light emitted by the phosphor can include a plurality of narrow emission lines distributed over the visible wavelength range such that the emitted light appears substantially white to an unaided human eye. The phosphor may be applied to the diode to form the LED as part of the composition. Alternatively or in addition to, the phosphor may be applied to the diode in a separate step, for example, the phosphor may be coated onto the diode prior to contacting the diode with the composition to form the encapsulant, i.e., the product.

[0091] An example of obtaining white light from an LED is to use a blue LED illuminating a phosphor that converts blue to both red and green wavelengths. A portion of the blue excitation light is not absorbed by the phosphor, and the residual blue excitation light is combined with the red and green light emitted by the phosphor. Another example of an LED is an ultraviolet (UV) LED illuminating a phosphor that absorbs and converts UV light to red, green, and blue light. Embodiments of the composition having groups that are small and have minimal UV absorption, e.g. methyl groups, are preferred for UV LEDs. Typically, both the phosphors, if included, and the diode, have refractive indexes that are higher than that of the product. Light scattering can be minimized by matching the refractive index of the product and the phosphors and/or the diode.

[0092] The following examples, illustrating the compositions and products of the present invention, are intended to illustrate and not to limit the present invention.

EXAMPLES

[0093] Examples of the compositions of the present invention were prepared. Components (A), (B), (C), (D), and the cure modifier were mixed in a reaction vessel to form the respective examples of the composition. The reaction vessel was a container capable of withstanding agitation and having resistance to chemical reactivity. The compositions were mixed using a high shear centrifical mixer for 1 to 3 minutes at 2000 to 3500 rpm. Viscosities of the compositions were determined using a Brookfield Cone and Plate Viscometer according to ASTM D-4287. The mixed compositions were heated to a temperature ranging from 80°C to 125°C to facilitate reaction of the compositions to form the respective products. The products cured, i.e., formed, in 30 to 120 minutes. Adhesion strengths of the products were determined by a die shear method using aluminum substrates. Refractive indices of the products were determined using a prism coupler. This method uses advanced optical wave guiding techniques to accurately measure refractive index at specific wavelengths. Optical transparency of the product was determined using a UV-spectrophotometer, using methods known to those skilled in the silicone art.

[0094] In inventive Example 1, zirconia nanoparticles having a particle size of 18nm (mean value) in toluene was mixed with a formulation of an organopolysiloxane component comprising 1,3-diphenyl-1,3-dimethyl-1,3-divinyldisiloxane, an organohydrogensiloxane component comprising a hydrogendimethylsiloxy group terminated phenylsilsesquioxane having the formula $T^{Ph}_{0.4}M^{H}_{0.6}$, a hydrosilylation catalyst comprising Pt, and a cure inhibitor comprising phenylbutynol (PBO), to form a composition. Both of the organopolysiloxane and organohydrogensiloxane components are commercially available from Dow Corning Corporation. After mixing the components of the composition, some amount of the toluene was removed from the composition. Next, the composition was coated on a quartz plate, followed by curing of the composition at 150° C for 1 hour. The resulting material formed from the cured composition was transparent and had a refractive index (RI) of 1.607.

[0095] Additional inventive Examples 2, 3 and 4 were also prepared. These compositions were similar to the inventive example immediately above, but different metal-oxide nanoparticles were employed in place of the zirconia nanoparticles, including zirconia nanoparticles having a particle size ranging from 20-40nm (mean value), and zirconia slurries employing the same. Some of these compositions, upon curing, resulted in materials with RIs up to 1.69.

[0096] The amount and type of each component used to form the compositions are indicated in Table 1 below with all values in parts by weight based on 100 parts by weight of the compositions unless otherwise indicated. The symbol '-' indicates that the component is absent from the formulation.

TABLE 1

Component	**Example**			
	1	**2**	**3**	**4**
Organopolysiloxane 1 (g)	0.11	0.05	-	-
Organopolysiloxane 2 (g)	-	0.18	0.13	0.12
Organopolysiloxane 3 (g)	-	0.05	-	-
Organopolysiloxane 4 (g)	-	-	0.015	-
Organohydrogensiloxane 1 (g)	0.14	-	-	-
Organohydrogensiloxane 2 (g)	-	0.05	0.12	0.11
Organohydrogensiloxane 3 (g)	-	-	0.030	0.025
Catalyst (ppm)	5	5	5	5
Cure modifier (ppm)	300	300	300	300
ZrO_2 Nanoparticles 1 (g)	1.0	1.5	-	-
ZrO_2 Nanoparticles 2 (g)	-	-	0.9	1.0

[0097] Organopolysiloxane 1 is 1,3-dimethyl-1,3-diphenyl-1,3-divinyldisiloxane, available from Dow Corning Corporation of Midland, MI.

[0098] Organopolysiloxane 2 is a silicone oligomer having the average formula $(D^{Ph})_4(M^{Vi})_2$, wherein D^{Ph} is $PhMeSiO_{2/2}$, M^{Vi} is $Me_2ViSiO_{1/2}$, Ph is a phenyl group, Vi is a vinyl group, and Me is a methyl group, available from Dow Corning Corporation.

[0099] Organopolysiloxane 3 is a silicone polymer having the formula $(ESiO_{3/2})_{0.4}(ViMeSiO_{2/2})_{0.4}(MeO_{1/2})_{0.2}$, wherein E is a 3-glycidoxypropyl group, Vi is a vinyl group, and Me is a methyl group.

[00100] Organopolysiloxane 4 is a silicone polymer having the formula $(EMeSiO_{2/2})_{0.29}(ViMe_2SiO_{1/2})_{0.18}(PhSiO_{3/2})_{0.53}$, wherein E is a 3-glycidoxypropyl group, Vi is a vinyl group, Ph is a phenyl group, and Me is a methyl group.

[00101] Organohydrogensiloxane 1 is a silicone resin having the formula $(T^{Ph})_{0.4}(M^{H})_{0.6}$, wherein T is $SiO_{3/2}$, M is $Me_2SiO_{1/2}$, Ph is a phenyl group, H is a hydrogen atom, and Me is a methyl group, available from Dow Corning Corporation.

[00102] Organohydrogensiloxane 2 is a silicone oligomer having the average formula $(D^{Ph})_4(M^H)_2$, wherein D^{Ph} is $PhMeSiO_{2/2}$, M^H is $Me_2HSiO_{1/2}$, Ph is a phenyl group, H is a hydrogen atom, and Me is a methyl group, available from Dow Corning Corporation.

[00103] Catalyst is a platinum catalyst.

[00104] Cure modifier is 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, available from Dow Corning Corporation.

[00105] ZrO_2 Nanoparticles 1 is a zirconia nanoparticle dispersion, having a D50 particle size of 18nm, commercially available from Sumitomo Osaka Cement Co., Ltd. The value shown in Table I is based on zirconia solids content.

[00106] ZrO_2 Nanoparticles 2 is a zirconia nanoparticle dispersion, having a D50 particle size of 31nm, commercially available from Sumitomo Osaka Cement Co., Ltd. The value shown in Table I is based on zirconia solids content.

[00107] Physical properties of the compositions are indicated in Table 2 below. The symbol '-' indicates that the property was not measured.

TABLE 2

	Example			
	1	**2**	**3**	**4**
Refractive Index (@ 632.8 nm)	1.607	1.603	1.698	1.733
Appearance	Transparent	Transparent	Transparent	Transparent
Thickness for transmittance (μm)	1084	694	11	10
Transmittance (% @ 450 nm wave length)	73.50	82.10	90.8	92.28
Adhesion property to aluminum substrate (MPa)	-	-	1.5	1.3

[00108] Examples 1-4 of the compositions were homogenous which were useful for easily dispensing and forming various shapes of the product. Optical transparency of all of the products was deemed to be at least 90% transparent at 450 nm wavelength with a thickness of 10 μm. The products formed from the examples had sufficient moduli and appropriate refractive indices for the application.

[00109] The compositions of the present invention provide excellent RIs and transparency for forming products such as encapsulants for LEDs, which provides for achieving excellent optical output efficiency. In addition, the compositions of the present invention generally have a low viscosity, which provides for increased efficiency in manufacturing encapsulants. Encapsulants formed from the products of the present invention generally have improved physical properties, including excellent modulus, refractive index, adhesion property, and optical transparency imparted by the compositions.

[00110] In contrast to the inventive examples described above, comparative examples (not shown) employing compositions including some amount of PDMS resulted in white inhomogeneous materials. It is believed that the lack of phenyl groups in PDMS is detrimental to the compositions formed therefrom.

[00111] In a comparative example, zirconia nanoparticles having a particle size of 18nm (mean value) in toluene was mixed with a formulation of an organopolysiloxane component comprising vinyldimethylsiloxy group and trimethylsiloxy group terminated silica, an organopolysiloxane component comprising vinyldimethylsiloxy terminated polydimethylsiloxane, an organohydrogensiloxane component comprising a trimethylsiloxy terminated methylhydrogensiloxane, a hydrosilylation catalyst comprising Pt, and a cure inhibitor comprising phenylbutynol (PBO), to form a composition. Both of the organopolysiloxane and organohydrogensiloxane components are commercially available from Dow Corning Corporation. After mixing the components of the composition, some amount of the toluene was removed from the composition. Next, the composition was coated on a quartz plate, followed by curing of the composition at 150° C for 1 hour. The resulting material formed from the cured composition was opaque in appearance.

[00112] It is to be understood that the appended claims are not limited to express and particular compounds, compositions, or methods described in the detailed description, which may vary between particular embodiments which fall within the scope of the appended claims. With respect to any Markush groups relied upon herein for describing particular features or aspects of various embodiments, it is to be appreciated that different, special, and/or unexpected results may be obtained from each member of the respective Markush group independent from all other Markush members. Each member of a Markush group may be relied upon individually and or in combination and provides adequate support for specific embodiments within the scope of the appended claims.

[00113] It is also to be understood that any ranges and subranges relied upon in describing various embodiments of the present invention independently and collectively fall within the scope of the appended claims, and are understood to describe and contemplate all ranges including whole and/or fractional values therein, even if such values are not expressly written herein. One of skill in the art readily recognizes that the enumerated ranges and subranges sufficiently describe and enable various embodiments of the present invention, and such ranges and subranges may be further delineated into relevant halves, thirds, quarters, fifths, and so on. As just one example, a range "of from 0.1 to 0.9" may be further delineated into a lower third, i.e., from 0.1 to 0.3, a middle third, i.e., from 0.4 to 0.6, and an upper third, i.e., from 0.7 to 0.9, which individually and collectively are within the scope of the appended claims, and may be relied upon individually and/or collectively and provide adequate support for specific embodiments within the scope of the appended claims. In addition, with respect to the language which defines or modifies a range, such as "at least," "greater than," "less than," "no more than," and the like, it is to be understood that such language includes subranges and/or an upper or lower limit. As another example, a range of "at least 10" inherently includes a subrange of from at least 10 to 35, a subrange of from at least 10 to 25, a subrange of from 25 to 35, and so on, and each subrange may be relied upon individually and/or collectively and provides adequate support for specific embodiments within the scope of the appended claims. Finally, an individual number within a disclosed range may be relied upon and provides adequate support for specific embodiments within the scope of the appended claims. For example, a range "of from 1 to 9" includes various individual integers, such as 3, as well as individual numbers including a decimal point (or fraction), such as 4.1, which may be relied upon and provide adequate support for specific embodiments within the scope of the appended claims. The subject matter of all combinations of independent and dependent claims, both singly and multiply dependent, is herein expressly contemplated.

[00114] The invention has been described in an illustrative manner, and it is to be understood that the terminology which has been used is intended to be in the nature of words of description rather than of limitation. Many modifications and variations of the present invention are possible in light of the above teachings, and the invention may be practiced otherwise than as specifically described.

CLAIMS

1. A composition comprising:

(A) an organopolysiloxane component having at least one aryl group and having an average of at least two alkenyl groups per molecule, with a number average molecular weight no greater than 1500;

(B) an organohydrogensiloxane component having at least one of an aryl group and an alkyl group and having an average of at least two silicon-bonded hydrogen atoms per molecule, with a number average molecular weight no greater than 1500;

(C) a catalytic amount of a hydrosilylation catalyst component; and

(D) metal-oxide nanoparticles other than titanium dioxide nanoparticles;

with the proviso that the composition has a molar ratio of alkyl groups to aryl groups ranging from 1:0.25 to 1:3.0.

2. The composition as set forth in claim 1, where the organopolysiloxane component comprises a disiloxane, a trisiloxane, a tetrasiloxane, a pentasiloxane, or a hexasiloxane, and has at least one of an alkyl group and an aryl group.

3. The composition of claim 1 or 2, where the molar ratio of alkyl groups to aryl groups ranges from 1:0.5 to 1:1.5.

4. The composition of any preceding claim, having a surface energy ranging from 19 to 33 dynes/cm.

5. The composition of any preceding claim, where the metal-oxide nanoparticles comprise zirconium dioxide (ZrO_2).

6. The composition of any one of claims 1-4, where the metal-oxide nanoparticles comprise Al_2O_3, V_2O_5, ZnO, SnO_2, or mixtures thereof.

7. The composition of any preceding claim, where the metal-oxide nanoparticles have an average particle size ranging from 1 to 50 nanometers.

8. The composition of any one of claims 1-6, where the metal-oxide nanoparticles have an average particle size less than 10 nanometers.

9. The composition of any preceding claim, where component (A) comprises the disiloxane having the formula:

(I) $R^1R^2R^3SiOSiR^1R^2R^3$

wherein each R^1, R^2, and R^3 independently comprises an alkyl group, an aryl group, or an alkenyl group.

10. The composition of claim 9, where the disiloxane has the formula:

(i) ViPhMeSiOSiViPhMe

wherein Vi is a vinyl group, Ph is a phenyl group, and Me is a methyl group.

11. The composition of any one of claims 1-8, where component (A) comprises at least one of the trisiloxane and the tetrasiloxane, each of the trisiloxane and the tetrasiloxane independently having the formula:

(II) $(R^1R^3_2SiO)_{4-a}SiR^4_a$

wherein each R^1 and R^3 independently comprises an alkyl group, an aryl group, or an alkenyl group, R^4 comprises an alkyl group or an aryl group, and subscript a is 0 for the tetrasiloxane or 1 for the trisiloxane.

12. The composition of claim 11, where each of the trisiloxane and the tetrasiloxane independently have the formula:

(ii) $(ViR^3_2SiO)_{4-a}SiR^4_a$

wherein Vi is a vinyl group, each R^3 and R^4 independently comprises a phenyl group or a methyl group, and subscript a is 0 for the tetrasiloxane or 1 for the trisiloxane.

13. The composition of any one of claims 1-8, where component (A) comprises at least one of the pentasiloxane and the hexasiloxane, each of the pentasiloxane and the hexasiloxane independently having the formula:

(III) $(R^1R^3_2SiO)_{6-a}SiR^4_a$

wherein each R^1, R^3, and R^4 independently comprises an alkyl group, an aryl group, or an alkenyl group, and subscript a is 0 for the hexasiloxane or 1 for the pentasiloxane.

14. The composition of claim 13, where each of the pentasiloxane and the hexasiloxane independently have the formula:

(iii) $(ViR^3_2SiO)_{6-a}SiR^4_a$

wherein Vi is a vinyl group, each R^3 and R^4 independently comprises a phenyl group or a methyl group, and subscript a is 0 for the hexasiloxane or 1 for the pentasiloxane.

15. The composition of any preceding claim, where component (B) comprises a silicone resin having the formula:

(IV) $(R^6R^7_2SiO_{1/2})_y(R^5SiO_{3/2})_x$

wherein each R^5 and R^6 independently comprises an alkyl group, an aryl group, an alkenyl group, or a hydrogen atom, each R^7 independently comprises an alkyl group, an aryl group, or an alkenyl group, subscript x ranges from 0.2 to 0.6, and $x + y = 1$.

16. The composition of claim 15, where the silicone resin has the formula:

(iv) $(HR^7{}_2SiO_{1/2})_y(R^5SiO_{3/2})_x$

wherein each R^5 and R^7 independently comprises a phenyl group or a methyl group, subscript x ranges from 0.2 to 0.6, and $x + y = 1$.

17. The composition of any one of claims 1-14, where component (B) comprises a siloxane having the formula:

(V) $(R^6R^7{}_2SiO)(R^5{}_2SiO)_z(SiR^6R^7{}_2)$

wherein each R^5 and R^6 independently comprises an alkyl group, an aryl group, an alkenyl group, or a hydrogen atom, each R^7 independently comprises an alkyl group, an aryl group, or an alkenyl group, and subscript $z \geq 1$.

18. The composition of claim 17, where the siloxane has the formula:

(v) $(HR^7{}_2SiO)(R^5{}_2SiO)_z(SiHR^7{}_2)$

wherein each R^5 and R^7 independently comprises a phenyl group or a methyl group, and $5 \geq z \geq 1$.

19. The composition of any preceding claim, where component (A) is present in an amount ranging from 20 to 50 parts by weight and component (B) is present in an amount ranging from 10 to 80 parts by weight, each based on 100 parts by weight of the composition.

20. The composition of any preceding claim, where component (C) is present in an amount sufficient to provide 2 to 10 ppm of a group VIII transition metal, based on 100 parts by weight of the composition.

21. The composition of any preceding claim, having a molar ratio of SiH groups to alkenyl groups ranging from 1.0 to 1.5.

22. The composition of any preceding claim, further comprising at least one of a co-crosslinker, an adhesion promoter, a filler, a treating agent, an optically active agent, a cure modifier, and a rheology modifier.

23. A composition comprising:

(A) an organopolysiloxane component having an average of at least two alkenyl groups per molecule and selected from the group of:

(I) $R^1R^2R^3SiOSiR^1R^2R^3$,

(II) $(R^1R^3_2SiO)_{4-a}SiR^4_a$,

(III) $(R^1R^3_2SiO)_{6-a}SiR^4_a$, and combinations thereof; and

(B) an organohydrogensiloxane component having an average of at least two silicon-bonded hydrogen atoms per molecule and selected from the group of:

(IV) $(R^6R^7_2SiO_{1/2})_y(R^5SiO_{3/2})_x$,

(V) $(R^6R^7_2SiO)(R^5_2SiO)_z(SiR^6R^7_2)$, and combinations thereof;

wherein each R^1, R^2, R^3, and R^7 independently comprises an alkyl group, an aryl group, or an alkenyl group, R^4 comprises an alkyl group or an aryl group, each R^5 and R^6 independently comprises an alkyl group, an aryl group, an alkenyl group, or a hydrogen atom, subscript a is 0 or 1, subscript y ranges from 0.2 to 0.6, $x + y = 1$, and subscript $z \geq 1$, provided component (A) has at least one aryl group and component (B) has at least one of an alkyl group and an aryl group;

(C) a catalytic amount of a hydrosilylation catalyst component; and

(D) metal-oxide nanoparticles other than titanium dioxide nanoparticles;

with the proviso that the composition has a molar ratio of alkyl groups to aryl groups ranging from 1:0.25 to 1:3.0.

24. The composition of claim 23, where

component (A) is selected from the group of:

(i) ViPhMeSiOSiViPhMe,

(ii) $(ViR^3_2SiO_{1/2})_{4-a}SiR^4_a$,

(iii) $(ViR^3_2SiO)_{6-a}SiR^4_a$, and combinations thereof; and

component (B) is selected from the group of:

(iv) $(HR^7_2SiO_{1/2})_y(R^5SiO_{3/2})_x$,

(v) $(HR^7_2SiO)(R^5_2SiO)_z(SiHR^7_2)$, and combinations thereof;

wherein Vi is a vinyl group, each R^3, R^4, R^5, and R^7 independently comprises a phenyl group or a methyl group, subscript a is 0 or 1, subscript x ranges from 0.2 to 0.6, $x + y = 1$, and $5 \geq z \geq 1$.

25. The composition of claim 23 or 24, having a surface energy ranging from 19 to 33 dynes/cm.

26. The composition of any one of claims 23-25, where the metal-oxide nanoparticles comprise ZrO_2, Al_2O_3, V_2O_5, ZnO, SnO_2, or mixtures thereof.

27. A product comprising the reaction product of:
a composition comprising

(A) an organopolysiloxane component having at least one aryl group and having an average of at least two alkenyl groups per molecule, with a number average molecular weight no greater than 1500; and

(B) an organohydrogensiloxane component having at least one of an aryl group and an alkyl group and having an average of at least two silicon-bonded hydrogen atoms per molecule, with a number average molecular weight no greater than 1500;

with the proviso that the composition has a molar ratio of alkyl groups to aryl groups ranges from 1:0.25 to 1:3.0;
in the presence of

(C) a catalytic amount of a hydrosilylation catalyst component; and

(D) metal-oxide nanoparticles other than titanium dioxide nanoparticles;
with the proviso that the product has a refractive index of at least 1.50 at 632.8 nm wavelength.

28. A product comprising the reaction product of:
a composition comprising

(A) an organopolysiloxane component having at least one aryl group and having an average of at least two alkenyl groups per molecule, with a number average molecular weight no greater than 1500; and

(B) an organohydrogensiloxane component having at least one of an aryl group and an alkyl group and having an average of at least two silicon-bonded hydrogen atoms per molecule, with a number average molecular weight no greater than 1500;

with the proviso that the composition has a molar ratio of alkyl groups to aryl groups ranges from 1:0.25 to 1:3.0;
in the presence of

(C) a catalytic amount of a hydrosilylation catalyst component; and

(D) metal-oxide nanoparticles other than titanium dioxide nanoparticles;
with the proviso that the product has a modulus greater than 8×10^5 dyn/cm^2.

29. The composition as set forth in claim 27 or 28, where the organopolysiloxane component comprises a disiloxane, a trisiloxane, a tetrasiloxane, a pentasiloxane, or a hexasiloxane, and has at least one of an alkyl group and an aryl group.

30. The product of any one of claims 27-29, having a refractive index ranging from 1.50 to 1.56 at 632.8 nm wavelength.

31. The product of any one of claims 27-30, having a Shore A hardness greater than 50.

32. The product of any one of claims 27-31, where the metal-oxide nanoparticles have an average particle size ranging from 1 to 50 nanometers.

33. The product of claim 29, where component (A) comprises the disiloxane having the formula:

(I) $R^1R^2R^3SiOSiR^1R^2R^3$

wherein each R^1, R^2, and R^3 independently comprises an alkyl group, an aryl group, or an alkenyl group.

34. The product of claim 29, where component (A) comprises at least one of the trisiloxane and the tetrasiloxane, each of the trisiloxane and the tetrasiloxane independently having the formula:

(II) $(R^1R^3{}_2SiO)_{4-a}SiR^4{}_a$

wherein each R^1 and R^3 independently comprises an alkyl group, an aryl group, or an alkenyl group, R^4 comprises an alkyl group or an aryl group, and subscript a is 0 for the tetrasiloxane or 1 for the trisiloxane.

35. The product of claim 29, where component (A) comprises at least one of the pentasiloxane and the hexasiloxane, each of the pentasiloxane and the hexasiloxane independently having the formula:

(III) $(R^1R^3{}_2SiO)_{6-a}SiR^4{}_a$

wherein each R^1, R^3, and R^4 independently comprises an alkyl group, an aryl group, or an alkenyl group, and subscript a is 0 for the hexasiloxane or 1 for the pentasiloxane.

36. The product of any one of claims 27-35, where component (B) comprises a silicone resin having the formula:

(IV) $(R^6R^7{}_2SiO_{1/2})_y(R^5SiO_{3/2})_x$

wherein each R^5 and R^6 independently comprises an alkyl group, an aryl group, an alkenyl group, or a hydrogen atom, each R^7 independently comprises an alkyl group, an aryl group, or an alkenyl group, subscript x ranges from 0.2 to 0.6, and $x + y = 1$.

37. The product of any one of claims 27-35, where component (B) comprises a siloxane having the formula:

(V) $(R^6R^7{}_2SiO)(R^5{}_2SiO)_z(SiR^6R^7{}_2)$

wherein each R^5 and R^6 independently comprises an alkyl group, an aryl group, an alkenyl group, or a hydrogen atom, each R^7 independently comprises an alkyl group, an aryl group, or an alkenyl group, and subscript $z \geq 1$.

38. The product of any one of claims 27-37, having a modulus ranging from 9.0×10^5 to 5.0×10^7 dyn/cm^2.

39. The product of any one of claims 27-38, where the metal-oxide nanoparticles comprise ZrO_2, Al_2O_3, V_2O_5, ZnO, SnO_2, or mixtures thereof.

40. A light emitting diode comprising:

a substrate; and

an encapsulant at least partially surrounding the substrate and comprising a reaction product of a composition comprising

(A) an organopolysiloxane component having at least one aryl group and having an average of at least two alkenyl groups per molecule, with a number average molecular weight no greater than 1500, and

(B) an organohydrogensiloxane component having at least one of an aryl group and an alkyl group and having an average of at least two silicon-bonded hydrogen atoms per molecule, with a number average molecular weight no greater than 1500,

with the proviso that the composition has a molar ratio of alkyl groups to aryl groups ranges from 1:0.25 to 1:3.0,

in the presence of

(C) a catalytic amount of a hydrosilylation catalyst component, and

(D) metal-oxide nanoparticles other than titanium dioxide nanoparticles,

with the proviso that the encapsulant has a refractive index of at least 1.50 at 632.8 nm wavelength.

41. The light emitting diode of claim 40, where the encapsulant has a Shore A hardness greater than 50.

42. The light emitting diode of claim 40 or 41, where the substrate is a light emitting diode source emitting in the range from UV to visible portions of the electromagnetic spectrum.

43. The light emitting diode of any one of claims 40-42, where the metal-oxide nanoparticles comprise ZrO_2, Al_2O_3, V_2O_5, ZnO, SnO_2, or mixtures thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/063446

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G77/20 C08L83/04 C08K3/20 C09D7/12 H01L23/29
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G C08L C08K C09D H01L

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 practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/036962 A1 (SASAKI YUUICHI [JP] ET AL) 15 February 2007 (2007-02-15) claims; examples 10,11 -----	1-43
A	US 2008/090947 A1 (SHIN HYEON JIN [KR] ET AL) 17 April 2008 (2008-04-17) the whole document -----	1-43

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"E" earlier document 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

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2011/063446

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2007036962 A1	15-02-2007	NONE	
US 2008090947 A1	17-04-2008	KR 20080033059 A	16-04-2008
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