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(54) Title: THERMALLY CONDUCTIVE SILICONE COMPOSITION AND THERMALLY CONDUCTIVE MEMBER

(57) Abstract: Problem: To provide, in cases where used as a thermally conductive member, particularly as a potting agent or the like of an electronic material, a thermally conductive silicone composition from which a cured product can be obtained that has superior bonding to substrates and is free of cracks, and also to provide a thermally conductive member obtained by curing said composition. Resolution Means: A thermally conductive silicone rubber composition comprising an aluminum hydroxide or magnesium oxide thermally conductive filler having a mass change, measured by thermogravimetric analyses (TGA) before and after being held at 250°C for 30 minutes, of less than 4.0 % by mass; and a thermally conductive member obtained by curing said composition.

THERMALLY CONDUCTIVE SILICONE COMPOSITION AND THERMALLY CONDUCTIVE MEMBER

TECHNICAL FIELD

[0001] The present invention relates to a thermally conductive silicone composition and a thermally conductive member obtained by curing said composition. Priorities are claimed on Japanese Patent Application No. 2012-274714 filed on Dec. 17, 2012, the content of which are incorporated herein by reference.

BACKGROUND ART

[0002] In recent years, high densification and increased integration of printed circuit boards and hybrid ICs on which transistors, ICs, memory elements, and other electronic parts are mounted has been taking place. As such, various types of thermally conductive silicone rubber compositions are used in order to effectively dissipate heat. Examples of such thermally conductive silicone rubber compositions that have been suggested include a thermally conductive silicone rubber composition comprising a vinyl group-containing organopolysiloxane, an organohydrogenpolysiloxane, a thermally conductive filler selected from alumina, quartz powder, magnesium oxide, boron nitride, and silicon carbide, an adhesion imparting agent selected from aminosilane, epoxysilane, and alkyl titanate, and a platinum-based catalyst (as described in Japanese Unexamined Patent Application Publication No. S61-157569); a thermally conductive silicone rubber composition comprising an organopolysiloxane having at least 0.1 mol% of aliphatic unsaturated groups in each molecule, an organohydrogenpolysiloxane having at least two silicon-bonded hydrogen atoms in each molecule, a spherical fine alumina powder having an average particle diameter of 10 to 50 μm, a spherical or non-spherical fine alumina powder having an average particle diameter of less than 10 μm, and a platinum or platinum-based compound (as described in Japanese Unexamined Patent Application Publication No. S63-251466); a thermally conductive silicone rubber composition comprising an alkenyl group-containing organopolysiloxane, an organohydrogenpolysiloxane, a fine, amorphous alumina powder having an average particle diameter of 0.1 to 5 μm, a spherical fine alumina powder having an average particle diameter of 5 to 50 μm, and a platinum-based catalyst (as described in Japanese Unexamined Patent Application Publication No. H02-041362); and a thermally conductive silicone rubber composition comprising an alkenyl group-containing organopolysiloxane having at least 0.5 alkenyl groups, on average, in each molecule, an organohydrogenpolysiloxane having at least two silicon-bonded hydrogen atoms in each molecule, a highly-pure fine alumina powder having an average particle diameter of not greater than 50 μm and a major axis to minor axis ratio of 1.0 to 1.4, and a platinum-based catalyst (as described in Japanese Unexamined Patent Application Publication No. H05-105814).

[0003] However, with these thermally conductive silicone rubber compositions, there are

problems in that surrounding substrates are contaminated by low-boiling components volatilized from the composition and oil components that bleed out from the composition during curing. There is another problem in that when the composition is cured and used as a thermally conductive member, bonding with the substrate is poor. Furthermore, there is a problem in that cracking occurs in cured products of the compositions, leading to breakage of the cured products.

[0004] As a countermeasure to these problems, Japanese Unexamined Patent Application Publication No. 2011-153252 suggests a thermally conductive silicone composition comprising an organopolysiloxane having at least two silicon-bonded alkenyl groups in each molecule and being free of silicon-bonded hydroxyl groups and alkoxy groups, a tetramer to eicosamer cyclic siloxane content in terms of mass units being not more than 1,000 ppm, an organopolysiloxane having at least two silicon-bonded hydrogen atoms in each molecule and being free of silicon-bonded alkenyl groups, hydroxyl groups, and alkoxy groups, an adhesion imparting agent, a thermally conductive filler, and a hydrosilylation catalyst.

Patent Documents

[0005] Patent Document 1: Japanese Unexamined Patent Application Publication No. S61-157569A

Patent Document 2: Japanese Unexamined Patent Application Publication No. S63-251466A

Patent Document 3: Japanese Unexamined Patent Application Publication No. H02-041362A

Patent Document 4: Japanese Unexamined Patent Application Publication No. H05-105814A

Patent Document 5: Japanese Unexamined Patent Application Publication No. 2011-153252A

SUMMARY OF INVENTION

Technical Problem

[0006] However, even with this thermally conductive silicone composition, there are problems in that bonding with the substrate is poor in cases where cured and used as a thermally conductive member and cracking occurs in a cured product, leading to breakage of the cured product.

[0007] In order to solve the problems described above, an object of the present invention is, in cases where used as a thermally conductive member, particularly as a potting agent or the like of an electronic material, to provide a thermally conductive silicone composition from which a cured product can be obtained that has superior bonding to substrates and is free of cracks, and also to provide a thermally conductive member obtained by curing said composition.

Solution To Problem

[0008] As a result of intensive investigation aimed at achieving the above object, the present inventors arrived at the present invention. That is, the object of the present invention is achieved by a thermally conductive silicone rubber composition comprising (A) an aluminum hydroxide or magnesium oxide thermally conductive filler having a mass change, measured by

thermogravimetric analyses (TGA) before and after being held at 250°C for 30 minutes, of less than 4.0 % by mass.

[0009] The thermally conductive silicone rubber composition of the present invention preferably further comprises:

(B) an organopolysiloxane having at least two silicon-bonded alkenyl groups in each molecule;
(C) an organopolysiloxane having at least two silicon-bonded hydrogen atoms in each molecule and being free of silicon-bonded alkenyl groups, hydroxyl groups, and alkoxy groups; and
(D) a hydrosilylation catalyst.

[0010] The component (B) is preferably an organopolysiloxane having silicon-bonded alkenyl groups at both molecular terminals.

[0011] The content of the component (A) is preferably from 100 to 2,000 parts by mass per 100 parts by mass of the component (B).

[0012] A content of the component (C) is preferably an amount whereby the amount of silicon-bonded hydrogen atoms is from 5 to 10 moles per 1 mol of the alkenyl groups in the component (B).

[0013] The thermally conductive silicone composition of the present invention can further comprise (E) an adhesion-imparting agent.

[0014] A total content of the component (C) and the component (E) is preferably from 0.5 to 10% by mass of a total content of the component (B), the component (C), and the component (E).

[0015] The thermally conductive silicone composition of the present invention can further comprise (F) a thermally conductive filler other than the component (A).

[0016] At least one component selected from the component (A) and the component (F) preferably is surface treated using a silicon surface treatment agent.

[0017] The present invention also relates to a thermally conductive member obtained by curing the thermally conductive silicone composition.

Advantageous Effects of Invention

[0018] The thermally conductive silicone composition of the present invention is characterized in that, a cured product can be obtained that has superior bonding to substrates and is free of cracks in cases where used as a thermally conductive member, particularly as a potting agent or the like of an electronic material. Additionally, heat dispersing materials fabricated using the thermally conductive silicone composition of the present invention is characterized by having superior thermal conductivity and few defects.

DESCRIPTION OF EMBODIMENTS

[0019] Component (A) is a thermally conductive filler for imparting thermal conductivity to the present composition, and specifically is an aluminum hydroxide or magnesium oxide having a mass change, measured by thermogravimetric analyses (TGA) before and after being held at 250°C for 30 minutes, of less than 4.0 % by mass. The component (A) is preferably aluminum

hydroxide. It is not preferable that a component having a mass change of 4.0% by mass or greater be used because stability at high temperatures of the resulting thermally conductive silicone rubber will be negatively affected, leading to poor bonding to substrates; and because cracking and similar breakages of cured products of the composition occur, leading to inferior quality of obtained heat dispersing materials.

[0020] The particle shape of the component (A) is not particularly limited, and examples thereof include spherical, needle-like, disc-like, rod-like, and irregular particle shapes. Among these, spherical and irregular shapes are preferable. Furthermore, the average particle diameter of the component (A) is not particularly limited but, when measured by microscopic observation or measurement using a laser diffraction/scattering type particle size distribution device, is preferably in a range of 0.01 to 100 μm, more preferably in a range of 0.01 to 50 μm, and even more preferably in a range of 0.5 to 25 μm.

[0021] In the present composition, the component (A) is preferably surface treated using a silicon-based surface treatment agent. Examples of the silicon-based surface treatment agent include alkoxysilanes such as methyl trimethoxysilane, vinyl trimethoxysilane, vinyl triethoxysilane, 3-Glycidoxypropyltrimethoxysilane, 3-methacryloxypropyl trimethoxysilane, 3-aminopropyl trimethoxysilane, 3-aminopropyl triethoxysilane, N-(2-aminoethyl)-3-aminopropyl trimethoxysilane, and the like; chlorosilanes such as methyl trichlorosilane, dimethyl dichlorosilane, trimethyl monochlorosilane, and the like; silazanes such as hexamethyldisilazane, hexamethylcyclotrisilazane, and the like; and siloxane oligomers such as a dimethylsiloxane oligomer capped at both molecular terminals with silanol groups, a dimethylsiloxane-methylvinylsiloxane copolymer oligomer capped at both molecular terminals with silanol groups, a methylvinylsiloxane oligomer capped at both molecular terminals with silanol groups, a methylphenylsiloxane oligomer capped at both molecular terminals with silanol groups, and the like.

[0022] Examples of the surface treatment method include treatment methods in which the component (A) and the silicon-based surface treatment agent are directly blended (dry treatment methods); treatment methods in which the silicon-based surface treatment agent is blended with the component (A) together with toluene, methanol, heptane, or a similar organic solvent (wet treatment methods); and treatment methods in which the component (A) is compounded in a mixture of the component (B) and the silicon-based surface treatment agent, or the silicon-based surface treatment agent is compounded in a mixture of the component (B) and the component (A) in order to surface treat the component (A) (in-situ treatment methods).

[0023] The component (A) may be a commercially available aluminum hydroxide or magnesium oxide selected from products that have the mass change properties recited in the present invention (e.g. CWL325LV, manufactured by Sumitomo Chemical Co., Ltd.) or may be obtained by heat treating a commercially available aluminum hydroxide or magnesium oxide. The heat treating conditions are not particularly limited, but the treatment is performed in an inert gas or in

vacuo preferably at 100 to 500°C and more preferably at 150°C to 300°C. Examples of the inert gas include nitrogen, helium, and argon. Note that the inert gas may contain hydrogen gas or similar reducing gases. Heating time is not particularly limited, but can be set to a range of 10 minutes to 10 hours, and preferably is set to a range of 30 minutes to 5 hours.

[0024] The content of the component (A) is in a range of 100 to 2,000 parts by mass and preferably is in a range of 200 to 1,600 parts by mass per 100 parts by mass of the component (B). This is because the thermal conductivity of the resulting silicone rubber is favorable when the content of the component (A) is greater than or equal to the lower limit of the range described above, and the handling workability of the resulting composition is favorable when the content is less than or equal to the upper limit of the range described above.

[0025] The organopolysiloxane component (B) is a base compound of the present composition and has at least two silicon-bonded alkenyl groups in each molecule. Examples of the silicon-bonded alkenyl groups in the component (B) include vinyl groups, allyl groups, butenyl groups, pentenyl groups, hexenyl groups, and heptenyl groups. Among these, vinyl groups are preferable. Examples of silicon-bonded organic groups other than the alkenyl groups in the component (B) include methyl groups, ethyl groups, propyl groups, butyl groups, pentyl groups, hexyl groups, heptyl groups, and similar alkyl groups; phenyl groups, tolyl groups, xylyl groups, naphthyl groups, and similar aryl groups; benzyl groups, phenethyl groups, and similar aralkyl groups; and chloromethyl groups, 3-chloropropyl groups, 3,3,3-trifluoropropyl groups, and similar halogenated alkyl groups. Among these methyl groups and phenyl groups are preferable. The molecular structure of the component (B) described above is not limited, and examples thereof include straight, partially branched straight, and branched structures. Among these, straight structures are preferable.

[0026] Viscosity at 25°C of the component (B) is not particularly limited, but is preferably in a range of 10 to 500,000 mPa·s, and more preferably in a range of 50 to 100,000 mPa·s. This is because the physical properties of the resulting silicone rubber are improved when the viscosity of the component (B) is greater than or equal to the lower limit of the range described above, and the handling workability of the resulting composition is favorable when the viscosity is less than or equal to the upper limit of the range described above. The viscosity at 25°C of the component (B) may, for example, be determined by measurement using a B type viscometer in accordance with JIS K 7117-1.

[0027] Tetramer to eicosamer cyclic siloxane content in terms of mass units in the component (B) is preferably not more than 1,000 ppm. This is because when the tetramer to eicosamer cyclic siloxane content in the component (B) is less than or equal to the upper limit of the range described above, low-boiling components that volatilize from the composition during curing (of the resulting composition) can be reduced. Examples of such a cyclic siloxane include cyclic dimethylsiloxane oligomers, cyclic methylvinylsiloxane oligomers, cyclic methylphenylsiloxane oligomers, and cyclic dimethylsiloxane-methylvinylsiloxane copolymer oligomers. The tetramer

to eicosamer cyclic siloxane content in the component (B) can be measured by gas chromatography or the like.

[0028] Examples of the organopolysiloxane component (B) include a copolymer of dimethylsiloxane and methylvinylsiloxane capped at both molecular terminals with trimethylsiloxy groups, a methylvinylpolysiloxane capped at both molecular terminals with trimethylsiloxy groups, a dimethylsiloxane-methylvinylsiloxane-methylphenylsiloxane copolymer capped at both molecular terminals with trimethylsiloxy groups, a dimethylpolysiloxane capped at both molecular terminals with dimethylvinylsiloxy groups, a methylvinylpolysiloxane capped at both molecular terminals with dimethylvinylsiloxy groups, copolymers of dimethylsiloxane and methylvinylsiloxane capped at both molecular terminals with dimethylvinylsiloxy groups, a dimethylsiloxane-methylvinylsiloxane-methylphenylsiloxane copolymer capped at both molecular terminals with dimethylvinylsiloxy groups; an organopolysiloxane copolymer consisting of siloxane units represented by the formula: $R^1_3SiO_{1/2}$, siloxane units represented by the formula: $R^1_2R^2SiO_{1/2}$, siloxane units represented by the formula: $R^1_2SiO_{2/2}$, and a small amount of siloxane units represented by the formula: $SiO_{4/2}$; an organopolysiloxane copolymer consisting of siloxane units represented by the formula: $R^1_2R^2SiO_{1/2}$, siloxane units represented by the formula: $R^1_2SiO_{2/2}$, and a small amount of siloxane units represented by the formula: $SiO_{4/2}$; an organopolysiloxane copolymer consisting of siloxane units represented by the formula: $R^1R^2SiO_{2/2}$, and a small amount of siloxane units represented by the formula: $R^1SiO_{3/2}$ or a small amount of siloxane units represented by the formula: $R^2SiO_{3/2}$; and mixtures of two or more types of these organopolysiloxanes. In the formulae above, R^1 is a monovalent hydrocarbon group other than an alkenyl group. Examples thereof include a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, and similar alkyl groups; a phenyl group, a tolyl group, a xylyl group, a naphthyl group, and similar aryl groups; a benzyl group, a phenethyl group, and similar aralkyl groups; and a chloromethyl group, a 3-chloropropyl group, a 3,3,3-trifluoropropyl group, and similar halogenated alkyl groups. Additionally, in the formulae above, R^2 is an alkenyl group. Examples thereof include a vinyl group, an allyl group, a butenyl group, a pentenyl group, a hexenyl group, and a heptenyl group.

[0029] The organopolysiloxane component (C) is the crosslinking agent in the present composition, and has at least two silicon-bonded hydrogen atoms in each molecule and is free of silicon-bonded alkenyl groups, hydroxyl groups, and alkoxy groups. Examples of the silicon-bonded organic groups in the component (C) include methyl groups, ethyl groups, propyl groups, butyl groups, pentyl groups, hexyl groups, heptyl groups, and similar alkyl groups; phenyl groups, tolyl groups, xylyl groups, naphthyl groups, and similar aryl groups; benzyl groups, phenethyl groups, and similar aralkyl groups; and chloromethyl groups, 3-chloropropyl groups, 3,3,3-trifluoropropyl groups, and similar halogenated alkyl groups. Among these methyl groups and phenyl groups are preferable. The molecular structure of the component (C) described above is not limited, and examples thereof include straight, partially branched straight, and

branched structures. Among these, straight structures are preferable.

[0030] Viscosity at 25°C of the component (C) is not particularly limited, but is preferably in a range of 1 to 500,000 mPa·s, and more preferably in a range of 5 to 100,000 mPa·s. This is because the physical properties of the resulting silicone rubber are favorable when the viscosity of the component (C) is greater than or equal to the lower limit of the range described above, and the handling workability of the resulting composition is favorable when the viscosity is less than or equal to the upper limit of the range described above. The viscosity at 25°C of the component (C) may, for example, be determined by measurement using a B type viscometer in accordance with JIS K 7117-1.

[0031] Examples of the organopolysiloxane component (C) include methylhydrogenpolysiloxane capped at both molecular terminals with trimethylsiloxy groups, a copolymer of dimethylsiloxane and methyl hydrogen siloxane capped at both molecular terminals with trimethylsiloxy groups, dimethylsiloxane-methylhydrogensiloxane-methylphenylsiloxane copolymer capped at both molecular terminals with trimethylsiloxy groups, dimethylpolysiloxane capped at both molecular terminals with dimethylhydrogensiloxy groups, dimethylsiloxane-methylphenylsiloxane copolymer capped at both molecular terminals with dimethylhydrogensiloxy groups, methylphenylpolysiloxane capped at both molecular terminals with dimethylhydrogensiloxy groups; an organopolysiloxane copolymer consisting of siloxane units represented by the formula: $R^1{}_3SiO_{1/2}$, siloxane units represented by the formula: $R^1{}_2HSiO_{1/2}$, and siloxane units represented by the formula: $SiO_{4/2}$; an organopolysiloxane copolymer consisting of siloxane units represented by the formula: $R^1{}_2HSiO_{1/2}$ and siloxane units represented by the formula: $SiO_{4/2}$; an organopolysiloxane copolymer consisting of siloxane units represented by the formula: $R^1HSiO_{2/2}$, and siloxane units represented by the formula: $R^1SiO_{3/2}$ or siloxane units represented by the formula: $HSiO_{3/2}$; and mixtures of two or more of these organopolysiloxanes. In the formulae above, R^1 is a monovalent hydrocarbon group other than an alkenyl group, and examples thereof are the same as the groups described above.

[0032] A content of the component (C) is a quantity whereby the amount of silicon-bonded hydrogen atoms in the component (C) is from 0.5 to 10 moles, preferably from 0.5 to 5 moles, and more preferably from 0.5 to 3 moles per 1 mole of alkenyl groups in the component (B). This is because curing of the resulting composition can be performed sufficiently when the content of the component (C) is greater than or equal to the lower limit of the range described above, and change over time of the physical properties of the resulting silicone rubber can be suppressed when the content is less than or equal to the upper limit of the range described above.

[0033] The component (D) is a hydrosilylation catalyst used to accelerate curing of the present composition. Examples of the component (D) include fine platinum powder, platinum black, silica supported fine platinum powder, activated carbon supported platinum, chloroplatinic acid, platinum tetrachloride, an alcohol solution of chloroplatinic acid, olefin complexes of platinum,

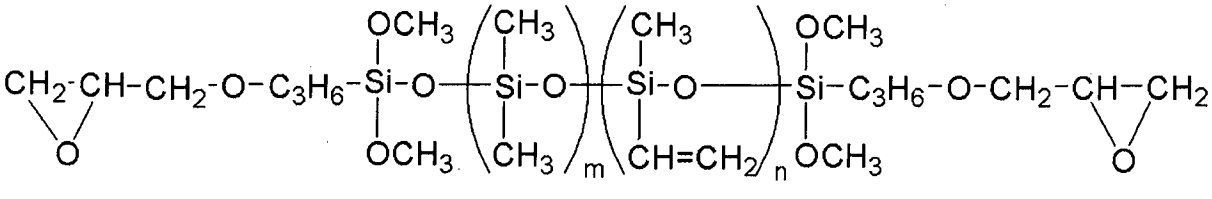
divinyltetramethyl disiloxane or similar alkenylsiloxane complexes of platinum, and similar platinum-based catalysts; tetrakis (triphenylphosphine) palladium and similar palladium-based catalysts; and rhodium-based catalysts; and, moreover, polystyrene resins, nylon resins, polycarbonate resins, silicone resins, and similar thermoplastic resin powders having a particle diameter of less than 10 μm comprising these metal-based catalysts.

[0034] The content of the component (D) is a catalytic quantity. For example, the content is, in terms of mass units, an amount such that the amount of metal atoms in the component (D) with respect to the component (B) is preferably in a range of 0.1 to 500 ppm and more preferably in a range of 1 to 50 ppm. This is because the curability of the resulting composition is favorable when the content of the component (D) is greater than or equal to the lower limit of the above-mentioned range and the resulting composition is sufficiently cured even when the content of the component (D) is less than or equal to the upper limit of the above-mentioned range.

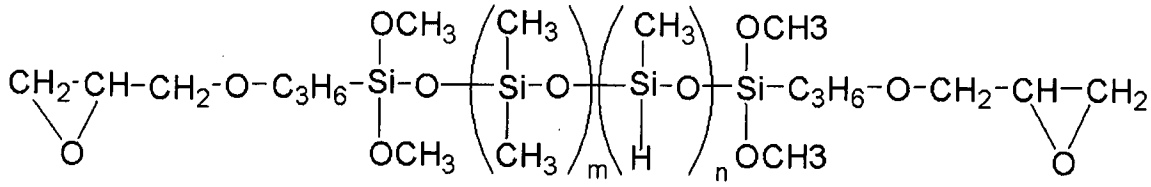
[0035] The component (E) is an adhesion imparting agent for imparting adhesivity to the present composition. The component (E) is not particularly limited, but preferably is an organosilicon compound having a silicon-bonded alkoxy group. Examples of the silicon-bonded alkoxy group in the component (E) include methoxy groups, ethoxy groups, propoxy groups, and butoxy groups. Among these, methoxy groups are preferable. Examples of the silicon-bonded organic group in the component (E) include methyl groups, ethyl groups, propyl groups, butyl groups, hexyl groups, octyl groups, and similar alkyl groups; vinyl groups, allyl groups, hexenyl groups, and similar alkenyl groups; phenyl groups, tolyl groups, xylyl groups, and similar aryl groups; 3,3,3-trifluoropropyl groups, 3-chloropropyl groups, and similar halogenated alkyl groups; 3-glycidoxypropyl groups, 3-methacryloxypropyl groups, 3-aminopropyl groups, N-(2-aminoethyl)-3-aminopropyl groups, and similar functional organic groups; trimethoxysilylethyl groups, methyldimethoxysilylethyl groups, and similar alkoxysilylalkyl groups; and silicon-bonded hydrogen atoms.

[0036] Examples of the component (E) include 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropyl methyldimethoxysilane, 3-methacryloxypropyl trimethoxysilane, 3-methacryloxypropylmethyldimethoxysilane, 3-aminopropyl trimethoxysilane, 3-aminopropyl triethoxysilane, N-(2-aminoethyl)-3-aminopropyl trimethoxysilane, and similar partially hydrolyzed condensates consisting of one or two or more types of alkoxysilanes; methylpolysilicate, ethylpolysilicate, an organosiloxane oligomer represented by the general formula:

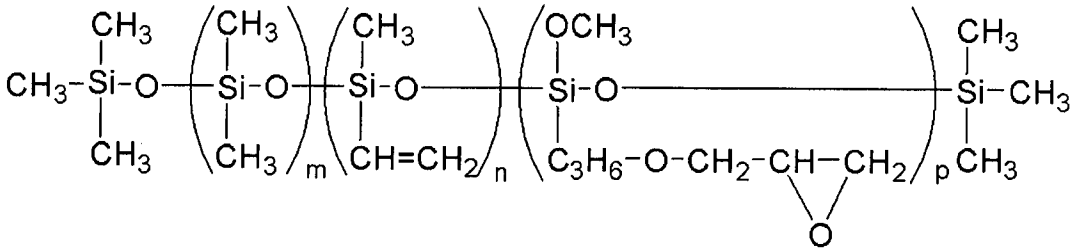
Formula 1



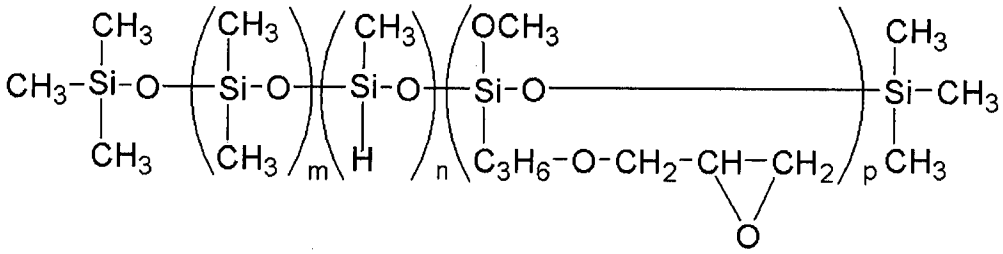
(wherein "m" is an integer of 0 or greater and "n" is an integer of 1 or greater);
an organosiloxane oligomer represented by the general formula:
Formula 2



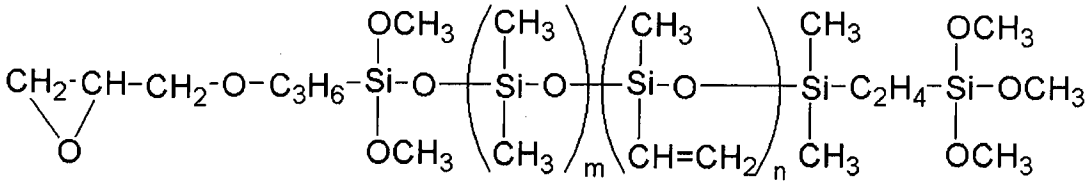
(wherein "m" is an integer of 0 or greater and "n" is an integer of 1 or greater);
an organosiloxane oligomer represented by the general formula:
Formula 3



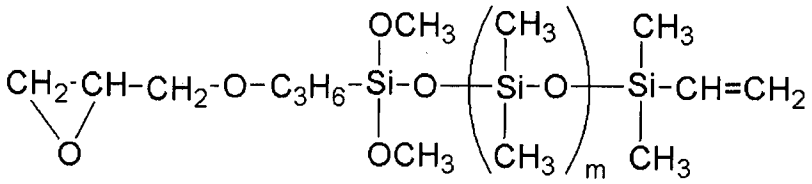
(wherein "m" is an integer of 0 or greater and "n" and "p" are each integers of 1 or greater);
an organosiloxane oligomer represented by the general formula:
Formula 4



(wherein "m" is an integer of 0 or greater and "n" and "p" are each integers of 1 or greater);
an organosiloxane oligomer represented by the general formula:
Formula 5



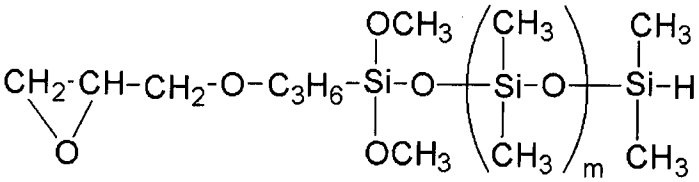
(wherein "m" is an integer of 0 or greater and "n" is an integer of 1 or greater);
an organosiloxane oligomer represented by the general formula:
Formula 6



(wherein "m" is an integer of 0 or greater); and

an organosiloxane oligomer represented by the general formula:

Formula 7



(wherein "m" is an integer of 0 or greater).

[0037] Particularly, the component (E) is preferably a mixture of (i) an organosilicon compound that contains a silicon-bonded alkoxy group and has a boiling point of 100°C or higher, and (ii) a diorganosiloxane oligomer that contains a silicon-bonded hydroxyl group and has at least one silicon-bonded alkenyl group in each molecule, or the component (E) is preferably a condensation reaction product of (i) and (ii).

[0038] This is because when the boiling point of the component (i) is 100°C or higher (note that the boiling point (normal boiling point) at 1 atmosphere is 100°C or higher), low-boiling components that volatilize from the composition during curing (of the resulting composition) can be reduced. Examples of the component (i) include 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropyl methyldimethoxysilane, 3-methacryloxypropyl trimethoxysilane, 3-methacryloxypropylmethyldimethoxysilane, 3-aminopropyl trimethoxysilane, 3-aminopropyl triethoxysilane, and N-(2-aminoethyl)-3-aminopropyl trimethoxysilane.

[0039] Additionally, preferably the component (ii) is a diorganosiloxane oligomer that has a silicon-bonded hydroxyl group (silanol group), and a content of the silanol group is no greater than 9% by mass. This is because when the content is 9% by mass or less, the adhesion of the resulting composition is favorable. Examples of the component (ii) include a methylvinylsiloxane oligomer capped at both molecular terminals with silanol groups, a dimethylsiloxane-methylvinylsiloxane copolymer oligomer capped at both molecular terminals with silanol groups, and a methylvinylsiloxane-methylphenylsiloxane copolymer oligomer capped at both molecular terminals with silanol groups.

[0040] The component (E) may be a mixture of the component (i) and the component (ii) or may be a reaction product resulting from a condensation reaction of components (i) and (ii). The method used for the condensation reaction of the component (i) and the component (ii) is not particularly limited, but the reaction is preferably carried out in the presence of potassium hydroxide, sodium hydroxide, or a similar basic catalyst.

[0041] A content of the component (E) is at least 0.05 parts by mass and is preferably at least 0.1

parts by mass per 100 parts by mass of the component (B). This is because the adhesion of the resulting composition is favorable when the content of the component (E) is greater than or equal to the lower limit of the range described above.

[0042] The component (F), like the component (A), is a thermally conductive filler for imparting thermal conductivity to the present composition. Examples of the component (F) include thermally conductive fillers other than the component (A) such as gold, silver, copper, aluminum, nickel, brass, shape memory alloys, solder, and similar metal powders; ceramics, glass, quartz, organic resin, and similar powders having gold, silver, nickel, copper, or a similar metal deposited or plated on the surface thereof; aluminum oxide, beryllium oxide, chromium oxide, zinc oxide, titanium oxide, crystalline silica, and similar metallic oxide-based powders; boron nitride, silicon nitride, aluminum nitride, and similar metal nitride-based powders; boron carbide, titanium carbide, silicon carbide, and similar metal carbide-based powders; magnesium hydroxide and similar metal hydroxide-based powders; carbon nanotube, carbon microfibers, diamonds, graphite, and similar carbon-based powders; and mixtures of two or more types of these powders. Particularly, the component (F) is preferably a metal-based powder, a metallic oxide-based powder, or a metal nitride-based powder, specifically, a silver powder, an aluminum powder, an aluminum oxide powder, a zinc oxide powder, or an aluminum nitride powder. Note that these thermally conductive fillers differ from aluminum hydroxide and magnesium oxide in that, in most cases, mass change of the filler that accompanies hydrated water and moisture absorption does not become a problem.

[0043] The particle shape of the component (F) is not particularly limited, and examples thereof include spherical, needle-like, disc-like, rod-like, and irregular particle shapes. Among these, spherical and irregular shapes are preferable. Furthermore, the average particle diameter of the component (F) is not particularly limited but is preferably in a range of 0.01 to 100 μm and more preferably in a range of 0.01 to 50 μm.

[0044] Additionally, the component (F) is preferably surface treated using a silicon-based surface treatment agent. The same silicon treatment agents recited for component (A) can be used as this silicon-based surface treatment agent. Moreover, the same methods recited in relation to the component (A) can be used as the surface treatment method. At least one component selected from the component (A) and the component (F) preferably is surface treated using a silicon surface treatment agent.

[0045] The content of the component (F) is in a range of 100 to 2,000 parts by mass and preferably is in a range of 200 to 1,600 parts by mass per 100 parts by mass of the component (B). This is because the thermal conductivity of the resulting silicone rubber is favorable when the content of the component (F) is greater than or equal to the lower limit of the range described above, and the handling workability of the resulting composition is favorable when the content is less than or equal to the upper limit of the range described above.

[0046] The present composition also preferably comprises a curing inhibitor for the purpose of

enhancing handling/workability. Examples of the curing inhibitor include 2-methyl-3-butyne-2-ol, 3,5-dimethyl-1-hexyne-3-ol, 2-phenyl-3-butyne-2-ol, and similar alkyne alcohols; 3-methyl-3-pentene-1-yne, 3,5-dimethyl-3-hexene-1-yne, and similar enyne compounds; and benzotriazole. The content of these curing inhibitors is preferably in a range of 10 to 50,000 ppm, in terms of mass units, relative to the component (B).

[0047] The method of preparing the thermally conductive silicone composition of the present invention is not particularly limited. For example, preparation method [1] wherein the component (A) is mixed with the component (B), the component (C) is added in small amounts thereto, and the resulting composition is mixed may be used or, alternatively, preparation method [2] wherein the component (A) is premixed with the component (C), and the component (B) is added in small amounts thereto may be used. However, preparation method [1] is particularly preferable. Various devices may be used as the mixing device but uniform mixing can be obtained by using a known kneading device such as a two roll mill, a Banbury mixer, a kneader/mixer, a planetary mixer, a Ross mixer, a Hobart mixer, a speed mixer, or the like. Among these use of a Ross mixer is preferable.

[0048] Provided that the objects of the present invention are not inhibited, the thermally conductive filler surface treatment agent and the thermally conductive silicone composition of the present invention may comprise the following various additives as optional components: fumed titanium oxide and similar reinforcing fillers; diatomaceous earth, aluminosilicate, iron oxide, zinc oxide, calcium carbonate, and similar non-reinforcing fillers; and surface-treated products of these fillers, treated using an organosilane, a polyorganosiloxane, or a similar organosilicon compound. Additionally, as necessary, methyl ethyl ketone, methyl isobutyl ketone, or a similar solvent, a pigment, a dye, a heat-resistant agent, a flame retardant, an internal release agent, a plasticizer, a mineral oil, a nonfunctional silicone oil, or similar additive commonly used in silicone compositions may be compounded.

EXAMPLES

[0049] The present invention is described in detail below based on examples, but the present invention is not limited to the examples. Note that in the Examples, physical properties are values measured at 25°C. Additionally, the particle diameters of the thermally conductive fillers are the values found in the product catalogues of each mentioned manufacturer.

[0050] Mass change of the thermally conductive filler (= % loss on heating)

The rate of loss in mass of each thermally conductive filler was measured under the following conditions after being held at 250°C for 30 minutes.

Device: TGA-50 Thermogravimetric Analyzer, manufactured by Shimadzu Corporation

Rate of temperature increase: 10°C/min from room temperature to 250°C

Temperature conditions: Held for 30 minutes after reaching 250°C

Measurement atmosphere: Nitrogen gas (flow rate: 50 ml/min)

Sample size: 10 mg

[0051] Stability evaluation of the thermally conductive silicone rubber (cured product) after the high temperature holding test

40 cc of each of the thermally conductive silicone rubber compositions was placed, respectively, in a 50 cc glass beaker and heat cured in an oven with internal air circulation at 150°C for 1 hour. Thus, thermally conductive silicone rubbers (samples) were obtained. The obtained samples were further stored at 180°C for 72 hours and, thereafter, the appearances thereof were visually confirmed. The samples were evaluated according to the following standards.

○: After storage, no pealing from the surface of the beaker (poor bonding) nor breakage of the sample (e.g. cracking) was observed.

×: After storage, obvious peeling from the surface of the beaker and breakage of the sample was observed.

[0052] Practical Example 1

100 parts by mass of dimethylpolysiloxane capped at both molecular terminals with dimethylvinylsiloxy groups having a viscosity of 400 mPa·s, 4.3 parts by mass of methyltrimethoxysilane, and 320 parts by mass of irregular shaped aluminum hydroxide microparticles having an average diameter of 25 μm and a loss on heating of 3.9% by mass (CWL325LV, manufactured by Sumitomo Chemical Co., Ltd.) were mixed at room temperature using a Ross mixer. Thereafter, the mixture was heated and mixed under reduced pressure at 150°C for 1 hour. Thus, a silicone rubber base was prepared. Next, 1 part by mass of copolymer of dimethylsiloxane and methyl hydrogen siloxane capped at both molecular terminals with trimethylsiloxy groups having a viscosity of 5 mPa·s (amount such that the amount of silicon-bonded hydrogen atoms in the present component is 0.8 moles per 1 mole of vinyl groups in the dimethylpolysiloxane contained in the silicone rubber base described above), 0.1 parts by mass of 2-phenyl-3-butyne-2-ol, and 1,3-divinyltetramethyl disiloxane platinum complex (at an amount such that the platinum metal in this component is, in terms of mass units, 30 ppm in the dimethylpolysiloxane included in the silicone rubber base) were added to the silicone rubber base and mixed uniformly at room temperature. Thus, a thermally conductive silicone rubber composition 1 was prepared.

[0053] Comparative Example 1

Aside from using irregular shaped aluminum hydroxide microparticles having an average diameter of 18 μm and a loss on heating of 4.4% by mass (HIGILITE H-31, manufactured by Showa Denko K.K.) in place of the aluminum hydroxide microparticles (CWL325LV) of Practical Example 1, a thermally conductive silicone rubber composition 2 of Comparative Example 1 was prepared in the same manner as that recited in Practical Example 1.

[0054] Practical Example 2

The irregular shaped aluminum hydroxide microparticles having an average diameter of 18 μm

and a loss on heating of 4.4% by mass (HIGILITE H-31, manufactured by Showa Denko K.K.) used in Comparative Example 1 were dried in an oven with internal air circulation at 250°C for 3 hours, thereby ultimately preparing irregular shaped aluminum hydroxide microparticles having an average diameter of 18 μm and a loss on heating of 1.4% by mass (hereinafter referred to as "baked H-31").

Aside from using this "baked H-31" in place of the aluminum hydroxide microparticles (CWL325LV) used in Practical Example 1, a thermally conductive silicone rubber composition 3 of Practical Example 2 was prepared in the same manner as that recited in Practical Example 1.

[0055] Comparative Example 2

Aside from using irregular shaped aluminum hydroxide microparticles having an average diameter of 9 μm and a loss on heating of 4.1% by mass (BF083, manufactured by Nippon Light Metal Company, Ltd.) in place of the aluminum hydroxide microparticles (CWL325LV) of Practical Example 1, a thermally conductive silicone rubber composition 4 of Comparative Example 2 was prepared in the same manner as that recited in Practical Example 1.

[0056] Comparative Example 3

Aside from using irregular shaped aluminum hydroxide microparticles having an average diameter of 3.6 μm and a loss on heating of 4.9% by mass (HP350, manufactured by Showa Denko K.K.) in place of the aluminum hydroxide microparticles (CWL325LV) of Practical Example 1, a thermally conductive silicone rubber composition 5 of Comparative Example 3 was prepared in the same manner as that recited in Practical Example 1.

[0057] Practical Example 3

The irregular shaped aluminum hydroxide microparticles having an average diameter of 3.6 μm and a loss on heating of 4.9% by mass (HP350, manufactured by Showa Denko K.K.) used in Comparative Example 3 were dried in an oven with internal air circulation at 250°C for 3 hours, thereby ultimately preparing irregular shaped aluminum hydroxide microparticles having an average diameter of 3.6 μm and a loss on heating of 2.1% by mass (hereinafter referred to as "baked HP350").

Aside from using this "baked HP350" in place of the aluminum hydroxide microparticles (CWL325LV) used in Practical Example 1, a thermally conductive silicone rubber composition 6 of Practical Example 3 was prepared in the same manner as that recited in Practical Example 1.

[0058] For Practical Examples 1 to 3 and Comparative Examples 1 to 3, the types, average diameters, and mass change (= % loss on heating) of the thermally conductive fillers in the obtained thermally conductive silicone rubber compositions, along with the stability evaluation of the thermally conductive silicone rubber (cured product) are shown in Table 1.

[0059] [Table 1]

	Practical Example 1	Comparative Example 1	Practical Example 2	Comparative Example 2	Comparative Example 3	Practical Example 3
Thermally conductive silicone rubber composition	1	2	3	4	5	6
Average diameter (μm)	25	18	18	9	3.6	3.6
Loss on heating (% by mass)	3.9	4.4	1.4	4.1	4.9	2.1
Stability evaluation after high temp. holding test	○	×	○	×	×	○

[0060] As shown in Table 1, it is clear that by using a thermally conductive filler having a loss on heating of less than 4.0% by mass, after the high temperature holding test, poor bonding of the thermally conductive silicone rubber cured product to the container (beaker) and breakage (cracking) of the sample were very effectively suppressed. In particular, as clear from a comparison of Practical Example 1 and Comparative Example 4, even when using similar types of aluminum hydroxide, the loss on heating of 4.0% marks the point where the high temperature stability of the obtained thermally conductive silicone rubber steeply declines and poor bonding and breakage of the cured product occurs.

INDUSTRIAL APPLICABILITY

[0061] The thermally conductive silicone rubber composition of the present invention has superior bonding to substrates, and cracking that accompanies curing can be suppressed. Therefore, the thermally conductive silicone rubber composition of the present invention is suitable for use as a heat dispersing adhesive for electrical and electronic parts including, for example, a potting material or adhesive for printed circuit boards and hybrid ICs on which transistors, ICs, memory elements, and similar electronic parts are mounted; an adhesive for semiconductor elements; and an adhesive or sealing agent for engine mounts.

CLAIMS

1. A thermally conductive silicone rubber composition comprising: (A) an aluminum hydroxide or magnesium oxide thermally conductive filler having a mass change, measured by thermogravimetric analyses (TGA) before and after being held at 250°C for 30 minutes, of less than 4.0 % by mass.
2. The thermally conductive silicone composition according to claim 1, further comprising:
(B) an organopolysiloxane having at least two silicon-bonded alkenyl groups in each molecule;
(C) an organopolysiloxane having at least two silicon-bonded hydrogen atoms in each molecule and being free of silicon-bonded alkenyl groups, hydroxyl groups, and alkoxy groups; and
(D) a hydrosilylation catalyst.
3. The thermally conductive silicone composition according to claim 2, wherein the component (B) is an organopolysiloxane having silicon-bonded alkenyl groups at both molecular terminals.
4. The thermally conductive silicone composition according to claim 2 or 3, wherein a content of the component (A) is from 100 to 2,000 parts by mass per 100 parts by mass of the component (B).
5. The thermally conductive silicone composition according to any one of claims 2 to 4, wherein a content of the component (C) is a quantity whereby the amount of silicon-bonded hydrogen atoms is from 0.5 to 10 moles per 1 mol of alkenyl groups in the component (B).
6. The thermally conductive silicone composition according to any one of claims 1 to 5, further comprising: (E) an adhesion-imparting agent.
7. The thermally conductive silicone composition according to claim 6, wherein a total content of the component (C) and the component (E) is from 0.5 to 10% by mass of a total content of the component (B), the component (C) and the component (E).
8. The thermally conductive silicone composition according to any one of claims 1 to 7, further comprising: (F) a thermally conductive filler other than the component (A).
9. The thermally conductive silicone composition according to claim 8, wherein at least one component selected from the component (A) and the component (F) is surface treated using a silicon surface treatment agent.
10. A thermally conductive member obtained by curing the thermally conductive silicone composition described in any one of claims 1 to 9.

INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2013/084177

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L83/04
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G C08L C09J C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 2 270 080 A1 (SHINETSU CHEMICAL CO [JP]) 5 January 2011 (2011-01-05) paragraph [0009] - paragraph [0045]	1-10

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

☒ See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/JP2013/084177

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