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(54) Thermally conductive grease composition

(57) A thermally conductive grease composition comprising (A) 100 weight parts of at least one base oil selected from liquid silicones, liquid hydrocarbons or fluorohydrocarbon oils and 500-1,000 weight parts of a thermally conductive filler mixture which is constituted of (B) an inorganic filler having Mohs' hardness of at least 6 and thermal conductivity of at least 100 W/m°K and (C) an inorganic filler having Mohs' hardness of at most 5 and thermal conductivity of at least 20 W/m°K, and in which the ratio of Component (C) to the sum total of Component (B) and Component (C) is from 0.05 to 0.5 by weight.

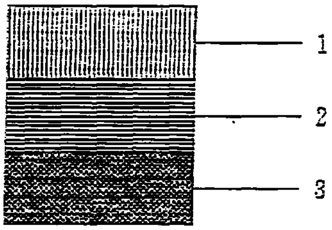

Fig.1

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Description

[0001] The present invention relates to a thermally conductive material and, more particularly, to a thermally conductive grease composition which comprises liquid silicone, liquid hydrocarbon or/and fluorohydrocarbon oil as base oil and has thermal conductivity adequate to the use for reduction of the heat from electronic parts.

[0002] Most electric and electronic appliances generate heat while they are used, so that the removal of the generated heat therefrom is necessary for their normal operation. With the intention of removing the generated heat from those appliances, many means have been proposed. For instance, in miniature electronic parts, especially electronic devices provided with integrated circuits, thermally conductive materials, such as thermally conductive grease and a thermally conductive sheet [Japanese Tokko Sho 57-36302 (U.S. Patent No. 4,265,775), wherein the term "Tokko" means an "examined patent publication", and Japanese Tokkai Sho 61-157587, wherein the term "Tokkai" means an "unexamined published patent application"], have been used as such means.

[0003] In general, an electronic device comprises integrated circuits and cap parts for protecting them, and a thermally conductive material is applied so as to contact directly with both the circuit element and the heat reducing part, or indirectly therewith via certain materials. Thus, the heat generated from integrated circuit chips during operation is transmitted in the thermally conductive material to be transferred directly or indirectly to the heat reducing part, and further radiated therefrom. A rough sectional view of such an electronic device, wherein a thermally conductive material is used, is shown in Fig. 1.

[0004] As the thermally conductive material mentioned above, there has already been known a heat-reducing grease of the type which uses a silicone oil as a base material and a zinc oxide or alumina powder as a thickener (Japanese Tokko Sho 52-33272 and Japanese Tokko Sho 59-52195). In recent years, aluminum nitride has been developed as a thickener which enables further improvement of thermal conductivity (as disclosed, e.g., in Japanese Tokkai Sho 52-125506).

[0005] Therein, however, the grease compositions undergo no great improvement in thermal conductivity by containing aluminum nitride instead of other known thickeners though the aluminum nitride itself has high thermal conductivity. This is because the permissible content of aluminum nitride in silicone oil is restricted within very narrow limits, or to the range of about 50 to about 95 weight parts per 100 weight parts of silicone oil used as a base oil, due to its insufficient oil-keeping power.

[0006] In Japanese Tokko Sho 57-36302 (U.S. Patent No. 4,265,775) is disclosed the thixotropic thermally conductive material comprising an oily organosilicone carrier, silica fiber in an amount effective for prevention of oily carrier exudation and a thermal conductivity-providing powder selected from a group consisting of dendrite-form zinc oxide, thin-leaf aluminum nitride, thin-leaf boron nitride and a mixture of two or more thereof. From this material also, sufficient improvement of thermal conductivity cannot be expected because it is inevitable to reduce the aluminum nitride powder content due to the incorporation of spherical silica fiber as an essential component for enhancement of oil keeping power.

[0007] This drawback can be mitigated by using a particular organopolysiloxane and a spherical aluminum nitride powder having a hexagonal crystal form and grain sizes in a specified range in combination to enable a very large amount of aluminum nitride to be incorporated in the silicone oil (Japanese Tokkai Hei 2-153995).

[0008] However, the effect produced by such an increase of the aluminum nitride powder content upon improvement of thermal conductivity is smaller than expected, and the thermal conductivity attained is of the order of 2.3 W/m°K which is still unsatisfactory. The reason therefor is that aluminum nitride is a very hard material having Mohs' hardness of from 7 to 9, and so there are spaces between aluminum nitride grains when they are coarse.

[0009] As a measure to solve this problem, the combined use of fine and coarse aluminum nitride powders is known (Japanese Tokkai Hei 3-14873). While the thermal conductivity is elevated in this case, the resulting composition is too small in consistency (too hard) as grease and has poor dispensation suitability; as a result, it is unsuitable for practical use.

[0010] Further, there are proposals such that organopolysiloxanes of the kind which can hold inorganic fillers in large amounts are employed as base oil and they are combined with at least one inorganic filler selected from the group consisting of ZnO, Al_2O_3, AlN and Si_3N_4 [e.g., Japanese Tokkai Hei 2-212556 (U.S. Patent No. 5,221,339) and Japanese Tokkai Hei 3-162493 (U.S. Patent No. 5,100,568)]. However, those combinations as heat-reducing grease are still unsatisfactory.

[0011] As a result of our intensive studies to further improve the dispensation suitability and the thermal conductivity of heat-reducing grease, it has been found that, when at least one base oil selected from the group consisting of liquid silicones, liquid hydrocarbons and fluorohydrocarbon oils is used in combination with a thermally conductive inorganic filler having Mohs' hardness of 6 or above and thermal conductivity of at least 100 W/m°K and a thermally conductive inorganic filler having Mohs' hardness of 5 or below and thermal conductivity of at least 20 W/m°K, the resulting grease composition can acquire excellent dispensation suitability as well as high thermal conductivity, thereby achieving the present invention.

[0012] Therefore, an object of the present invention is to provide a thermally conductive grease having both high thermal conductivity and excellent dispensation suitability.

[0013] The above-described object of the present invention is attained with a thermally conductive grease composition comprising:

(A) 100 weight parts of at least one base oil selected from the group consisting of liquid silicones, liquid hydrocarbons and fluorohydrocarbon oils, and
500-1,000 weight parts of a thermally conductive filler mixture constituted of (B) an inorganic filler having Mohs' hardness of at least 6 and thermal conductivity of at least 100 W/m°K and (C) an inorganic filler having Mohs' hardness of at most 5 and thermal conductivity of at least 20 W/m°K;
wherein the ratio of Component (C) to the sum total of Component (B) and Component (C) is from 0.05 to 0.5 by weight.

[0014] In a thermally conductive grease composition according to the present invention, the gaps among hard particles of thermal conductive inorganic filler having Mohs' hardness of at least 6 and thermal conductivity of at least 100 W/m°K are filled up with soft particles of thermal conductive inorganic filler having Mohs' hardness of at most 5 and thermal conductivity of at least 20 W/m°K; as a result, high thermal conductivity is secured and dispensation suitability is improved. Thus, it is easy for the present composition to acquire the oil separation degree reduced to 0.01 % or below and the thermal conductivity higher than 2.5 W/m°k.

[0015] Fig. 1 is a schematic view showing the removal of heat generated from electronic parts by the use of thermally conductive grease. Therein, the figures 1, 2 and 3 represent a heat-releasing member, thermally conductive grease and heat-generating electronic parts respectively.

[0016] The following are characteristics which the base oil used as Component (A) in the present invention is required to have:

1) Appropriate viscosity characteristics, including a slight change of viscosity with temperature and solidification at a low temperature (a low pour point),
2) Low volatility at high temperatures and a high flash point,
3) High stability against oxidation and satisfactory thermal stability, more specifically good receptiveness to the benefit from antioxidants and no changes in color and properties upon heating up to about 200°C,
4) Good oiliness,
5) Slight aggravating influences upon surrounding materials, such as sealing materials and resinous or ceramic cover, and
6) Good affinity for fillers (thickeners).

[0017] As examples of a base oil having the foregoing characteristics, mention may be made of base oils generally used for lubricating oil, including liquid silicones, such as silicone oils containing methyl groups or/and phenyl groups, and mineral oils of naphthene and paraffin types. Besides these oils, a wide variety of synthetic oils as recited below are suitable for the base oil of grease or the like to be used under temperatures covering a wide range because of their excellent fluidity, viscosity index and thermal stability.

[0018] The liquid silicone used as base oil in the present invention can be properly selected from known silicones which are liquid at room temperature, such as organopolysiloxanes, polyorganosilalkylenes, polyorganosilanes and copolymers thereof. From the viewpoint of ensuring heat resistance, stability and electric insulation, however, it is desirable to use organopolysiloxanes, particularly an organopolysiloxane represented by compositional formula $R_aSiO_{(4-a)/2}$. Each R in this formula is a group selected from monovalent organic groups, and all R groups may be the same or different.

[0019] Examples of a monovalent organic group as R include monovalent unsubstituted or substituted hydrocarbon groups having 1 to 30 carbon atoms, such as alkyl groups (e.g., methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, etc.), cycloalkyl groups (e.g., cyclohexyl, etc.), alkenyl groups (e.g., vinyl, allyl, etc.), aryl groups (e.g., phenyl, naphthyl, tolyl, etc.), and groups formed by substituting halogen atom(s), cyano group(s), hydroxyl group(s) or/and so on for part or all of the hydrogen atoms attached to carbon atoms present in the above-recited groups (e.g., chloromethyl, 3,3,3-trifluoropropyl, cyanopropyl, phenol, hindered phenol, etc.); and organic functional groups, such as an organic group having an amino group, an organic group having a polyether group and an organic group having an epoxy group. Of these organic groups, a methyl group, a phenyl and an alkyl groups having 6 to 14 carbon atoms are preferred over the others.

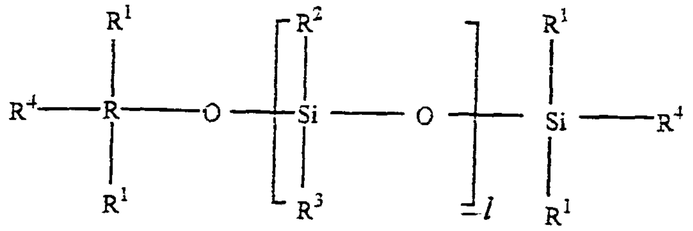
[0020] Further, "a" in the above formula is a number of 1.8-2.3.

[0021] For acquiring satisfactory grease characteristics, it is desirable that the viscosity of the foregoing organopolysiloxane be from 50 to 500,000 cs, particularly from 50 to 300,000 cs, at 25°C. When the viscosity is below 50 cs at 25°C, the grease obtained shows a strong tendency to oil separation; while, when it is above 500,000 cs at °C, the grease prepared is so high in viscosity that it cannot possibly be dispensed to a substrate in a satisfactory condition.

[0022] The organopolysiloxane used in the present invention can have any of linear, branched and cyclic structures, and it is not necessarily a single compound, but it can be a mixture of two or more of organopolysiloxanes different in structure. Although "a" may be from 1.8 to 2.3, it is desirable for the organopolysiloxane to have "a" in the range of 1.9 to 2.1, because this range enables the organopolysiloxane to have a linear structure or a structure close thereto.

[0023] Suitable examples of such an organopolysiloxane include dimethylpolysiloxane, diethylpolysiloxane, methylphenylpolysiloxane, dimethylsiloxane-diphenylsiloxane copolymer, and alkyl-modified methylpolysiloxanes. Of these polysiloxanes, homopolymers and copolymers produced from dimethylsiloxane, alkylmethylsiloxane, methylphenylsiloxane or/and diphenylsiloxane and blocked at their molecular-chain ends with trimethylsilyl or dimethylhydrosilyl groups are preferred in particular.

[0024] More specifically, such organopolysiloxanes are represented by, e.g., the following formula (I):



$$R^4-\underset{R^1}{\overset{R^1}{R}}-O-\left[\underset{R^3}{\overset{R^2}{Si}}-O\right]_l-\underset{R^1}{\overset{R^1}{Si}}-R^4 \qquad (I)$$

wherein each of R^1 groups is a group selected from monovalent unsubstituted or substituted hydrocarbon groups having 1 to 30 carbon atoms, such as alkyl groups (e.g., methyl, ethyl, propyl, butyl, amyl, octyl, etc.), alkenyl groups (e.g., vinyl, allyl, etc.), aryl groups (e.g., phenyl, tolyl, etc.) and groups formed by substituting halogen atom(s), cyano group(s), hydroxyl group(s) or/and so on for part or all of the hydrogen atoms attached to carbon atoms present in the above-recited groups (e.g., chloromethyl, 3,3,3-trifluoropropyl, cyano-propyl, phenol, hindered phenol, etc.); R^2 and R^3 groups are the same or different, and each of them is the same monovalent hydrocarbon group as R^1 represents, an amino group-containing organic group, a polyether group-containing organic group or an epoxy group-containing organic group; R^4 is a hydrogen atom, the same monovalent hydrocarbon group as R^1 represents or the same monovalent organic group as R^2 or R^3 represents; and ℓ is a positive number to ensure the viscosity of from 50 to 500,000 cs at 25°C in the organopolysiloxane.

[0025] It is desirable for the organopolysiloxane used in the present invention to be blocked with trimethylsilyl groups at the molecular-chain ends thereof. As R^1, R^2 and R^3 each, an alkyl group such as methyl or ethyl, an aryl group such as phenyl or tolyl, or a group formed by substituting hydroxyl group(s) for a part of the hydrogen atoms of the group as recited above, particularly a methyl group, a phenyl group or an alkyl group having 6 to 14 carbon atoms, is preferable with respect to easiness of synthesis and thermal resistance and electric insulation of the oil obtained.

[0026] The organopolysiloxane oil as mentioned above can be produced in accordance with known methods. For instance, dimethylpolysiloxane oil can be produced by subjecting a low molecular cyclic siloxane, such as octamethylcyclotetrasiloxane or decamethylcyclopentasiloxane, to a ring-opening reaction in the presence of an acid catalyst, such as sulfuric acid, chlorosulfonic acid, nitric acid, phosphoric acid, activated clay, acid clay or trifluoroacetic acid, or an alkaline catalyst, such as potassium hydroxide, sodium hydroxide, rubidium hydroxide, caesium hydroxide, potassium oxide, potassium acetate or calcium silanolate, and then polymerizing the reaction product.

[0027] In order to produce a dimethylpolysiloxane oil having the intended viscosity by controlling the polymerization degree in the foregoing method, a low molecular weight siloxane having a terminal blocking group, such as hexamethyldisiloxane, octamethyltrisiloxane or decamethyltetrasiloxane, can be added properly at the stage of polymerization.

[0028] As for the production of organopolysiloxanes having carbon functional groups, on the other hand, an amino group-containing organopolysiloxane can be produced by the dealcoholating condensation reaction between an organopolysiloxane having at least one silanol group and an amino group-containing alkoxysilane, and an epoxy group- or polyether group-containing organopolysiloxane can be produced by subjecting a compound having both epoxy or polyether group and an unsaturated group, such as vinyl group, and an organohydrogenpolysiloxane having hydrogen-attached silicon atom(s) to an addition reaction in the presence of a platinum catalyst.

[0029] However, the organopolysiloxane oils produced in accordance with the foregoing methods generally contain low molecular weight siloxanes having at most 12 siloxane units in a proportion of about 10 %, because they are obtained as equilibrated mixtures of polysiloxanes produced with the progress of polymerization which are various in their polymerization degrees.

[0030] After the syntheses using the foregoing methods, therefore, the products obtained generally undergo a stripping treatment at a temperature of 120-250°C under a reduced pressure to remove the low molecular weight siloxanes therefrom. Even after the stripping treatment, however, the low molecular weight siloxanes still remain in a quantity of

500-20,000 ppm. These low molecular weight siloxanes have a strong adsorbing power, compared with nonpolar combustible gases, so that their vapors are adsorbed strongly by various electrical contact parts and so on.

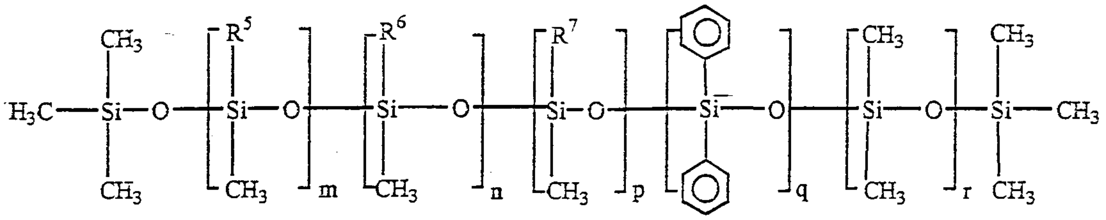
[0031] The low molecular weight siloxanes adsorbed to electrical contact parts are converted into $SiO_2 \cdot nH_2O$ by undergoing oxidation, and further accumulated in the form of αSiO_2 on the surface of the contact parts to cause a contact point disturbance. Therefore, the presence of low molecular weight siloxanes is already known to be undesirable.

[0032] In addition, it is also known that such a trouble can be prevented by reducing each of the contents of low molecular weight siloxanes having no more than 12 siloxane units to at most 50 ppm.

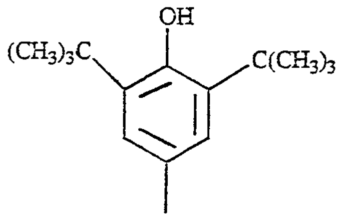
[0033] The removal of the foregoing low molecular weight siloxanes can be effected by subjecting an organopolysiloxane oil produced by the foregoing conventional method to a stripping treatment at a high temperature of 150-300°C under a reduced pressure of 50 mmHg or below in an atmosphere of dried nitrogen gas, or by extracting the low molecular weight siloxanes contained in the foregoing organopolysiloxane oil with an alcohol or ketone solvent. Thus, each of the contents of low molecular weight siloxanes in the organopolysiloxane oil produced in the foregoing manner can be reduced to less than 50 ppm, and the total content of the low molecular weight siloxanes having from 2 to 12 siloxane units can be reduced to less than 500 ppm.

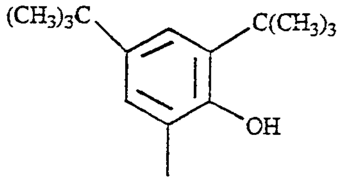
[0034] From the standpoint of improving, e.g., the thermal resistance, R^1 in formula (I) may be a monovalent substituted hydrocarbon group having the hindered phenol structure as described in Japanese Tokko Hei 3-131692.

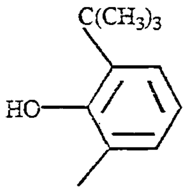
[0035] Examples of a liquid silicone suitable for the present invention include those represented by the following formula (II), but these examples should not be construed as limiting on the scope of the present invention anyway:

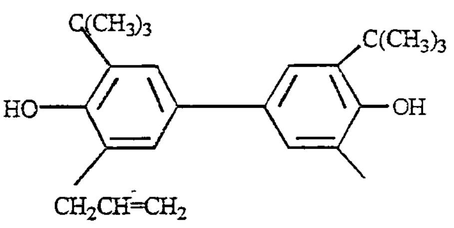

(II)

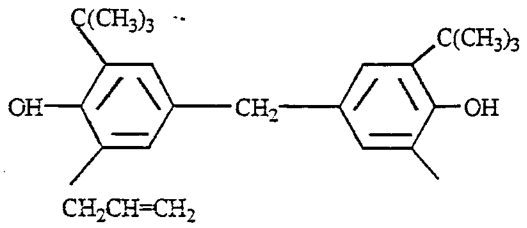
wherein R^5 is $-C_4H_9$, $-C_6H_{13}$, $-C_8H_{17}$, $-C_{10}H_{21}$, $-C_{12}H_{25}$, $-C_{15}H_{31}$ or $-C_{18}H_{37}$; R^6 is $-(CH_2)_s-Q$; s is an integer of 1 to 6; Q is a group selected from the following monovalent organic groups having hindered phenol structures,









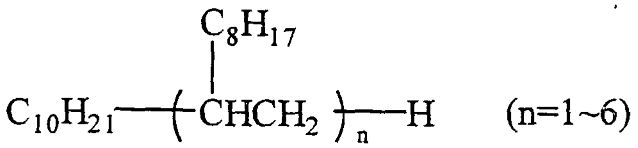


R^7 is a 2-phenylethyl group or a 2-phenylpropyl group; and m, n, p, q and r are each a number satisfying the following equations: $0 \leq m \leq 1{,}000$, $0 \leq n \leq 100$, $0 \leq p \leq 1{,}000$, $0 \leq q \leq 1{,}000$, $0 \leq r \leq 2{,}000$ and $5 \leq m+n+p+q+r \leq 2{,}000$.

[0036] From the viewpoint of consistency and dispensation property required for a silicone grease composition, it is desirable that the liquid silicone used in the present invention have its viscosity in the range of 50 to 500,000 cs, particularly 100 to 100,000 cs, at 25°C.

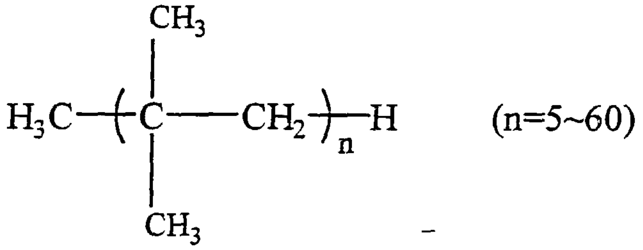
[0037] Examples of mineral oil and synthetic oil usable as base oil in the present invention include paraffin oil, naphthene oil, α-olefin oligomers (poly-α-olefins), polybutenes (polyisobutylenes), substituted aromatic compounds, polyalkylene glycols (polyglycol, polyether, polyalkylene oxides), diesters (dibasic acid esters), polyol esters (neopentylpolyol esters and hindered esters), phosphoric acid esters (phosphate esters), fluorinated compounds, such as chlorofluorocarbons, fluoroesters and perfluoroalkyl ethers (fluoropolyglycols, perfluoropolyethers, polyperfluoroalkylethers), and polyphenylether.

[0038] With respect to the synthetic oils recited above, the α-olefin oligomers include those represented by the following formula (III), the polybutenes include those represented by the following formula (IV), the substituted aromatic compounds include those represented by the following formula (V) and the polyalkylene glycols include those represented by the following formula (VI):



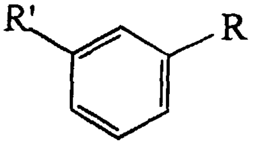
$$C_{10}H_{21}-\left(\overset{\overset{\textstyle C_8H_{17}}{|}}{C}HCH_2\right)_n-H \quad (n=1\sim6)$$

(III)



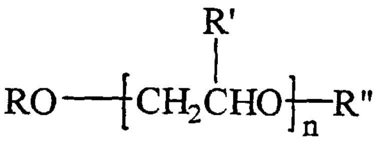
$$H_3C-\left(\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}-CH_2\right)_n-H \quad (n=5\sim60)$$

(IV)



R, R': $C_{10\text{-}18}$ alkyl

(V)



$$RO-\left[CH_2\overset{\overset{\textstyle R'}{|}}{C}HO\right]_n-R''$$

(VI)

[0039] In the above formula (VI), R, and R" each are generally H or CH_3, R' is H, CH_3 or C_2H_5, and n is from 1 to 200. In general, the polyalkylene glycol of formula (VI) is polyethylene glycol or polypropylene glycol. Further, it may be a copolymer of these two glycols.

[0040] The diesters (dibasic acid esters) are generally produced by the esterification reaction between alcohols and dibasic acids as shown below;

$$2\ ROH + HOOCR'COOH \rightarrow ROOCR'COOR + 2\ H_2O$$

wherein R is H or a $C_{4\text{-}18}$ alkyl group and R' is a $C_{4\text{-}18}$ alkylene group or an arylene group.

[0041] The dibasic acids used as starting material are generally those represented by formula, $HOOC(CH_2)_nCOOH$, with examples including adipic acid (n=4), azelaic acid (n=7), sebacic acid (n=8) and dodecane diacid (n=10). The alcohols used in combination with those acids are 7-13C primary alcohols having a side chain, with examples including 2-ethylhexanol (C_8), isodecanol (C_{10}) and tridecanol (C_{13}).

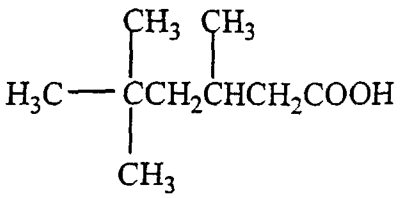
[0042] By using those acids and alcohols in different combinations, various diesters can be obtained. Examples thereof include diisodecyl phthalate, di-2-ethylhexyl phthalate, dibutyl phthalate, diisodecyl adipate, diisononyl adipate, diisobutyl adipate, mixed acid esters of 2-ethylhexanol, di-2-hexyl sebacate, dibutyl sebacate, di-2-ethylhexyl azelate, di-n-hexyl azelate, di-2-hexyl dodecanoate and dibutoxyethoxyethyl adipate.

[0043] The polyol esters, including neopentylpolyol esters and hindered esters, are monobasic fatty acid esters of polyhydric alcohols, such as neopentylpolyols.

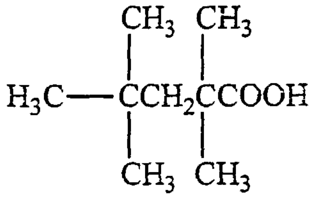
[0044] In producing polyol esters, neopentylpolyols which are mass-produced as the starting material for syntheses of alkyd resin and surfactants can be employed as raw materials of alcohols. Specifically, neopentyl glycol (NPG), trimethylolpropane (TMP), trimethylolethane (TME), pentaerithritol (PE) and dipentaerithritol (DPE) can be used as polyhydric alcohol.

[0045] The monobasic fatty acids usable as the other starting material in the polyol ester synthesis include straight-chain and branched C_{3-13} carboxylic acids. For instance, as C_9 carboxylic acids are exemplified the following acids having a straight-chain structure, a branched structure and a structure having a neopentyl type branch respectively:

$$CH_3(CH_2)_7COOH$$



$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}CH_2\overset{CH_3}{C}HCH_2COOH$$



$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}CH_2\underset{CH_3}{\overset{CH_3}{C}}COOH$$

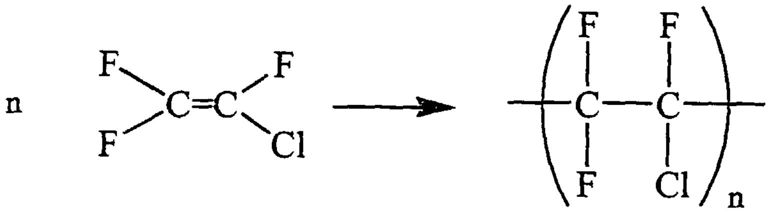
[0046] By variously combining the above-recited compounds as starting materials, a wide variety of polyol esters can be synthesized. In particular, the esters produced by the reaction of an acid having a neopentyl type branch with an alcohol having a neopentyl type branch have the advantage of high thermal stability.

[0047] Additionally, by the comparative experiment on stability against pyrolysis between di(isooctyl)azelate as an ester produced from an alcohol having no neopentyl type branch and an acid having no neopentyl type branch, bis(2,2-dimethyloctyl)azelate as an ester produced from an alcohol having a neopentyl type branch and an acid having no neopentyl type branch, and bis(2,2-dimethylpentyl)-2,2,8,8-tetraethylazelate as an ester produced from an alcohol having a neopentyl type branch and an acid having neopentyl type branches, it is known that the last ester as the neopentyl type-neopentyl type combination has the highest thermal stability.

[0048] The phosphoric acid esters include esters prepared from phosphoric acid as an inorganic acid and phenols or alcohols. With respect to the phenyl phosphate, as triphenyl phosphate is in a solid state at ordinary temperature, the phenyl phosphates in a liquid state can be generally prepared by using phenols substituted by alkyl group(s). Examples of such a liquid phenyl phosphate include tricresyl phosphate (TCP), trixylenyl phosphate, tripropylphenyl phosphate and tributylphenyl phosphate.

[0049] Suitable examples of an alkyl phosphate include tributyl phosphate (TBP) and tri-2-ethylhexyl phosphate (TOP).

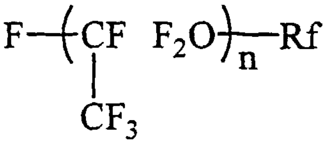
[0050] The chlorofluorocarbons have a structure such that hydrogen atoms of n-paraffin are replaced by fluorine atoms and chlorine atoms, and can be produced by polymerizing chlorotrifluoroethylene in a low polymerization degree as shown in the following reaction scheme:



[0051] The chlorofluorocarbon produced has a viscosity depending on the polymerization degree, and the viscosity can be varied over a wide range.

[0052] Examples of a fluoroester usable in the present invention include sebacic acid esters of C_7 perfluoroalcohols, pyromellitic acid esters of perfluoroalcohols and camphoric acid esters of perfluoroalcohols.

[0053] The perfluoroalkyl ethers are generally represented by the following formula (VII) or (VIII):



$$F\!-\!\left(\underset{\displaystyle CF_3}{\underset{|}{CF}}\;F_2O\right)_n\!-\!Rf \qquad (Rf : CF_3 \text{ or } C_2F_5) \qquad \text{(VII)}$$

$$RfO-\left(CF_2C\ _2O\right)_m\left(CF_2O\right)_n-Rf \quad (Rf : CF_3 \text{ or } C_2F_5) \qquad \text{(VIII)}$$

[0054] It is possible to produce perfluoroalkyl ethers having from low to high viscosities by changing the polymerization degree.

[0055] From the viewpoints of consistency and dispensation suitability required for thermally conductive grease, it is desirable that the liquid hydrocarbons and/or fluorinated hydrocarbon oil used in the present invention have their viscosity in the range of 50 to 500,000 cs, especially 100 to 100,000 cs, at 25°C.

[0056] The Component (B) of the present grease composition is a thermally conductive inorganic filler having Mohs' hardness of at least 6 and thermal conductivity of at least 100 W/m°K (in theory). As the Component (B) is used for conferring high thermal conductivity on the grease composition, it is the more advantageous to the composition to use a filler having higher thermal conductivity.

[0057] In order to provide a thermally conductive material useful for the heat removal from heat-generating electronic parts, which is an object of the present invention, it is required for the filler to have theoretical thermal conductivity of at least 100 W/m°K, preferably at least 300 W/m°K. Further, it is required for the filler as Component (B) to have Mohs' hardness of at least 6, though inorganic fillers having such high thermal conductivity are generally high in Mohs' hardness. When the filler used as Component (B) has Mohs' hardness lower than 6, it cannot have good compatibility with an inorganic filler having low Mohs' hardness used as Component (C). Examples of a filler suitable for Component (B) include an aluminum nitride powder, a diamond powder and a silicon carbide powder.

[0058] The aluminum nitride powder used as a thermal conductivity providing filler in the present invention is a nitride of Group III-V metal which generally has a crystal structure of hexagonal system or wurtzite type, and colored white or grayish white in appearance. The particle shape of the powder is polygonal or spherical depending on the preparation method adopted.

[0059] Such an aluminum nitride powder is prepared using, e.g., a direct nitriding method in which a metallic aluminum powder is allowed to react directly with nitrogen or ammonia, an alumina reduction method in which a mixture of alumina and carbon powders is heated in an atmosphere of nitrogen or ammonia to undergo reduction and nitriding reactions at the same time, a method of reacting aluminum vapor directly with nitrogen, or the pyrolysis of $AlCl_3 \cdot NH_3$.

[0060] In the present invention can also be used a highly pure aluminum nitride ceramic prepared by using as a raw material an aluminum nitride powder prepared by the method as mentioned above and sintering the raw material. In preparing such a highly pure aluminum nitride ceramic, the aluminum nitride powder used as a raw material is required to be susceptible to sintering by having high purity and being a fine powder having a uniform primary particle size of the order of 0.5 μm.

[0061] The aluminum nitride powders prepared by any methods can be used in the present invention, although they differ in characteristics, including the chemical composition (impurities), the particle shape and the particle size distribution, depending on the preparation method adopted. Also, the powders prepared by different methods may be used as a mixture.

[0062] The thus obtained aluminum nitride powder is a very hard material, and has an excellent thermal conductivity, electric insulation and mechanical strength.

[0063] The aluminum nitride powders having their average particle sizes in a wide range of 0.5 to 5 μm can be used in the present invention. In view of the dispersibility in a base oil, however, it is preferable for the aluminum nitride powder to have an average particle size in the range of 1 to 4 μm, particularly 2 to 4 μm.

[0064] When the average particle size of an aluminum nitride powder used is smaller than 0.5 μm, the powder is undesirable because of its too great viscosity-increasing effect. In other words, the grease obtained using such a powder has low consistency (or high hardness and poor dispensation suitability). When the average particle size is larger than 5 μm, on the other hand, the thermally conductive material obtained is poor in uniformity and stability and, what is worse, the base oil separates therefrom to a considerable extent (namely, the material obtained has a high oil-separation degree). Therefore, it is a matter of course that good grease cannot be obtained in the foregoing cases.

[0065] Further, it is desirable for such a powder to have a specific surface area of from 1 to 5 m^2/g. In particular, the specific surface area ranging from 2 to 4 m^2/g is preferred from the viewpoint of compatibility with a base oil.

[0066] In general, aluminum nitride is very hard, and the Mohs' hardness thereof is within the range of 7 to 9. Any aluminum nitride can be used in the present invention as far as the Mohs' hardness thereof is in the foregoing range. In particular, the aluminum nitride having Mohs' hardness of from 8 to 9 is used to advantage.

[0067] The thermal conductivity of aluminum nitride is 320 W/m°K in theory, but the actually measured value is lower than the theoretical value, specifically 250 W/m°K or below, because the aluminum nitride powder obtained in practice is more or less contaminated with impurities and contains voids and bubbles. It is required for the aluminum nitride powder used in the present invention to have a thermal conductivity of at least 100 W/m°K at room temperature. In particular, it is desirable that the thermal conductivity thereof be at least 150 W/m°K, especially at least 200 W/m°K, at room temperature. When the thermal conductivity of an aluminum nitride powder used is below 100 W/m°K, the thermal conductivity of the grease or sheet obtained cannot reach such a high value as to be aimed at by the present invention.

[0068] Examples of aluminum nitride which can be used in the present invention include US, UF and UM, trade names, produced by Toyo Aluminum Co., Ltd., XUS-55548, trade name, produced by Dow Chemical Co., Ltd., H-grade and F-grade, trade names, produced by K.K. Tokuyama, FA and ES-10, trade names, produced by Nippon Light Metal Co., Ltd., and A-100WR, A-100 and AG-SD, trade names, produced by Advanced Refractory Technologies Inc.

[0069] The diamond powder used as a thermal conductivity providing filler in the present invention is a synthetic diamond powder which is generally produced on an industrial scale. The synthetic diamond powders have a density of about 3.5 and a hexahedral or octahedral crystal shape originating in diamond structure, and produced according to the ultra-high pressure synthesis method or low pressure synthesis method using graphite as a starting material.

[0070] The synthetic diamond changes its crystal shape depending on the synthesis condition including the combination of pressure and temperature, and the crushing characteristic value thereof depends on the crystal shape. Accordingly, the synthesis condition can be chosen so as to achieve the grain form and the grain size distribution adapted for the use intended. Thus, synthetic diamond powders various in grain form and grain size distribution are procurable. In the present invention, it is possible to employ diamond powders in micron sizes which are generally used for slurry, paste and tape. As for the diamond powders of micron sizes, there are known diamond powders the grain size of which ranges from 0.1 to 60 μm and the bulk density of which ranges from 1.4 to 2.1.

[0071] The synthetic diamond powders usable in the present invention are those various in average grain size. Specifically, their average grain sizes are in the range of 0.2 to 5 μm. From the viewpoint of dispersibility in base oils, it is desirable for their average grain sizes to range from 0.5 to 4 μm, particularly from 1 to 3 μm. Moreover, it is favorable to prepare such a diamond powder by properly mixing a relatively coarse diamond powder having a grain size of from 8 to 20 μm, a diamond powder having a medium grain size of from 1 to 8 μm and a relatively fine diamond powder having a grain size of from 0.1 to 1 μm, because the mixture obtained can have a broad grain size distribution to ensure excellent dispensation suitability in the heat-reducing grease as the dispersion thereof in a base oil. Additionally, the theoretical thermal conductivity of synthetic diamond, though depends on its crystal form, is very high, specifically in the range of 900 to 2,000 W/m°K.

[0072] Silicon carbide powders usable as a thermal conductivity providing filler in the present invention are generally obtained by producing high-purity α-SiC ingot from silica and coke as the main raw materials by means of an electric resistance furnace (Acheson furnace) and subjecting the thus produced ingot to pulverizing, decarburizing, iron-removing and sieving steps in succession. According to this process, silicon carbide powders various in grain size distribution can be produced depending on the intended uses. Further, an ultra fine silicon carbide powder can be prepared by choosing a powder having a moderate particle size distribution as starting material, thoroughly grinding the powder into fine particles of sub-micron order in size, sieving them, and further purifying by a chemical treatment.

[0073] The grain size and the grain size distribution of silicon carbide are determined by the methods defined in JIS R6001, JIS R6002 and JIS R6124. The average particle size of a silicon carbide powder usable in the present invention, though it may be in a wide range of 0.4 to 10 μm, is desirably in the range of 0.4 to 5 μm from the viewpoints of securing high dispersibility in base oil and preventing oil separation. The silicon carbide powders are bluish black in appearance, have a crystal form of trigonal prism, and are generally hard. The theoretical thermal conductivity of silicon carbide is 100 W/m°K. The silicon carbide powders having Mohs' hardness in the range of 8 to 9 are usable in the present invention.

[0074] As a thermally conductive inorganic filler having Mohs' hardness of at least 6 and a theoretical thermal conductivity of at least 100 W/m°K, which is referred to as Component (B) of the present invention, the above-recited fillers are exemplified. However, these exemplified fillers should not be construed as limiting the scope of the present invention in any way. Additionally, the fillers as recited above may be used alone or in combination to constitute the Component (B).

[0075] In particular, as it is required for the Component (B) to have a thermal conductivity of at least 100 W/m°K, especially at least 200 W/m°K in order to impart excellent thermal properties upon the grease composition, it is desirable that the aluminum nitride and diamond powders having high thermal conductivity be used alone as Component (B) or the Component (B) comprises such powders in appropriate proportions.

[0076] The Component (C) of the present invention is a thermally conductive inorganic filler having Mohs' hardness of no higher than 5 and theoretical thermal conductivity of at least 20 W/m°K. This Component (C) enables the Component (B) to have a high filling factor when used in combination with the Component (B). More specifically, when the present thermally conductive composition is used as heat-reducing grease, the Component (C) functions so as to secure satisfactory dispensation suitability and, at the same time, attain a high filling factor of thermally conductive inorganic filler.

[0077] In order to fulfil such a function, the Component (C) is required to have Mohs' hardness of no higher than 5, desirably in the range of 1 to 5. When the Mohs' hardness thereof is higher than 5, the Component (C) cannot have good compatibility with the Component (B) having high hardness. In addition, the Component (C) is required to have theoretical thermal conductivity of at least 20 W/m°K. When the Component (C) has theoretical thermal conductivity lower than 20 W/m°K, it is hard to obtain a composition having the high thermal conductivity aimed at by the present invention. Examples of an inorganic filler as Component (C) which can meet the foregoing requirements include a boron nitride powder and a zinc oxide powder.

[0078] The zinc oxide usable in the present invention is a white zinc oxide powder having a hexagonal or wurtzite crystal structure, generally referred to as "Zinc White". Such a zinc oxide powder can be prepared using known methods. For instance, one of the known methods is an indirect method in which the zinc vapor generally produced by heating metallic zinc to 1,000°C is oxidized with hot air, and another thereof is a direct method wherein the zinc oxide obtained by roasting zinc ore is reduced by coal or the like and the zinc vapor produced is oxidized with hot air, or wherein the slag obtained by the leaching of zinc ore with sulfuric acid is admixed with coke and then heated in an electric furnace, and further the zinc vapor produced thereby is oxidized with hot air.

[0079] The zinc oxide produced using any of the foregoing methods is cooled by passing through an air condenser equipped with a blower, and fractionated according to the grain size. As still another production method of zinc oxide, there is known a wet method in which a zinc salt solution is admixed with an alkali carbonate solution to precipitate zinc hydroxycarbonate and the zinc hydroxycarbonate obtained is roasted.

[0080] The thus obtained zinc oxide powders are defined in accordance with the Japanese Industrial Standards, JIS K1410 and K5102, or American standards, ASTM-D79.

[0081] In the present invention, the zinc oxide powders produced by any of the aforementioned methods can be used alone, or a mixture of zinc oxide powders produced by different methods may be used.

[0082] In general the zinc oxide powder is used not only as a vulcanization accelerator for rubber but also in the fields of coating color, ceramics, enameled ware, glass, ferrite, cosmetics and medicines. Further, it is known to use a zinc oxide powder as a thermal conductivity providing filler in a thermally conductive grease [Japanese Tokkai Sho 51-55870, Sho 54-116055, Sho 55-45770, Sho 56-28264, Sho 61-157587, Hei 2-212556 (U.S. Patent No. 5,221,339), Hei 3-162493 (U.S. Patent No. 5,100,568) and Hei 4-202496].

[0083] The average grain size of a zinc oxide powder which can be used in the present invention is in a wide range of 0.2 to 5 μm. In the view of the dispersibility in base oil and the relation with the powders used in combination, such as an aluminum nitride powder, it is desirable to use a zinc oxide powder having a grain size in the range of 0.3 to 4 μm, particularly 0.3 to 3 μm. By using the zinc oxide powder having such a grain size, the oil separation degree of the thermal conductive material obtained can be reduced to 0.01 % or below. Further, it is desirable for the zinc oxide used to have Mohs' hardness of from 4 to 5.

[0084] The boron nitride powders usable in the present invention are boron nitride powders having a hexagonal crystal structure similar to that of graphite, or a hexagonal network laminate which are produced by heating boric acid or a borate in combination with a nitrogen-containing organic compound or ammonia. The boron nitride of hexagonal system has characteristics such that it retains high lubricity even in a high temperature range, has high thermal conductivity as well as high electrical insulating capacity, and further is chemically stable and hardly wetted with fused metal or glass. Accordingly, it is used as an electrical insulating filler having high thermal conductivity, a solid lubricant, a filler for modification of resins, or the like.

[0085] These boron nitride powders having a crystal structure ox hexagonal system are white in appearance, the average grain size thereof is from 1 to 10 μm, and they are generally soft. In the present invention, the boron nitride powders having Mohs' hardness in the range of 1 to 3 are usable. In particular, the boron nitride powders having Mohs' hardness of the order of 2 are used to advantage.

[0086] The boron nitride powders usable in the present invention have their average grain sizes in a wide range of 1 to 10 μm. In viewing the dispersibility in base oil and the prevention of oil separation, however, it is desirable for the powder used in the present invention to have an average particle size in the range of 1 to 5 μm.

[0087] On the other hand, the hexagonal boron nitride as described above is converted to cubic boron nitride based on the same structural principle of diamond when it undergoes a high temperature-ultrahigh pressure processing. The boron nitride having a crystal structure of cubic system has the hardness second to that of diamond, and its powdered products available on the market are from liver brown to black in appearance and the average particle size thereof is in the range of several μm to 800 μm.

[0088] Such cubic boron nitride powders also are usable in the present invention, but they are not favorable because their thermal conductivity is in a low range of 0.5 to 3.6 W/m °K; as a result, even if they are incorporated in grease or sheet, the achievement of the thermal conductivity satisfactory to the present invention is difficult. Another reason for this difficulty is that the thermal conductivity of the present thermal conductive material depends also on the filling rate of thermal conductivity providing fillers in the base oil used.

[0089] In order to achieve high thermal conductivity which is an object of the present invention, it is required that the filling rate of fillers, especially an aluminum nitride or diamond powder as Component (B), be heightened. To the attainment of a high filling rate without causing damage to grease characteristics, the shape and size of filler particles are of great importance. In the case of preparing grease, apart from sheet, increasing a filling rate renders the resulting composition highly viscous to tend to fair dispensation suitability.

[0090] The term "dispensation suitability" as used herein indicates the ease of the work in coating a grease on a substrate. When the grease has an inferior dispensation suitability, the ease of the coating work using a cylinder-form apparatus equipped with a grease extruding means is reduced and it becomes difficult to form a thin coating of the grease on a substrate. In the case where a thermally conductive material is used as grease, therefore, the shape as well as the size of filler particles constitutes a very important factor for achieving a high filling rate while securing a dispensation suitability.

[0091] However, each of aluminum nitride and diamond powders consists of square- or flake-shaped particles rather than spherical particles due to the production process and crystal structure thereof, so that the powder tends to increase the viscosity of a thermally conductive material with a rise in the filling rate. In other words, the rise in the filling rate causes an increase in the viscosity, or a drop in consistency, of the thermally conductive material to impair the dispensation suitability required for a thermally conductive grease.

[0092] On the other hand, the theoretical thermal conductivity of zinc oxide or boron nitride as Component (C) is in the range of 20 to 60 W/m°K. In other words, this range is much lower than the thermal conductivity required for the filler as Component (B), or about 1/(5-15) as high as the thermal conductivity 300 W/m°K which an aluminum nitride or diamond powder as Component (B) can have. Therefore, zinc oxide and boron nitride powders have rarely been used in the fields where high thermal conductivity is needed. As for the hardness, however, these powders are softer than the powders used as Component (B). Accordingly, if the Component (C) is used in combination with the Component (B), every individual soft particle of Component (C) can be arranged among hard particles of Component (B) to function so as to confer a mobility on the close-packed structure to enable an improvement in dispensation suitability.

[0093] In mixing a filler as Component (B) with a filler as Component (C), it is desirable that the ratio of the filler as Component (C) to the total fillers, or the Component (C)/(Component (B) + Component (C)) ratio, be from 0.05 to 0.5 by weight, particularly from 0.1 to 0.3. When the filler as Component (C) is mixed in a proportion lower than 5 weight %, it cannot fill up sufficiently the gaps among hard filler particles as Component (B) to fail in not only efficiently improving the thermal conductivity but also imparting satisfactory dispensation suitability to a thermally conductive material intended for grease.

[0094] When the filler as Component (C) is mixed in a proportion higher than 50 weight %, on the other hand, it becomes difficult to produce an improvement in thermal conductivity, because the thermal conductivity of zinc oxide or boron nitride used as Component (C), specifically 20-60 W/m °K in theory, is considerably low, compared with the theoretical thermal conductivity of 300 W/m°K or above the filler used as Component (B), such as aluminum nitride or diamond, has.

[0095] By mixing a filler as Component (B) with a filler as Component (C) in a proper ratio according to the present invention, the fillers can be most appropriately dispersed into a base oil used as component (A) to enable the heat-reducing grease obtained to have a moderate consistency and to avoid deterioration in the dispensation suitability. As a result, the present thermal conductive grease can acquire thermal conductivity of at least 2.5 W/m°K which is in the optimum range for the removal of the heat from highly heat-generating electronic parts.

[0096] It is required that the proportion of a filler mixture of Component (B) with Component (C) be from 500 to 1,000 parts by weight, preferably from 800 to 1,000 parts by weight, to 100 parts by weight of base oil as Component (A). When the content of a filler mixture in the present composition is less than 500 parts by weight, the thermal conductivity of the composition obtained is in almost the same level as those of conventional grease compositions; while, when it is increased beyond 1,000 parts by weight, the resulting composition becomes hard and poor in dispensation suitability although high in thermal conductivity, so that it is unfit for grease.

[0097] To the present thermally conductive grease compositions each may further be added various agents, such as a thixotropy providing agent, an antioxidant, metallic powders, metallic fibers, a flame retardant, heat-resistant additives, pigments, a blowing agent, a cross-linking agent, a curing agent, a vulcanizing agent and a mold-releasing agent, if desired. Specific examples of such additives include reinforcing fillers (such as aerosol silica, precipitated silica, diatomaceous earth and non-conductive carbon black), aluminum oxide, mica, clay, zinc carbonate, glass beads, polydimethylsiloxane, alkenyl group-containing polysiloxanes, and polymethylsilsesquioxane. These additives can be properly chosen according to the necessity or usefulness, and mixed under heat or reduced pressure. In kneading the present components with those additives, a closed kneader, a two-rod roll, a three-rod roll, or a colloid mill can be used to disperse them homogeneously.

[0098] The present thermally conductive material can be prepared with each in the following manner: The foregoing Components (A), (B) and (C), e.g., liquid silicone, aluminum nitride powder and zinc oxide powder, are weighed out in proper amounts, admixed with additives such as an antioxidant, if needed, and then kneaded together using a planetary mixer or the like so that the gaps among aluminum nitride particles as Component (B) are filled up with zinc oxide particles as Component (C) to ensure the consistency of from 200 to 400 in the composition prepared. In view of dispensation suitability, it is desirable for the grease to have the consistency of from 200 to 400, particularly from 250 to 350.

[0099] In applying the grease prepared in the foregoing manner to an electronic apparatus which generates heat during the operation, it is desirable to use an injector-like coating device which is fitted up with a means to push the grease charged therein towards the outlet. In particular, the grease can be easily applied to an electronic apparatus by users if the foregoing coating device is in advance charged with the present grease.

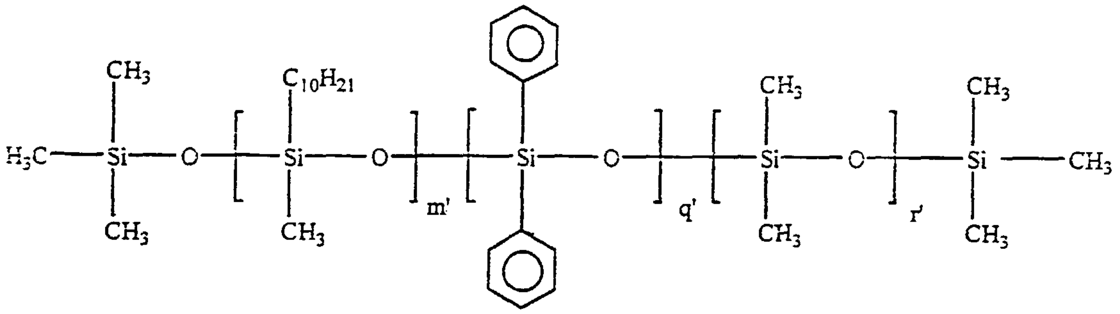
[0100] The present invention will now be illustrated in greater detail by reference to the following examples.

[0101] The entire disclosure of all applications, patents and publications, cited above and below, and of corresponding Japanese applications No. Hei 10-64581, filed February 27, 1998, and No. Hei 10-64582, filed February 27, 1998, is hereby incorporated by reference.

[0102] Additionally, all "pars" and "%" in the following examples and comparative examples are by weight unless otherwise noted.

EXAMPLE 1-14

[0103] The liquid silicones represented by the following formula (III), having the viscosities set forth in Table 1, were each used as base oil (Component (A)) in the amount of 100 parts.



(III)

Table 1

Symbol of Liquid Silicone	Viscosity (cs) at 25°C	Average	Polymerization	Degree
		m'	q'	r'
A - 1	450	20	0	25
A - 2	1,000	80	0	100
A - 3	500	0	0	240
A - 4	400	0	3	9
A - 5	10,000	0	0	800

[0104] Thermally conductive silicone composition samples according to the present invention were each prepared as follows; A filler as Component (B), the species and average particle size of which are set forth in Table 2, and a filler as Component (C), the species and average particle size of which are also set forth in Table 2, were weighed out in their respective amounts as set forth in Table 2, and added to a base oil as specified above. Then, these three components were thoroughly mixed for 20 minutes by means of a planetary mixer, and further subjected to a kneading process for three times by means of a three-rod roll.

[0105] The silicone composition samples thus prepared were each examined for consistency and oil separation degree in accordance with JIS-K-2220 with the intention of using them as grease, and further the thermal conductivities thereof were measured with a hot-wire instrument for measuring thermal conductivity, Model TCW-1000, made by Shinku Riko Co., Ltd. The results obtained are shown in Table 2.

[0106] Additionally, the symbols B-1 and B-2 used in Table 2 to represent Component (B) are pulverized AlN (average particle size: 0.1-15 μm) and a synthetic diamond powder (average particle size: 0.1-5 μm) respectively; while the symbols C-1 and C-2 used therein to represent Component (C) are a zinc oxide powder (average particle size: 0.05-5 μm) and a hexagonal boron nitride powder (average particle size: 0.1-5 μm).

Table 2

	Component (A) (100wt%)		Component (B)			Component (C)						
	Species	Viscosity 25℃ (cs)	Species	Average particle size μm	Amount added (wt%)	Species	Average particle size μm	Amount added (wt%)	$\frac{(C)}{((B)+(C))}$	Consistency	Oil Separation Degree 150℃/24hr	Thermal Conductivity W/m° K
Example 1	A-1	450	B-1	1.2	630	C-1	0.3	270	0.30	290	0	3.72
Example 2	A-1	450	B-1	2.0	720	C-1	0.05	180	0.20	135	0	2.72
Example 3	A-2	1,000	B-1	5.0	620	C-1	0.2	180	0.20	315	0.01	3.77
Example 4	A-3	500	B-1	0.5	460	C-1	5.0	190	0.29	310	0	3.72
Example 5	A-4	400	B-1	1.5	846	C-1	0.2	54	0.06	260	0	3.68
Example 6	A-5	10,000	B-1	1.0	500	C-1	2.0	100	0.17	315	0	2.97
Example 7	A-1	450	B-1	1.2	585	C-2	0.3	315	0.35	310	0	3.77
Example 8	A-2	1,000	B-1	5.0	810	C-2	0.2	90	0.10	320	0	3.64
Example 9	A-3	500	B-1	0.5	488	C-2	4.5	162	0.25	310	0	2.80
Example10	A-4	400	B-1	1.8	325	C-2	1.2	325	0.50	330	0	2.72
Example11	A-3	500	B-2	3.0	280	C-1	0.2	280	0.50	345	0	3.56
Example12	A-4	400	B-2	1.8	460	C-1	1.2	100	0.18	290	0	3.89
Example13	A-1	450	B-2	2.0	488	C-2	0.3	162	0.25	300	0	3.97
Example14	A-4	400	B-2	2.2	280	C-2	0.2	280	0.50	320	0	3.77

COMPARATIVE EXAMPLES 1-14

[0107] Other thermally conductive silicone composition samples were prepared in the same manner as in the aforementioned Examples, except that the amounts of fillers used as Components (B) and (C) were each changed variously. The consistency, oil separation degree and thermal conductivity of each composition prepared were measured in the same ways as in each Example, and the measurement results obtained are shown in Table 3.

[0108] Additionally, the symbols A-1 to A-5, B-1, B-2, C-1 and C-2 used in Table 3 represent the same ingredients as those in each Example, respectively.

Table 3

	Component (A) (100wt%)		Component (B)			Component (C)			$\frac{(C)}{((B)+(C))}$	Consistency	Oil Separation Degree	Thermal Conductivity
	Species	Viscosity 25℃ (cs)	Species	Average particle size μm	Amount added (wt%)	Species	Average particle size μm	Amount added (wt%)			150℃/24hr	W/m°K
Compar.Ex.1	A-1	450	B-1	2.5	720	C-1	0.5	30	0.04	340	2.3	2.13
Compar.Ex.2	A-1	450	B-1	11.0	630	-	-	-	0	125	2.0	3.14
			B-1	0.1	270							
Compar.Ex.3	A-2	1,000	-	-	-	C-1	0.2	550	1.00	335	0	1.05
Compar.Ex.4	A-2	1,000	B-1	2.0	825	C-1	0.3	275	0.25	85	0.5	2.85
Compar.Ex.5	A-2	1,000	-	-	-	C-2	2.5	550	1.00	340	0	1.26
Compar.Ex.6	A-3	500	B-1	2.0	360	C-2	0.5	90	0.20	350	0.2	1.72
Compar.Ex.7	A-2	1,000	B-1	2.5	770	C-2	1.0	330	0.30	90	3.5	2.93
Compar.Ex.8	A-4	400	B-1	1.5	340	C-1	1.0	410	0.55	195	0.9	0.88
Compar.Ex.9	A-5	10,000	B-1	2.0	405	C-1	3.0	495	0.55	238	0.4	2.09
Compar.Ex.10	A-3	500	B-2	1.8	280	-	-	-	0	305	2.0	1.21
Compar.Ex.11	A-4	400	B-2	2.0	280	-	-	-	0	330	2.0	1.30
Compar.Ex.12	A-1	450	B-2	3.0	530	C-1	0.5	20	0.04	340	2.6	2.05
Compar.Ex.13	A-1	450	B-2	2.2	250	C-1	0.5	300	0.55	145	3.0	2.01
Compar.Ex.14	A-1	450	B-2	1.8	250	C-2	2.5	300	0.55	free of grease character		

[0109] As can be seen from the data shown in Tables 2 and 3, the present thermally conductive silicone grease compositions had their thermal conductivity in the range of 2.72 to 3.97 W/m°K. In other words, the present compositions underwent considerable improvement in thermal conductivity over conventional grease compositions and the comparative compositions. Further, the present compositions had the consistency on the practically optimum level for the use as grease and satisfactory dispensation suitability.

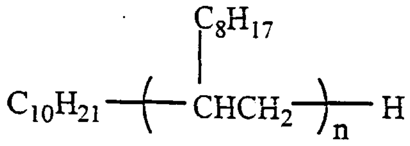
EXAMPLE 15-27

[0110] The liquid hydrocarbons and fluorohydrocarbon oils having the structural formulae illustrated below and the viscosities set forth in Table 4 were each used as base oil (Component (A)) in the amount of 100 parts.

Table 4

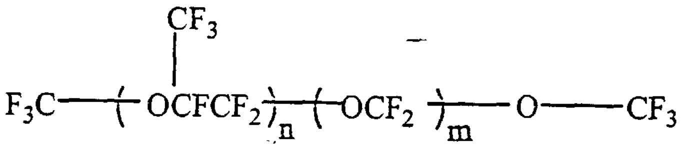
Symbol of Base Oil	Trade Name	Viscosity (Cst) at 40°C	Specific Gravity
A - 6	ETHYLFLO* 174	395	0.836
A - 7	ETHYLFLO* 180	1,400	0.856
A - 8	FOBRIN** Y45	200	1.91
A - 9	DEMNUM*** S-200	200	1.89

* Product of U.S. ETHYL Co., having the following structural formula;



$$C_{10}H_{21}-\left(\overset{\overset{C_8H_{17}}{|}}{C}HCH_2\right)_n-H$$

** Product of AUSIMONT S.p.A., having the following structural formula;



$$F_3C-\left(O\overset{\overset{CF_3}{|}}{C}FCF_2\right)_n-\left(OCF_2\right)_m-O-CF_3$$

*** Product of DAIKIN KOGYO CO., LTD., having the following structural formula;

$$F-\left(CF_2CF_2CF_2O\right)_n-CF_2CF_3$$

[0111] Thermally conductive grease compositions according to the present invention were each prepared as follows; A filler as Component (B), the species and average particle size of which are set forth in Table 5, and a filler as Component (C), the species and average particle size of which are also set forth in Table 5, were weighed out in their respective amounts as set forth in Table 5, and added to a base oil as specified above. Then, these three components were thoroughly mixed for 20 minutes by means of a planetary mixer, and further subjected to a kneading process for three times by means of a three-rod roll.

[0112] The thermally conductive composition samples thus prepared were each examined for consistency and oil separation degree in accordance with JIS-K-2220 with the intention of using them as grease, and further the thermal conductivities thereof were measured with a hot-wire instrument for measuring thermal conductivity, Model TCW-1000, made by Shinku Riko Co., Ltd. The results obtained are shown in Table 5.

[0113] Additionally, the symbols B-1 and B-2 used in Table 5 to represent Component (B) are pulverized AlN (average particle size: 0.1-5 μm) and a synthetic diamond powder (average particle size: 0.1-5 μm) respectively; while the symbols C-1 and C-2 used therein to represent Component (C) are a zinc oxide powder (average particle size: 0.05-5 μm) and a hexagonal boron nitride powder (average particle size: 0.1-5 μm).

Table 5

	Component (A) (100wt%)		Component (B)			Component (C)						
	Species	Viscosity 25℃ (cs)	Species	Average particle size μm	Amount added (wt%)	Species	Average particle size μm	Amount added (wt%)	$\frac{(C)}{((B)+(C))}$	Consis-tency	Oil Separation Degree 150℃/24hr	Thermal Conduc-tivity W/m° K
Example15	A-6	395	B-1	0.5	630	C-1	0.3	270	0.30	315	0	3.18
Example16	A-6	395	B-1	1.2	720	C-1	0.2	180	0.20	280	0	2.85
Example17	A-6	395	B-2	2.8	630	C-1	2.0	270	0.30	305	0	3.64
Example18	A-6	395	B-2	2.5	810	C-1	0.2	90	0.10	320	0	3.93
Example19	A-6	395	B-1	0.5	630	C-2	0.3	270	0.30	300	0	2.80
Example20	A-6	395	B-2	2.2	488	C-2	0.3	162	0.25	310	0	3.97
Example21	A-7	1,400	B-1	0.5	720	C-1	0.2	180	0.20	295	0	3.14
Example22	A-7	1,400	B-1	0.5	488	C-2	0.3	162	0.25	335	0	2.59
Example23	A-8	200	B-1	0.5	630	C-1	0.2	270	0.30	310	0	2.93
Example24	A-8	200	B-1	1.0	630	C-2	0.3	270	0.30	345	0	2.97
Example25	A-8	200	B-2	2.0	720	C-2	0.3	180	0.20	290	0	4.02
Example26	A-9	200	B-1	0.5	630	C-1	0.2	270	0.30	300	0	3.10
Example27	A-9	200	B-1	1.0	630	C-2	0.3	270	0.30	285	0	3.51

COMPARATIVE EXAMPLES 15-25

[0114] Other thermally conductive grease composition samples were prepared in the same manner as in the aforementioned Examples 15-27, except that the amounts of fillers used as Components (B) and (C) were each changed variously. The consistency, oil separation degree and thermal conductivity of each composition prepared were measured in the same ways as in each Example, and the measurement results obtained are shown in Table 6.

[0115] Additionally, the symbols A-6 to A-9, B-1, B-2, C-1 and C-2 used in Table 6 represent the same ingredients as those in Examples 15-27, respectively.

Table 6

	Component (A) (100wt%)		Component (B)			Component (C)						
	Species	Viscosity 25℃ (cs)	Species	Average particle size μm	Amount added (wt%)	Species	Average particle size μm	Amount added (wt%)	$\frac{(C)}{((B)+(C))}$	Consistency	Oil Separation Degree 150℃/24hr	Thermal Conductivity W/m°K
Compar.Ex.14	A-6	395	B-1	0.5	900	-	-	-	0	95	3.0	3.26
Compar.Ex.15	A-6	395	B-1	1.5	720	C-1	0.5	30	0.04	380	3.5	2.59
Compar.Ex.16	A-6	395	-	-	-	C-1	0.3	600	1.00	358	0	0.38
Compar.Ex.17	A-6	395	B-2	2.8	580	-	-	-	0	305	2.0	2.51
Compar.Ex.18	A-6	395	B-2	2.8	250	C-1	0.3	330	0.57	130	3.0	1.63
Compar.Ex.19	A-6	395	B-2	2.5	250	C-2	0.3	330	0.57	80	2.5	1.72
Compar.Ex.20	A-7	1,400	B-1	1.5	900	-	-	-	0	free of grease character		
Compar.Ex.21	A-8	200	B-1	0.5	825	C-1	0.3	275	0.25	78	1.0	2.93
Compar.Ex.22	A-8	200	B-1	0.5	360	C-1	0.3	90	0.20	340	0.5	1.80
Compar.Ex.23	A-9	200	-	-	-	C-2	2.5	580	1.00	355	0	1.13
Compar.Ex.24	A-9	200	B-2	2.0	250	C-2	0.5	300	0.55	free of grease character		

[0116] As can be seen from the data shown in Tables 5 and 6, the present thermally conductive silicone grease compositions had their thermal conductivity in the range of 2.59 to 4.02 W/m°K. In other words, the present compositions underwent considerable improvement in thermal conductivity over conventional grease compositions and the comparative compositions. Further, the present compositions had the consistency on the practically optimum level for the use as grease and satisfactory dispensation suitability.

Claims

1. A thermally conductive grease composition comprising:

(A) 100 weight parts of at least one base oil selected from the group consisting of liquid silicones, liquid hydrocarbons and fluorohydrocarbon oils, and
500-1,000 weight parts of a thermally conductive filler mixture constituted of (B) an inorganic filler having Mohs' hardness of at least 6 and thermal conductivity of at least 100 W/m°K and (C) an inorganic filler having Mohs' hardness of at most 5 and thermal conductivity of at least 20 W/m°K;
wherein the ratio of Component (C) to the sum total of Component (B) and Component (C) is from 0.05 to 0.5 by weight.

2. A thermally conductive grease composition according to claim 1, wherein the base oil is a liquid silicone, liquid hydrocarbon or fluorohydrocarbon oil having a viscosity of from 50 to 500,000 cs at 25°C.

3. A thermally conductive grease composition according to claim 1 or 2, wherein the base oil is a liquid silicone selected from organopolysiloxanes having compositional formula $R_aSiO_{(4-a)/2}$ wherein each R is a monovalent organic group and a is a number of from 1.8 to 2.3.

4. A thermally conductive grease composition according to claim 3, wherein the monovalent organic group as R is a methyl group, a phenyl group or an alkyl group containing 6 to 14 carbon atoms.

5. A thermally conductive grease composition according to claim 1 or 2, wherein the base oil is at least one liquid hydrocarbon selected from the group consisting of paraffin oil, naphthene oil, α-olefin oligomers, polybutenes, substituted aromatic compounds, polyalkylene glycols, diesters, polyol esters and phosphoric acid esters.

6. A thermally conductive grease composition according to claim 1 or 2, wherein the base oil is at least one fluorohydrocarbon oil selected from the group consisting of chlorofluorocarbons, fluoroesters and perfluoroalkyl ethers.

7. A thermally conductive grease composition according to any of claims 1 to 4, wherein the base oil as Component (A) is a liquid silicone and the thermally conductive inorganic filler as Component (B) is at least one filler selected from the group aluminum nitride powders or diamond powders.

8. A thermally conductive grease composition according to any of claims 1, 2, 5 and 6, wherein the base oil as Component (A) is a liquid hydrocarbon or a fluorohydrocarbon oil and the thermally conductive inorganic filler as Component (B) is at least one filler selected from consisting of aluminum nitride powders, silicon carbide powders and diamond powders.

9. A thermally conductive grease composition according to any of the preceding claims 1 to 8, wherein the thermally conductive inorganic filler as Component (C) is at least one filler selected from boron nitride powders or zinc oxide powders.

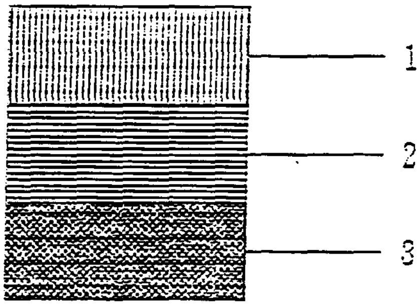


Fig.1

European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 98 30 8489

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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A	DATABASE WPI Section Ch, Week 8714 Derwent Publications Ltd., London, GB; Class A26, AN 87-096686 XP002104988 & JP 62 043492 A (TOSHIBA SILICONE KK) , 25 February 1987 * abstract * ---	1-4,8	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	4 June 1999	Kazemi, P

CATEGORY OF CITED DOCUMENTS

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 98 30 8489

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