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54 **Silicone grease compositions used for assisting heat radiation.**

57 A grease composition used for assisting radiation of heat from electronic devices or machines comprises, by weight,

(1) 100 parts of a photocurable organopolysiloxane having a viscosity at 25°C of 0.5 - 1000 m².s⁻¹ (50-100,000 cSt) and (i) represented by the general formula R¹_aR²_bR³_cSiO_{(a+b+c)/2} where a, b and c are defined respectively by 0.01 <a,b< 0.1 and 1.9 <c< 2.0, R¹ is a monofunctional mercaptoalkyl group represented by -(CH₂)_nSH wherein n is 1 - 8 (preferably 3), R² is a monofunctional hydrocarbon group containing a C2-8 aliphatic unsaturated group (e.g. vinyl), and R³ is an optionally substituted (e.g. halogenated) monofunctional C1-18 hydrocarbon group and/or (ii) a combination of organopolysiloxanes each of said viscosity and one containing at least 2 mercaptoalkyl groups as defined for R¹ and another containing at least 2 monofunctional hydrocarbon groups as defined for R²,

(2) 100-900 (preferably 150-400) parts of a thickener which is a powdered inorganic compound having good heat conductivity, e.g. ZnO, Al₂O₃, AlN, BN or SiC, and optionally

(3) a curing accelerator or photosensitizer.

The mixed composition readily cures in natural or artificial light. It is used to assist removal of heat generated in the use of electronic components used in electrical appliances, audio systems and industrial equipment; the grease which is squeezed or bled to the exterior is there photocured and does not soil the surrounding area.

This invention concerns a photocurable silicone grease composition which is suitable for assisting heat radiation from electronic components and to a method of using the composition for this purpose in which the bleeding out of the composition can be prevented.

In apparatus or devices containing such components it is known to use, for assisting the radiation away of harmful heat, silicone greases comprising mainly dimethylpolysiloxane, dimethyldiphenylpolysiloxane or dimethyldecylmethylpolysiloxane, blended with zinc oxide, alumina, aluminum nitride, boron nitride, silicon carbide or the like as a thickening agent, see JP Examined Published Patent ("Tokko") No. 33272/77) and JP Unexamined Laid-Open Patent Applications ("Tokkai") Nos. 43492/87, 43493/87 and 153995/90.

However, with these known compositions the grease tends to be squeezed or to leak or bleed out of the device when it becomes hot in use, and the leaked siloxane grease tends to infiltrate undesirably into other parts of the apparatus or the surroundings after long periods of use. In some cases, mechanical contacts are soiled so that the contacts were damaged, or the contact region between the commutator and brushes in a micromotor was soiled so that the motor no longer rotated properly. In addition, the loss of the siloxane leads to a progressive deterioration in the amount of heat radiated away from the device.

To overcome the above disadvantages, a method has been proposed to confer adhesive properties on the siloxane grease. This method is effective in suppressing the leakage, but is not fully satisfactory over long periods of use.

A method is also known wherein an organopolysiloxane containing mercapto groups and an organopolysiloxane containing aliphatic unsaturated hydrocarbon groups are cured by the action of radiation or ultraviolet light, for example a composition of an organopolysiloxane containing mercaptoalkyl groups and one containing vinyl groups is cured in the presence of photosensitizing compounds by means of exposure to intense radiation such as ultraviolet light (JP Tokko No. 6512/79 and Tokkai Nos. 61386/75 and 79265/87). These techniques are primarily intended to obtain thin film coating agents, but a thick film coating agent is also known consisting of a curable organopolysiloxane using silica or carbon black as a filler (Tokko No. JP 23941/86). In this case organic salts of e.g. manganese are used as curing catalysts, and the composition cures even when it is not irradiated with ultraviolet light.

It is however not known to use such curable organopolysiloxane compositions as greases for assisting heat radiation.

We have made studies to inhibit the creep of the siloxane in greases used to assist heat radiation from devices, and have found that when an organopolysiloxane containing mercapto-substituted hydrocarbon group and aliphatic unsaturated bonds was used as the grease, excess grease which was leaked or squeezed out to the exterior of a device becomes cured at the surface under irradiation by natural light or ultraviolet light so as to inhibit the subsequently leakage of the base oil, thus achieving the present invention.

It is therefore an object of the invention to provide a method of inhibiting the leakage of a silicone grease from a device where it is present to assist radiation of heat.

It is a further object to provide a silicone grease composition for assisting heat radiation, e.g. from an electronic device, which, by inhibiting the leakage of the base oil, exhibits a stable heat conduction performance over long periods of time without causing damage to contacts or other components of the device.

According to the invention we provide a photocuring silicone grease composition comprising alone or principally: (1) 100 parts by weight of a photocuring organopolysiloxane consisting essentially of an organopolysiloxane having a viscosity of 50 - 100,000 cSt (0.5 - 1000 m².s⁻¹) at 25°C and represented by the general formula $R^1_a R^2_b R^3_c SiO_{(4-(a+b+c))/2}$ (where a, b and c are defined respectively by the conditions 0,01 < a, b < 0,1 and 1,9 < c < 2,0, R¹ is a monofunctional mercaptoalkyl group represented by $-(CH_2)_n SH$ (wherein n is equal to 1 - 8), R² is a monofunctional hydrocarbon group containing an aliphatic unsaturated group having 2 - 8 carbon atoms, and R³ is a substituted or unsubstituted monofunctional hydrocarbon group having 1 - 18 carbon atoms), and/or a combination of an organopolysiloxane having a viscosity of 50 - 100,000 cSt at 25°C and containing in its molecule at least 2 mercaptoalkyl groups represented by $-(CH_2)_n SH$ (wherein n is equal to 1 - 8) with an organopolysiloxane having a viscosity of 50 - 100,000 cSt at 25°C and containing in its molecule at least 2 monofunctional hydrocarbon groups having an aliphatic unsaturated group with 2 - 8 carbon atoms, and (2) 100 - 900 parts by weight of at least one powdered inorganic compound with good heat conduction properties.

The silicone grease composition of the invention undergoes rapid curing in the light-exposed parts. The silicone grease in the internal parts of a device which are not exposed to light is therefore prevented from moving outside due to leakage or bleeding of the composition, and as a result the heat irradiating functioning of the grease remains stable.

Only the excess grease squeezed out from a heat radiating surface is cured when the composition of the invention is used. As a result, the leakage of the siloxane is inhibited, and the heat radiation-assisting function of the grease is therefore stable over long periods of time. Further, in addition to the fact that there is no soiling due to grease infiltrating the area around locations where it is used, there is no damage to contacts, etc. of the

machine or device and the reliability of equipment is increased.

As the curable organopolysiloxane (a silicone grease or "base oil"), the following are particularly suitable from the viewpoint of heat radiation properties and durability:

In the organopolysiloxane represented by the aforesaid general formula, $R^1_a R^2_b R^3_c SiO_{(4-(a+b+c))/2}$, which can be used as the first component, R^1 is a monofunctional mercaptoalkyl group represented by $-(CH_2)_n SH$ wherein n must be 1 - 8, but mercaptopropyl wherein $n = 3$ is particularly preferable.

R^2 designates a monofunctional hydrocarbon group containing an aliphatic unsaturated group having 2 - 8 carbon atoms, the vinyl group being particularly preferable,

R^3 designates a substituted or unsubstituted monofunctional hydrocarbon group having 1 - 18 carbon atoms, specific examples being aliphatic hydrocarbon groups such as methyl, ethyl, propyl, hexyl, octyl, decyl, dodecyl and tetradecyl, aromatic hydrocarbon groups such as phenyl and tolyl, and halogenated hydrocarbon groups such as trifluoropropyl, chloromethyl and chlorophenyl.

The viscosity of the organopolysiloxanes which constitute the first component is 50 - 100,000 cSt, but more preferably 200 - 3,000 cSt. When it is less than 50 cSt, the silicone grease composition for assisting heat radiation obtained by kneading the first component together with the second component has poor homogeneity. When on the other hand the viscosity is higher than 100,000 cSt, the blending proportion of the thickener added to confer suitable extensibility on the silicone grease composition thus obtained has to be reduced to a low level, and the grease no longer exhibits satisfactory heat radiation properties when it is used to assist heat radiation.

The thickener which is the second component is a powdered inorganic compound with good heat conduction properties, and for example may consist of one or more of a compound chosen from zinc oxide or alumina, aluminum nitride, boron nitride or silicon carbide. The blending proportion of this second component is 100 - 900 parts by weight, and more preferably 150 - 400 parts by weight, with respect to 100 parts by weight of the first component. When the proportion is less than 100 parts by weight, the grease does not exhibit satisfactory heat radiation properties. When on the other hand the proportion is higher than 900 parts by weight, the resulting grease is extremely stiff so that it has poor extensibility which has an adverse effect on its performance.

In this invention, accelerators such as organic acid salts, for example, of manganese, iron, cobalt, nickel or copper, and photosensitizers such as benzophenone, acetophenone, anthraquinone, methylantraquinone, 1,4-naphthoquinone, 2-hydroxy-2-methyl-1-phenyl-propane-1-one, 1-(4-isopropylphenyl)-2-hydroxy-2-methyl-propane-1-one, 1-(4-dodecylphenyl)-2-hydroxy-2-methyl-propane-1-one, 1-{4-(2-hydroxyethoxy)phenyl}-2-hydroxy-2-methyl-propane-1-one and the like, may be added as a third component if desired, in the proportion of 0.001 - 10 parts by weight with respect to 100 parts by weight of organopolysiloxanes.

Further, antioxidants, rustproofing agents, coloring pigments, dyes and the like may be added as a fourth component if desired, provided that they do not interfere with the curing reaction.

The method of manufacturing the photocuring silicone grease composition of the invention consists of measuring out, into a planetary mixer, the organopolysiloxanes which are the first component and the thickener which is the second component, adding the third and fourth components if necessary, heating if necessary, and blending the components together. After blending, the mixture is kneaded to render it homogeneous. The kneader employed may be a three-rod roller mill, colloid mill, sand grinder, Gaulin Homogenizer or the like, a three-rod roller mill being particularly preferable.

The composition obtained as described hereintofore, and the silicone grease composition used in this invention, undergo a curing reaction under even very mild conditions such as exposure to natural light, e.g. sunlight or roomlight, e.g. U.V. When the composition is used for example as a grease for assisting heat radiation, therefore, the excess grease squeezed out from the heat radiating surface rapidly undergoes surface curing. This inhibits bleed of the base oil so that the grease exhibits a stable heat conduction performance over long periods of time, and in addition it greatly improves the reliability of instrumentation.

Further, as damage to mechanical contacts and interference with the proper operation of micromotors, etc., resulting from soiling of the environment due to bleed of the base oil or low volatility components in the grease, is thereby avoided, the silicone grease composition of the invention is highly suitable as a grease for assisting heat radiation from transistors, IC, diodes, thermistors and the like used in household electrical appliances, audio systems and various types of industrial equipment.

EXAMPLES

This invention will now be described in further detail by means of the following examples.

The various properties in the examples and comparative examples were measured according to the following methods.

* Thickness and Oil Separation

Thickness and oil separation were measured according to the method described in JIS(JAPANESE INDUSTRIAL STANDARDS)-K-2220 "Grease".

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* Oil bleed and Curing of Excess Grease

A grease was applied between a heat radiating fin of size 130 x 150 x 50 mm and a transistor (2SD113). The distance over which the base oil had spread after leaving the assembly in a room for 40 days after applying a tightening force of 5 kgf was judged visually, and taken as the oil bleed. Further, the curing of the excess grease was judged by touching it.

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* Thermal Conductivity

The thermal conductivity was measured by a Shinku Riko Inc. TCW-1000 heating coil type thermal conductivity meter.

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Examples 1 - 7

The first and second components of the grease composition of the invention were measured out into a planetary mixer in the blending proportions shown in Table 1. After blending well together, the mixture obtained was kneaded three times by a three-rod roller mill, and the thickness, oil separation, oil bleed and thermal conductivity were evaluated. The results are shown in Table 2.

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After measuring the oil bleed after 40 days, the transistor was peeled off from the heat radiation fin. When the grease between the fin and the transistor was observed, it was found that it had not cured and it exhibited satisfactory contact properties. This result was found for all the greases in Examples 1 - 7.

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From this, it was concluded that curing took place only in the excess grease which was exposed to room light. It was also concluded that the grease composition of the invention not only had excellent thermal conductivity, but also that the base oil had little oil bleed and therefore presented no risk of contaminating the environment.

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TABLE 2

Example	Thickness (Mixture)	Oil Separation (%)	Oil Bleed (mm)	Thermal Conductivity (cal / cm · sec · °C)	Curing Property of Excess Grease
1	3 1 2	0	0	2.31×10^{-3}	Cured in 2 days.
2	3 5 8	0	0	1.94×10^{-3}	Cured in 2 days.
3	3 4 0	0	0	3.50×10^{-3}	Cured in 2 days.
4	3 2 5	0	0	1.70×10^{-3}	Cured in 2 days.
5	3 5 9	0	0	2.33×10^{-3}	Cured in 3 days.
6	3 7 2	0	0	1.95×10^{-3}	Cured in 3 days.
7	3 6 3	0	0	2.30×10^{-3}	Cured in 5 days.

Oil Separation in the table is the value under an environment of 150°C, 24 hours.

Comparative Examples 1 - 3

5 The first and second components of the grease composition of the invention were measured out into a planetary mixer in the blending proportions shown in Table 3. After blending well together, the mixture obtained was kneaded three times by a three-roller mill, and the thickness, oil separation, oil bleed and thermal conductivity of the samples obtained were evaluated. The results are shown in Table 4.

10 As is clear from the results of the Examples and Comparative Examples, the silicone grease of the present invention loses almost no oil, the base oil has very little bleed, and moreover the composition has an excellent thermal conductivity.

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TABLE 3

Comparative Example	Base oil			Thickener	
	Structure	Viscosity (cSt)	Parts by weight	Specie	Parts by weight
1	$ \begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_3)_3\text{SiO} - \text{SiO} - \text{Si}(\text{CH}_3)_3 \\ \qquad \qquad \\ \text{CH}_3 \qquad \qquad \text{CH}_3 \\ \left[\qquad \qquad \right]_m \end{array} $	5 0 0	2 5	ZnO	7 5
2	$ \begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_3)_3\text{SiO} - \text{SiO} - \text{Si}(\text{CH}_3)_3 \\ \qquad \qquad \\ \text{CH}_3 \qquad \qquad \text{CH}_3 \\ \left[\qquad \qquad \right]_m \end{array} $	1. 0 0 0	3 0	Al ₂ O ₃	7 0
3	$ \begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_3)_3\text{SiO} - \text{SiO} - \text{Si}(\text{CH}_3)_3 \\ \qquad \qquad \\ \text{CH}_3 \qquad \qquad \text{C}_6\text{H}_5 \\ \left[\qquad \qquad \right]_m \qquad \left[\qquad \qquad \right]_n \\ \text{C}_6\text{H}_5 \end{array} $	4 5 0	5 0	BN	5 0

Viscosities in the table is the value at 25 °C.

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TABLE 4

Example	Thickness (Mixture)	Oil Separation (%)	Oil Bleed (mm)	Thermal Conductivity (cal/cm · sec · °C)	Curing Property of Excess Grease
1	3 2 2	0. 3 0	3 5	$1. 8 4 \times 1 0^{-3}$	not cured
2	3 4 4	1. 3 0	2 8	$1. 9 1 \times 1 0^{-3}$	not cured
3	3 0 5	2. 4 0	3 2	$1. 8 1 \times 1 0^{-3}$	not cured

Oil Separation in the table is the value under an environment of 150°C, 24 hours.

Claims

1. A photocurable silicone grease composition comprising by weight (1) 100 parts of a photocurable organopolysiloxane consisting essentially of an organopolysiloxane having a viscosity at 25°C of 0.5 - 1000 m².S⁻¹ (50-100,000 cSt) and (i) represented by the general formula R¹aR²_bR³_cSiO_{(a+b+c)/2} where a, b and c are defined respectively by the conditions 0.01 < a, b < 0.1 and 1.9 < c < 2.0, R¹ is a monofunctional mercaptoalkyl group represented by -(CH₂)_n-SH wherein n is equal to 1 - 8, R² is a monofunctional hydrocarbon group containing an aliphatic unsaturated group having 2 - 8 carbon atoms, and R³ is an optionally substituted monofunctional hydrocarbon group having 1 - 18 carbon atoms and/or (ii) a combination of organopolysiloxanes each of said viscosity and one containing in its molecule at least 2 mercaptoalkyl groups as defined for R¹ and another containing in its molecule at least 2 monofunctional hydrocarbon groups as defined for R², and
(2) 100 - 900 parts of a thickener consisting of at least one powdered inorganic compound having good heat conduction properties.
2. A silicone grease composition as claimed in Claim 1, wherein R¹ is -(CH₂)₃SH.
3. A silicone grease composition as claimed in Claim 1 or 2, wherein R² is a vinyl group.
4. A silicone grease composition as claimed in Claim 1, 2 or 3, wherein R³ is an aliphatic hydrocarbon group, an aromatic hydrocarbon group or a halogenated hydrocarbon group.
5. A silicone grease composition as claimed in any preceding claim, wherein R³ is selected from methyl, ethyl, propyl, hexyl, octyl, decyl, dodecyl, tetradecyl, phenyl tolyl, trifluoropropyl, chloromethyl and chlorophenyl groups.
6. A silicone grease composition as claimed in any preceding claim, wherein the viscosity of said organopolysiloxane(s) is from 2 to 30 m².s⁻¹ (200 to 3,000 cSt).
7. A silicone grease composition as claimed in any preceding claim, wherein the powdered inorganic compound used as thickener is selected from zinc oxide, alumina, aluminum nitride, boron nitride and silicon carbide.
8. A silicone grease composition as claimed in any preceding claim, wherein the amounts by weight are 150-400 parts of the thickener per 100 parts of the first component.
9. A silicone grease composition as claimed in any preceding claim, which additionally contains a photosensitizing agent in an amount of 0.001-10 parts by weight per 100 parts by weight of the organopolysiloxanes as the first component.
10. A silicone grease composition as claimed in Claim 9, wherein the photosensitizing agent consists of at least one compound selected from benzophenone, acetophenone, anthraquinone, methylanthraquinone, 1,4-naphthoquinone, 2-hydroxy-2-methyl-1-phenyl-propane-1-one, 1-(4-isopropyl-phenyl)-2-hydroxy-2-methyl-propane-1-one, 1-(4-dodecyl-phenyl)-2-hydroxy-2-methyl-propane-1-one and 1-(4-(2-hydroxy-ethoxy)phenyl)-2-hydroxy-2-methyl-propane-1-one.
11. A silicone grease composition as claimed in any preceding claim, which additionally contains a curing accelerator in an amount of 0.001-10 parts by weight per 100 parts by weight of the organopolysiloxanes used as the component (1).
12. A silicone grease composition as claimed in Claim 11, wherein the curing accelerator consists of at least one salt selected from organic acid salts of manganese, iron, cobalt, nickel or copper.
13. A silicone grease composition as claimed in any preceding claim, when utilized for assisting heat radiation from a machine or device.
14. A method of inhibiting the bleeding out of a composition from a machine or device wherein heat is generated and wherein the composition is used to assist radiation of the heat so as to cool the machine or device,

which method comprises utilising as said composition a silicone grease composition as claimed in any preceding claim, and irradiating with light the grease composition which has become squeezed or bled out to the surface of the machine or device during use thereof so as to photocure the composition on the said surface and prevent further bleeding of the grease composition.

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 9533

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-3 873 499 (K.W MICHAEL) * column 1, line 13 - column 2, line 63 * * column 4, line 17 - line 21 * ---	1-5	C10M169/00 C10M169/02 //(C10M169/00, 107:50,113:00, 129:24,129:26) C10N30:00,40:00, 50:10
D,A	WORLD PATENTS INDEX LATEST Week 8627, Derwent Publications Ltd., London, GB; AN 83-756434 & JP-B-61 023 941 (SHINETSU CHEM IND KK) 9 June 1986 * abstract *	1-5, 11, 12	
D,A	PATENT ABSTRACTS OF JAPAN & JP-A-62 043 492 (TOSHIBA SILICONE CO LTD) 25 February 1987 * abstract *	1,7,13	
A	EP-A-0 284 340 (SHIN-ETSU CHEMICAL) * page 3, line 4 - line 6 * * page 3, line 16 - line 18 * * page 3, line 42 - line 47 *	1,6,7,13	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	FR-A-2 246 608 (DOW CORNING CORPORATION) * page 2, line 5 - page 3, line 40 * * page 4, line 30 *	1-5,9,10	C10M C08L H01B
A	EP-A-0 030 098 (DOW CORNING CORPORATION) * page 8; example V * * page 13; example XII * * page 15, line 11 - line 18; claims 1,2 *	1-5,11, 12	
A	US-A-4 401 491 (F.J MODIC) * column 6, line 8 - line 35 * * column 8, line 10 * * column 13, line 23 - line 43 * -----	1,7,13	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 30 DECEMBER 1991	Examiner HILGENGA K, J.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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