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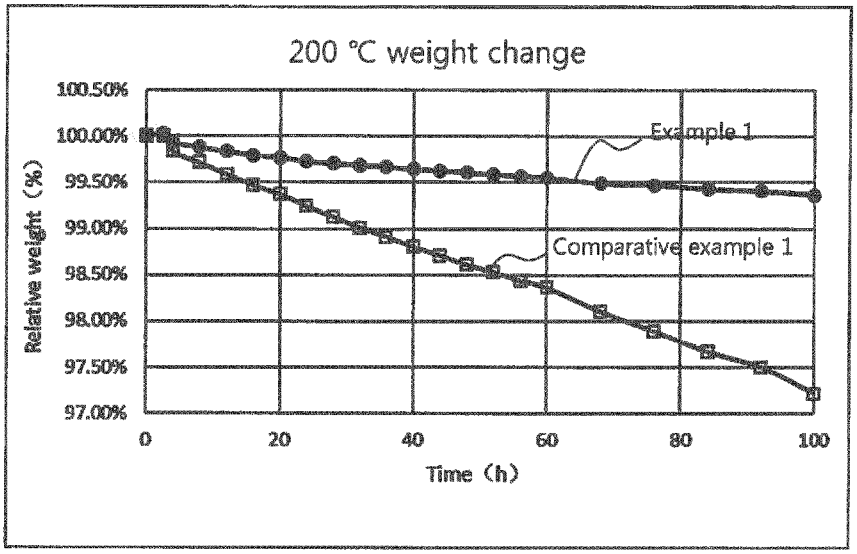
Fig. 3



(57) Abstract: Disclosed is a curable organopolysiloxane composition, a Light Emitting Diode (LED) encapsulant and a semiconductor device.

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CURABLE ORGANOPOLYSILOXANE COMPOSITION, ENCAPSULANT AND SEMICONDUCTOR DEVICE

Technical Field

The present invention relates to a curable organopolysiloxane composition, an LED encapsulant, and a semiconductor device, and more particularly, the present invention relates to a curable organopolysiloxane composition with excellent thermal resistance and crack resistance, an LED encapsulant with excellent reliability using the same, and a semiconductor device.

Background Art

A LED package is generally composed of a chip, an adhesive, an encapsulant, a phosphor, and a heat radiation material. Among them, the encapsulant basically serves to protect a LED device, and allows light to pass through the LED device and emit light outside the device.

As a basic material for the LED encapsulant, curable silicone compositions and curable epoxy compositions have been used. Particularly, the silicone compositions curable by the hydrosilylation reaction, which gives optically clear silicone products, have been mainly used for good properties such as resistance to heat, moisture, and light.

Recently, as high power output has been demanded in the field of LED such high power output of LED's has caused problems with LED package materials due to their lack of thermal resistance. Further, when heat is continuously added to the LED package, the material in the LED encapsulant is additionally subjected to a curing reaction, so that the hardness of the LED encapsulant may be changed, or the weight

loss of the LED encapsulant may occur. And thus, cracks may occur on the LED encapsulant.

Disclosure of Invention

An object of the present invention is to provide a curable organopolysiloxane composition with excellent thermal resistance and excellent crack resistance to thermal aging, an LED encapsulant with excellent reliability using the same, and a semiconductor device.

The present invention provides a curable organopolysiloxane composition including:

(A) a cerium (Ce)-containing branched organopolysiloxane;

(B) a branched organopolysiloxane;

(C) a linear organopolysiloxane with both terminal ends of the molecular chain blocked by silicon-bonded hydrogen atoms, having at least one silicon-bonded aryl group per molecule;

(D) a hydrosilylation reaction catalyst; and

(E) a low molecular weight siloxane having at least one silicon-bonded alkenyl group per molecule, represented by the following average formula:

[average formula]

$(R^8{}_3SiO_{1/2})_f(R^8{}_2SiO_{2/2})_g(R^8SiO_{3/2})_h(SiO_{4/2})_i$

(where each R^8 can be the same or different and is independently selected from a substituted or unsubstituted monovalent hydrocarbon group, in which at least one of R^8 per molecule is an alkenyl group, with the proviso that the ratio between alkenyl groups and silicon atoms is from 0.3 to 1,

f, g, h, and i are independently 0 or a positive number,

in which f+g+h+i is 1, and

the weight average molecular weight Mw of the siloxane is 1,000 g/mol or less).

Further, the present invention provides an LED encapsulant including the above-described curable organopolysiloxane composition.

In addition, the present invention provides a semiconductor device including a semiconductor element coated with a cured product of the above-described curable organopolysiloxane composition.

Effects of Invention

The composition according to the present invention shows less change in weight and hardness at high temperature and thus may be cured as a cured product with excellent thermal stability. Therefore, the present invention may provide an LED silicon encapsulant which is stable against light generated from LED chips and heat generated during the operation. Furthermore, the present invention has high hardness and flexibility at high temperature and thus may improve the reliability of the LED.

Brief Description of the Drawings

Fig. 1 is a photograph illustrating whether cracks occur on LED encapsulants of Example 1 and Comparative Example 1.

Fig. 2 is a photograph illustrating whether cracks occur on a cured product of Example 1 and Comparative Example 1 in an aluminum pan.

Figs. 3 and 4 are graphs showing a change in hardness and weight of cured silicone in Example 1 and Comparative Example 1 at 200°C.

Detailed Description of the Invention

Hereinafter, an exemplary embodiment of the present invention will be described in detail. However, the exemplary embodiment of the present invention may be modified in various forms, and the scope of the present invention is not limited to an exemplary embodiment to be described below.

The present invention is a curable organopolysiloxane composition, including: (A) a cerium (Ce)-containing branched organopolysiloxane; (B) a branched organopolysiloxane; (C) a linear organopolysiloxane with both terminal ends of the molecular chain blocked by silicon-bonded hydrogen atoms, having at least one silicon-bonded aryl group per molecule; (D) a hydrosilylation reaction catalyst; and (E) a low molecular weight siloxane having at least one silicon-bonded alkenyl group per molecule, represented by the average formula.

Hereinafter, each component and composition of the curable organopolysiloxane composition will be described.

Component (A)

In the composition according to the present invention, the cerium (Ce)-containing branched organopolysiloxane (hereinafter, 'component (A)') imparts thermal stability while imparting strength to a silicone cured product obtained by curing the composition.

Specifically, since component (A) is a kind of branched organopolysiloxane, the present invention may obtain a silicone cured product with excellent strength as compared to a composition including a linear organopolysiloxane. Furthermore, in the

present invention, cerium is not a separate single material, but is contained in the form of cerium ions in the branched organopolysiloxane, so that cerium is stably dispersed in the composition without being precipitated or sedimentation. Further, since cerium takes part in a reaction when the composition is cured, cerium is stably included as one component of the silicone cured product after the curing. In addition, when the cerium (Ce)-containing branched organopolysiloxane is prepared, the content of cerium may be easily controlled according to the content of silanol groups in an alkali metal salt of a silanol group-containing branched organopolysiloxane. Accordingly, since a silicone cured product obtained by curing the composition of the present invention shows less change in weight loss and hardness, the occurrence of cracks due to the thermal aging is minimized or suppressed, and accordingly, when the silicone cured product is applied to an encapsulant of an LED, reliability of the LED may be improved.

In component (A), the content of cerium is not particularly limited, and may be, for example, 0.1 to 2 % by weight based on the total weight of the curable organopolysiloxane composition. If the content of cerium in component (A) is less than 0.1 % by weight, the effect may be insignificant, and while, if the content of cerium in component (A) exceeds 2 % by weight, the value of b* of the cured product becomes 2 or more, and as a result, it is difficult to use the composition of the present invention as an LED encapsulant. According to one example, the content of cerium in component (A) may be about 5 to 300 ppm as a mass unit based on the total weight of the curable organopolysiloxane composition. In this case, the silicone cured product according to the present invention has excellent thermal stability, and a change in light emission color may be minimized when the silicone cured product is used in an optical semiconductor device.

This component (A) is a material obtained by reacting an alkali metal salt of a silanol group-containing branched organopolysiloxane with cerium chloride or cerium salt of carboxylic acid.

In this case, the mixing ratio of an alkali metal salt of the silanol group-containing branched organopolysiloxane to cerium chloride (or cerium salt of carboxylic acid) is not particularly limited, and may be, for example, a molar ratio of 0.1 to 2 : 1.

Examples of the cerium salts of carboxylic acid which may be used in the present invention include cerium 2-ethylhexanoate, cerium naphthenate, cerium oleate, cerium laurate, cerium stearate, and the like, but are not limited thereto. These cerium salts may be used either alone or in a mixture of two or more thereof.

Further, examples of the alkali metal salts of the silanol group-containing branched organopolysiloxane which may be used in the present invention include sodium salt of the silanol group-containing branched organopolysiloxane, potassium salt of the silanol group-containing branched organopolysiloxane, and the like, but are not limited thereto.

According to one example, the alkali metal salt of the silanol group-containing branched organopolysiloxane may be an alkali metal salt of a branched organopolysiloxane having at least one silanol group, at least one silicon-bonded alkenyl group, and at least one silicon-bonded aryl group per molecule, and having siloxane units represented by the following general formula 1:

[general formula 1]

$RSiO_{3/2}$

where R is a substituted or unsubstituted monovalent hydrocarbon group.

In the alkali metal salt of the silanol group-containing branched organopolysiloxane, the alkenyl groups have 2 to 12 carbon atoms, examples thereof include vinyl, allyl, methallyl, butenyl, pentenyl, and hexenyl group, specific examples thereof include vinyl, and allyl group, and more specific examples thereof include vinyl group.

Further, the aryl groups have 6 to 20 carbon atoms, examples thereof include phenyl, naphthyl, anthryl, phenanthryl, indenyl, benzophenyl, fluorenyl, xanthenyl, and anthronyl; aryloxyaryl groups such as o-phenoxyphenyl and p-phenoxyphenyl; alkaryl groups such as o-tolyl, m-tolyl, p-tolyl, xylyl, and ethylphenyl; and aralkyl groups such as benzyl, α-phenylethyl, and β-phenylethyl, and specific examples thereof include phenyl group.

Further, in addition to the above-described alkenyl groups and aryl groups, examples of the silicon-bonded organic groups in the silanol group-containing branched organopolysiloxane include substituted or unsubstituted C_1 to C_{20} monovalent hydrocarbon groups, specific examples thereof include C_1 to C_{20} alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl, and heptyl; and C_1 to C_{20} halogenated alkyl groups such as chloromethyl, 3-chloropropyl, and 3,3,3-trifluoropropyl, and more specific examples thereof include methyl groups. In this case, the monovalent hydrocarbon groups may be unsubstituted or substituted with one or more substituents selected from the group consisting of C_1 to C_{20} alkyl groups, C_2 to C_{20} alkenyl group, C_6 to C_{20} aryl groups, C_7 to C_{20} aralkyl groups, and C_1 to C_{20} halogenated alkyl groups.

In the siloxane unit represented by general formula 1, R is C_1 to C_{20} monovalent hydrocarbon groups. Examples of the C_1 to C_{20} monovalent hydrocarbon groups include C_1 to C_{20} alkyl groups, C_2 to C_{20} alkenyl group, C_6 to C_{20} aryl groups, C_7 to C_{20} aralkyl

groups, and C_1 to C_{20} halogenated alkyl groups. In this case, the C_1 to C_{20} monovalent hydrocarbon groups may be unsubstituted or substituted with one or more substituents selected from the group consisting of C_1 to C_{20} alkyl groups, C_2 to C_{20} alkenyl groups, C_6 to C_{20} aryl groups, C_7 to C_{20} aralkyl groups, and C_1 to C_{20} halogenated alkyl groups, and specifically, may be unsubstituted or substituted with one or more substituents selected from the group consisting of C_1 to C_{20} alkyl groups and C_6 to C_{20} aryl groups.

According to another example, the alkali metal salt of the silanol group-containing branched organopolysiloxane may be an alkali metal salt of an organopolysiloxane represented by the following average unit formula 1.

[average unit formula 1]

$(R^1R^1R^3SiO_{1/2})_a(R^1{}_2SiO_{2/2})_b(R^2SiO_{3/2})_c(SiO_{4/2})_d(X^1O_{1/2})_e$

In the formula above,

each of R^1, R^2, and R^3 can be the same or different and is independently selected from a substituted or unsubstituted monovalent hydrocarbon group,

with the proviso that at least one of R^1, R^2, and R^3 per molecule is a silanol group,

at least one of R^1, R^2, and R^3 per molecule is a C_2 to C_{12} alkenyl group, and

at least one of R^1, R^2, and R^3 per molecule is a C_6 to C_{20} aryl group.

The monovalent hydrocarbon groups have 1 to 20 carbon atoms, and examples thereof include the above-described C_1 to C_{20} alkyl groups, the above-described C_2 to C_{20} alkenyl group, the above-described C_6 to C_{20} aryl groups, the above-described C_7 to C_{20} aralkyl groups, and the above-described C_1 to C_{20} halogenated alkyl groups.

Further, the content of the silanol groups per molecule is not particularly limited, but may be, for example, 1 to 3 mol% of R^1, R^2, and R^3 per molecule. If the content of

the silanol groups per molecule in the alkali metal salt of the silanol group-containing branched organopolysiloxane is within the above-described range, thermal stability of the cured product may be improved.

Further, the content of the alkenyl groups per molecule is not particularly limited, but may be, for example, 0.1 to 40 mol%, specifically 5 to 25 mol%, of R^1, R^2, and R^3 per molecule. If the content of the alkenyl groups per molecule in the alkali metal salt of the silanol group-containing branched organopolysiloxane is within the above-described range, the reactivity of component (A) may be improved.

Further, the content of the aryl groups per molecule is not particularly limited, but may be, for example, 10 mol% or more of R^1, R^2, and R^3 per molecule. If the content of the aryl groups per molecule in the alkali metal salt of the silanol group-containing branched organopolysiloxane is within the above-described range, it is possible to minimize attenuation due to light refraction, reflection, scattering, etc. in the cured product obtained by curing. In particular, in the siloxane units represented by the general formula $R^2SiO^{3/2}$, it is even more preferable that not less than 30 mol % of R^2 should be represented by the above-mentioned aryl groups, with R^2 other than the alkenyl and aryl groups being preferably represented by methyl groups.

In addition, in the formula above, X^1 is a hydrogen atom or C_1 to C_{20} alkyl group, a is 0 or a positive number, b is 0 or a positive number, c is a positive number, d is 0 or a positive number, e is 0 or a positive number, b/c is a number between 0 and 10, a/c is a number between 0 and 0.5, d/(a+b+c+d) is a number between 0 and 0.3, and e/(a+b+c+d) is a number between 0 and 0.4.

According to another example, the alkali metal salt of the silanol group-containing branched organopolysiloxane may be an alkali metal salt of an

organopolysiloxane represented by the following average unit formula 2.

[average unit formula 2]

$(R^1R^1R^3SiO_{1/2})_a(R^1{}_2SiO_{2/2})_b(R^2SiO_{3/2})_c$

In the formula above,

R^1 is a C_1 to C_{12} alkyl group,

R^2 is a C_6 to C_{20} aryl group or a C_7 to C_{20} aralkyl group,

R^3 is a C_2 to C_{12} alkenyl group,

a is 0 or a positive number,

b is 0 or a positive number, and

c is a positive number,

with the proviso that at least one of R^1, R^2, and R^3 per molecule is a silanol group.

The content of the silanol groups in the alkali metal salt of the above-described silanol group-containing branched organopolysiloxane is not particularly limited, and may be, for example, 1 to 3 mol% per molecule. If the content of the silanol groups in the alkali metal salt of the silanol group-containing branched organopolysiloxane is within the above-described range, thermal stability of the cured product may be improved.

The weight average molecular weight of the cerium-containing branched organopolysiloxane is not particularly limited, and may be, for example, about 1,000 to 3,000 g/mol, specifically about 1,500 to 2,500 g/mol.

In the composition of the present invention, the content of component (A) is not particularly limited, but may be, for example, about 0.01 to 5 parts by weight, based on 100 parts by weight of the composition.

Component (B)

In the composition according to the present invention, the branched organopolysiloxane (hereinafter, 'component (B)') imparts strength to a silicone cured product obtained by curing the composition.

Component (B) represents a branched organopolysiloxane having at least one silicon-bonded alkenyl group and at least one silicon-bonded aryl group per molecule, and having siloxane units represented by the general formula 2:

[general formula 2]

$RSiO_{3/2}$

where R is a substituted or unsubstituted monovalent hydrocarbon group having 1 to 20 carbon atoms.

In component (B), the alkenyl groups have 1 to 20 carbon atoms. Examples of the C1 to C20 alkenyl groups include vinyl, allyl, methallyl, butenyl, pentenyl, and hexenyl group, preferably vinyl and allyl group, particularly preferred vinyl group.

In component (B), the aryl groups have 6 to 20 carbon atoms. Examples of the C6 to C20 aryl groups include phenyl, naphthyl, anthryl, phenanthryl, indenyl, benzophenyl, fluorenyl, xanthenyl, anthronyl; aryloxyaryl groups such as o- or p-phenoxyphenyl; alkaryl groups such as o-, m-, p-tolyl, xylyl and ethylphenyl; aralkyl groups such as benzyl, α- and β-phenylethyl. Preferably the aryl group is phenyl group.

In addition, examples of silicon-bonded organic groups of component (B) other than the alkenyl and aryl groups include substituted or unsubstituted monovalent hydrocarbon groups having 1 to 20 carbon atoms, examples of which include methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, and other alkyl groups; and halogenated alkyl groups having 1 to 20 carbon atoms such as chloromethyl, 3-chloropropyl, and 3,3,3-

trifluoropropyl, with methyl being particularly preferable.

In the siloxane units of component (B) represented by the general formula 2 $RSiO_{3/2}$, R is a substituted or unsubstituted monovalent hydrocarbon group having 1 to 20 carbon atoms. Substituents of hydrocarbon groups may include the above-mentioned C1 to C20 alkyl groups, the above-mentioned C2 to C20 alkenyl groups, the above-mentioned C6 to C20 aryl groups, the above-mentioned C7 to C20 aralkyl groups, and the above-mentioned C1 to C20 halogenated alkyl groups, particularly preferably the above-mentioned C1 to C20 alkyl groups and the above-mentioned C6 to C20 aryl groups.

As component (B), an organopolysiloxane represented by the average unit formula 3:

$(R^4R^4R^6SiO_{1/2})_a(R^4{}_2SiO_{2/2})_b(R^5SiO_{3/2})_c(SiO_{4/2})_d(X^2O_{1/2})_e$

is preferable.

In the formula above, each of R^4, R^5, and R^6 can be the same or different and is independently selected from a substituted or unsubstituted monovalent hydrocarbon group having 1 to 20 carbon atoms, wherein at least one of R^4, R^5 or R^6 per molecule is an C2 to C12 alkenyl group and at least one of R^4, R^5 or R^6 per molecule is an C6 to C20 aryl group.

The monovalent hydrocarbon group having 1 to 20 carbon atoms may be more specifically exemplified by the above-mentioned C1 to C20 alkyl groups, the above-mentioned C2 to C20 alkenyl groups, the above-mentioned C6 to C20 aryl groups, the above-mentioned C7 to C20 aralkyl groups, and the above-mentioned C1 to C20 halogenated alkyl groups.

Preferably 0.1 to 40 mol%, more preferably 5 to 25 mol%, of R^4, R^5, and R^6 per

molecule is the above-mentioned C2 to C12 alkenyl groups. This is due to the fact that when the content of the alkenyl groups is below the lower limit or exceeds the upper limit of the above-mentioned range, its reactivity with component (B) tends to decrease.

Also, in order to achieve low attenuation due to light refraction, reflection, scattering etc. in the cured product obtained by curing preferably not less than 10 mol% of R^4, R^5, and R^6 should be the above-mentioned C6 to C20 aryl groups, and, in particular, in siloxane units represented by the general formula $R^5SiO_{3/2}$, it is even more preferable that not less than 30 mol % of R^5 should be represented by the above-mentioned aryl groups, with R^5 other than the alkenyl and aryl groups being preferably represented by methyl groups.

In addition, in the formula above,

X^2 is a hydrogen atom or C1 to C20 alkyl group, a is 0 or a positive number, b is 0 or a positive number, c is a positive number, d is 0 or a positive number, e is 0 or a positive number, b/c is a number between 0 and 10, a/c is a number between 0 and 0.5, d/(a+b+c+d) is a number between 0 and 0.3, and e/(a+b+c+d) is a number between 0 and 0.4.

As component (B), an organopolysiloxane with the average unit formula 4:

$$(R^4R^4R^6SiO_{1/2})_a(R^4{}_2SiO_{2/2})_b(R^5SiO_{3/2})_c$$

is particularly preferable.

In the formula above, R^4 is a C_1 to C_{12} alkyl group, R^5 is a C_6 to C_{20} aryl group or a C_7 to C_{20} aralkyl group, R^6 is a C_2 to C_{12} alkenyl group, a is 0 or a positive number, b is 0 or a positive number, and c is a positive number.

Although there are no limitations concerning the molecular weight of component (B), when converted to standard polystyrene, its weight average molecular

weight (Mw) should preferably be in the range of from 500 g/mol to 10,000 g/mol, and, especially preferably, in the range of from 700 g/mol to 7,000 g/mol, more preferably in the range from 1,000 g/mol to 5,000 g/mol, particularly from 1,500 to 3,000 g/mol.

In the composition of the present invention, the content of component (B) is not particularly limited, but may be, for example, about 60 to 85 parts by weight based on 100 parts by weight of the composition. According to one example, the content of component (B) may be about 54 to 80 % by weight, based on the sum of the amounts of components (A), (B), and (C).

Component (C)

Component (C) is the curing agent of the present composition.

Component (C) is a linear organopolysiloxane with both terminal ends of the molecular chain blocked by silicon-bonded hydrogen atoms having at least one silicon-bonded aryl group per molecule. By using a linear organopolysiloxane as the curing agent, instead of a branched organopolysiloxane, a good elongation performance may be obtained.

In Component (C), the aryl groups have 6 to 20 carbon atoms. Examples of the C6 to C20 aryl groups of component (C) are the same as those described above. Phenyl group is especially preferable.

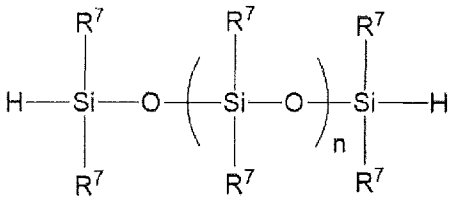
In addition, examples of silicon-bonded organic groups of component (C) other than the aryl groups include substituted or unsubstituted C1 to C20 monovalent hydrocarbon groups with the exception of alkenyl groups, such as the above-described C1 to C20 alkyl groups, the above-described C7 to C20 aralkyl groups, and the above-described C1 to C20 halogenated alkyl groups, with methyl being particularly

preferable.

In order to achieve low attenuation due to light refraction, reflection, scattering, etc. in the cured product obtained by curing the content of the silicon-bonded aryl groups among all the silicon-bonded organic groups in component (C) should preferably be not less than 15 mol % and, particularly preferably, not less than 30 mol%. Although there are no limitations concerning the viscosity of component (C) at 25 °C, it is preferably in the range of from 1 to 1,000 mPa·s, and, especially preferably, in the range of from 2 to 500 mPa·s. This is due to the fact that when the viscosity of component (C) is below the lower limit of the above-mentioned range, it may tend to volatilize and the makeup of the resultant composition may be unstable, and, on the other hand, when it exceeds the upper limit of the above-mentioned range, the handling properties of the resultant composition tend to deteriorate.

An organopolysiloxane represented by the general formula 3:

[general Formula 3]



is preferable as component (C).

In the formula above, each R^7 can be the same or different and is independently selected from a hydrogen atom or a substituted or unsubstituted monovalent hydrocarbon group with the exception of alkenyl groups.

The monovalent hydrocarbon group has 1 to 20 carbon atoms. Examples of the monovalent hydrocarbon groups of R^7 include the above-mentioned C1 to C20 alkyl

groups, the above-mentioned C6 to C20 aryl groups, and the above-mentioned C1 to C20 halogenated alkyl groups.

Here, at least one R^7 per molecule must be one of the above-mentioned C6 to C20 aryl groups, preferably, phenyl.

In addition, n in the formula above is an integer of 0 or more, preferably, an integer in the range of from 0 to 20, and, especially preferably, an integer in the range of from 0 to 10. This is due to the fact that when the value of n exceeds the upper limit of the above-mentioned range, the toughness of the resultant composition, or the adhesive properties of the cured product, tend to deteriorate. It is most preferable that n is 1 to 4, particularly, 1, that is, the component (C) represents trisiloxane.

By having M unit as the repeating unit, instead of Q or T unit, a good elongation performance may be obtained.

Component (C) is preferably present in an amount of 1 to 30 % by weight, more preferably 10 to 30 % by weight, particularly prefered, 15 to 25 % by weight, based on the sum of the amounts of components (A), (B) and (C).

It is preferable that the molar ratio of Si-H groups in component (C)/ alkenyl groups, for example, vinyl groups, in components (A) and (B) $\left[\left| \frac{M_1}{M_2} \right| \right]$, where M_1 is a number of moles of the alkenyl group in components (A) and (B), and M_2 is a number of moles of the hydrosilyl group in component (C)] is 1 to 1.2 to reduce the reactive residual silicone hydride.

In the composition of the present invention, the content of component (C) is not particularyl limited, but may be, for example, about 10 to 30 parts by weight, based on 100 parts by weight of the composition.

Component (D)

Component (D) is a hydrosilylation reaction catalyst.

The hydrosilylation reaction catalyst of component (D) is used to promote the reaction of the alkenyl groups of component (B) with the silicon-bonded hydrogen atoms of component (A).

Examples of component (D) include platinum catalysts, rhodium catalysts, and palladium catalysts. Platinum catalysts are preferable because of their ability to significantly stimulate the cure of the present composition. Examples of the platinum catalysts include platinum micropowder, chloroplatinic acid, alcohol solutions of chloroplatinic acid, platinum/alkenylsiloxane complexes, platinum/olefin complexes, and platinum/carbonyl complexes, preferably, platinum/alkenylsiloxane complexes. Examples of the alkenylsiloxanes include 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, alkenylsiloxanes obtained by substituting groups such as ethyl, phenyl etc. for some of the methyl groups of the above-mentioned alkenylsiloxanes, and alkenylsiloxanes obtained by substituting groups such as allyl, hexenyl, etc. for the vinyl groups of the above-mentioned alkenylsiloxanes. 1,3-divinyl-1,1,3,3-tetramethyldisiloxane is particularly preferable because of the excellent stability of the platinum/alkenylsiloxane complex. Also, due to the improvement in the stability of the complex that their addition may bring, it is desirable to add 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, 1,3-diallyl-1,1,3,3-tetramethyldisiloxane, 1,3-divinyl-1,3-dimethyl-1,3-diphenyldisiloxane, 1,3-divinyl-1,1,3,3-tetraphenyldisiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane and other alkenylsiloxanes and organosiloxane oligomers such as dimethylsiloxane oligomers to the platinum/alkenylsiloxane complex, with alkenylsiloxanes being

particularly preferable.

There are no limitations on the content of component (D) as long as the amount promotes curing of the present composition. According to one example, in the present composition, the content of component (D) may be about 0.001 to 0.3 parts by weight, based on 100 parts by weight of the composition. According to another example, in the present composition, component (D) is preferably present in an amount resulting in a platinum content of 0.05 to 100 ppm (parts per million) by weight, more preferably 0.1 to 10 ppm by weight, particularly preferred 0.1 to 5 ppm by weight, relative to 100 parts by weight of the total of components (A), (B) and (C). This is due to the fact that when the content of component (D) is below the lower limit of the above-mentioned range, the present composition tends to fail to completely cure, and, on the other hand, when it exceeds the upper limit of the above-mentioned range, problems may arise in terms imparting various colors to the resultant cured product.

Component (E)

Component (E) is an additive, which is a low molecular weight siloxane having at least one silicon-bonded alkenyl group per molecule, represented by the average formula 1:

[average formula 1]

$(R^8{}_3SiO_{1/2})_f(R^8{}_2SiO_{2/2})_g(R^8SiO_{3/2})_h(SiO_{4/2})_i$

where each R^8 can be the same or different and is independently selected from a substituted or unsubstituted monovalent hydrocarbon group, wherein at least one of R^8 per molecule is an alkenyl group, with the proviso that the ratio between alkenyl groups and silicon atoms is from 0.3 to 1,

f, g, h, and i are independently 0 or positive, wherein f+g+h+i is 1, and

the weight average molecular weight Mw of the siloxane is less than 1,000 g/mol, preferably less than 800 g/mol, more preferably less than 500 g/mol.

Preferably component (E) is selected from the group consisting of $D^{alkenyl}_4$, $M^{alkenyl}_4Q$, $M^{alkenyl}_6Q_2$, $M^{alkenyl}_3T$. Preferably the alkenyl group is vinyl (=Vi). Particularly preferred as component (E) are cyclotetrasiloxane D^{Vi}_4, and M^{Vi}_4Q, especially D^{Vi}_4. Herein, D unit is $R^5_2SiO_{2/2}$, M unit is $R^5_3SiO_{1/2}$, Q unit is $SiO_{4/2}$, and T unit is $R^5SiO_{3/2}$.

It is assumed that component (E) serves to react with an unreacted site (Si-H), thereby protecting additional reaction of the unreacted site due to heat or light. As a result, in the composition comprising component (E), color change and mechanical strength change to high temperature may be remarkably reduced.

In the composition according to prior art, which has no component (E), materials often show an increase in hardness after curing during storage at high temperature, which can be attributed to a post-curing reaction of remaining reactive sites and/or show a weight loss by evaporation of low molecular weight species that did not crosslink into the polymer network. Due to the change in hardness and weight loss, the materials were not stable under operating conditions. In the present invention, a reaction of component (E) with unreacted site (Si-H) leads to better stability such as less change in hardness, low weight loss, and discoloration, at high temperature.

Component (E) also gives a filling effect, which makes it possible to lower gas and vapor transmission. The encapsulant further comprising component (E) provides stablity to sulfur and such effect is expected to be obtained from the filing effect.

As a result, an LED package with excellent reliability may be obtained.

Component (E) is both reactive and small enough to react with residual silicone hydride. At the same time, component (E) crosslinks into the siloxane network and thus does not increase the proportion of volatile components in the cured material. Component (E) is preferably used in an amount of at most 10 parts by weight, more preferably at most 7 parts by weight, and even more preferably at most 5 parts by weight relative to 100 parts by weight of the total of components (A), (B) and (C). If component (E) is included in higher amounts, compatibility with the other components would be lower and thus, transmittance would be lower. Preferably, component (E) is used in an amount of at least 1 parts by weight relative to 100 parts by weight of the total of components (A), (B) and (C). The amount of the component (E) may be adequately selected in consideration of the specific formulation and the feature.

Preferably, the composition of the present invention comprises about 0.5 to 10 parts by weight of component (E), based on 100 parts by weight of the composition.

The curable silicone composition of the present invention may not comprise as flexibilizing units, a linear organopolysiloxane having at least two silicon-bonded alkenyl groups and at least one silicon-bonded aryl group per molecule. It is assumed that since bulky branched organopolysiloxane such as component (B) is used as resin instead of a linear organopolysiloxane, the present curable silicone composition provides excellent hardness and toughness. That is, bulky branched organopolysiloxane is directly connected to unreacted Si-H site.

The curable organopolysiloxane composition of the present invention may further comprise a crosslinking agent, which is generally used in this field.

The curable organopolysiloxane composition of the present invention may

further comprise a curing inhibitor, a catalyst, and a phosphor, which are generally used in this field.

The present composition may also contain silica, glass, quartz, cristobalit, alumina, zinc oxide and other inorganic fillers; micropowders of organic resins such as polymethacrylate resin; heat-stabilizers, dyes, pigments, flame retardants, solvents, etc. as optional components, so long as this does not impair the purpose of this invention.

The compositions described above may be prepared by mixing the components generally used in this art, for example, by mixing all the components at ambient temperature.

An LED encapsulant of the present invention comprises the curable organopolysiloxane composition as described above. Encapsulation for light emitting devices in the present invention is well known to the art and may be used in the present invention. For example, casting, dispensing, molding may be used.

In a semiconductor device of the present invention, semiconductor elements are coated with a cured product of the curable organopolysiloxane composition as described above. Such semiconductor elements are exemplified by semiconductor elements used in diodes, transistors, thyristors, solid-state image pickup elements, monolithic ICs and in hydride ICs. In particular, it is preferable that semiconductor elements are light-emitting elements.

Examples of such semiconductor devices included diodes, light-emitting diodes, transistors, thyristors, photocouplers, CCDs, monolithic IICs, hybrid ICs, LSIs, and VLSIs.

Hereinafter, the present invention will be described in more detail with exemplary embodiments. However, the following exemplary embodiments are given for illustrative purposes only, and the scope of the present invention is not limited to these exemplary embodiments.

Examples

<Analytical Methods>

(1) Description of ^{29}Si-NMR measurement

* Solvent: C_6D_6 99,8%d/CCl_4 1:1 v/v with 1 % w/w $Cr(acac)_3$ as reagent for relaxation

* Sample concentration: ca. 2 g / 1.5 mL solvent in 10 mm NMR tube

* Spectrometer: Bruker Avance 300

* Sample head: 10 mm $^{1}H/^{13}C/^{15}N/^{29}Si$ glassfree QNP-Head (Bruker)

* Measurement parameter: Pulprog = zgig60, TD = 64k, NS = 1024, SW = 200 ppm, AQ = 2.75 s, D1 = 4 s, SFO1 = 300.13 MHz, O1 = -50 ppm

* Processing-Parameter: SI = 64k, WDW = EM, LB = 0.3 Hz

(2) Viscosity

Viscosity data is measured with a rheometer model MCR302 manufactured by the company Anton Paar, D-Ostfildern, according to DIN EN ISO 3219 in rotation with a cone-plate measurement system. Measurements were performed in a range where the samples behavior is newtonian. Viscosity data are given for a temperature of 25 °C and an ambient pressure of 1013 mbar.

(3) Molecular weight

Molecular weight is determined as weight average molecular weight Mw and number average molecular Mn by Size Exclusion Chromatography SEC. Polystyrene is

used as standard. The detector is a RI detector. THF is used as solvent. Sample concentration is 5 mg / mL.

[Example 1]

1-1. Synthesis of Branched Organopolysiloxane

After phenyl triethoxy silane, dimethyl dimethoxy silane, and divinyl tetramethyl disiloxane as monomers were introduced into a glass reactor at a molar ratio of 7 : 1 : 1, water was introduced thereinto in an amount of 1 part by weight relative to the content of the phenyl triethoxy silane, and then hydrochloric acid (HCl) as a catalyst was introduced thereinto in an amount of 0.0009 part by weight relative to the content of the water. Thereafter, after the mixture was refluxed for 2 hours and heated, sodium hydroxide was introduced thereinto in an amount of 0.0016 part by weight relative to the content of water used, and then the resulting mixture was subjected to condensation polymerization by being refluxed and heated.

After the reaction solution was neutralized with hydrochloric acid until the time point when the acidity of the reaction solution became acidic, a solution containing a branched organopolysiloxane was obtained by removing the aqueous layer of the solution cooled to room temperature, and introducing toluene thereinto in an amount of 1 part by weight relative to the content of the phenyl triethoxy silane used above.

The solvent was removed from the solution containing the branched organopolysiloxane obtained above under vacuum, and ^{29}Si NMR of the remaining solid content (the branched organopolysiloxane) was ($Me_2ViSiO_{1/2}$): 20%, ($Me_2SiO_{2/2}$): 10%, ($PhSiO_{3/2}$): 70%.

1-2. Preparation of Branched Organopolysiloxane Including Cerium Salt

The content of the solid content in the solution containing the branched organopolysiloxane obtained in Example 1-1 was measured, and the content of branched organopolysiloxane used was estimated based on this content. Thereafter, the solution containing the branched organopolysiloxane was introduced together with methanol into a glass reactor. In this case, methanol was used in an amount of 0.25 part by weight relative to the content of toluene used in Example 1-1. Thereafter, sodium hydroxide was introduced into the glass reactor in an amount of 0.028 part by weight relative to the estimated content of the branched organopolysiloxane, and then the mixture was stirred at room temperature for 2 hours.

Thereafter, cerium ethylhexanoate was introduced in an amount of 0.057 part by weight relative to the estimated content of the branched organopolysiloxane compound, and then the mixture was allowed to react while being stirred at 50°C for 2 hours.

After the reaction was terminated, the solution was cooled, the aqueous layer was removed, and then a branched vinylsiloxane compound containing cerium salt $[(Me_2ViSiO_{1/2})_{(0.2-x)}(Me_2SiO_{2/2})_{(0.1-y)}(PhSiO_{3/2})_{(0.7-z)}(Ce_{1/3}Me_2SiO_{2/2})_{(x+y+z)}]$ was prepared by filtering and distilling the remaining solution.

1-3. Preparation of Curable Organopolysiloxane

2.5 parts by weight of the branched vinylsiloxane compound containing cerium salt obtained in Example 1-2 as component (A), 73.55 parts by weight of the branched vinylsiloxane compound obtained in Example 1-1 as component (B), 21 parts by weight of 1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane as component (C), 0.03 parts by weight of a platinum(0)-1,3-divinyl-1,1,3,3,-tetramethyl-disiloxane complex as component (D), 3 parts by weight of D^{Vi}_4 as component (E), 0.76 parts by weight of 3-

Glycidoxypropyltrimethoxysilane as additive (1) which is adhesion promoter, 0.76 parts by weight of 3-Methacryloxypropyltrimethoxysilane as additive (2) which is adhesion promoter, and 0.9 parts by weight of 2-Methyl-3-butyn-2-ol as additive (3) which is curing inhibitor were mixed to prepare a curable organopolysiloxane composition. In this case, the content of each component was based on 100 parts by weight of the sum of the amounts of components (B), (C), (D), (E), and additive (1) to (3).

[Comparative Example 1]

73.55 parts by weight of the branched vinylsiloxane compound obtained in Example 1-1 as component (B), 21 parts by weight of 1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane as component (C), 0.03 parts by weight of a platinum(0)-1,3-divinyl-1,1,3,3,-tetramethyl-disiloxane complex as component (D), 3 parts by weight of D^{Vi}_4 as component (E), 0.76 parts by weight of 3-Glycidoxypropyltrimethoxysilane as additive (1) which is adhesion promoter, 0.76 parts by weight of 3-Methacryloxypropyltrimethoxysilane as additive (2) which is adhesion promoter, and 0.9 parts by weight of 2-Methyl-3-butyn-2-ol as additive (3) which is curing inhibitor were mixed to prepare a curable organopolysiloxane composition. In this case, the content of each component was based on 100 parts by weight of the sum of the amounts of components (B), (C), (D), (E), and additive (1) to (3).

[Experimental Example 1: Crack test]

For the compositions in Example 1 and Comparative Example 1, it was determined whether cracks occurred. Specimens of LED packages and specimens of cured silicone each contained in an aluminum pan were prepared, and then it was

observed whether cracks occurred on the specimens at the time of quenching the specimens from 250°C to room temperature (about 22.5°C) at an interval of 4 hours. The results each are shown in Figs. 1 and 2.

As shown in Figs. 1 and 2, even though the quenching of the composition in Example 1 from 250°C to room temperature was repeated 25 times (100 hours), any crack did not occur. On the contrary, when the quenching of the composition in Comparative Example 1 from 250°C to room temperature was repeated 6 times (24 hours), cracks occurred.

[Experimental Example 2: Hardness and weight change test]

For the composition according to example 1 and comparative example 1, change of hardness and weight after storage at 200 °C was determined. Specimens of cured silicone are prepared and stored at 200 °C. Then, change of hardness and weight of the specimens were measured. The result is shown in the Figs. 3 and 4.

As shown in Figs. 3 and 4, the composition according to example 1 shows almost no change of hardness and weight at 200 °C, whereas the composition according to comparative example 1 shows increase of hardness and weight.

WHAT IS CLAIMED IS:

1. A curable organopolysiloxane composition comprising:

(A) a cerium (Ce)-containing branched organopolysiloxane;

(B) a branched organopolysiloxane;

(C) a linear organopolysiloxane with both terminal ends of the molecular chain blocked by silicon-bonded hydrogen atoms, having at least one silicon-bonded aryl group per molecule;

(D) a hydrosilylation reaction catalyst; and

(E) a low molecular weight siloxane having at least one silicon-bonded alkenyl group per molecule, represented by the following average formula 1:

[average formula 1]

$(R^8_3SiO_{1/2})_f(R^8_2SiO_{2/2})_g(R^8SiO_{3/2})_h(SiO_{4/2})_i$

(where

each R^8 is the same or different and is independently selected from a substituted or unsubstituted monovalent hydrocarbon group,

wherein at least one of R^8 per molecule is an alkenyl group,

with the proviso that a ratio between alkenyl groups and silicon atoms is from 0.3 to 1 : 1,

f, g, h, and i are independently 0 or a positive number,

wherein f+g+h+i is 1, and

the weight average molecular weight Mw of the siloxane is 1,000 g/mol or less).

2. The curable organopolysiloxane composition of claim 1, wherein in component (A), a content of cerium is 0.1 to 2% by weight based on the total weight of the curable

organopolysiloxane composition.

3. The curable organopolysiloxane composition of claim 1, wherein component (A) is a material formed by allowing an alkali metal salt of a silanol group-containing branched organopolysiloxane to react with cerium chloride or cerium salt of carboxylic acid.

4. The curable organopolysiloxane composition of claim 3, wherein a molar ratio of the cerium chloride (or cerium salt of carboxylic acid) to the alkali metal salt of the silanol group containing-branched organopolysiloxane is 1 : 0.1 to 2.

5. The curable organopolysiloxane composition of claim 3, wherein a content of silanol groups in the alkali metal salt of the silanol group-containing branched organopolysiloxane is 1 to 3 mol% per molecule.

6. The curable organopolysiloxane composition of claim 3, wherein the alkali metal salt of the silanol group-containing branched organopolysiloxane is an alkali metal salt of a branched organopolysiloxane having at least one silanol group, at least one silicon-bonded alkenyl group, and at least one silicon-bonded aryl group per molecule, and having siloxane units represented by the following general formula 1:

[general formula 1]

$RSiO_{3/2}$

(where R is a C_1 to C_{20} monovalent hydrocarbon group).

7. The curable organopolysiloxane composition of claim 3, wherein the alkali metal salt of the silanol group-containing branched organopolysiloxane is an alkali metal salt of an organopolysiloxane represented by the following average unit formula 1:

[average unit formula 1]

$(R^1R^1R^3SiO_{1/2})_a(R^1{}_2SiO_{2/2})_b(R^2SiO_{3/2})_c(SiO_{4/2})_d(X^1O_{1/2})_e$

(where each of R^1, R^2, and R^3 is the same or different and is independently selected from a substituted or unsubstituted C_1 to C_{20} monovalent hydrocarbon group,

with the proviso that at least one of R^1, R^2, and R^3 per molecule is a silanol group, at least one of R^1, R^2, and R^3 per molecule is a C_2 to C_{12} alkenyl group, and at least one of R^1, R^2, and R^3 per molecule is a C_6 to C_{20} aryl group,

X^1 is a hydrogen atom or a C_1 to C_{20} alkyl group,

a is 0 or a positive number,

b is 0 or a positive number,

c is a positive number,

d is 0 or a positive number,

e is 0 or a positive number,

b/c is a number between 0 and 10,

a/c is a number between 0 and 0.5,

d/(a+b+c+d) is a number between 0 and 0.3, and

e/(a+b+c+d) is a number between 0 and 0.4).

8. The curable organopolysiloxane composition of claim 3, wherein the alkali metal salt of the silanol group-containing branched organopolysiloxane is an alkali

metal salt of an organopolysiloxane represented by the following average unit formula 2:

[average unit formula 2]

$(R^1R^1R^3SiO_{1/2})_a(R^1{}_2SiO_{2/2})_b(R^2SiO_{3/2})_c$

(where R^1 is a C_1 to C_{12} alkyl group,

R^2 is a C_6 to C_{20} aryl group or a C_7 to C_{20} aralkyl group,

R^3 is a C_2 to C_{12} alkenyl group,

a is 0 or a positive number,

b is 0 or a positive number, and

c is a positive number,

with the proviso that at least one of R^1, R^2, and R^3 per molecule is a silanol group).

9. The curable organopolysiloxane composition of claim 7, wherein a content of the silanol groups is 1 to 3 mol% of R^1, R^2, and R^3 per molecule.

10. The curable organopolysiloxane composition of claim 1, wherein the cerium-containing branched organopolysiloxane has a weight average molecular weight of 1,000 to 3,000 g/mol.

11. The curable organopolysiloxane composition of claim 1, in which the component (B) is a branched organopolysiloxane having at least one silicon-bonded alkenyl group and at least one silicon-bonded aryl group per molecule, and having siloxane units represented by the general formula 2:

[general formula 2]

$RSiO_{3/2}$

where R is a substituted or unsubstituted monovalent a C_1 to C_{20} hydrocarbon group

12. The curable organopolysiloxane composition of claim 1, in which the component (B) is an organopolysiloxane represented by the average unit formula 3:

[average unit formula 3]

$(R^4R^4R^6SiO_{1/2})_a(R^4{}_2SiO_{2/2})_b(R^5SiO_{3/2})_c(SiO_{4/2})_d(X^2O_{1/2})_e$

where each of R^4, R^5, and R^6 can be the same or different, and is independently selected from a substituted or unsubstituted a C_1 to C_{20} monovalent hydrocarbon group, wherein at least one of R^4, R^5, or R^6 per molecule is a C_1 to C_{12} alkenyl group and at least one of R^4, R^5, or R^6 per molecule is a C_1 to C_{20} aryl group,

X^2 is a hydrogen atom or a C_1 to C_{20} alkyl group,

a is 0 or a positive number,

b is 0 or a positive number,

c is a positive number,

d is 0 or a positive number,

e is 0 or a positive number,

b/c is a number between 0 and 10,

a/c is a number between 0 and 0.5,

d/(a+b+c+d) is a number between 0 and 0.3, and

e/(a+b+c+d) is a number between 0 and 0.4.

13. The curable organopolysiloxane composition of claim 1, in which component (B) is an organopolysiloxane with the average unit formula 4:

[average unit formula 4]

$(R^4R^4R^6SiO_{1/2})_a(R^4{}_2SiO_{2/2})_b(R^5SiO_{3/2})_c$

where R^4 is a C_1 to C_{12} alkyl group,

R^5 is a C_6 to C_{20} aryl group or C_7 to C_{20} aralkyl group,

R^6 is a C_2 to C_{12} alkenyl group,

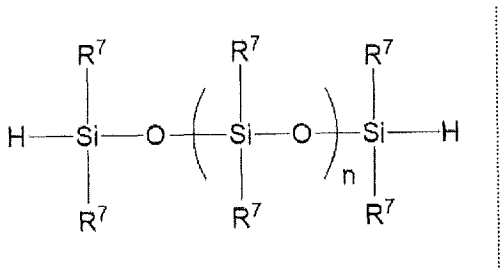
a is 0 or a positive number,

b is 0 or a positive number, and

c is a positive number.

14. The curable organopolysiloxane composition of claim 1, in which component (C) is an organopolysiloxane represented by the general formula 3:

[general formula 3]



where each R^7 can be the same or different and is independently selected from a hydrogen atom or a substituted or unsubstituted C_1 to C_{20} monovalent hydrocarbon group with the exception of alkenyl groups, wherein at least one R^7 per molecule is a C_6 to C_{20} aryl group, and

n is an integer of 0 or more.

15. The curable organopolysiloxane composition of claim 1, in which component (E) is selected from the group consisting of D^{Vi}_4, M^{Vi}_4Q, $M^{Vi}_6Q_2$, M^{Vi}_3T.

16. The curable organopolysiloxane composition of claim 1, in which component (E) comprises D^{Vi}_4.

17. The curable organopolysiloxane composition of claim 1, wherein based on 100 parts by weight of the composition, the curable organopolysiloxane composition comprises:

0.01 to 5 parts by weight of the component (A);

60 to 85 parts by weight of the component (B);

10 to 30 parts by weight of the component (C);

0.001 to 0.3 parts by weight of the component (D); and

0.5 to 10 parts by weight of the component (E).

18. The curable organopolysiloxane composition of claim 1, wherein the molar ratio of the hydrosilyl group in component (C) with respect to the alkenyl group in components (A) and (B) [$\left|\frac{M_1}{M_2}\right|$, where M_1 is a number of moles of the alkenyl group in components (A) and (B), and M_2 is a number of moles of the hydrosilyl group in component (C)] is 1 to 1. 2.

19. The curable organopolysiloxane composition of claim 1, further comprising at

least one selected from the group consisting of a crosslinking agent, a curing inhibitor, a catalyst, and a phosphor.

20. An LED encapsulant comprising the curable organopolysiloxane composition according to any one of claims 1 to 19.

21. A semiconductor device, in which semiconductor elements are coated with a cured product of the curable organopolysiloxane composition according to any one of claims 1 to 19.

22. The semiconductor device according to claim 21, in which said semiconductor elements are light-emitting elements.

Fig. 1

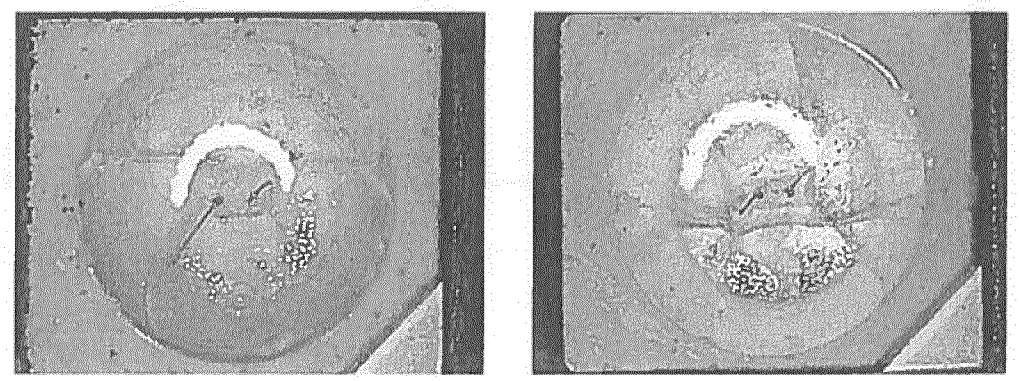


Fig. 2

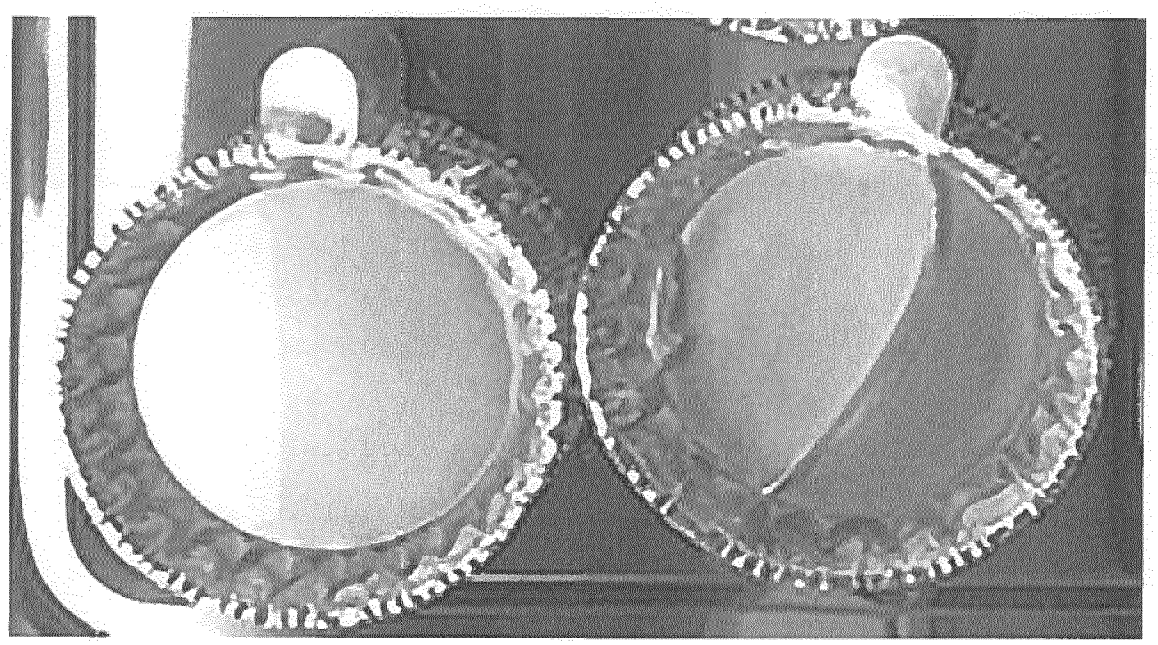


Fig. 3

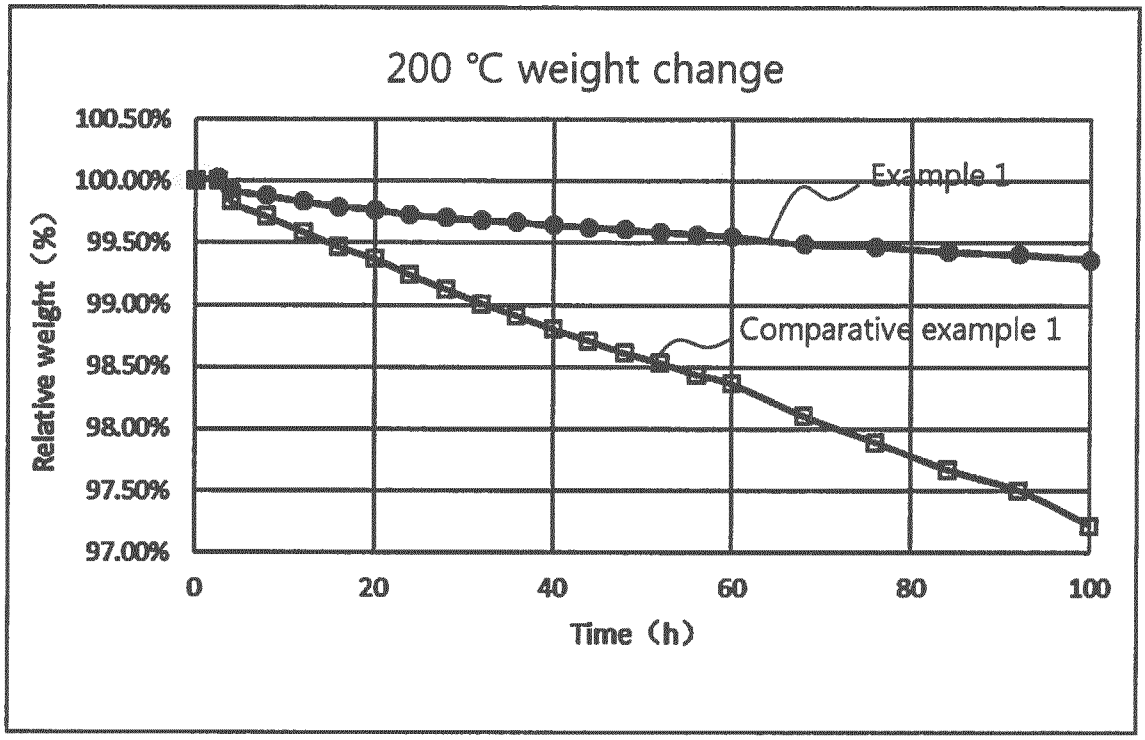
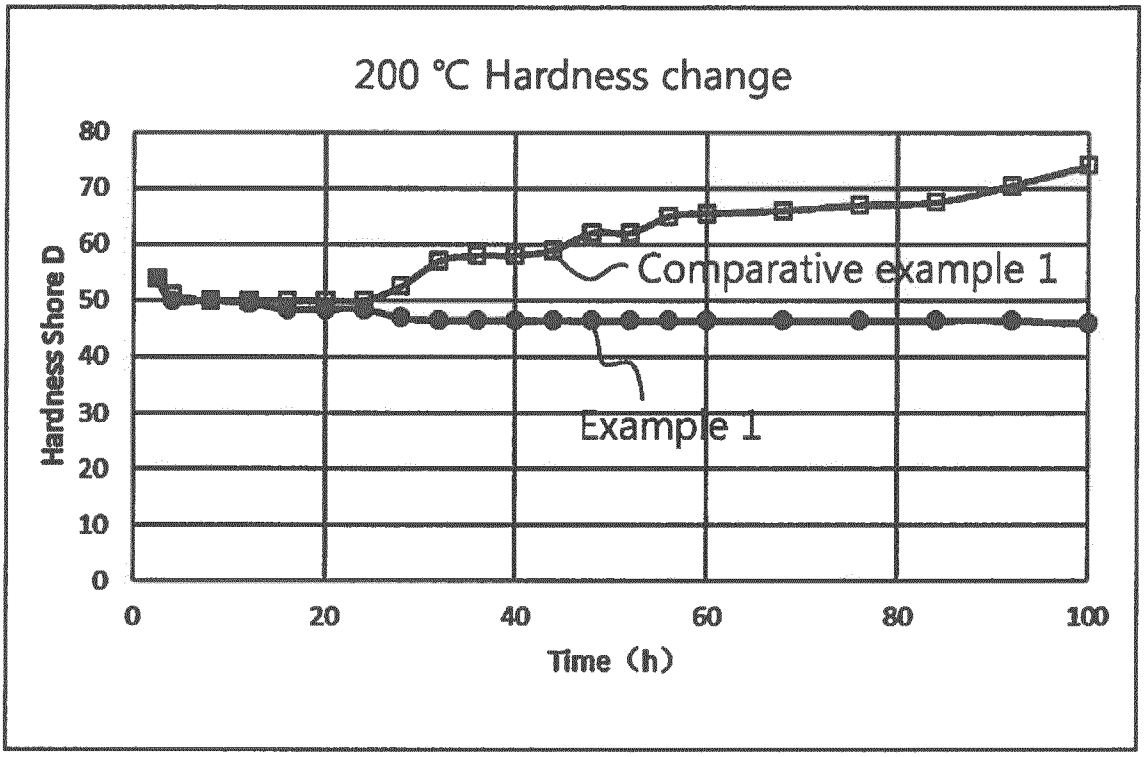

200 °C weight change
100.50%
100.00%
99.50%
99.00%
98.50%
98.00%
97.50%
97.00%
Relative weight (%)
0
20
40
60
80
100
Time (h)
Example 1
Comparative example 1

Fig. 4


200 °C Hardness change
Hardness Shore D
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
Time (h)
Comparative example 1
Example 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/073487

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D183/04 C09D183/06 C09D183/08 C08G77/12 C08G77/20
C08G77/398 C08L83/04 C08L83/08 H01L23/31 H01L33/56
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)
C09D C08K H01L C08G 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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2018/028792 A1 (WACKER CHEMIE AG [DE]) 15 February 2018 (2018-02-15) page 3, lines 5-24 page 4, lines 7-14 page 14, line 23 - page 15, line 2 page 21, lines 1-24 example 1	1-22
Y	CN 107 629 460 A (GUANGZHOU HUMAN CHEMICALS CO LTD) 26 January 2018 (2018-01-26) the whole document	1-22
Y	GB 1 393 078 A (TORAY SILICONE CO) 7 May 1975 (1975-05-07) page 1, lines 11-19 page 2, lines 9-43 example 4	1-22

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[X] Further documents are listed in the continuation of Box C.

[X] 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
14 March 2019	22/03/2019

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	Denis, Cécile

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/073487

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2014/130784 A1 (DOW CORNING TORAY CO LTD [JP]; DOW CORNING [US]) 28 August 2014 (2014-08-28) page 2, paragraph 6 - page 3, paragraph 7 page 3, paragraph 10 - page 4, paragraph 12 page 11, paragraph 42 page 9, paragraph 38 - page 10, paragraph 39 examples 1-9,10-11 -----	1-22

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2018/073487

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		WO 2018028792 A1	15-02-2018
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