

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
6 August 2009 (06.08.2009)

PCT

(10) International Publication Number
WO 2009/096436 A1

(51) International Patent Classification:

C10M 169/02 (2006.01) **C10N 30/00** (2006.01)
C09K 5/14 (2006.01) **C10N 30/08** (2006.01)
H01L 23/373 (2006.01) **C10N 40/14** (2006.01)
C08L 83/04 (2006.01) **C10N 50/10** (2006.01)
C08L 83/14 (2006.01)

(21) International Application Number:

PCT/JP2009/051399

(22) International Filing Date: 22 January 2009 (22.01.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

2008-019864 30 January 2008 (30.01.2008) JP

(71) Applicant (for all designated States except US): **DOW CORNING TORAY CO., LTD.** [JP/JP]; 1-3, Marunouchi 1-chome, Chiyoda-ku, Tokyo, 1000005 (JP).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **NAKAYOSHI, Kazumi** [JP/JP]; c/o Dow Corning Toray Co., Ltd., 2-2, Chigusaigaigan, Ichihara-shi, Chiba, 2990108 (JP). **KATO, Tomoko** [JP/JP]; c/o Dow Corning Toray Co., Ltd., 2-2, Chigusaigaigan, Ichihara-shi, Chiba, 2990108 (JP).

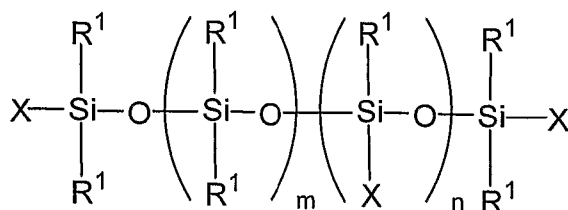
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, KE, KG, KM, KN,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

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

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(54) Title: THERMALLY CONDUCTIVE SILICONE GREASE COMPOSITION

(57) Abstract: A thermally conductive silicone grease composition comprising at least the following components: an organopolysiloxane (A) represented by the following general formula : [wherein R₁ designates identical or different univalent hydrocarbon groups; X designates identical or different univalent hydrocarbon groups or alkoxy-silyl-containing groups of the following general formula: -R²-SiR¹_a(OR₃)_(3-a) (wherein R¹ designates the previously mentioned groups; R² designates oxygen atoms or alkylene groups; R³ designates alkyl groups;

and 'a' is an integer ranging from 0 to 2); and 'm' and 'n' are integers equal to or greater than 0, respectively]; a thermally conductive filler (B); and an organopolysiloxane (C) having silicon-bonded hydrogen atoms on both molecular terminals and in the molecular chains; is characterized by excellent resistance to heat and reduced oil bleeding.



WO 2009/096436 A1

DESCRIPTION

THERMALLY CONDUCTIVE SILICONE GREASE COMPOSITION

Technical Field

[0001] The present invention relates to a thermally conductive silicone grease composition which is characterized by excellent resistance to heat and reduced oil bleeding.

Background Art

[0002] In recent years, following an increase in the degree of density and integration of hybrid ICs and printed circuit boards that carry transistors, ICs, memory elements, and other electronic components, various thermally conductive silicone grease compositions comprising an organopolysiloxane and a thermally conductive filler such as an aluminum oxide powder, zinc oxide powder or the like have been used in order to achieve efficient heat transfer from such devices (see Japanese Unexamined Patent Application Publications (hereinafter referred to as "Kokai") Sho 50-105573, Sho 51-55870, and Sho 61-157587).

However, a problem associated with conventional silicone grease compositions is that a part of the oil bleeds out, and this impairs reliability of the respective electronic devices.

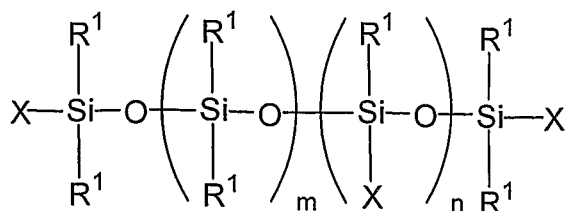
[0003] On the other hand, in order to increase content of a thermally conductive filler in a thermally conductive silicone grease composition, it was proposed to use a thermally conductive silicone grease composition comprising an organopolysiloxane, a thermally conductive filler, and an organohydrogenpolysiloxane having in one molecule at least three silicon-bonded hydrogen atoms (see Kokai Hei 4-202496). However, such a thermally conductive silicone grease composition was subject either to oil bleeding or to dripping from thick coating layers or from vertical surfaces under the effect of heat.

[0004] It is an object of the present invention to provide a thermally conductive silicone grease composition which is characterized by excellent resistance to heat and reduced oil bleeding.

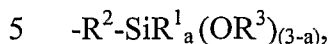
Disclosure of Invention

[0005] The above problems are solved by the present invention that provides a thermally conductive silicone grease composition comprising at least the following components:

100 parts by mass of an organopolysiloxane (A) represented by the following general formula:



[wherein R¹ designates identical or different univalent hydrocarbon groups; X designates identical or different univalent hydrocarbon groups or alkoxysilyl-containing groups of the following general formula:



(wherein R¹ designates the previously mentioned groups; R² designates oxygen atoms or alkylene groups; R³ designates alkyl groups; and “a” is an integer ranging from 0 to 2); and “m” and “n” are integers equal to or greater than 0, respectively];

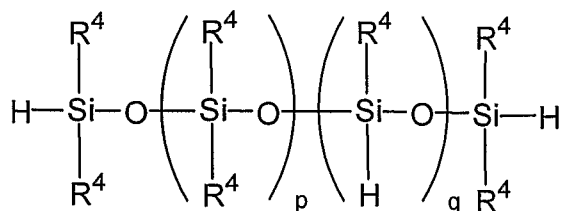
400 to 3,500 parts by mass of a thermally conductive filler (B); and

10 1 to 100 parts by mass of an organopolysiloxane (C) having silicon-bonded hydrogen atoms on both molecular terminals and in the molecular chains.

[0006] The aforementioned component (A) may have a viscosity ranging from 5 to 100,000 mPa·s at 25 °C.

[0007] The aforementioned component (B) may have an average particle size ranging
15 from 0.01 to 100 μm. Component (B) may comprise a metal-based powder, metal oxide-based powder, or a metal nitride-based powder. In particular, this may be a silver powder, aluminum powder, aluminum oxide powder, zinc oxide powder, or aluminum nitride powder.

[0008] Aforementioned component (C) may comprise an organopolysiloxane of the
20 following general formula:



(wherein R⁴ designates identical or different univalent hydrocarbon groups, which are free of unsaturated aliphatic bonds; “p” is an integer equal to or greater than 0; and “q” is an integer equal to or greater than 1).

[0009] The thermally conductive silicone grease composition of the invention may further contain a silica-based filler (D) in an amount of 1 to 100 parts by mass for 100 parts by mass of component (A).

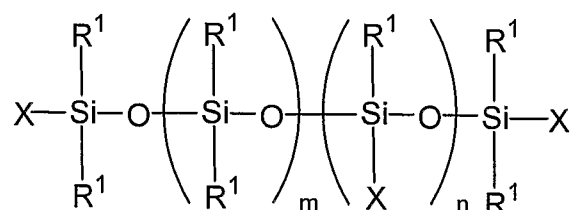
[0010] The thermally conductive silicone grease composition of the invention may further contain a coupling agent (E) in an amount of 0.1 to 10 parts by mass for 100 parts by mass of component (A).

Effects of Invention

[0011] The thermally conductive silicone grease composition of the invention is characterized by excellent resistance to heat and reduced oil bleed.

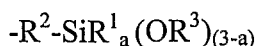
10 Detailed Description of the Invention

[0012] The organopolysiloxane of component (A) is one of the main components of the composition and is represented by the following general formula:



[0013] In this formula, R¹ may represent identical or different univalent hydrocarbon groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, and other linear alkyl groups; isopropyl, tertiary butyl, isobutyl, 2-methyl undecyl, 1-hexyl heptyl, and other branched alkyl groups; cyclopentyl, cyclohexyl, cyclododecyl, and other cyclic alkyl groups; vinyl, allyl, butenyl, pentenyl, hexenyl, and other alkenyl groups; phenyl, tolyl, xylyl, and other aryl groups; benzyl, phenethyl, 2-(2,4,6-trimethylphenyl) propyl, and other aralkyl groups; 3,3,3-trifluoropropyl, 3-chloropropyl, and other halogenated alkyl groups. Preferably, such groups are alkyl, alkenyl, or aryl groups, and especially preferably, methyl, vinyl, or phenyl.

[0014] In the above formula, X designates identical or different univalent hydrocarbon groups or alkoxysilyl-containing groups of the following general formula:



The univalent hydrocarbon groups designated by X may be the same as aforementioned groups designated by R¹, of which preferable are alkyl, alkenyl, and aryl groups, especially methyl, vinyl, or phenyl groups. In the alkoxysilyl-containing groups, R¹ are the same as

those mentioned above and preferably are alkyl groups, especially methyl groups. R^2 designates oxygen atoms or alkylene groups such as ethylene, propylene, butylenes, or methylethylene groups, of which preferable are ethylene and propylene groups. R^3 designates alkyl groups such as methyl, ethyl, propyl, or butyl groups, of which preferable are methyl and ethyl groups. In the formula, "a" is an integer ranging from 0 to 2, of which 0 is preferable.

[0015] There are no special limitations on the viscosity of component (A) at 25 °C. However, the viscosity is preferably within the range from 5 to 100,000 mPa·s, more preferably, within the range from 5 to 50,000 mPa·s, and most preferably, within the range from 10 to 50,000 mPa·s. This is due to the fact that when the viscosity at 25 °C is less than the lower limit of the above-mentioned range, the physical properties of the resultant compositions tend to markedly decrease, and, on the other hand, when the viscosity exceeds the upper limit of the above-mentioned range, the handleability of the resultant compositions tends to decrease.

[0016] Specific examples of aforementioned component (A) are the following: a diorganopolysiloxane capped at both molecular terminals with trimethylsiloxy groups; a dimethylpolysiloxane capped at both molecular terminals with dimethylphenylsiloxy groups; a copolymer of a dimethylsiloxane and a methylphenylsiloxane capped at both molecular terminals with trimethylsiloxy groups; a copolymer of a dimethylsiloxane and a methylphenylsiloxane capped at both molecular terminals with dimethylphenylsiloxy groups; a methyl (3,3,3-trifluoropropyl) polysiloxane capped at both molecular terminals with trimethylsiloxy groups; a dimethylpolysiloxane capped at both molecular terminals with dimethylvinylsiloxy groups; a dimethylpolysiloxane capped at both molecular terminals with methylphenylvinylsiloxy groups; a copolymer of a dimethylsiloxane and a methylphenylsiloxane capped at both molecular terminals with dimethylvinylsiloxy groups; a copolymer of a dimethylsiloxane and a methylvinylsiloxane capped at both molecular terminals with dimethylvinylsiloxy groups; a copolymer of a dimethylsiloxane and a methylvinylsiloxane capped at both molecular terminals with trimethylsiloxy groups; a methyl (3,3,3-trifluoropropyl) polysiloxane capped at both molecular terminals with dimethylvinylsiloxy groups; a dimethylpolysiloxane capped at both molecular terminals with trimethoxysiloxy groups; a copolymer of a dimethylsiloxane and a methylphenylsiloxane capped at both molecular terminals with trimethoxysiloxy groups; a dimethylpolysiloxane capped at both molecular terminals with methyldimethoxysiloxy

groups; a dimethylpolysiloxane capped at both molecular terminals with triethoxysiloxy groups; a dimethylpolysiloxane capped at both molecular terminals with trimethoxysilylethyl groups; a dimethylpolysiloxane having one molecular terminal capped with a trimethylsiloxy group and another one with a trimethoxysilylethyl group; a
5 dimethylpolysiloxane having one molecular terminal capped with a dimethylvinylsiloxy group and another one with a trimethoxysilylethyl group; a dimethylpolysiloxane capped at both molecular terminals with methyldimethoxysilylethyl groups; a copolymer of a dimethylsiloxane and a methylphenylsiloxane capped at both molecular terminals with methyldimethoxysilylethyl groups; or combinations of two or more of the above
10 compounds.

[0017] When component (A) is an alkoxysilyl-containing organopolysiloxane, it works as a surface-treatment agent for component (B). As a result, handleability of the obtained composition is not impaired, even though component (B) has high content.

[0018] Component (B) is a thermally conductive filler used for imparting heat-
15 conductive properties to the composition of the invention. This component can be exemplified by a metal powder based on the use of gold, silver, copper, aluminum, nickel, brass, shape-memory alloy, solder, or the like; powdered ceramic, glass, quartz, organic resin, or the like surface coated with gold, silver, nickel, copper, or a similar metal applied by a vapor deposition or a metal plating method; aluminum oxide, magnesium oxide,
20 beryllium oxide, chromium oxide, zinc oxide, titanium oxide, crystalline silica, or similar metal oxide powders; boron nitride, silicon nitride, aluminum nitride, or a similar powdered metal nitride; boron carbide, titanium carbide, silicon carbide, or a similar powdered metal carbide; aluminum hydroxide, magnesium hydroxide, or a similar metal hydroxide; carbon nanotubes, carbon microfibers, diamond, graphite, or similar carbon-
25 based powders; or combinations of two or more of the above substances. Most preferable for component (B) are metal powders, metal oxide powders, or metal nitride powders, in particular, silver powder, aluminum powder, aluminum oxide powder, zinc oxide powder, or aluminum nitride powder. When it is required that the composition have electrical insulating properties, it is recommended to use metal oxide powders or metal nitride
30 powders, in particular an aluminum oxide powder, zinc oxide powder, or an aluminum nitride powder.

[0019] There are no special restrictions with regard to the shape of particles of component (B) which may be spherical, needle-shaped, disk-shaped, rod-like, or irregular

in shape. There are no limitations also concerning the average particle size of component (B), which is preferably in the range from 0.01 to 100 μm and, more preferably, in the range from 0.01 to 50 μm .

[0020] In the present composition, the content of component (B) should be in the range of 400 to 3,500 parts by mass and, most preferably, 400 to 3,000 parts by mass for 100 parts by mass of component (A). This is due to the fact that when the content of Component (B) is less than the lower limit of the above-mentioned range, the thermal conductivity of the resultant compositions tends to be insufficient, and, on the other hand, when it exceeds the upper limit of the above-mentioned range, the viscosity of the resultant compositions becomes too high and it will impair handleability of the composition.

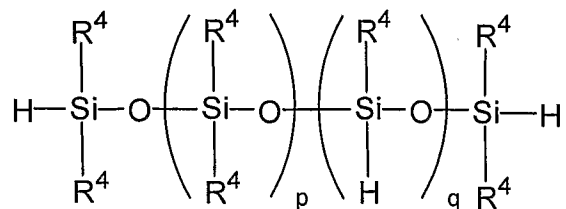
[0021] The organopolysiloxane of component (C) is used for suppressing oil bleeding from the composition. This organopolysiloxane has silicon-bonded hydrogen atoms at molecular terminals and in the chains. Other silicon-bonded groups contained in component (C) may comprise univalent hydrocarbon groups which are free of unsaturated aliphatic groups. Examples of these groups are the following: methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, and other linear alkyl groups; isopropyl, tertiary butyl, isobutyl, 2-methyl undecyl, 1-hexyl heptyl, and other branched alkyl groups; cyclopentyl, cyclohexyl, cyclododecyl, and other cyclic alkyl groups; phenyl, tolyl, xylyl, and other aryl groups; benzyl, phenethyl, 2-(2,4,6-trimethylphenyl) propyl, and other aralkyl groups; 3,3,3-trifluoropropyl, 3-chloropropyl, and other halogenated alkyl groups. Preferably, such groups are alkyl or aryl groups, and especially preferably, methyl or phenyl.

[0022] There are no special limitations on the viscosity of component (C) at 25°C.

However, the viscosity is preferably within the range from 1 to 10,000 mPa·s, more preferably, within the range from 1 to 1,000 mPa·s, and most preferably, within the range from 5 to 1,000 mPa·s. This is due to the fact that when the viscosity at 25°C is less than the lower limit of the above-mentioned range, the physical properties of the resultant compositions tend to markedly decrease, and, on the other hand, when the viscosity exceeds the upper limit of the above-mentioned range, the handleability of the resultant compositions tends to decrease.

[0023] If component (C) has silicon-bonded hydrogen atoms at molecular terminals and in the chains, no restrictions exist with regard to the molecular structure of this

component which may be a linear, partially-branched linear, or a branched molecular structure. The linear molecular structure is preferable. Component (C) is represented by the following general formula:



- 5 In this formula, R⁴ designates identical or different univalent hydrocarbon groups, which are free of unsaturated aliphatic bonds; “p” is an integer equal to or greater than 0; and “q” is an integer equal to or greater than 1.

[0024] Component (C) can be exemplified by a methylhydrogenpolysiloxane capped at both molecular terminals with dimethylhydrogensiloxy groups, a copolymer of a
10 dimethylsiloxane and a methylhydrogensiloxane capped at both molecular terminals with dimethylhydrogensiloxy groups, a copolymer of a methylphenylsiloxane and a methylhydrogensiloxane capped at both molecular terminals with dimethylhydrogensiloxy groups, and a copolymer of a dimethylsiloxane, a methylphenylsiloxane, and a methylhydrogensiloxane capped at both molecular terminals with dimethylhydrogensiloxy
15 groups.

[0025] In the present composition, the content of component (C) should be in the range of 1 to 100 parts by mass, preferably 1 to 90 parts by mass, and most preferably 1 to 85 parts by mass for 100 parts by mass of component (A). This is due to the fact that
20 when the content of component (C) is less than the lower limit of the above-mentioned range, the resultant compositions will be subject to oil bleeding, and, on the other hand, when it exceeds the upper limit of the above-mentioned range, this will impair heat-resistant properties of the composition.

[0026] The composition may contain an arbitrary component in the form of a silica-based filler (D) which may comprise fumed silica, fused silica, precipitated silica, or the
25 aforementioned silicas which have been surface treated with an organic silicon compound such as an organoalkoxysilane, organochlorosilane, organosilazane, or the like.

[0027] In the present composition, there are no limitations concerning the content of component (D), but preferably it should be in the range of 1 to 100 parts by mass and, most

preferably, 1 to 50 parts by mass, and most preferably, 1 to 20 parts by mass for 100 parts by mass of component (A).

[0028] If necessary, the composition may also contain another arbitrary component in the form of a coupling agent (E) that can be exemplified by methyltrimethoxysilane,

5 butyltrimethoxysilane, hexyltrimethoxysilane, octyltrimethoxysilane, 3-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, 3-mercaptopropyltrimethoxysilane, or a similar silane coupling agent; tetrabutyltitanate, tetraisopropyltitanate, or a similar titanate
10 coupling agent.

[0029] Although there are no special restrictions with regard to the content of component (E), it may be recommended to add this component in an amount of 0.1 to 10 parts by mass, preferably 0.1 to 5 parts by mass for 100 parts by mass of component (A).

[0030] Within the limits not contradicting with the objects of the invention, the
15 composition may contain other arbitrary components such as carbon black, red iron oxide, or similar pigments, as well as dyes, fluorescent dyes, heat-resistant agents, flame retarders, plasticizer, or adhesion promoters.

[0031] There are no special restrictions with regard to the method used for the preparation of the composition. For examples, the following methods are possible:

20 component (C) can be added to a preliminarily prepared mixture of components (A) and (B); components (A), (B), and (C) are mixed simultaneously; component (C) can be added to a preliminarily prepared mixture of components (A), (B), and (E); or component (C) can be added to a preliminarily prepared mixture of components (A), (B), and (D). It is recommended to mix components (A) and (B) under heating conditions, in particular, with
25 heating at 100 to 200 °C under a reduced pressure. When component (A) is an alkoxysilane-containing organopolysiloxane, in order to accelerate surface coating of component (B), the process is carried out either under heating conditions or with an addition of a catalytic quantity of acidic substances such as acetic acid, phosphoric acid, or the like, or with an addition of catalytic quantities of basic substances such as
30 trialkylamine, tertiary ammonium salt, ammonia gas, ammonium carbonate, or the like.

Examples

[0032] The thermally conductive silicone grease composition of the present invention will be now explained in more details by referring to Practical Examples. Additionally, it

should be noted that the physical characteristics described in the Practical Examples are represented by values obtained at 25 °C.

[Viscosity]

[0033] Viscosity of the thermally conductive silicone grease composition was measured by using the rheometer AR550 of TA Instruments, Ltd., having geometry defined by a 20 mm diameter plate. Viscosity was measured at the shear rate of 10 (1/s).

[Oil Bleeding Characteristics]

[0034] The thermally conductive silicone grease composition was applied in an amount of about 0.2 cm³ onto a frosted surface of a square (5 cm side) glass plate frosted one side (the product of Paltec Co., Ltd.), the coating was covered by a square (1.8 cm side) cover glass (the product of Matsunami Glass Co., Ltd.), and by using a micrometer (the product of Mitsutoyo Co., Ltd.), the thickness of the coating was adjusted to 300 µm. The obtained specimen was held for 3 days at 25 °C, and then the oil-bleed characteristics of the composition were evaluated as a ratio of a diameter of an oil spot bled out from the thermally conductive silicone grease composition to the initial diameter of the area occupied by thermally conductive silicone grease composition.

[Thermal Conductivity]

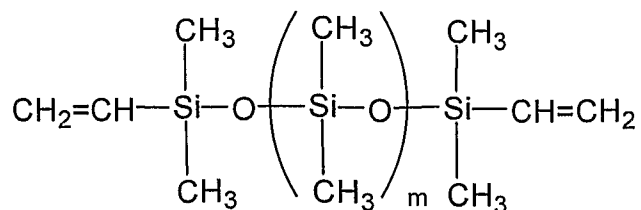
[0035] 0.6 cm³ of the thermally conductive silicone grease composition was sandwiched between a copper-made test panel having dimensions of 25 x 75 x 1 mm (the product of Paltec Co., Ltd.) and a cover glass having dimensions of 25 x 75 x 1 mm (the product of Matsunami Glass Co., Ltd.), and the thickness of the composition layer was adjusted to 1 mm by spacers. The obtained specimen was arranged vertically and subjected to a heat-shock test under the following conditions: minus -40 °C/+125 °C/500 cycles. Thermal conductivity was evaluated by observing the presence or absence of the composition drips.

[Thermal Conductivity]

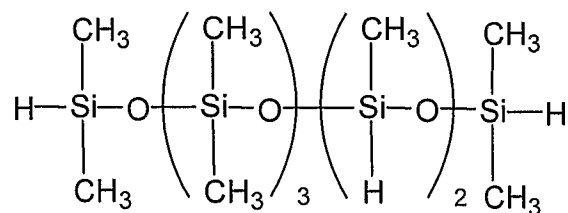
[0036] Thermal conductivity of the thermally conductive silicone grease composition was determined as thermal resistance of the composition measured by means of a resin thermal resistance tester of Hitachi Seisakusho Co., Ltd. at 50 °C using a layer of the composition having a 1 cm x 1 cm area and thickness of 200 µm and 500 µm.

[Practical Example 1]

[0037] 100 parts by mass of a dimethylpolysiloxane represented by the following general formula:



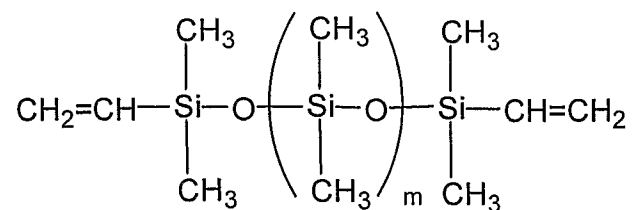
(wherein "m" is a value that occurs at viscosity of 2,000 mPa·s) and 2,360 parts by mass of a spherical aluminum oxide powder having an average particle diameter of 12 μm were premixed for 30 min. at room temperature and then mixed for another 60 min. under a reduced pressure and at a temperature of 150 °C. Following this, the product was cooled to room temperature and mixed with 80 parts by mass of a copolymer of a methylhydrogensiloxane and a dimethylsiloxane having viscosity of 10 mPa·s and represented by the following formula:



whereby a thermally conductive silicone grease composition was obtained.

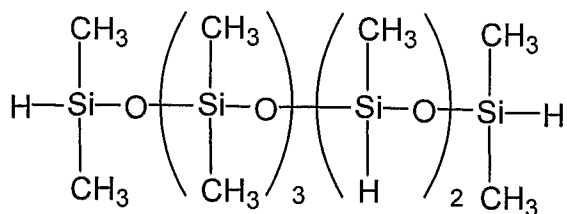
[Practical Example 2]

[0038] 100 parts by mass of a dimethylpolysiloxane represented by the following general formula:



(wherein "m" is a value that occurs at viscosity of 10,000 mPa·s), 1,240 parts by mass of a spherical aluminum oxide powder having an average particle diameter of 12 μm, and 70 parts by mass an irregular-shaped zinc oxide powder having an average particle size of 0.1 μm were premixed for 30 min. at room temperature and then mixed for another 60 min. under a reduced pressure and at a temperature of 150 °C. Following this, the product was

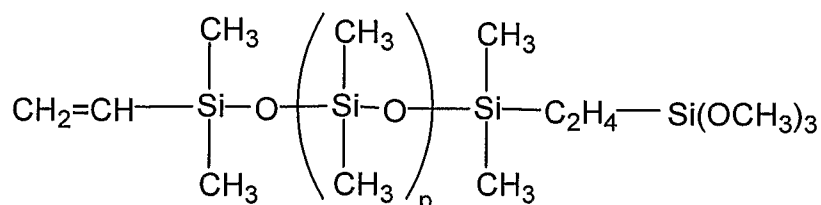
cooled to room temperature and mixed with 14 parts by mass of a copolymer of a methylhydrogensiloxane and a dimethylsiloxane having viscosity of 10 mPa·s and represented by the following formula:



5 whereby a thermally conductive silicone grease composition was obtained.

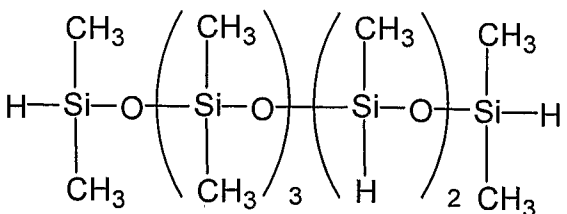
[Practical Example 3]

[0039] 100 parts by mass of a dimethylpolysiloxane represented by the following general formula:



10 (wherein “p” is a value that occurs at viscosity of 20 mPa·s), 2,560 parts by mass of a spherical aluminum oxide powder having an average particle diameter of 12 μm, 360 parts by mass of an irregular-shaped zinc oxide powder having an average particle size of 0.1 μm, and 7 parts by mass of a methyltrimethoxysilane were premixed for 30 min. at room temperature and then mixed for another 60 min. under a reduced pressure and at a

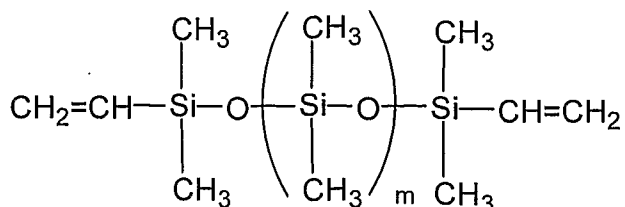
15 temperature of 150 °C. Following this, the product was cooled to room temperature and mixed with 2.7 parts by mass of a copolymer of a methylhydrogensiloxane and a dimethylsiloxane having viscosity of 10 mPa·s and represented by the following formula:



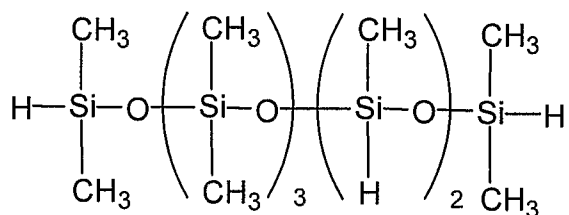
whereby a thermally conductive silicone grease composition was obtained.

20 [Practical Example 4]

[0040] 100 parts by mass of a dimethylpolysiloxane represented by the following general formula:



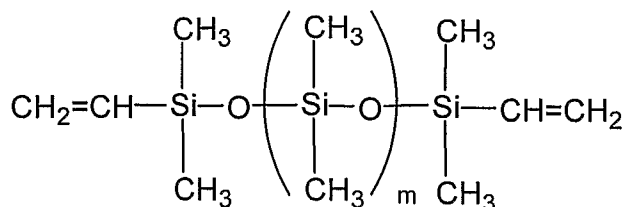
(wherein “m” is a value that occurs at viscosity of 900 mPa·s), 500 parts by mass of a spherical aluminum oxide powder having an average particle diameter of 12 μm, and 10 parts by mass of a fumed silica having BET specific surface area of 200 m²/g and hydrophobically surface-treated with a hexamethyldisilazane were premixed for 30 min. at room temperature and then mixed for another 60 min. under a reduced pressure and at a temperature of 150 °C. Following this, the product was cooled to room temperature and mixed with 5 parts by mass of a copolymer of a methylhydrogensiloxane and a dimethylsiloxane having viscosity of 10 mPa·s and represented by the following formula:



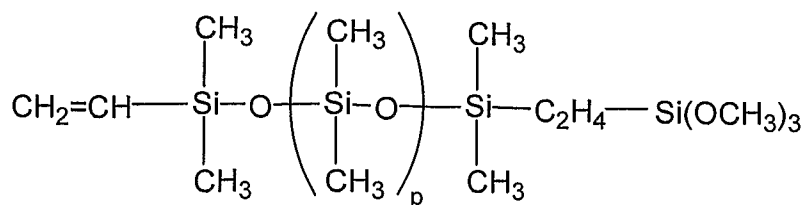
whereby a thermally conductive silicone grease composition was obtained.

[Practical Example 5]

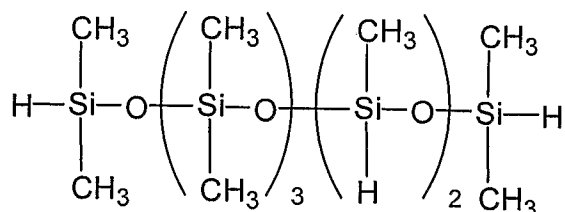
[0041] 100 parts by mass of a dimethylpolysiloxane represented by the following general formula:



(wherein “m” is a value that occurs at viscosity of 2,000 mPa·s), 650 parts by mass of an irregular aluminum nitride powder having an average particle diameter of 3 μm, 5 parts by mass of a dimethylpolysiloxane represented by the following formula:



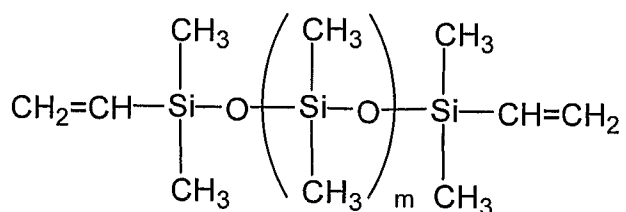
(wherein "p" is a value that occurs at viscosity of 20 mPa·s), and 5 parts by mass of a methyltrimethoxysilane were premixed for 30 min. at room temperature and then mixed for another 60 min. under a reduced pressure and at a temperature of 150 °C. Following this, the product was cooled to room temperature and mixed with 10 parts by mass of a copolymer of a methylhydrogensiloxane and a dimethylsiloxane having viscosity of 10 mPa·s and represented by the following formula:



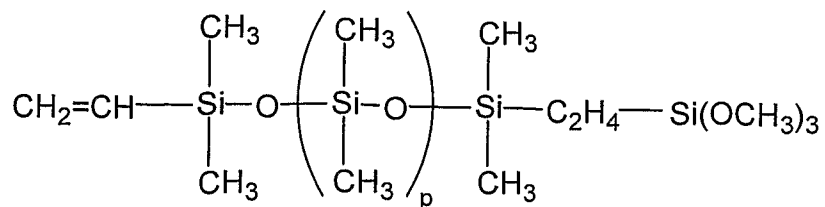
whereby a thermally conductive silicone grease composition was obtained.

10 [Practical Example 6]

[0042] 100 parts by mass of a dimethylpolysiloxane represented by the following general formula:

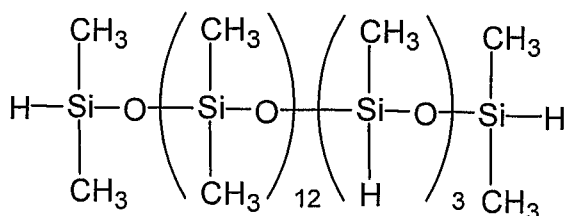


(wherein "m" is a value that occurs at viscosity of 2,000 mPa·s), 1,250 parts by mass of a spherical aluminum oxide powder having an average particle diameter of 12 μm, and 3 parts by mass of a dimethylpolysiloxane represented by the following formula:



(wherein “p” is a value that occurs at viscosity of 20 mPa·s), and 3 parts by mass of a dimethylpolysiloxane were premixed for 30 min. at room temperature and then mixed for another 60 min. under a reduced pressure and at a temperature of 150 °C. Following this, the product was cooled to room temperature and mixed with 7 parts by mass of a

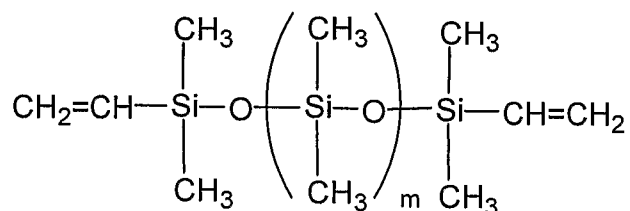
5 copolymer of a methylhydrogensiloxane and a dimethylsiloxane having viscosity of 10 mPa·s and represented by the following formula:



whereby a thermally conductive silicone grease composition was obtained.

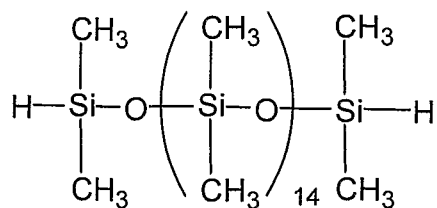
[Comparative Example 1]

- 10 **[0043]** 100 parts by mass of a dimethylpolysiloxane represented by the following general formula:



(wherein “m” is a value that occurs at viscosity of 2,000 mPa·s), 1,740 parts by mass of a spherical aluminum oxide powder having an average particle diameter of 12 μm, and 4

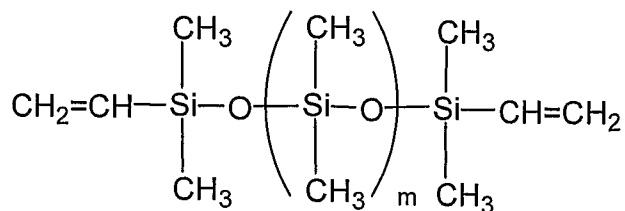
15 parts by mass of a methyltrimethoxysilane were premixed for 30 min. at room temperature and then mixed for another 60 min. under a reduced pressure and at a temperature of 150 °C. Following this, the product was cooled to room temperature and mixed with 38 parts by mass of a dimethylsiloxane having viscosity of 10 mPa·s and represented by the following formula:



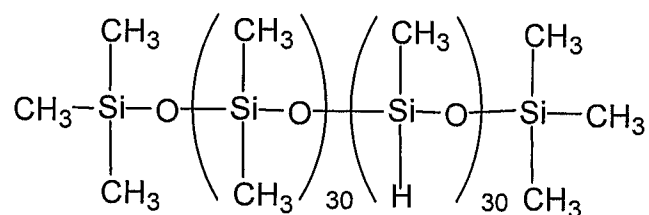
20 whereby a thermally conductive silicone grease composition was obtained.

[Comparative Example 2]

[0044] 100 parts by mass of a dimethylpolysiloxane represented by the following general formula:



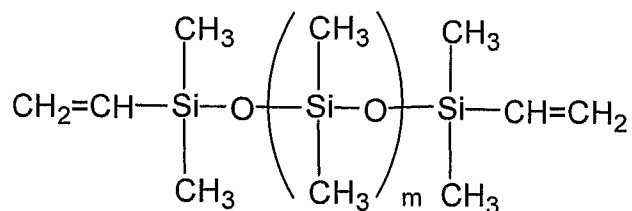
- 5 (wherein “m” is a value that occurs at viscosity of 2,000 mPa·s) and 1,850 parts by mass of a spherical aluminum oxide powder having an average particle diameter of 12 μm were premixed for 30 min. at room temperature and then mixed for another 60 min. under a reduced pressure and at a temperature of 150 °C. Following this, the product was cooled to room temperature and mixed with 40 parts by mass of a copolymer of a
- 10 methylhydrogensiloxane and a dimethylsiloxane having viscosity of 60 mPa·s and represented by the following formula:



whereby a thermally conductive silicone grease composition was obtained.

[Comparative Example 3]

- 15 [0045] 100 parts by mass of a dimethylpolysiloxane represented by the following general formula:



- (wherein “m” is a value that occurs at viscosity of 10,000 mPa·s) and 550 parts by mass of a spherical aluminum oxide powder having an average particle diameter of 12 μm were
- 20 premixed for 30 min. at room temperature and then mixed for another 60 min. under a

reduced pressure and at a temperature of 150 °C. whereby a thermally conductive silicone grease composition was obtained.

[0046]

[Table 1]

Examples	Practical Examples						Comparative Examples		
Properties	1	2	3	4	5	6	1	2	3
Viscosity (Pa·s)	210	750	800	550	380	600	450	450	720
Oil bleeding properties	1.1	1.0	1.0	1.0	1.1	1.0	2.2	1.8	1.5
Resistance to heat	Did not change						Drips		Did not change
Coefficient of thermal conductivity (W/mK)	4.5	4.2	8.5	1.2	1.6	4.5	4.5	4.5	1.6

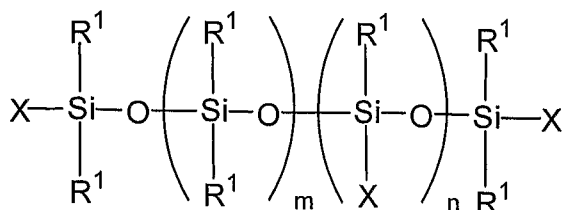
5 Industrial Applicability

[0047] Since the thermally conductive silicone grease composition of the invention is characterized by excellent resistance to heat and reduced oil bleeding, this composition is suitable for use as a heat-removing medium in electrical and electronic devices.

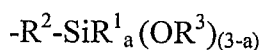
CLAIMS

1. A thermally conductive silicone grease composition comprising at least the following components:

100 parts by mass of an organopolysiloxane (A) represented by the following
5 general formula:



[wherein R¹ designates identical or different univalent hydrocarbon groups; X designates identical or different univalent hydrocarbon groups or alkoxy-silyl-containing groups of the following general formula:



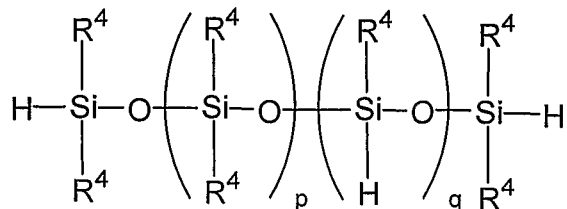
(wherein R¹ designates the previously mentioned groups; R² designates oxygen atoms or alkylene groups; R³ designates alkyl groups; and “a” is an integer ranging from 0 to 2); and “m” and “n” are integers equal to or greater than 0, respectively];

400 to 3,500 parts by mass of a thermally conductive filler (B); and

15 1 to 100 parts by mass of an organopolysiloxane (C) having silicon-bonded hydrogen atoms at both molecular terminals and in the molecular chains.

2. The thermally conductive silicone grease composition according to Claim 1, wherein component (A) has a viscosity ranging from 5 to 100,000 mPa·s at 25 °C.
3. The thermally conductive silicone grease composition according to Claim 1, wherein component (B) has an average particle size ranging from 0.01 to 100 μm.
4. The thermally conductive silicone grease composition according to Claim 1, wherein component (B) is a metal-based powder, metal oxide-based powder, or a metal nitride-based powder.
5. The thermally conductive silicone grease composition according to Claim 1, wherein component (B) is a silver powder, aluminum powder, aluminum oxide powder, zinc oxide powder, or an aluminum nitride powder.

6. The thermally conductive silicone grease composition according to Claim 1, wherein component (C) is an organopolysiloxane of the following general formula:



(wherein R^4 designates identical or different univalent hydrocarbon groups, which are free of unsaturated aliphatic bonds; “p” is an integer equal to or greater than 0; and “q” is an integer equal to or greater than 1).

7. The thermally conductive silicone grease composition according to Claim 1, further containing a silica-based filler (D) in an amount of 1 to 100 parts by mass for 100 parts by mass of component (A).
8. The thermally conductive silicone grease composition according to Claim 1, further containing a coupling agent (E) in an amount of 0.1 to 10 parts by mass for 100 parts by mass of component (A).

INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2009/051399

A. CLASSIFICATION OF SUBJECT MATTER		
INV. C10M169/02	C09K5/14	H01L23/373 C08L83/04 C08L83/14
ADD. C10N30/00	C10N30/08	C10N40/14 C10N50/10
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) C10M C09K H01L C08L		
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		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 352 947 A1 (SHINETSU CHEMICAL CO [JP]) 15 October 2003 (2003-10-15) example 4; table 2	1-8
A	US 2002/140082 A1 (MATAYABAS JAMES C [US]) MATAYABAS JR JAMES C [US] 3 October 2002 (2002-10-03) paragraphs [0001] - [0010], [0019], [0021], [0028] claims 1-7,10; figures 1-3	1-8
A	EP 1 254 924 A1 (SHINETSU CHEMICAL CO [JP]) 6 November 2002 (2002-11-06) paragraphs [0009] - [0031]; claims	1-8
	-/--	
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier 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		
Date of the actual completion of the international search 30 June 2009		Date of mailing of the international search report 08/07/2009
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Keipert, Olaf

INTERNATIONAL SEARCH REPORT

International application No

PCT/JP2009/051399

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 496 419 A2 (SHINETSU CHEMICAL CO [JP]) 29 July 1992 (1992-07-29) page 2, line 34 - line 50 page 3, line 4 - page 6, line 9 examples -----	1-8
A	PRASHER R S ET AL: "Thermal contact resistance of cured gel polymeric thermal interface material" THERMAL AND THERMOMECHANICAL PHENOMENA IN ELECTRONIC SYSTEMS, 2004. IT HERM '04. THE NINTH INTERSOCIETY CONFERENCE ON LAS VEGAS, NV, USA JUNE 1-4, 2004, PISCATAWAY, NJ, USA, IEEE, 1 January 2004 (2004-01-01), pages 28-35, XP010714845 ISBN: 978-0-7803-8357-9 the whole document -----	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/JP2009/051399

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1352947	A1	15-10-2003	JP 4130091 B2	06-08-2008
			JP 2003301189 A	21-10-2003
			TW 276665 B	21-03-2007
			US 2003195124 A1	16-10-2003
US 2002140082	A1	03-10-2002	NONE	
EP 1254924	A1	06-11-2002	DE 60200630 D1	22-07-2004
			DE 60200630 T2	30-06-2005
			JP 3580366 B2	20-10-2004
			JP 2002327116 A	15-11-2002
			US 2003049466 A1	13-03-2003
EP 0496419	A2	29-07-1992	DE 69223659 D1	05-02-1998
			DE 69223659 T2	14-05-1998
			SG 64338 A1	27-04-1999
			US 5276087 A	04-01-1994