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(54) Title: THERMALLY CONDUCTIVE SILICONE COMPOSITION

(57) Abstract: A thermally conductive composition contains, based on the weight of the thermally conductive composition, (A) from 1.0 to 4.0 weight-percent of an alkenyl-functional polyorganosiloxane; (B) a silyl-hydride functional polysiloxane crosslinker that contains at least two silyl-hydride groups per molecule; (C) from 93 to 96 weight-percent of thermally conductive fillers containing specific amounts of (C1-a) aluminum oxide particles having a D50 in a range of 10 to 40 micrometers, and optionally (C1-b) aluminum nitride particles having a D50 in a range of 10 to 40 micrometers, (C2) spherical aluminum particles having a D50 in a range of 1 to 5 micrometers, and (C3) a third thermally conductive filler having a D50 in a range of 0.1 to 0.6 micrometer and selected from the group consisting of zinc oxide particles, aluminum oxide particles, and mixtures thereof; and (D) a filler treating agent.

THERMALLY CONDUCTIVE SILICONE COMPOSITION

FIELD

The present invention relates to a thermally conductive silicone composition that contains thermally conductive fillers including a novel combination of at least three different thermally conductive
5 particles.

INTRODUCTION

An industry drive to smaller and more powerful electronic devices has increased demands on thermally conductive compositions useful for dissipating heat generated in such devices. The heat generated by the high power in the smaller devices would damage the device if not efficiently dissipated.
10 Particularly, advanced integrated circuit devices like CPU in consumer devices produce large amounts of heat due to the acceleration of operating speed. Thermally conductive interface materials are often used in electronics to thermally couple heat generating components and heat dissipating components.

A challenge with silicone grease compositions is to provide a combination of good thermal conductivity properties to efficiently transfer heat between coupled components, at the same time, being
15 easily extrudable or dispensable so as to allow precise application of the thermally conductive material on small components. In particular, it is desirable to provide a thermally conductive interface material that has an extrusion rate of at least 40 grams per minute as measured using the Extrusion Rate Test defined herein below and that cures to a material that has a thermal conductivity (TC) of at least 6.0 Watts per meter*Kelvin (W/m*K) as measured using a hot disk according to ISO 22007-2 and a thermal resistance
20 (TR) of no more than 0.12 degree Celsius square centimeter per Watt (°C*cm^2/W) as determined by ASTM D-5470. Aluminum (Al) filler particles have a high thermal conductivity of 200 W/m*K and can be used to afford the silicone composition with the above described high TC in applications where electrical insulation properties are not needed. However, due to the electrical conductivity of aluminum, addition of greater than 30% by weight of aluminum particles based on the silicone composition weight usually
25 compromises the electrical insulating properties of the silicone composition and the cured product, which make them not suitable for heat transfer involving high-voltage applications.

A thermally conductive grease compositions is usually applied between an electronic component and a member such as heat sink for efficiently releasing the heat from the electronic component. Incumbent silicone grease compositions usually comprise silicone fluids loaded with alumina (Al_2O_3) filler. When
30 such silicone grease compositions are targeted to achieve a thin bond line thickness (BLT) of 80 micrometers (μm) or less, the average particle size of Al_2O_3 filler needs to be in an appropriate range, enabling the composition to be compressed to fill thin gaps and meet the thermal resistance requirement (≤0.12 °C*cm^2/W). However, when using Al_2O_3 filler with an average particle size of 40 μm or less, it usually requires a high filler loading (e.g., greater than 94.5% by weight relative to composition weight)
35 for the silicone composition is to achieve the desired thermal conductivity of at least 6.0 W/m*K, which reduces the extrusion rate of the composition which can even become a powdery paste. Further, such a highly viscous composition cannot conform to fine irregularities on the surface of electronic components

and/or heat sinks, resulting in an increase of thermal resistance properties. Therefore, meeting these performance parameters is particularly challenging.

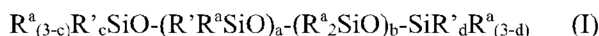
There remains a need to identify a thermally conductive composition that can simultaneously achieve the above described extrusion rate and thermal conductivity properties.

SUMMARY

The present invention provides a thermally conductive composition that has an extrusion rate (ER) of 40 grams per minute (g/min) or more as measured using the Extrusion Rate Test defined herein below and that cures to a material that has a thermal resistance (TR) of no greater than 0.12 degree Celsius square centimeter per Watt (°C*cm^2/W) according to ASTM D-5470 and a thermal conductivity (TC) of at least 6.0 Watts per meter*Kelvin (W/m*K) using a hot disk according to ISO 22007-2. The composition of the present invention is particularly suitable for use as a thermally conductive silicone grease that can achieve a Bond Line Thickness (BLT) of 80 μm or less, while still meeting the TR and TC requirements. Surprisingly, it has been determined such a composition can be prepared from a polysiloxane composition (also as "thermally conductive composition") that comprises a novel combination of specific amounts of at least three thermally conductive fillers different in types and/or particle size.

In a first aspect, the present invention is a thermally conductive composition comprising, based on the weight of the thermally conductive composition,

(A) from 1.0 to 4.0 weight-percent of an alkenyl-functional polyorganosiloxane having a viscosity in a range of 25 to 500 millipascal*seconds as determined by ASTM D445-21 at 25 degrees Celsius, wherein the alkenyl-functional polyorganosiloxane has an average chemical structure (I):



$$R^a_{(3-c)}R'_cSiO\text{-}(R'R^aSiO)_a\text{-}(R^a_2SiO)_b\text{-}SiR'_dR^a_{(3-d)} \qquad (I)$$

where R^a is independently in each occurrence an alkyl group having 1 to 6 carbon atoms or an aryl group having 6 to 10 carbon atoms, R' is independently in each occurrence an alkenyl group, subscript a $\geq$ 0, subscript b > 0, subscript c is 0 or 1, subscript d is 0 or 1, and $(a+c+d) \geq 2$;

(B) a silyl-hydride functional polysiloxane crosslinker that contains at least two silyl-hydride groups per molecule and that is present at a concentration to provide a molar ratio of silicon-bonded hydrogen atoms to alkenyl groups for the composition of 0.4:1 to 1.5:1;

(C) from 93 to 96 weight-percent of thermally conductive fillers comprising:

(C1-a) from 15 to 65 weight-percent of aluminum oxide particles having a D50 in a range of 10 to 40 micrometers,

(C1-b) from 0 to 40 weight-percent of aluminum nitride particles having a D50 in a range of 10 to 40 micrometers,

wherein the combined concentration of the aluminum oxide particles (C1-a) and the aluminum nitride particles (C1-b) is in a range of from 45 to 65 weight-percent;

(C2) from 10 to 30 weight-percent of spherical aluminum particles having a D50 in a range of 1 to 5 micrometers;

(C3) from 10 to 25 weight-percent of a third thermally conductive filler having a D50 in a range of

0.1 to 0.6 micrometer, wherein the third thermally conductive filler is selected from the group consisting of zinc oxide particles, aluminum oxide particles, and mixtures thereof; and

(D) a filler treating agent selected from the group consisting of a trialkoxysilyl diorganopolysiloxane, an alkyl trialkoxysilane, and mixtures thereof.

5 In a second aspect, the present invention is a process for using the thermally conductive composition of the first aspect. The process comprises the steps of: a) applying the thermally conductive composition on an electronic component, and b) curing the thermally conductive composition by heat.

In a third aspect, the present invention is an electronic article comprising the thermally conductive composition of the first aspect between and in contact with two components of the electronic article, 10 wherein the thermally conductive composition is in either a cured or non-cured form.

DETAILED DESCRIPTION

Test methods refer to the most recent test method as of the priority date of this document when a date is not indicated with the test method number. References to test methods contain both a reference to the testing society and the test method number. The following test method abbreviations and identifiers 15 apply herein: ASTM refers to ASTM International methods and ISO refers to International Organization for Standards.

Products identified by their tradename refer to the compositions available under those tradenames on the priority date of this document. "And/or" means "and, or as an alternative". All ranges include endpoints unless otherwise indicated. Unless otherwise stated, all weight-percent (wt%) values are relative 20 to composition weight.

"Spherical" shaped particles refer to particles that have an aspect ratio of 1.0 +/- 0.2. The aspect ratio of a particle is determined using scanning electron microscope (SEM) imaging and by taking the average ratio of the longest dimension (major axis) and shortest dimension (minor axis) of at least ten particles.

25 "Roundish" refers to a shape in which the corners of the particles are small, and the entire particles are single grain with less crystal edges. The roundish particles have an aspect ratio other than 1.0 +/- 0.2, may be elliptical, or the like, but does not include a sphere.

"Polyhedron" refers to a shape surrounded by a plurality of planes such as a hexahedron, an octahedron, and a dodecahedron. Each plane does not necessarily have the same shape.

30 "Irregular" shaped particles refer to a shape that does not have a fixed shape such as "spherical", "roundish", or "polyhedron". The irregular particles have an aspect ratio other than 1.0 +/- 0.2 and have sharp, uneven, different shape corners evident by SEM imaging.

Particle size of thermally conductive fillers (which is used interchangeable with "average particle size" and "D50") refers to the volume-weighted median value of particle diameter distribution (D50). D50 35 can be measured using a laser diffraction particle size analyzer such as a Mastersizer™ (trademark of Malvern Instruments Limited) 3000 laser diffraction particle size analyzer from Malvern Instruments.

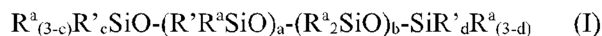
Viscosity of a polysiloxane is determined according to ASTM D445-21 at 25 degrees Celsius (°C)

unless otherwise stated. For example, a glass capillary Cannon-Fenske type viscometer can be used to determine the viscosity.

The thermally conductive composition of the present invention is a curable composition, that is, can undergo a crosslinking reaction ("curing"). In the present composition, the crosslinking reaction is a hydrosilylation reaction between alkenyl-functional polyorganosiloxane components and silyl-hydride (SiH) functional polysiloxane crosslinker.

The thermally conductive composition of the present invention comprises an alkenyl-functional polyorganosiloxane that has two or more alkenyl groups per molecule (component (A)). "Alkenyl" means a branched or unbranched, monovalent hydrocarbon group having one or more carbon-carbon double bonds. The alkenyl groups can be terminal, pendant, or a combination of both terminal and pendant. "Terminal" groups are on end siloxane groups of a molecule. "End" siloxane groups are attached to only one other siloxane group. "Pendant" groups are on interior siloxane group – siloxane groups bound to at least two other siloxane groups of the molecule. "Siloxane group" is a group containing SiO that is bound to another Si through the oxygen of the SiO. Desirably, the alkenyl-functional polydiorganosiloxane has an average of one or more terminally alkenyl groups per molecule. The alkenyl-functional polyorganosiloxane has a viscosity in a range of 25 to 500 millipascal*seconds (mPa*s). If the viscosity is too low, then separation of polymer matrix and fillers tends to occur, therefore, hurting physical properties of the composition. If the viscosity is too high, it may be difficult to incorporate sufficient fillers so as to achieve the desired TC and ER properties. The viscosity of the alkenyl-functional polyorganosiloxane is 25 to 500 mPa*s, and can be 25 mPa*s or more, 30 mPa*s or more, 40 mPa*s or more, 50 mPa*s or more, 60 mPa*s or more, 70 mPa*s or more, 75 mPa*s or more, 78 mPa*s or more, even 80 mPa*s or more while at the same time is 500 mPa*s or less, and can be 400 mPa*s or less, 300 mPa*s or less, 200 mPa*s or less, 150 mPa*s or less, 100 mPa*s or less, 90 mPa*s or less, even 80 mPa*s or less, desirably 30 to 100 mPa*s, as determined according to ASTM D445-21 at 25 °C, e.g., using a glass capillary Cannon-Fenske type viscometer. The alkenyl-functional polyorganosiloxane may be a combination of two or more alkenyl-functional polyorganosiloxanes that may differ in one or more properties selected from molecular weight, structure, siloxane units and sequence. When the alkenyl-functional polyorganosiloxane is a combination of more than one alkenyl-functional polyorganosiloxane then the viscosity is the combined viscosity of alkenyl-functional polyorganosiloxanes.

The alkenyl-functional polyorganosiloxane (A) useful in the present invention has an average chemical structure (I):



$$R^a_{(3-c)}R'_cSiO-(R'R^aSiO)_a-(R^a_2SiO)_b-SiR'_dR^a_{(3-d)} \quad (I)$$

where R^a is independently in each occurrence an alkyl group of 1 to 6 carbon atoms or an aryl group of 6 to 10 carbon atoms, R' is independently in each occurrence an alkenyl group, subscript a is zero or more (≥ 0), subscript b is greater than zero (>0), subscript c is 0 or 1, subscript d is 0 or 1, (a+c+d) is 2 or more (≥ 2).

Suitable alkyl groups for R^a may include, for example, methyl, ethyl, propyl (e.g., iso-propyl and/or

n-propyl), butyl (e.g., isobutyl, n-butyl, tert-butyl, and/or sec-butyl), pentyl (e.g., isopentyl, neopentyl, and/or tert-pentyl), hexyl, as well as branched saturated alkyl groups of 6 carbon atoms. Suitable aryl groups for R^a are exemplified by phenyl, tolyl, xylyl, naphthyl, benzyl, and dimethyl phenyl. Each R^a may be the same or different. Each R^a can be an alkyl group. Desirably, each R^a is independently methyl, ethyl, or propyl, and more desirably, each R^a is methyl.

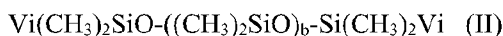
The alkenyl group for R' typically has from 2 to 8 carbon atoms, from 2 to 6 carbon atoms or from 2 to 4 carbon atoms. Suitable alkenyl groups may include vinyl, allyl, butenyl, and hexenyl. Particularly suitable alkenyl groups for R' vinyl, allyl, butenyl, and hexenyl. R' groups may be the same or different. Desirably, each R' is selected from vinyl or hexenyl. More desirably, each R' is vinyl.

Desirably, subscript a is zero, subscript c is 1, subscript d is 1, and each R^a is methyl.

Subscript a is the average number of ($R'R^aSiO$) groups per molecule. Subscript b is the average number of (R^a_2SiO) groups per molecule. Desirably, a quantity (a+b) is 20 to 600, and can be 25 or more, 30 or more, 40 or more, 50 or more, 60 or more, 70 or more, 80 or more, 90 or more, 100 or more, 120 or more, 140 or more, 160 or more, even 180 or more while at the same time is typically 600 or less, and can be 560 or less, 500 or less, 400 or less, 350 or less, 200 or less, 180 or less, 160 or less, 140 or less, 120 or less, 100 or less, 80 or less, 60 or less, even 40 or less, desirably, 25 to 60. Desirably, the value of subscript b is as described above for (a+b). Desirably, a quantity (a+c+d) is 2 or more, even 3 or more while at the same time is typically 30 or less, and can be 20 or less, 10 or less, or even 3 or less.

Examples of suitable alkenyl-functional polyorganosiloxanes include i) vinyldimethylsiloxy-terminated polydimethylsiloxane, ii) dimethylvinylsiloxy-terminated poly(dimethylsiloxane/methylvinylsiloxane), iii) dimethylvinylsiloxy-terminated polymethylvinylsiloxane, iv) trimethylsiloxy-terminated poly(dimethylsiloxane/methylvinylsiloxane), v) trimethylsiloxy-terminated polymethylvinylsiloxane, vi) dimethylvinylsiloxy-terminated poly(dimethylsiloxane/methylvinylsiloxane), or mixtures thereof.

Desirably, the alkenyl-functional polyorganosiloxane comprises, or consists of, one or any combination of more than one vinyldimethylsiloxy-terminated polydimethylpolysiloxane (A1) of an average chemical structure (II):

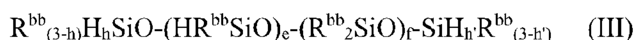


$$Vi(CH_3)_2SiO\text{-}((CH_3)_2SiO)_b\text{-}Si(CH_3)_2Vi \quad (II)$$

where Vi represents vinyl, and subscript b is the average number of ($(CH_3)_2SiO$) groups per molecule and has a value of 20 to 600, and can be 20 or more, 25 or more, 30 or more, 40 or more, 45 or more, 50 or more, 60 or more, 70 or more, 80 or more, 90 or more, 100 or more, 120 or more, 140 or more, 160 or more, even 180 or more while at the same time typically have a value of 600 or less, and can be 560 or less, 500 or less, 400 or less, 350 or less, 200 or less, 180 or less, 160 or less, 140 or less, 120 or less, 100 or less, 80 or less, 60 or less, 45 or more, even 40 or less, desirably from 20 to 200. For example, the alkenyl-functional polyorganosiloxane can be a vinyldimethylsiloxy terminated polydimethylsiloxane having a viscosity of 60 mPa*s and containing 1.55 weight-percent (wt%) vinyl groups relative to molecular weight such as that available from Gelest under the name HMS-501.

The concentration of component (A) the alkenyl-functional polyorganosiloxane may be from 1.0 to 4.0 wt%, and can be 1.0 wt% or more, 1.5 wt% or more, 1.8 wt% or more, 2.0 wt% or more, 2.4 wt% or more, 2.5 wt% or more, 2.6 wt% or more, 2.7 wt% or more, 2.8 wt% or more, 2.9 wt% or more, even 3.0 wt% or more while at the same time is generally 4.0 wt% or less, and can be 3.8 wt% or less, 3.5 wt% or less, 3.3 wt% or less, 3.0 wt% or less, 2.9 wt% or less, 2.8 wt% or less, 2.7 wt% or less, or even 2.6 wt% or less, desirably, from 1.8 to 2.8 wt%, based on the weight of the thermally conductive composition.

The thermally conductive composition of the present invention comprises a silyl-hydride (SiH) functional polysiloxane crosslinker (component (B), also referred to as "SiH crosslinker"). The SiH functional polysiloxane crosslinker contains at least two silyl-hydride groups (i.e., containing at least two silicon-bonded hydrogen atoms), or even 3 or more, per molecule. The SiH groups can be pendant, terminal or a combination of both pendant and terminal. The SiH functional polysiloxane crosslinker can have an average chemical structure (III):



$$R^{bb}_{(3-h)}H_hSiO\text{-}(HR^{bb}SiO)_e\text{-}(R^{bb}_2SiO)_f\text{-}SiH_{h'}R^{bb}_{(3-h')} \quad \text{(III)}$$

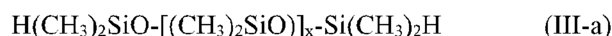
where R^{bb} is independently in each occurrence selected from an alkyl group having from 1 to 6 carbon atoms and phenyl; subscripts h and h' each are independently in each occurrence selected from a value in a range of zero to 3 provided that the combination of e, h, and h' is at least 2; subscript e is zero to 30; and subscript f is 5 to 200.

The R^{bb} group can have one carbon or more, 2 carbons or more, 3 carbons or more, 4 carbons or more, even 5 carbons or more while at the same time 6 carbons or fewer, 5 carbons or fewer, 4 carbons or fewer, 3 carbons or fewer, even 2 carbons or fewer. Desirably, the R^{bb} group is independently in each occurrence selected from methyl and phenyl. H is a hydrogen atom.

Subscripts h and h' refer to the average number of terminal hydrogen atoms on either end and each are independently in each occurrence selected from a value in a range of zero to 3 provided that the combination of e, h, and h' is at least 2. Desirably, h and h' are independently in each occurrence 0 or more, 1 or more, even 2 or more while at the same time 3 or less, 2 or less, even 1 or less. More desirably, h and h' have the same value. Most desirably, h and h' are both zero. Subscript e is the average number of $(HR^{bb}SiO)$ groups per molecule. If h and h' are both zero then e is in a range of 2 to 30. If h and h' are both non-zero then subscript e can be zero to 30 provided the combination of e, h and h' is 2 or more. Desirably, subscript e is 1 or more, and can be 2 or more and can be 3 or more, 4 or more, 5 or more, 6 or more, 7 or more, 8 or more, even 9 or more while at the same time typically is 30 or less, and can be 25 or less, 20 or less, 15 or less, 10 or less, 9 or less, 8 or less, 7 or less, 6 or less, 5 or less, 4 or less, 3 or less, even 2 or less. Subscript f is the average number of (R^{bb}_2SiO) groups per molecule. Generally, subscript f is 5 or more, 10 or more, 20 or more, 25 or more, 30 or more, 40 or more, 50 or more, and can be 75 or more, 100 or more, 125 or more, 150 or more, 175 or more, even 190 or more while at the same time is typically 200 or less, 175 or less, 150 or less, 125 or less, 100 or less, 75 or less, 50 or less, 40 or less, 30 or less, 25 or less, or even 20 or less.

Desirably, the SiH functional polysiloxane crosslinker comprises one or more polysiloxane having

chemical structures selected from (III-a), (III-b), or combinations thereof:


$$H(CH_3)_2SiO\text{-}[(CH_3)_2SiO)]_x\text{-}Si(CH_3)_2H \quad \text{(III-a)}$$

$$(CH_3)_3SiO\text{-}[(CH_3)HSiO]_y[(CH_3)_2SiO]_z\text{-}Si(CH_3)_3 \quad \text{(III-b)}$$

where subscript x is 10 to 100, and can be 10 to 60, 10 to 40, or 10 to 20; subscript y is 2 to 30, and can be 2 to 20, 2 to 10, or 2 to 5; and subscript z is 3 to 100, and can be 3 to 30, 3 to 20, or 3 to 10.

Desirably, component (B) is a combination of a SiH crosslinker of (III-a) and a SiH crosslinker of (III-b).

The SiH functional polysiloxane crosslinker may have a silicon-bonded hydrogen atom ("SiH") content (i.e., SiH content) of 0.01 wt% to 1.0 wt%, and can be 0.01 wt% or more, 0.05% wt% or more, 0.1 wt% or more, 0.11 wt% or more, 0.15 wt% or more, 0.20 wt% or more, 0.25 wt% or more, 0.30 wt% or more, even 0.35 wt% or more while at the same time is generally 1.0 wt% or less, and can be 0.9 wt% or less, 0.8 wt% or less, 0.7 wt% or less, 0.6 wt% or less, 0.5 wt% or less, 0.4 wt% or less, even 0.36 wt% or less, desirably, 0.1 wt% to 0.8 wt%. SiH content refers to weight percentages of the silicon bonded hydrogen atoms relative to the molecular weight of the SiH functional polysiloxane crosslinker and can be determined using Fourier Transfer Infra-Red (FTIR) spectroscopy.

Suitable SiH functional polysiloxane crosslinkers may include, for example, trimethylsiloxy-terminated poly(dimethylsiloxane/methylhydrogensiloxane), trimethylsiloxy-terminated polymethylhydrogensiloxane, hydrogen-terminated polydimethylsiloxane, hydrogen-terminated poly(dimethylsiloxane/methylhydrogensiloxane), or mixtures thereof. The crosslinker may be a combination of two or more crosslinkers that may differ in one or more properties selected from molecular weight, structure, siloxane units and sequence, such as a mixture of trimethyl terminated dimethyl-co-hydrogen methyl polysiloxane and a hydride terminated polydimethylsiloxane. Specific examples of SiH crosslinkers include those having average chemical structure of $Me_3SiO(Me_2SiO)_7(MeHSiO)_3SiMe_3$, $Me_3SiO(Me_2SiO)_{108}(MeHSiO)_{10}SiMe_3$, $Me_3SiO(Me_2SiO)_{22}(MeHSiO)_2SiMe_3$, $HMe_2SiO(Me_2SiO)_{25}(MeHSiO)_1SiMe_2H$, or $H(Me)_2SiO\text{-}[Me_2SiO)]_{14}\text{-}SiMe_2H$, where Me represents methyl, or mixtures thereof. Suitable commercially available SiH crosslinkers include those available under the names HMS-071, HMS-501 and DMS-H11 all available from Gelest. Desirably, the SiH crosslinker can be one or a combination of both polymers selected from a group consisting of: (B-i) trimethyl terminated dimethyl-co-hydrogen methyl polysiloxane with a viscosity of 10 to 14 mPa*s at 25 °C and a SiH content of 0.36 wt%; and (B-ii) hydride terminated polydimethylsiloxane having a viscosity in a range of 7-10 mPa*s 25 °C and a SiH content of 0.16 wt%.

The concentration of the SiH functional polysiloxane crosslinker is sufficient to provide a molar ratio of silicon-bonded hydrogen atoms from the crosslinker to alkenyl groups (desirably, vinyl groups) in the thermally conductive composition (also as "SiH/Vi ratio") in a range of from 0.4:1 to 1.5:1, and can be 0.4:1 or higher, 0.5:1 or higher, 0.6:1 or higher, 0.7:1 or higher, 0.8:1 or higher, even 0.9:1 or higher while at the same time is 1.5:1 or less, and can be 1.4:1 or less, 1.2:1 or less, 1:1 or less, 0.9:1 or less, 0.8:1 or less, 0.7:1 or less, or even 0.6:1 or less. Desirably, the SiH/Vi ratio is 0.6:1 to 1.2:1. The SiH/Vi ratio

determines the extent of crosslinking that occurs when the thermally conductive composition cures. If the SiH/Vi ratio is too low, then the composition tends not to be sufficiently cured. If the SiH/Vi ratio is too high then the composition cures so much it may become brittle and suffer from surface cracking.

The thermally conductive composition of the present invention comprises thermally conductive fillers (component (C)). Component (C) comprises, and can consist of, a combination of at least three, or even four, different thermally conductive fillers, i.e., (C1), (C2), and (C3), and optionally (C4), described below.

The thermally conductive fillers (C) comprise the first thermally conductive filler (C1) that comprises (C1-a) aluminum oxide particles having a D50 in a range of 10 to 40 μm, and optionally (C1-b) aluminum nitrite particles having a D50 in a range of 10 to 40 μm. The aluminum oxide particles (C1-a) and the aluminum nitrite particles (C1-b) may each independently have a D50 particle size of 10 μm to 40 μm, and can have a D50 of 10 μm or more, 12 μm or more, 15 μm or more, 20 μm or more, 25 μm or more, 30 μm or more, even 35 μm or more while at the same time have a D50 particle size of 40 μm or less, and can have a D50 of 38 μm or less, 35 μm or less, 32 μm or less, 30 μm or less, 28 μm or less, 25 μm or less, 22 μm or less, 20 μm or less, 18 μm or less, or even 15 μm or less. Desirably, the aluminum oxide particles (C1-a) have a D50 in a range of 15 to 35 μm, and more desirably, 20 to 35 μm. Desirably, the aluminum nitride particles (C1-b) have a D50 in a range of 10 to 30 μm, more desirably, 10 to 20 μm. The concentration of the aluminum oxide particles (C1-a) is from 15 to 65 wt%, and can be 15 wt% or more, 20 wt% or more, 25 wt% or more, 30 wt% or more, 35 wt% or more, 40 wt% or more, 45 wt% or more, 50 wt% or more, 55 wt% or more, even 58 wt% or more while at the same time is 65 wt% or less, and can be 62 wt% or less, 60 wt% or less, 58 wt% or less, 55 wt% or less, 52 wt% or less, 50 wt% or less, 45 wt% or less, 40 wt% or less, 35 wt% or less, 30 wt% or less, or even 28 wt% or less, desirably, 25 wt% to 60 wt%, more desirably, 40 wt% to 60 wt%, based on the weight of the thermally conductive composition. The concentration of aluminum nitride particles (C1-b) is in a range of from zero to 40 wt%, and can be 5 wt% or more, 15 wt% or more, even 24 wt% or more while at the same time is 40 wt% or less, and can be 30 wt% or less, 27 wt% or less, 20 wt% or less, 18 wt% or less, or even 10 wt% or less, desirably, zero to 30 wt% or 20 wt% to 30 wt%, based on the weight of the thermally conductive composition. The combined concentration of the aluminum oxide particles (C1-a) and the aluminum nitride particles (C1-b) (i.e., the total concentration of the first thermally conductive filler (C1)) is from 45 to 65 wt%, and can be 46 wt% or more, 48 wt% or more, 50 wt% or more, 51 wt% or more, 52 wt% or more, 53 wt% or more, 54 wt% or more, 55 wt% or more, 56 wt% or more, 57 wt% or more, even 58% or more while at the same time is 65 w% or less, and can be 64 wt% or less, 63 wt% or less, 62 wt% or less, 61 wt% or less, 60 wt% or less, 59 wt% or less, or even 58 wt%, based on the total weight of the thermally conductive composition. The first thermally conductive filler (C1) can consist of the aluminum oxide particles (C1-a). Alternatively, the thermally conductive filler (C1) can be a blend of from 25 to 45 wt% of the aluminum oxide particles (C1-a) and from 15 to 30 wt% of the aluminum nitride particles (C1-b). The first thermally conductive filler (C1) may comprise irregular, spherical, roundish, or polyhedron particles, or combinations of two or more

thermally conductive fillers different in type, shape or particle size as long as each having a D50 within 10 to 40 μm. The first thermally conductive filler (C1) can be roundish, spherical, irregular, and combinations thereof. Desirably, the first thermally conductive filler (C1) comprises roundish or spherical aluminum oxide particles.

5 The second thermally conductive filler (C2) is spherical aluminum particles having a D50 particle size of from 1 to 5 μm, and can have a D50 of 1 μm or more, 1.1 μm or more, even 1.5 μm or more while at the same time has a D50 particle size of 5 μm or less, and can have a D50 of 4.5 μm or less, 4 μm or less, 3.5 μm or less, 3 μm or less, 2.5 μm or less, even 2 μm or less, or even 1.5 μm or less, desirably, from 1 to 3 μm. The concentration of the spherical aluminum particles (C2) is from 10 to 30 wt%, and can be 10 10 wt% or more, 12 wt% or more, 14 wt% or more, 15 wt% or more, 16 wt% or more, 18 wt% or more, 20 wt% or more, 21 wt% or more, 22 wt% or more, even 23 wt% or more while at the same time is 30 wt% or less, and can be 29 wt% or less, 27 wt% or less, 25 wt% or less, 23 wt% or less, or even 21 wt% or less, desirably from 15 to 30 wt%, more desirably from 20 to 25 wt%, based on the weight of the thermally conductive composition.

15 The third thermally conductive filler (C3) is a thermally conductive filler having a D50 in a range of from 0.1 to 0.6 μm, and can have a D50 of 0.1 μm or more, 0.12 μm or more, 0.15 μm or more, 0.2 μm or more, 0.3 μm or more, even 0.4 μm or more while at the same time has a D50 particle size of 0.6 μm or less, and can be 0.5 μm or less, 0.4 μm or less, 0.3 μm or less, 0.2 μm or less, or even 0.15 μm or less, desirably, from 0.1 to 0.5 μm. The third thermally conductive filler particles can have any shape such as 20 spherical, irregular, roundish or polyhedron. The third thermally conductive filler may be selected from one or any combination of more than one of zinc oxide and aluminum oxide. Desirably, the third thermally conductive filler is zinc oxide particles, such as irregular zinc oxide. The concentration of the third thermally conductive filler (C3) may be from 10 to 25 wt%, and can be 10 wt% or more, 11 wt% or more, 12 wt% or more, 13 wt% or more, 14 wt% or more, even 14.5 wt% or more while at the same time is 25 25 wt% or less, and can be 23 wt% or less, 22 wt% or less, 20 wt% or less, 21 wt% or less, 19 wt% or less, 18 wt% or less, 17 wt% or less, 15 wt% or less, or even 14.7 wt% or less, desirably, from 14 to 22 wt%, more desirably, from 14 to 20 wt%, based on the weight of the thermally conductive composition. Desirably, the third thermally conductive filler (C3) is irregular zinc oxide.

The thermally conductive filler may comprise or be free of (C4) a fourth thermally conductive filler 30 that is other than (C1), (C2), and (C3) described above. The concentration of the fourth thermally conductive filler (C4) is zero to 10 wt%, and can be 1 wt% or more, 2 wt% or more, 4 wt% or more, 6 wt% or more, even 8 wt% or more while at the same time is 10 wt% or less, and can be 9 wt% or less, 7 wt% or less, 5 wt% or less, 3 wt% or less, or even 1 wt% or less, based on the weight of the thermally conductive composition. The thermally conductive filler (C4) may have a D50 particle size in a range of from 10 to 40 35 μm, and can have a D50 of 10 μm or more, 20 μm or more, 30 μm or more, even 35 μm or more while at the same time has a D50 particle size of 40 μm or less, and can have a D50 of less than 40 μm, 25 μm or less, or even 15 μm or less. The fourth thermally conductive filler (C4) may be selected from one or any

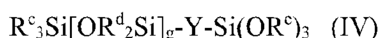
combination of more than one of boron nitride, diamond, magnesium oxide, and additional aluminum particles that is other than (C2), e.g., aluminum particles having different shapes and/or D50 from (C2). Desirably, the fourth thermally conductive filler (C4) is boron nitride particles. The fourth thermally conductive filler (C4) particles can have any shape such as spherical, irregular, roundish or polyhedron. Desirably, the total concentration of aluminum particles (including (C2) and additional aluminum particles for (C4) if used) in the composition is less than 40 wt%, less than 35 wt%, or even less than 30 wt%, based on the weight of the thermally conductive composition.

Desirably, the thermally conductive filler (C) comprises or consists of: from 45 to 60 wt% of spherical or roundish aluminum oxide particles having a D50 of 15 to 35 µm, from 20 to 25 wt% of spherical aluminum particles having a D50 in a range of 1 to 5 µm, and from 14 to 20 wt% of irregular zinc oxide particles having a D50 in a range of 0.1 to 0.5 µm, based on the weight of the thermally conductive composition.

Alternatively, the thermally conductive filler (C) may comprise or consist of: (C1) from 25 to 45 wt% of (C1-a) the aluminum oxide particles having a D50 in a range of 15 to 35 µm, and from 15 to 30 wt% of (C1-b) the aluminum nitride particles having a D50 in a range of 10 to 20 µm; (C2) from 15 to 30 wt% of spherical aluminum particles having a D50 in a range of 1 to 5 µm; and (C3) from 14 to 22 wt% of irregular zinc oxide particles having a D50 in a range of 0.1 to 0.5 µm, based on the weight of the thermally conductive composition.

The total concentration of thermally conductive fillers in the thermally conductive composition may be from 93 to 96 wt%, and can be 93 wt% or more, 93.5 wt% or more, 94 wt% or more, 94.4 wt% or more, 94.5 wt% or more, 95 wt% or more, 95.4 wt% or more, even 95.5 wt% or more while at the same time is 96 wt% or less, and can be 95.5 wt% or less, 95 wt% or less, even 94.5 wt% or less, based on the weight of the thermally conductive composition. Desirably, the thermally conductive fillers (C) in the composition are selected from the group consisting of aluminum oxide, aluminum nitride, aluminum, and zinc oxide; more desirably, the thermally conductive fillers are selected from the group consisting of aluminum oxide, aluminum, and zinc oxide.

The thermally conductive composition of the present invention comprises a filler treating agent (component (D)). Component (D) may be selected from a trialkoxysilyl diorganopolysiloxane, an alkyl trialkoxysilane, or mixtures thereof. Component (D) is one or a combination of more than one filler treating agent. Component (D) the filler treating agent may comprise, or consists of, one or any combination of more than one trialkoxysilyl diorganopolysiloxane, which is a diorganopolysiloxane that contains a -$Si(OR^e)_3$ group, where R^e is independently in each occurrence as described for R^e herein below in (IV). Desirably, the trialkoxysilyl diorganopolysiloxane is a mono-trialkoxysiloxy terminated diorganopolysiloxane. Suitable monotrialkoxysiloxy-terminated diorganopolysiloxanes include those having the average chemical structure (IV):



$$R^c_3Si[OR^d_2Si]_g\text{-}Y\text{-}Si(OR^e)_3 \quad (IV)$$

where R^c, R^d, and R^e are each independently in each occurrence hydrocarbon groups (hydrocarbyls)

having 1 to 10 carbon atoms such as alkyl and aryl groups, for example, having 1 or more, 2 or more, 3 or more, 4 or more, 5 or more, 6 or more, 7 or more, even 8 or more carbon atoms while at the same time typically having 10 or fewer, 8 or fewer, 6 or fewer, 4 or fewer, even 2 or fewer carbon atoms; and subscript g typically has a value of 20 to 150, can be 20 or more, 25 or more, 30 or more, 40 or more, 50 or more, 60 or more, 70 or more, 80 or more, 90 or more, 100 or more, or even 110 or more, while at the same time typically has a value of 150 or less, and can be 130 or less, 125 or less, 120 or less, 110 or less, 100 or less, 90 or less, 80 or less, 70 or less, 60 or less, 50 or less, 40 or less, or even 30 or less; and Y is O or $[OSiR^d_2](CH_2)_n$, where R^d is described above and subscript n has a value of 3 to 20, 3 to 10, or 3 to 6; desirably Y is O. Desirably, subscript g has a value in a range of 25 to 110. Each R^c, R^d, and R^e can be the same or different. Suitable alkyl groups for R^c, R^d, and R^e are exemplified by methyl, ethyl, propyl (e.g., iso-propyl and/or n-propyl), butyl (e.g., isobutyl, n-butyl, tert-butyl, and/or sec-butyl), pentyl (e.g., isopentyl, neopentyl, and/or tert-pentyl), hexyl, as well as branched saturated hydrocarbon groups of 6 carbon atoms. R^c, R^d, and R^e each can be independently an alkyl group such as methyl, ethyl, and propyl. Desirably, each R^c, R^d, and R^e is methyl. Suitable aryl groups for R^c, R^d, and R^e may include phenyl and dimethyl phenyl. A particularly desirable monotrialkoxysiloxy-terminated diorganopolysiloxane is a monotrimethoxysiloxy and trimethylsiloxy terminated polydimethylsiloxane such as those having the average chemical formula $(CH_3)_3SiO[(CH_3)_2SiO]_{30}Si(OCH_3)_3$. Suitable mono-trialkoxysiloxy terminated dimethylpolysiloxanes can be synthesized according to the teachings in US2006/0100336.

Component (D) the filler treating agent may comprise or be free of one or a combination of more than one alkyl trialkoxysilane. Suitable alkyl trialkoxysilanes include those having the chemical formula (V):

$$R^fSi(OR^g)_3 \qquad (V)$$

where R^f is independently in each occurrence an alkyl group having 1 to 20 carbon atoms, and can be 6 or more, 7 or more, 8 or more, 9 or more, or even 10 or more carbon atoms, while at the same time having 20 or less, and can be 18 or less, 16 or less, 14 or less, 12 or less, or even 10 or less carbon atoms; and R^g is independently in each occurrence an alkyl having 1 to 6 carbon atoms, and can be 1 or more, 2 or more, 3 or more, 4 or more, even 5 or more carbon atoms while at the same time generally having 6 or less, 5 or less, 4 or less, 3 or less, or even 2 or less carbon atoms. Desirably, R^f is independently in each occurrence an alkyl group having 6 to 12 carbon atoms. R^g is desirably methyl so as to form methoxyl groups attached to the silicon atom. A particularly desirable alkyl trialkoxysilane is n-decyltrimethoxysilane, n-octyltrimethoxysilane, or a mixture thereof. Suitable alkyl trialkoxysilanes include n-decyltrimethoxysilane available from The Dow Chemical Company as DOWSIL™ Z-6210 Silane or under the name SID2670.0 from Gelest (DOWSIL is a trademark of The Dow Chemical Company).

Component (D) the filler treating agent useful in the present invention may be present at a total concentration of from 0.5 to 2.5 wt%, and can be 0.5 wt% or more, 0.6 wt% or more, 0.7 wt% or more, 0.8 wt% or more, 0.9 wt% or more, 1.0 wt% or more, 1.2 or more, 1.3 wt% or more, 1.4 wt% or more, 1.5 wt%

or more, 1.6% or more, even 1.7% or more while at the same time is typically 2.5 wt% or less, and can be 2.4% or less, 2.3 wt% or less, 2.2 wt% or less, 2.1 wt% or less, 2.0 wt% or less, or even 1.9 wt% or less, based on the weight of the thermally conductive composition. Desirably, the monotrialkoxysiloxy-terminated diorganopolysiloxane is present at a concentration of from 0.5 to 2.5 wt%, and can be 0.5 wt% or more, 0.6 wt% or more, 0.7 wt% or more, 0.8 wt% or more, 0.9 wt% or more, 1.0 wt% or more, 1.1 wt% or more, 1.2 wt% or more, 1.5 wt% or more even 1.6 wt% or more while at the same time is typically present at a concentration of 2.5 wt% or less, and can be 2.4 wt% or less, 2.2 wt% or less, 2.0 wt% or less, 1.8 wt% or less, even 1.7 wt% or less, based on the weight of the thermally conductive composition. At the same time, or alternatively, the alkyltrialkoxysilane may be present at a concentration of from zero to 0.4 wt%, and can be zero or more, 0.01 wt% or more, 0.05 wt% or more, 0.1 wt% or more, 0.14 wt% or more, even 0.15 wt% or more while at the same time is typically present at a concentration of 0.5 wt% or less, and can be 0.4 wt% or less, 0.3 wt% or less, or even 0.2 wt% or less, based on the weight of the thermally conductive composition. Desirably, the filler treating agent (D) comprises from 1.5 to 2.0 wt% of the monotrialkoxysiloxy-terminated diorganopolysiloxane and from 0.1 to 0.3 wt% of the alkyltrialkoxysilane, based on the weight of the thermally conductive composition.

The thermally conductive composition of the present invention may comprise or be free of one or more platinum (Pt)-based hydrosilylation reaction catalyst (component (E)). Such hydrosilylation reaction catalyst may include compounds and complexes such as platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Karstedt's catalyst), H_2PtCl_6, di-μ.-carbonyl di-.π.-cyclopentadienyldinickel, platinum-carbonyl complexes, platinum-divinyltetramethyldisiloxane complexes, platinum cyclovinylmethylsiloxane complexes, platinum acetylacetonate (acac), platinum black, platinum compounds such as chloroplatinic acid, chloroplatinic acid hexahydrate, a reaction product of chloroplatinic acid and a monohydric alcohol, platinum bis(ethylacetoacetate), platinum bis(acetylacetonate), platinum dichloride, and complexes of the platinum compounds with olefins or low molecular weight organopolysiloxanes or platinum compounds microencapsulated in a matrix or core-shell type structure. The hydrosilylation reaction catalyst can be part of a solution that includes complexes of platinum with low molecular weight organopolysiloxanes that include 1,3-diethenyl-1,1,3,3-tetramethyldisiloxane complexes with platinum. These complexes may be microencapsulated in a resin matrix (typically, in a phenyl resin) or non-encapsulated. The resin matrix for microencapsulating the complexes can be a phenyl resin, an acrylate polymer, a polycarbonate, or other resin matrix which has a melting point less than 150 °C to release Pt during heat curing. Exemplary hydrosilylation reaction catalysts are described in U.S. Patents 3,159,601 and 3,220,972, and encapsulated platinum catalysts described in WO2014017671A1. The catalyst can be 1,3-diethenyl-1,1,3,3-tetramethyldisiloxane complex with platinum. Platinum-based hydrosilylation reaction catalysts are commercially available, for example, SYL-OFF™ 4000 Catalyst, SYL-OFF 4500 Catalyst, and SYL-OFF 2700 Catalyst are available from The Dow Chemical Company (SYL-OFF is a trademark of The Dow Chemical Company). Two different catalysts (e.g., E1 and E2) that activate at different temperatures can be added. The two different catalysts may be

(E1) 1,3-diethenyl-1,1,3,3-tetramethyldisiloxane complex with platinum, and (E2) an encapsulated platinum catalyst, such as 1,3-diethenyl-1,1,3,3-tetramethyldisiloxane complex with platinum which is encapsulated in dimethyl siloxane with phenyl silsesquioxane.

The amount of component (E) the platinum-based hydrosilylation reaction catalyst is sufficient to provide 0.5 part per million (ppm) to 30 ppm, and can be 0.5 ppm or more, 5 ppm or more, 10 ppm or more, 20 ppm or more, even 30 ppm or more while at the same time is generally even 30 ppm or less, of the platinum, by weight based on the weight of the thermally conductive composition. Alternatively, the amount of the platinum-based hydrosilylation reaction catalyst may be 0.01 wt% to 0.6 wt%, and can be 0.01 wt% or more, 0.03 wt% or more, 0.04 wt% or more, 0.05 wt% or more, even 0.06 wt% or more while at the same time is typically 0.6 wt% or less, and can be 0.5 wt% or less, 0.4 wt% or less, 0.3 wt% or less, 0.2 wt% or less, 0.1 wt% or less, 0.09 wt% or less, 0.08 wt% or less, 0.07 wt% or less, or even 0.06 wt% or less, based on the weight of the thermally conductive composition.

The thermally conductive composition of the present invention may comprise or be free of one or a combination of more than one hydrosilylation reaction inhibitor (Component (F), also as "inhibitor"). Inhibitors can serve to stabilize the thermally conductive composition from premature curing and provide storage stability to the composition. Examples of suitable inhibitors include any one or any combination of more than one of acetylene-type compounds such as 2-methyl-3-butyn-2-ol; 3-methyl-l-butyn-3-ol; 3,5-dimethyl- l-hexyn-3-ol; 2-phenyl-3-butyn-2-ol;3-phenyl-l-butyn-3-ol; 1-ethynyl-1-cyclohexanol; 1,1-dimethyl-2-propynyl)oxy)trimethylsilane; and methyl(tris(l,l-dimethyl-2-propynyloxy))silane; ene-yne compounds such as 3-methyl-3-penten-l-yne and 3,5-dimethyl-3-hexen-l-yne; triazols such as benzotriazole; hydrazine-based compounds; phosphines-based compounds; mercaptan-based compounds; cycloalkenylsiloxanes including methylvinylcyclosiloxanes such as l,3,5,7-tetramethyl-1,3,5,7-tetravinyl cyclotetrasiloxane and l,3,5,7-tetramethyl-l,3,5,7-tetrahexenyl cyclotetrasiloxane.

The concentration of component (F) the inhibitor may be zero to 0.1 wt%, and can be 0.001 wt% or more, 0.002 wt% or more, even 0.003 wt% or more while at the same time is typically 0.1 wt% or less, and can be 0.05 wt% or less, 0.01 wt% or less, 0.005 wt% or less, 0.004 wt% or less, even 0.003 wt% or less, based on the weight of the thermally conductive composition.

The thermally conductive composition of the present invention may comprise or be free of other optional components including any one or any combination of more than one of the following components: heat stabilizers and/or pigments (such as copper phthalocyanine powder), thixotropic agents, fumed silica (desirably, surface treated), and spacer additives (such as glass beads). The total concentration for these additional components can be in a range of from zero to 0.6 wt%, and can be zero or more, 0.1 wt% or more, 0.2 wt% or more, 0.3 wt% or more, 0.4 wt% or more, even 0.5 wt% or more while at the same time is typically 0.6 wt% or less, and can be 0.5 wt% or less, 0.4 wt% or less, 0.3 wt% or less, 0.2 wt% or less, 0.1 wt% or less, or even 0.05 wt% or less, based on the weight of the thermally conductive composition.

The thermally conductive composition of the present invention may comprise or be free of one or a combination of more than one solvent. The concentration of solvent can be less than 0.01 wt%, less than

0.005 wt%, or even zero, based on the weight of the thermally conductive composition. Desirably, the thermally conductive composition is substantially free of a solvent, i.e., contains no solvent or may contain trace amounts of residual solvents from delivery of starting materials in the composition. The concentration of the solvent can be measured by gas chromatography (GC). If the amount of solvents is too high, voids tend to be generated during curing the thermally conductive composition, which gives poor surface appearance or even results in a decreased thermal conductivity. The solvent can be an organic solvent such as an aliphatic or aromatic hydrocarbon, which is saturated or unsaturated, such as benzene, toluene, xylene, hexane, heptane, octane, iso-paraffin, hydrocarbon compounds of 8 to 18 carbon atoms and at least one aliphatic unsaturation per molecule such as tetradecene; a ketone such as acetone, methyl ethyl ketone, or methyl isobutyl ketone; an ester acetate such as ethyl acetate or isobutyl acetate; an ether such as a glycol ether such as propylene glycol methyl ether, dipropylene glycol methyl ether, and propylene glycol n-butyl ether, diisopropyl ether or 1,4-dioxane; a cyclic or linear siloxane having an average degree of polymerization from 3 to 10 such as hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, and/or decamethylcyclopentasiloxane; or mixtures thereof. The thermally conductive composition does not require the use of any solvents such as those described above while still achieving the desired ER (i.e., good processability) and TC properties below.

The thermally conductive composition of the present invention achieves an extrusion rate (ER) of 40 g/min or more. At the same time, the thermally conductive composition of the present invention, upon curing, provides a thermal resistance (TR) of no more than 0.12 °C*cm^2/W and a thermal conductivity (TC) of at least 6.0 W/m*K. Determine extrusion rates herein at a pressure of 0.62 MegaPascals (MPa) and 25 °C with a standard 30 cubic centimeters EFD syringe package. The thermally conductive composition can have an extrusion rate of 40 g/min or more, can be 45 g/min or more, 55 g/min or more, 60 g/min or more, 80 g/min, 90 g/min or more, or even 100 g/min or more. ER is a useful characteristic as a measure of extrudability, viscosity, dispensability, which, for example, makes the thermally conductive composition easily dispensable for applying onto another material such as electronic components or heat sinks and ensures application efficiency during a production process. TR can be measured according to ASTM D-5470 at a pressure of 40 psi (275.8 kilopascals), for example, at 80 °C for 15 minutes using a thermal resistance and conductivity measurement apparatus such as LonGwin Model LW 9389 TIM thermal conductivity and resistance tester. The thermally conductive composition can provide a TR of 0.11 °C*cm^2/W or less, 0.10 °C*cm^2/W or less, 0.09 °C*cm^2/W or less, or even 0.08 °C*cm^2/W or less. TC properties can be measured using a hot disk according to ISO 22007-2 with cured samples. The thermally conductive composition can provide a TC of 6.0 W/m*K or more, 6.5 W/m*K or more, 7 W/m*K or more, or even 8.0 W/m*K or more. The thermally conductive composition can achieve a Bond Line Thickness (BLT) of 80 micrometers (μm) or less, and can have a BLT of 70 μm or less, 60 μm or less, or even 50 μm or less. Further details for evaluating the above properties may be found in the Examples section below. Having such a high ER (being easily dispensable), at the same time, both a low TR and a high TC (affording an efficient thermal dissipation) makes the thermally conductive composition

particularly useful as a thermally conductive interface material to efficiently transfer heat between two components with a thin gap up to 80 μm or less. Thermally conductive interface materials are typically used to thermally couple heat generating components and heat dissipating components, especially in electronics.

5 The present invention also relates to a method of preparing the thermally conductive composition, the method comprising: admixing the alkenyl-functional polyorganosiloxane, the SiH crosslinker, the thermally conductive fillers, the filler treating agent, and optionally, the hydrosilylation reaction catalyst and the inhibitor and other optional components described above.

The present invention also includes a process for using the thermally conductive composition 10 described above. The process comprises the steps of: a) applying the thermally conductive composition on an electronic component, and b) curing the thermally conductive composition by heat. The applying of the thermally conductive composition may involve dispensing or extruding the thermally conductive composition. Due to the above described properties of the thermally conductive composition such as excellent dispensability and conformability as indicated by the high ER above, the process allows for 15 automated dispensing and assembly (i.e., increased productivity) with minimal stress applied to fill in intricate geometries and diverse gaps, therefore avoiding potential damages to the electronic components. The low BTL described above also enables the composition to be applied to thin gaps.

The two components where the thermally conductive composition is the components of an electronic article. The thermally conductive composition can be between and in contact with one electronic 20 component and a heat dissipating component such as a heat sink, or between and in contract with two electronic components of the electronic device, where at least one electronic component generates heat when the electronic device is in operation. Examples of the electronic components which generate heat during the electronic device is operated include central processing units (CPU), graphics processing units (GPU), memory chips, driver chips and optical modules. The thermally conductive composition can be 25 applied on one or two electronic components which generate heat. Examples of the heat dissipating components include a heat sink, cooling plate/pad, cooling tube, and metal cover.

The curing of the thermally conductive composition can be conducted at room temperature or by heat, for example, at temperatures greater than 25 °C, and can be greater than 40 °C, or greater than 80 °C. The duration time for curing may vary depending on the temperatures, typically 0.5 to 24 hours. The 30 thermally conductive composition can be cured at room temperature, or by heat generated by the electronic component. Desirably, when the electronic device is in operation, the heat generated from at least one electronic component cures the thermally conductive composition typically within several hours, thereby forming the cured material.

Due to the low concentration or absence of the solvent in the thermally conductive composition, 35 the process does not involve (that is, is free of) an extra procedure for removal of the solvent, e.g., stripping off or evaporating the solvent. While still affording the resulting composition with desired ER and TC properties as described above, the thermally conductive composition enables the process for using the

composition without the aid of a solvent and also makes it applicable to dispense (e.g., by extrusion) the composition directly onto components of articles without requiring addition of solvents to the composition before use.

The present invention further includes an electronic article comprising the thermally conductive composition and at least the two components where the thermally conductive composition is between and in contact with the two components of the article. The thermally conductive composition can be in either a cured or non-cured form. The article of is useful as a device benefiting from efficient thermal conduction and good electrical insulation between components, such as a heat generating device and at least one of a heat sink, cooling plate, metal cover or other heat dissipating component. The two components can be the same or different. The electronic article is useful as an electronic device. Examples of the electronic devices include optical modules, smartphones, digital cameras, computers, pad devices, servers and base stations for communication, power inverters, DC (direct current)-to-DC converters, advanced driver assistance systems (ADAS), and battery packs in electric vehicles (EV).

EXAMPLES

Some embodiments of the invention will now be described in the following Examples, wherein all percentages (%) are by weight relative to the weight of a composition and all particle sizes of fillers are D50 particle sizes, unless otherwise specified. Table 1 lists the materials for use in the thermally conductive composition of the samples described herein below. Note: "Vi" represents vinyl, "Me" represents methyl, and "TC filler" refers to thermally conductive filler. SYL-OFF is a trademark of The Dow Chemical Company.

Table 1

Component	Description	Source
Vi Polymer A-1	Vinyl dimethyl terminated polydimethylsiloxane (PDMS) with a viscosity of 60 mPa*s at 25 °C and 1.55 wt% of vinyl relative to molecular weight, having an average chemical structure: $ViMe_2SiO-[Me_2SiO]_{45}-SiMe_2Vi$.	Available under the name ANDISIL™ VS 50 from AB Specialty Silicones (Nantong) Co., Ltd. of China
SiH Crosslinker B-1	Trimethyl terminated dimethyl-co-hydrogen methyl polysiloxane with a viscosity of 14 mPa*s at 25 °C and 0.36 wt% of H from SiH	Available from Gelest under the name HMS-501
SiH Crosslinker B-2	Hydride terminated PDMS with a viscosity of 7-10 mPa*s at 25 °C and 0.16 wt% of H from SiH	Available from Gelest under the name DMS-H11
Treating Agent D-1	n-Decyltrimethoxysilane	Available from Gelest under the name SID2670.0
Treating Agent D-2	Monotrimethoxysiloxy and trimethylsiloxy terminated PDMS having an average molecular structure: $Me_3SiO[Me_2SiO]_{30}Si(OMe_3)_3$	Synthesized according to the teachings in US2006/0100336 (such as paragraphs 101-103)
TC Filler C1-1	Roundish aluminum oxide ("Al_2O_3") with a D50 of 20 μm	Available from ZRI of China
TC Filler C1-2	Roundish $Al_2O_3$with a D50 of 35 μm	Available from ZRI of China
TC Filler C1-3	Spherical $Al_2O_3$with a D50 of 15 μm	Available from Denka of Japan
TC Filler C1-4[C]	Spherical Al_2O_3 with a D50 of 5 μm	Available from Denka of Japan
TC Filler C1-5[C]	Spherical Al_2O_3 with a D50 of 70 μm	Available from Denka of Japan
TC Filler C1-6[C]	Spherical aluminum ("Al") with a D50 of 16 μm	Available from Jiweixin of China
TC Filler C1-7	Spherical AlN with a D50 of 20 μm	Available from Bestry of China
TC Filler C2-1	Spherical Al with a D50 of 1.5 μm	Available from Jiweixin of China
TC Filler C2-2[C]	Spherical Al with a D50 of 9 μm	Available from Jiweixin of China
TC Filler C2-3[C]	Irregular aluminum nitride ("AlN") particles with a D50 of 1.5 μm	Available from Maruwa Ceramic Co. Ltd. of Japan
TC Filler C3-1	Irregular zinc oxide ("ZnO") particles with a D50 of 0.12 μm	Available from Zochem, Inc.
TC Filler C1-8	Irregular AlN particles with a D50 of 10 μm	Available from Foxsine of China
TC Filler C1-9[C]	Roundish AlN particles with a D50 of 5 μm	Available from Maruwa Ceramic Co. Ltd. of Japan
Catalyst E-1	Karstedt's Catalyst composition	Available under the name SYL-OFF™ 4000 Catalyst from The Dow Chemical Company
Inhibitor F-1	Methyl(tris(1,1-dimethyl-2-propynyloxy))silane dispersed in the Vi Polymer A1-1 above at a concentration of 2.5 wt%	Methyl(tris(1,1-dimethyl-2-propynyloxy))silane available under the name ACM83817714 from Alfa Chemistry

Note: Viscosities were measured by ASTM D445-21 at 25 °C using a glass capillary Cannon-Fenske type viscometer. D50 was measured using a Mastersizer™ 3000 laser diffraction particle size analyzer from Malvern Instruments.

5 Inventive Example (IE) 1-7 and Comparative Example (CE) 1-8 Samples

Formulations for the samples are in Tables 2 and 3, with the amount of each component reported in grams (g). Samples were prepared by using a SpeedMixer™ DAC 400 FVZ mixer from FlackTek Inc. (South Carolina, USA) to mix the components together. To a cup of the SpeedMixer add the Vi Polymer A-1, SiH Crosslinkers B-1 and B-2, Treating Agents D-1 and D-2, TC filler C3, and TC filler C4 if present.
10 Mix at 1000 revolutions per minute (RPM) for 20 seconds, then 1500 RPM for 20 seconds. Add TC fillers

C2 and mix at 1000 RPM for 20 seconds, then 1500 RPM for 20 seconds. Add TC filler C1 and mix in the same way. The resulting composition in the cup was scraped to ensure homogenous mixing and then Catalyst E-1, and Inhibitor F-1 were added and mixed in like manner to obtain the thermally conductive composition samples. The obtained thermally conductive composition samples were evaluated for
5 extrusion rate and thermal conductivity, and appearance according to the following test methods:

Thermal Resistance Test

Thermal resistance ("TR") was measured according to ASTM D-5470 using LonGwin Model LW 9389 TIM thermal resistance and conductivity measurement apparatus from Longwin Science and Technology Corporation, Taiwan. Liquid samples were applied between a guarded central hot and cold
10 plates where the hot plate was set at 80 °C and maintained for 15 minutes (min). A pressure of 40 psi was used to maintain contact to the plates. Thermal resistance was recorded. Acceptable thermal resistance is 0.12 °C*cm^2/W or less.

Bond Line Thickness Test

Bond line thickness ("BLT") was measured using ARES G2 Rheometer by dispensing a sample
15 material on a substrate, pressing a plate (with a diameter of 8 mm) onto the sample with a pressure of 40 psi, compressing the sample to the minimum bondline thickness, and recording the bondline thickness of the sample after 180 seconds.

Extrusion Rate Test

Extrusion rate ("ER") for a sample was determined using Nordson EFD dispensing equipment. The
20 sample material was packaged into a 30 cubic centimeter syringe with a 2.54 millimeter (mm) opening (EFD syringe form Nordson Company). The sample was dispensed at 25 °C through the opening by applying a pressure of 0.62 MPa to the syringe. The mass of the sample in grams (g) extruded after one minute corresponds to the extrusion rate in grams per minute (g/min). The objective of the present invention is to achieve an extrusion rate of at least 40 g/min. Notably, some samples were powdery pastes that could
25 not be extruded so they are reported as having an ER of 0 (and other properties were not measured, thus reporting as "NA").

Thermal Conductivity Test

Thermal conductivity ("TC") was determined using a hot disk according to ISO 22007-2. The thermal conductivity of cured samples was measured by Hot Disk TPS 2500 S instrument with a 3.189 mm
30 Kapton sensor (model 5465). The cured samples were prepared by curing the curable thermally conductive composition samples prepared above at 100 °C for 60 min with dimension of 25mm*25mm*8mm. The objective of the present invention is to achieve a thermal conductivity of at least 6.0 Watts per meter*Kelvin (W/m*K).

Appearance Evaluation Test

35 Surface condition of each thermally conductive composition sample obtained above was evaluated by visual inspection and rated as follows:

V: The grease composition surface is uniform and smooth.

M: The grease composition surface is coarse and granular.

X: The grease composition is powdery and cannot form a paste.

Each sample was characterized for extrusion rate using the Extrusion Rate Test, thermal conductivity using the Thermal Conductivity Test, and thermal resistance using the Thermal Resistance Test, BLT using the Bond Line Thickness Test, and Appearance using the Appearance Evaluation Test described herein, above.

Table 2 contains characterization results for IEs 1-6 samples. As shown in Table 2, all IEs samples comprise the novel combination of specific amounts of at least three TC fillers including (C1) Al_2O_3 particles with a D50 in a range of 10-40 μm, (C2) spherical Al particles with a D50 in a range of 1-5 μm, and (C3) ZnO particles with a D50 in a range of 0.1-0.6 μm where IEs 1, 3 and 7 further comprise AlN filler with a D50 of 10 μm or 20 μm. All IEs samples with uniform and smooth surface achieved TC of at least 6 W/m*K, TR of no higher than 0.12 °C*cm^2/W, and ER of at least 40 g/min or even greater than 53 g/min (IEs 2 and 4-6). Moreover, all IE samples achieved a BLT of 80 μm or less.

Table 2

Component	**IE 1**	**IE 2**	**IE 3**	**IE 4**	**IE 5**	**IE 6**	**IE 7**
Vi Polymer A-1	2.50	2.32	2.46	2.32	2.32	2.32	2.64
SiH Crosslinker B-1	0.02	0.03	0.03	0.03	0.03	0.03	0.02
SiH Crosslinker B-2	0.61	0.56	0.59	0.56	0.56	0.56	0.65
Treating Agent D-1	0.20	0.19	0.20	0.19	0.19	0.19	0.20
Treating Agent D-2	1.70	1.60	1.70	1.60	1.74	1.60	1.70
TC Filler C1-1					51.91	58.02	15.88
TC Filler C1-2				58.49			
TC Filler C1-3	25.99	58.49	36.00				
TC Filler C2-1	22.99	21.70	23.00	21.70	28.45	16.60	22.97
TC Filler C3-1	15.89	15.00	15.90	15.00	14.70	20.57	15.88
TC Filler C1-7	29.99						39.95
TC Filler C1-8			20.00				
Catalyst E-1	0.06	0.06	0.06	0.06	0.06	0.06	0.06
Inhibitor F-1	0.06	0.06	0.06	0.06	0.06	0.06	0.06
Characterization							
SiH/Vi ratio	0.631	0.646	0.646	0.646	0.646	0.646	0.636
Wt% filler	94.9	95.2	94.9	95.2	95.1	95.2	94.68
Vol% filler	83.7	83.7	83.5	83.7	83.7	83.2	83.34
Wt% Al filler (1-5 μm)	23.0	21.7	23.0	21.7	28.5	16.6	23.0
ER (g/min)	53	57	45	105	65	98	41
TC (W/m*K)	8.547	6.904	6.889	7.119	6.797	7.175	9.367
TR (°C*cm^2/W)	0.08	0.099	0.095	0.112	0.085	0.088	0.062
BLT at 40 psi (μm)	42	48	55	68	49	53	40
Appearance	V	V	V	V	V	V	V

Note: In Table 2 and Table 3 below:
"Wt% filler" refers to weight percentage of total thermally conductive fillers relative to the total weight of all components in the sample.
"Vol% filler" refers to volume percentage of total thermally conductive fillers relative to the total volume of all components in the sample.
"SiH/Vi ratio" refers to molar ratio of SiH functionality from the crosslinker to vinyl functionality in the sample.
"Wt% Al filler (1-5 μm)" refers to wt% of aluminum particles with a D50 in a range of 1 to 5 μm relative to the total

weight of all components in the sample.
"ER", "TC", "TR", "BLT", and "Appearance" were evaluated according to the test methods described above.

In contrast, as shown in Table 3, all CE samples failed to meet one or more of the requirements for
5 ER, TC, and TR. CE 1 sample comprising spherical Al filler (D50: 1.5 μm) at a lower concentration of 7.6% failed to achieve both the ER and TR requirements. CE 2 sample that contains TC filler C1 with a D50 of 10-40 μm in an amount less than the claimed concentration gave an undesirably low ER and high TR. CE 3 sample comprising spherical Al filler with a D50 of 1.5 μm at a concentration higher than the claimed concentration failed to meet the requirement for ER. CE 4 sample using spherical Al filler with a D50 of 9
10 μm to replace spherical Al filler with a D50 of 1-5 μm gave poor processability, thermal performance cannot be measured due to the powdery state. CE 5 sample comprising Al_2O_3 particles with a D50 of 5 μm that is smaller than 10 μm gave lower TC and ER than the requirements. CE 6 sample that does not comprise Al_2O_3 with a D50 in a range of 10 to 40 μm but just larger spherical Al_2O_3 particles with a D50 of 70 μm failed to achieve both the ER and TR requirements. CE 7 sample that does not comprise spherical Al filler
15 with a D50 of 1-5 μm but irregular AlN gave a powdery paste (that is poor processability) and TC cannot be measured. CE 8 sample comprising 40 wt% of spherical Al filler with a D50 of 16 μm and 40 wt% of spherical Al filler with a D50 of 1.5 μm at a total concentration of Al fillers of 80 wt% gave undesirably low ER.

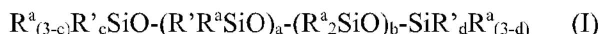
Table 3

Component	CE 1	CE 2	CE 3	CE 4	CE 5	CE 6	CE 7	CE 8
Vi Polymer A1	2.32	2.460	2.32	2.32	2.32	2.32	2.41	3.280
SiH Crosslinker B-1	0.03	0.030	0.03	0.03	0.03	0.03	0.03	0.110
SiH Crosslinker B-2	0.56	0.590	0.56	0.56	0.56	0.56	0.58	0.590
Treating Agent D-1	0.19	0.200	0.19	0.19	0.19	0.19	0.20	0.200
Treating Agent D-2	1.60	1.700	1.60	1.74	1.60	1.60	1.67	1.700
TC Filler C1-1	72.92		43.11	51.91				
TC Filler C1-3		36.000					50.98	
TC Filler C1-4[C]					58.49			
TC Filler C1-5[C]						58.49		
TC Filler C1-6[C]								40.0
TC Filler C2-1	7.55	23.000	36.79		21.70	21.70		40.0
TC Filler C2-2[C]				28.45				
TC Filler C2-3[C]							28.43	
TC Filler C3-1	14.72	15.900	15.28	14.70	15.00	15.00	15.59	14.0
TC Filler C1-9[C]		20.000						
Catalyst E-1	0.06	0.060	0.06	0.06	0.06	0.06	0.06	0.06
Inhibitor F-1	0.06	0.060	0.06	0.06	0.06	0.06	0.06	0.06
Characterization								
SiH/Vi ratio	0.646	0.646	0.646	0.646	0.646	0.646	0.646	0.638
Wt% filler	95.2	94.9	95.2	95.1	95.2	95.2	95.0	94.0
Vol% filler	82.8	83.5	84.6	83.7	83.7	83.7	82.6	83.7
Wt% Al filler (1-5 μm)	7.6	23.0	36.8	0.0	21.7	21.7	0.0	40
ER (g/min)	5	27	4	0	23	33	0	23
TC (W/m*K)	7.493	6.169	6.948	NA	5.193	8.643	NA	7.962
TR (°C*cm^2/W)	0.2	0.213	0.09	NA	0.067	0.216	NA	0.04
BLT at 40 psi (μm)	88	86	48	NA	15	162	NA	33
Appearance	M	V	M	X	V	V	X	V

CLAIMS:

1. A thermally conductive composition comprising, based on the weight of the thermally conductive composition,

(A) from 1.0 to 4.0 weight-percent of an alkenyl-functional polyorganosiloxane having a viscosity in a range of 25 to 500 millipascal*seconds as determined by ASTM D445-21 at 25 degrees Celsius, wherein the alkenyl-functional polyorganosiloxane has an average chemical structure (I):



$$R^{a}_{(3-c)}R'_{c}SiO\text{-}(R'R^{a}SiO)_{a}\text{-}(R^{a}_{2}SiO)_{b}\text{-}SiR'_{d}R^{a}_{(3-d)} \quad (I)$$

where R^{a} is independently in each occurrence an alkyl group having 1 to 6 carbon atoms or an aryl group having 6 to 10 carbon atoms, R' is independently in each occurrence an alkenyl group, subscript $a \geq 0$, subscript $b > 0$, subscript c is 0 or 1, subscript d is 0 or 1, and $(a+c+d) \geq 2$;

(B) a silyl-hydride functional polysiloxane crosslinker that contains at least two silyl-hydride groups per molecule and that is present at a concentration to provide a molar ratio of silicon-bonded hydrogen atoms to alkenyl groups for the composition of 0.4:1 to 1.5:1;

(C) from 93 to 96 weight-percent of thermally conductive fillers comprising:

(C1-a) from 15 to 65 weight-percent of aluminum oxide particles having a D50 in a range of 10 to 40 micrometers,

(C1-b) from 0 to 40 weight-percent of aluminum nitride particles having a D50 in a range of 10 to 40 micrometers,

wherein the combined concentration of the aluminum oxide particles (C1-a) and the aluminum nitride particles (C1-b) is in a range of from 45 to 65 weight-percent;

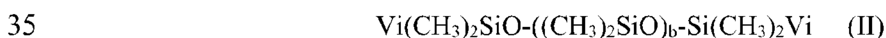
(C2) from 10 to 30 weight-percent of spherical aluminum particles having a D50 in a range of 1 to 5 micrometers;

(C3) from 10 to 25 weight-percent of a third thermally conductive filler having a D50 in a range of 0.1 to 0.6 micrometer, wherein the third thermally conductive filler is selected from the group consisting of zinc oxide particles, aluminum oxide particles, and mixtures thereof; and

(D) a filler treating agent selected from the group consisting of a trialkoxysilyl diorganopolysiloxane, an alkyl trialkoxysilane, and mixtures thereof.

2. The thermally conductive composition of claim 1, wherein the composition further comprises, based on the weight of the thermally conductive composition, one or both of the following components: (E) a platinum-based hydrosilylation reaction catalyst in an amount sufficient to provide 0.5 to 30 ppm of the platinum, and (F) from 0.001 to 0.1 weight-percent of a hydrosilylation reaction inhibitor.

3. The thermally conductive composition of claim 1 or 2, wherein the alkenyl-functional polyorganosiloxane comprises a vinyldimethylsiloxy-terminated polydimethylpolysiloxane having an average chemical structure (II):

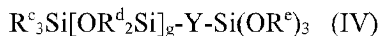


$$Vi(CH_3)_2SiO\text{-}((CH_3)_2SiO)_b\text{-}Si(CH_3)_2Vi \quad (II)$$

where Vi represents vinyl and subscript b has a value of 20 to 200.

4. The thermally conductive composition of any one of claims 1-3, wherein the filler treating agent

comprises, based on the weight of the curable thermally conductive composition, 0.5 to 2.5 weight-percent of a mono-trialkoxysiloxy terminated diorganopolysiloxane of an average chemical structure (IV):



$$R^c_3Si[OR^d_2Si]_g\text{-}Y\text{-}Si(OR^e)_3 \quad (IV)$$

where R^c, R^d, and R^e are independently in each occurrence selected from hydrocarbon groups having from 1 to 10 carbon atoms; subscript g has a value of 25 to 110; and Y is O or $[OSiR^d_2](CH_2)_n$, where subscript n has a value of 3 to 20.

5. The thermally conductive composition of any one of claims 1-4, wherein the third thermally conductive filler is irregular zinc oxide.

6. The thermally conductive composition of any one of claims 1-5, wherein, based on the weight of the thermally conductive composition, the concentration of the aluminum oxide particles (C1-a) is in a range of from 25 to 45 weight-percent and the concentration of the aluminum nitride particles (C1-b) is in a range of from 15 to 30 weight-percent.

7. The thermally conductive composition of any one of claims 1-5, wherein the thermally conductive composition comprises, based on the weight of the thermally conductive composition, from 45 to 60 weight-percent of spherical or roundish aluminum oxide particles having a D50 of 15 to 35 micrometers, from 20 to 25 weight-percent of the spherical aluminum particles having a D50 in a range of 1 to 5 micrometers, and from 14 to 20 weight-percent of irregular zinc oxide particles having a D50 in a range of 0.1 to 0.5 micrometer.

8. The thermally conductive composition of any one of claims 1-5, wherein the thermally conductive composition comprises, based on the weight of the thermally conductive composition, from 25 to 45 weight-percent of spherical or roundish aluminum oxide particles having a D50 in a range of 15 to 35 micrometers, from 15 to 30 weight-percent of the aluminum nitride particles having a D50 in a range of 10 to 20 micrometers, from 15 to 30 weight-percent of the spherical aluminum particles having a D50 in a range of 1 to 5 micrometers, and from 14 to 22 weight-percent of irregular zinc oxide particles having a D50 in a range of 0.1 to 0.5 micrometer.

9. A process for using the thermally conductive composition of any one of claims 1-8, comprising the steps of:

a) applying the thermally conductive composition on an electronic component, and

b) curing the thermally conductive composition by heat.

10. An electronic article comprising the thermally conductive composition of any one of claims 1-8 between and in contact with two components of the electronic article, wherein the thermally conductive composition is in either a cured or non-cured form.

INTERNATIONAL SEARCH REPORT

International application No
PCT/CN2023/122025

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

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

B. FIELDS SEARCHED

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

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2023/212447 A1 (BHAGWAGAR DORAB [US] ET AL) 6 July 2023 (2023-07-06) paragraph [0008] - paragraph [0011] paragraph [0038] - paragraph [0043] Samples 1-17 -----	1-10
A	US 2023/032719 A1 (FRANKEL ERICA A [US] ET AL) 2 February 2023 (2023-02-02) paragraph [0007] - paragraph [0010] paragraph [0022] paragraph [0034] - paragraph [0041] claim 1 -----	1-10

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

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 March 2024	25/03/2024

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Stinchcombe, John

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/CN2023/122025

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2023212447 A1	06-07-2023	CN 116323803 A	23-06-2023
		EP 4237494 A1	06-09-2023
		JP 2023539538 A	14-09-2023
		KR 20230084585 A	13-06-2023
		TW 202229501 A	01-08-2022
		US 2023212447 A1	06-07-2023
		WO 2022087878 A1	05-05-2022
US 2023032719 A1	02-02-2023	CN 115135709 A	30-09-2022
		EP 4114892 A1	11-01-2023
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		WO 2021178119 A1	10-09-2021