

DESCRIPTION

Title of Invention:

CURABLE RESIN COMPOSITION AND CURED PRODUCT THEREOF

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Technical Field

[0001]

The present invention relates to a curable resin composition and a cured product thereof, suitable for electric and electronic materials uses, particularly optical semiconductor uses.

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Background Art

[0002]

Hitherto, as an encapsulating material for optical semiconductor elements of LED products and the like, epoxy resin compositions have been adopted in view of balance between performance and economic efficiency. Particularly, there have been widely used glycidyl ether-type epoxy resin compositions including bisphenol A-type epoxy resins as representatives, which are excellent in balance of heat resistance, transparency and mechanical strength.

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However, as a result of the advancement of shortening of emission wavelength of LED products (480 nm or less in LED products mainly emitting a blue light), it has been pointed out that the encapsulating material is colored on an LED chip by the influence of the short wavelength light and finally illuminance as the LED products decreases.

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Consequently, since alicyclic epoxy resins including 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexylcarboxylate as a representative are excellent in transparency as compared with glycidyl ether-type epoxy resin compositions having an aromatic ring, aggressive investigation as LED encapsulating materials have been performed (Patent Documents 1 and 2).

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[0003]

In general, as curing agents for epoxy resins to be used in such a field, acid anhydride-based compounds are mentioned. Particularly, acid anhydrides formed of saturated hydrocarbons are frequently utilized because cured products therewith are excellent in light resistance. As such acid anhydrides, alicyclic acid anhydrides such as methyltetrahydrophthalic anhydride, hexahydrophthalic anhydride and tetrahydrophthalic anhydride are common. Of these, methylhexahydrophthalic anhydride, methyltetrahydrophthalic anhydride and the like that are liquid at ordinary temperature have been mainly used owing to easiness in handling.

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However, in the case where the above alicyclic acid anhydrides are used as curing

agents, since these curing agents have high vapor pressure and vaporize in part at curing, at the time of thermal curing in an open system using them as curing agents for epoxy resins, there arise problems that they themselves vaporize into the air to cause not only environmental pollution and adverse effects on the human body through the release of harmful substances into the air but also pollution of product lines and poor curing of epoxy resin compositions resulting from the absence of a predetermined amount of carboxylic anhydrides (curing agents) in cured products, and also characteristic properties thereof remarkably change depending on curing conditions, so that it is difficult to obtain cured products having objective performance stably.

[0004]

Moreover, cured products using conventional curing agents remarkably show the problems at the time when LED, particularly SMD (Surface Mounted Device) is encapsulated and, owing to the small amount of the resin to be used, there arises a problem that concave(s) are generated and, in the severe case, wires are exposed due to the aforementioned vaporization problem. Furthermore, there is a problem that, owing to cracks, detachment and the like at solder reflow and further insufficient curing, it is difficult to endure long-term lighting.

[0005]

Moreover, as another problem, since brightness has been further heightened for illumination, backlight for TV sets, and the like in recent LED products and much heat generation has been involved at the time when LED is lighted, even in the case of a resin composition using the alicyclic epoxy resin, coloration has occurred on the LED chip and finally illuminance as the LED products has decreased, so that a problem still remains even in view of durability (Patent Document 3).

[0006]

Because of the durability problem of the epoxy resins, there have been performed investigations in which resins to which a siloxane skeleton (specifically a skeleton having an Si-O bond) has been introduced, including silicone resins, silicone-modified epoxy resins and the like as representatives, are used as encapsulating materials (Patent Document 3).

In general, it is known that resins to which the siloxane skeleton has been introduced are more stable against heat and light than epoxy resins. Therefore, it has been said that, in the case of the application to the encapsulating agent for LED products, durability is more excellent than in the case of epoxy resins from the viewpoint of the coloration on the LED chip. However, problems exist.

The resins to which the siloxane skeleton has been introduced are apt to exhibit brittleness remarkably as compared with usual epoxy resins. Therefore, reflow resistance is poor and cracks at reflow are noticeable.

Furthermore, the resins to which the siloxane skeleton has been introduced are inferior in gas permeation resistance to usual epoxy resins. Therefore, in the case where a silicone resin or a silicone-modified epoxy resin is used as an LED encapsulating material, there arises a problem that deterioration and coloration of interior constituent members occur, although the coloration on the LED chip is not a problem. Particularly, in the case where the resin is used in living environment, various compounds are floating therein and the permeation of such compounds into the inside triggers off the occurrence of a trouble. For example, in the case where the resin is used in illumination uses, there is a problem that a silver component (silver plating is performed for increasing reflectance) plated on a metal lead frame that is a constituent member in an LED package is discolored or blackened by the permeation of gases in the environment through the encapsulating material for LED and finally, performance as an LED product is lowered (Patent Documents 4 and 5).

[0007]

In order to solve the problem of the gas permeation resistance, Patent Documents 4 and 5 use a method of coverage with a gas permeation-resistant protecting agent, a method of covering a metal part with an inorganic material, or the like. However, there is a problem that not only steps increase and productivity becomes worse but also light extraction efficiency decreases due to the difference in refractive index between the covered part and the encapsulating agent.

Related Art

Patent Documents

[0008]

Patent Document 1: JP-A-9-213997

Patent Document 2: Japanese Patent No. 3618238

Patent Document 3: WO 2005/100445

Patent Document 4: JP-A-2007-324256

Patent Document 5: JP-A-2000-174347

Summary of the Invention

Problems to Be Solved by the Invention

[0009]

An object of the invention is to obtain a cured product which exhibits little vaporization at curing, is excellent in optical properties as LED and corrosive gas resistance, and is excellent in toughness.

5 Means for Solving the Problems

[0010]

As a result of the extensive studies in consideration of such real circumstances as mentioned above, the present inventors have accomplished the invention.

Namely, the invention relates to the followings.

- 10 (1) A curable resin composition, comprising:
an epoxy resin (A);
a polyhydric carboxylic acid (B); and
a zinc salt and/or a zinc complex (C) as essential components, provided that the
polyhydric carboxylic acid (B) and the zinc salt and/or the zinc complex (C) satisfy the
15 following requirements respectively:
Polyhydric carboxylic acid (B): a polyhydric carboxylic acid having at least two
carboxyl groups and having a siloxane skeleton as a main skeleton; and
Zinc salt and/or zinc complex (C): a zinc carboxylate, a zinc salt of a phosphate
ester or phosphoric acid and/or a zinc complex having the acid or ester as a ligand.
20 (2) The curable resin composition as described in the above item (1),
wherein the polyhydric carboxylic acid (B) has a linear polysiloxane structure and
has carboxylic acids at both terminals.
(3) The curable resin composition as described in the above item (1) or (2),
wherein the polyhydric carboxylic acid (B) is a compound obtained by a reaction
25 of a carbinol-modified compound having a linear polysiloxane structure with a cyclic
saturated aliphatic acid anhydride.
(4) The curable resin composition as described in any one of the above items (1)
to (3), comprising:
a hindered amine-based photo-stabilizer; and
30 a phosphorus-containing antioxidant.
(5) A cured product, which is obtained by curing the curable resin composition
as described in any one of the above items (1) to (4).

Effects of the Invention

35 [0011]

Since the curable resin composition of the invention is excellent in corrosive gas resistance, the composition is extremely useful as particularly an adhering material and an

encapsulating material for particularly optical semiconductors (LED products etc.) to be used in living environment, for example, illumination, among optical materials.

Embodiments for Carrying Out the Invention

[0012]

The following will describe the curable resin composition of the invention.

The curable resin composition of the invention comprises an epoxy resin (A), a polyhydric carboxylic acid (B), and a zinc salt and/or a zinc complex (C) as essential components.

As the epoxy resin (A), there may be mentioned novolak-type epoxy resins, bisphenol A-type epoxy resins, biphenyl-type epoxy resins, triphenylmethane-type epoxy resins, phenolaralkyl-type epoxy resins and the like. Specifically, there may be mentioned solid or liquid epoxy resins including bisphenol A, bisphenol S, thiodiphenol, fluorene bisphenol, terpene diphenol, 4,4'-biphenol, 2,2'-biphenol, 3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'-diol, hydroquinone, resorcin, naphthalenediol, tris-(4-hydroxyphenyl)methane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, polycondensates of phenols (phenol, alkyl-substituted phenols, naphthol, alkyl-substituted naphthaols, dihydroxybenzene, dihydroxynaphthalene, etc.) with formaldehyde, acetaldehyde, bezaldehyde, p-hydroxybenzaldehyde, o-hydroxybenzaldehyde, p-hydroxyacetophenone, o-hydroxyacetophenone, dicyclopentadiene, furfural, 4,4'-bis(chloromethyl)-1,1'-biphenyl, 4,4'-bis(methoxymethyl)-1,1'-biphenyl, 1,4-bis(chloromethyl)benzene, 1,4-bis(methoxymethyl)benzene or the like and modified compounds thereof, halogenated bisphenols such as tetrabromobisphenol A, glycidyl etherified compounds derived from alcohols, alicyclic epoxy resins, glycidylamine-based epoxy resins, glycidyl ester-based epoxy resins, polysiloxane-type epoxy resins (epoxy resins having a glycidyl group and/or epoxycyclohexane structure in a siloxane structure of chain, cyclic or ladder one, or a mixed structure of two or more thereof) and the like, but the epoxy resins are not limited thereto. They may be used singly or two or more thereof may be used in combination.

[0013]

Particularly, it is mainly purposed that the curable resin composition of the invention is used in optical uses. In the case where the composition is used in optical uses, it is preferred to use the alicyclic epoxy resins or the organopolysiloxane-type epoxy resins. In the case of the alicyclic epoxy resins, the resins are preferably compounds having an epoxycyclohexane structure in the skeleton and particularly preferably epoxy resins obtained by oxidation reaction of compounds having a cyclohexane structure.

As the alicyclic epoxy resins, there may be mentioned those obtained by oxidation of compounds that can be produced by the esterification reaction of cyclohexenecarboxylic acid with alcohols or the esterification reaction of cyclohexenemethanol with carboxylic

acids (procedures described in Tetrahedron vol. 36 p.2409 (1980), Tetrahedron Letter p.4475 (1980) and the like), or the Tishchenko reaction of cyclohexenealdehyde (procedures described in JP-A-2003-170059, JP-A-2004-262871 and the like), or further the ester-exchange reaction of cyclohexenecarboxylate esters (procedures described in JP-A-2006-052187 and the like).

The alcohols are not particularly limited as long as they are compounds having an alcoholic hydroxyl group but there may be mentioned diols such as ethylene glycol, propylene glycol, 1,3-propanediol, 1,2-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, cyclohexanedimethanol, 2,4-diethylpentanediol, 2-ethyl-2-butyl-1,3-propanediol, neopentyl glycol, tricyclodecanedimethanol and norbornenediol; triols such as glycerin, trimethylolethane, trimethylolpropane, trimethylolbutane, 2-hydroxymethyl-1,4-butanediol; tetraols such as pentaerythritol and ditrimethylolpropane; and the like. Moreover, as the carboxylic acids, there may be mentioned oxalic acid, maleic acid, fumaric acid, phthalic acid, isophthalic acid, adipic acid, cyclohexanedicarboxylic acid and the like but the acids are not limited thereto.

[0014]

Further, there may be mentioned acetal compounds obtained by the acetalization reaction of cyclohexenealdehyde derivatives with alcohol compounds.

[0015]

Also, there may be mentioned those obtained by oxidation of alicyclic multivalent olefins such as vinylcyclohexene or limonene, dicyclopentadiene, tricyclopentadiene, methyldicyclopentadiene, bicyclohexene and octadiene, and the like.

[0016]

Specific examples of these epoxy resins include ERL-4221, ERL-4299 (all trade names, all manufactured by Dow Chemical), Epolead GT401, EHPE3150, EHPE3150CE (all trade names, all manufactured by Daicel Chemical Industries, Co., Ltd.) and dicyclopentadiene diepoxide and the like but they are not limited thereto (Reference Literature: Sosetsu Epokisi Rejin Kiso-hen I p76-85).

They may be used singly or two or more thereof may be used in combination.

[0017]

The organopolysiloxane-type epoxy resin is not particularly designated as long as it is an organopolysiloxane having an epoxycyclohexane structure. In the invention, there may be particularly mentioned a compound obtained by a sol-gel reaction using as a raw material an alkoxysilane having an epoxycyclohexyl group.

Specifically, there may be mentioned silsesquioxane-type organopolysiloxanes having a three-dimensionally spreading reticular structure, described in JP-A-2004-256609, JP-A-2004-346144, WO2004/072150, JP-A-2006-8747, WO2006/003990, JP-A-2006-104248, WO2007/135909, JP-A-2004-10849, JP-A-2004-359933, WO2005/100445, JP-A-

2008-174640, and the like.

The structure of the organopolysiloxane is not particularly limited but, since a siloxane compound having a simple three-dimensional reticular structure is too hard, a structure that reduces the hardness is desired.

In the invention, a block structural body having a silicone segment and the aforementioned silsesquioxane structure obtained by a sol-gel reaction in one molecule is particularly preferred. As a production process of the compound, there may be mentioned a production process and a structure described in WO2010/026714.

Specifically, in the invention, the structure is not particularly limited but, since an organopolysiloxane structure having a simple three-dimensional reticular structure is too hard, a structure that reduces the hardness is desired. In the invention, a block structural body having a silicone segment and the aforementioned silsesquioxane structure of the coupling agent in one molecule is particularly preferred (hereinafter referred to as block-type siloxane compound (A1)).

[0018]

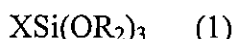
The block-type siloxane compound (A1) is not a compound having repeating units linearly as in usual block copolymers but has a three-dimensionally spreading reticular structure in which a silsesquioxane structure is a core and a chain silicone segment is extended and bonded to the next silsesquioxane structure. The present structure is effective for imparting a balance between hardness and flexibility to a cured product of the curable resin composition of the invention.

[0019]

The block-type siloxane compound (A1) can be, for example, produced using an alkoxysilane compound (a) represented by the general formula (1) and a silicone oil (b) represented by the general formula (2) as raw materials and, according to need, an alkoxysilane compound (c) represented by the general formula (3) can be used as a raw material. The chain silicone segment of the block-type siloxane compound (A1) is formed from the silicone oil (b) and the three-dimensional reticular silsesquioxane segment is formed from the alkoxysilane (a) (and the alkoxysilane (c) to be added according to need). The following will explain individual raw materials in detail.

[0020]

The alkoxysilane compound (a) is represented by the following general formula (1):



As X in the general formula (1) is not particularly limited as long as it is an organic group having an epoxy group. Examples thereof include glycidoxy alkyl groups having 1 to 4 carbon atoms, such as β -glycidoxyethyl, γ -glycidoxypropyl and γ -glycidoxybutyl, a glycidyl group, alkyl groups having 1 to 5 carbon atoms substituted with

a cycloalkyl group of 5 to 8 carbon atoms having an oxirane group, such as a β -(3,4-epoxycyclohexyl)ethyl group, a γ -(3,4-epoxycyclohexyl)propyl group, a β -(3,4-epoxycycloheptyl)ethyl group, a β -(3,4-epoxycyclohexyl)propyl group, a β -(3,4-epoxycyclohexyl)butyl group and a β -(3,4-epoxycyclohexyl)pentyl group. Of these, alkyl groups having 1 to 3 carbon atoms substituted with a glycidoxy group and alkyl groups having 1 to 3 carbon atoms substituted with a cycloalkyl group of 5 to 8 carbon atoms having an epoxy group, for example, a β -glycidoxyethyl group, a γ -glycidoxypropyl group, and a β -(3,4-epoxycyclohexyl)ethyl group are preferred, and particularly, a β -(3,4-epoxycyclohexyl)ethyl group is preferred.

[0021]

A plurality of R_2 groups present in the general formula (1) may be the same or different from each other and represent a linear, branched or cyclic alkyl group having 1 to 10 carbon atoms. Examples thereof include a methyl group, an ethyl group, an n-propyl group, an i-propyl group, an n-butyl group, an i-butyl group, a tert-butyl group, an n-pentyl group, an n-hexyl group, a cyclopentyl group, a cyclohexyl group, and the like. As these R_2 groups, from the viewpoints of reaction conditions such as compatibility and reactivity, a methyl group or an ethyl group is preferred and particularly, a methyl group is preferred.

[0022]

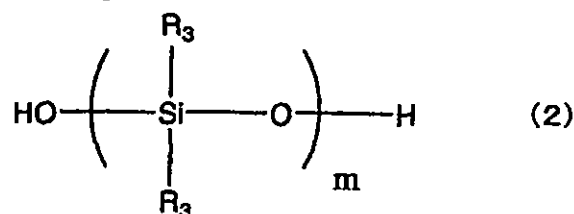
Preferable specific examples of the alkoxysilane (a) include β -glycidoxyethyltrimethoxysilane, β -glycidoxyethyltriethoxysilane, γ -glycidoxypropyltrimethoxysilane, γ -glycidoxypropyltriethoxysilane, β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, β -(3,4-epoxycyclohexyl)ethyltriethoxysilane and the like. Particularly, β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane is preferred. These alkoxysilane compounds (a) may be used singly or two or more thereof may be used, or they may be used in combination with an alkoxysilane (c) to be mentioned below.

[0023]

The silicone oil (b) is a chain silicone oil having a silanol group at the terminal, which has a structure represented by the following general formula (2).

[0024]

[Chem. 1]



[0025]

In the general formula (2), a plurality of R_3 groups present may be the same or different from each other and represent an alkyl group having 1 to 10 carbon atoms, an aryl group having 6 to 14 carbon atoms, or an alkenyl group having 2 to 10 carbon atoms.

The alkyl group having 1 to 10 carbon atoms includes linear, branched or cyclic alkyl groups having 1 to 10 carbon atoms. Examples thereof include a methyl group, an ethyl group, an n-propyl group, an i-propyl group, an n-butyl group, an i-butyl group, a sec-butyl group, a t-butyl group, an n-pentyl group, an i-pentyl group, an amyl group, an n-hexyl group, a cyclopentyl group, a cyclohexyl group, an octyl group, a 2-ethylhexyl group, a nonyl group, a decyl group and the like. Of these, in consideration of light resistance, a methyl group, an ethyl group and a cyclohexyl group are preferred.

Examples of the aryl group having 6 to 14 carbon atoms include a phenyl group, an o-tolyl group, an m-tolyl group, a p-tolyl group, a xylyl group and the like.

Examples of the alkenyl group having 2 to 10 carbon atoms include alkenyl groups such as a vinyl group, a 1-methylvinyl group, an allyl group, a propenyl group, a butenyl group, a pentenyl group and a hexenyl group.

From the viewpoints of light resistance and heat resistance, R_3 is preferably a methyl group, a phenyl group, a cyclohexyl group or an n-propyl group and particularly preferably a methyl group or a phenyl group.

[0026]

m in the compound of the general formula (2) represents 3 to 200 as an average value and is preferably 3 to 100, more preferably 3 to 50. When m is less than 3, the cured product becomes too hard and low elastic modulus properties decrease. When m is more than 200, the mechanical properties of the cured product tend to deteriorate, so that the case is not preferred.

[0027]

With regard to the weight-average molecular weight (M_w) of the silicone oil (b), preferred are those having a weight-average molecular weight ranging from 300 to 18,000 (a value measured by gel permeation chromatography (GPC)). Of these, in consideration of elastic modulus at low temperature, those having a molecular weight of 300 to 10,000 are preferred and further, in consideration of compatibility at the preparation of the composition, those having a molecular weight of 300 to 5,000 are more preferred, those having a molecular weight of 500 to 3,000 are particularly preferred. When the weight-average molecular weight is less than 300, the characteristic properties of the chain silicone part of the characteristic segment are difficult to exhibit and the characteristic properties as a block type may be impaired. When the molecular weight exceeds 18,000, a severe layer separated structure is formed, so that transparency becomes worse for use in optical materials and thus the use becomes difficult. In the invention, as the molecular weight of the silicone oil (b), using GPC (gel permeation chromatography), the weight-average molecular weight (M_w) was calculated as a value in terms of polystyrene measured under the following conditions.

Various conditions for GPC

Manufacturer: Shimadzu Corporation

Column: guard column SHODEX GPC LF-G LF-804 (3 columns)

Flow rate: 1.0 ml/min.

Column temperature: 40°C

5 Used solvent: THF (tetrahydrofuran)

Detector: RI (differential refractometry detector)

[0028]

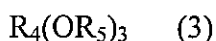
The kinematic viscosity of the silicone oil (b) is preferably in the range of 10 to 200 cSt, more preferably 30 to 90 cSt. When it is less than 10 cSt, the viscosity of the
10 block-type siloxane compound (A1) is too low and it is not suitable as an optical semiconductor encapsulating agent in some cases. When the kinematic viscosity is more than 200 cSt, the viscosity of the block-type siloxane compound (A1) increases and a trouble on workability tends to occur, so that the cases are not preferred.

[0029]

15 As preferable specific examples as the silicone oil (b), the following product names can be mentioned. Examples thereof include PRX413 and BY16-873 as those manufactured by Dow Corning Toray SILICONE Co.; X-21-5841 and KF-9701 as those manufactured by Shin-Etsu Chemical Co., Ltd.; XC96-723, TSR160, YR3370, YF3800, XF3905, YF3057, YF3807, YF3802, YF3897, YF3804 and XF3905 as those manufactured
20 by Momentive Company; DMS-S12, DMS-S14, DMS-S15, DMS-S21, DMS-S27, DMS-S31, DMS-S32, DMS-S33, DMS-S35, DMS-S42, DMS-S45, DMS-S51, PDS-0332, PDS-1615 and PDS-9931 as those manufactured by Gelest Company; and the like. Of the above ones, from the viewpoints of the molecular weight and the kinematic viscosity, PRX413, BY16-873, X-21-5841, KF-9701, XC96-723, YF3800, YF3804, DMS-S12,
25 DMS-S14, DMS-S15, DMS-S21 and PDS-1615 are preferred. Of these, from the viewpoint of the molecular weight for imparting a characteristic feature of flexibility of the silicone segment, X-21-5841, XC96-723, YF3800, YF3804, DMS-S14 and PDS-1615 are particularly preferred. These silicone oils (b) may be used singly or two or more thereof may be used in combination.

30 [0030]

The following will describe the alkoxysilane (c) in detail. The alkoxysilane (c) has a structure of the following general formula (3):



R_4 in the general formula (3) represents a methyl group or a phenyl group.

35 [0031]

A plurality of R_5 groups present in the general formula (3) may be the same or different from each other and represent each a linear, branched or cyclic alkyl group having 1 to 10 carbon atoms. Examples thereof include a methyl group, an ethyl group, an n-

propyl group, an i-propyl group, an n-butyl group, an i-butyl group, a tert-butyl group, an n-pentyl group, an n-hexyl group, a cyclopentyl group, a cyclohexyl group and the like. From the viewpoints of reaction conditions such as compatibility and reactivity, R₅ is preferably a methyl group or an ethyl group.

5 [0032]

Preferable specific examples of the alkoxysilane (c) include methyltrimethoxysilane, phenyltrimethoxysilane, methyltriethoxysilane, phenyltriethoxysilane and the like. Of the above ones, methyltrimethoxysilane and phenyltrimethoxysilane are preferred.

10 [0033]

In the invention, the alkoxysilane (c) can be used in combination with the alkoxysilane (a), for controlling the molecular weight of the block-type siloxane compound (A1), the compatibility at the formation of the composition, and the heat resistance, light resistance, low moisture permeability, low gas permeability and the like of the cured

15 product.
[0034]

In the case where the alkoxysilane (c) is used in combination with the alkoxysilane (a), the alkoxysilane (c) is used in the range of preferably 5 to 70% by mol, further preferably 5 to 50% by mol and particularly preferably 10 to 40% by mol based on the total mol of the alkoxysilane (a) and the alkoxysilane (c). When the content is more than

20 70% by mol, crosslinking density of the cured product decreases and mechanical strength lowers, so that the case is not preferred.
[0035]

As the reaction ratio of the alkoxysilane (a), the silicone oil (b) and the alkoxysilane (c), the reaction is preferably carried out with the equivalent value of the alkoxy group in the alkoxysilane (a) (and the alkoxysilane (c) to be added according to need) being 1.5 to 200, preferably 2 to 200, particularly preferably 2 to 100 relative to 1 equivalent of the silanol group in the silicone oil (b).

When the equivalent value exceeds 200, the cured product using the block-type siloxane compound (A1) becomes too hard and thus the objective low elastic modulus properties decrease.

30 [0036]

The following will specifically refer to a preferable production process of the block-type siloxane compound (A1).

35 [0037]

The production process of the block-type siloxane compound (A1) preferably includes the following production steps represented by the following (i) and (ii):

Production step (i): a step of performing dealcoholization condensation of a

silanol-terminated silicone oil with a silicon compound having an alkoxy group, and
Production step (ii): a step of adding water to perform hydrolytic condensation
between the alkoxy groups of silicon compounds having an alkoxy group.

The production steps (i) and (ii) may be performed in any order as long as the
5 steps are included.

[0038]

As preferable production processes, specifically, the following three kinds of
production processes may be mentioned.

<Production process (a)>

10 A process for producing the block-type siloxane compound (A1), wherein
first, as the production step (i), a step of obtaining an alkoxysilane-modified
compound (d) is performed by modifying the silicone oil terminal with an alkoxysilane
through a dealcoholization condensation reaction of the silicone oil (b) having a silanol
group at the terminal with the alkoxysilane (a) (and the alkoxysilane (c) to be added
15 according to need) that is a silicon compound having an alkoxy group, and
subsequently, as the production step (ii), a step of adding water to the alkoxysilane
(a) (and the alkoxysilane (c) to be added according to need) that is a silicon compound
having an alkoxy group and the alkoxysilane-modified compound (d) of the silicone oil
obtained in the production step (i) to carry out the hydrolytic condensation reaction
20 between the alkoxy groups is performed.

<Production process (b)>

A process for producing the block-type siloxane compound (A1), wherein
first, as the production step (ii), a step of obtaining a silsesquioxane (e) having an
alkoxy group in the molecule is performed by carrying out the hydrolytic condensation
25 reaction between the alkoxy groups of the alkoxysilane (a) (and the alkoxysilane (c) to be
added according to need) that is a silicon compound having an alkoxy group by adding
water, and

subsequently, as the production step (i), a step of reacting the silicone oil (b)
having a silanol group at the terminal with the silsesquioxane (e) to carry out the
30 dealcoholization condensation reaction of the alkoxy group remaining in the silsesquioxane
structure with the silanol group is performed.

<Production process (c)>

A process for producing the block-type siloxane compound (A1), wherein
first, as the production step (i), the silicone oil terminal is modified with an
35 alkoxysilane by the dealcoholization condensation reaction of the silicone oil (b) having a
silanol group at the terminal with the alkoxysilane (a) (and the alkoxysilane (c) to be added
according to need) that is a silicon compound having an alkoxy group to form an
alkoxysilane-modified compound (d), and then, water is added in the system, as the

production step (ii), the hydrolytic condensation reaction between the alkoxy groups of the remaining alkoxysilane (a) (the alkoxysilane (c)) and the alkoxysilane-modified compound (d) is carried out in one pot.

[0039]

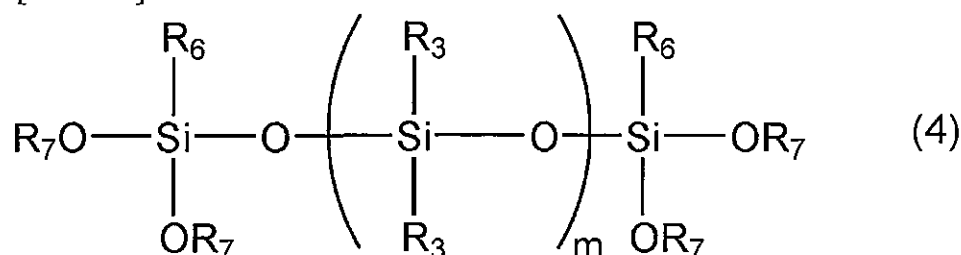
5 In the invention, from the viewpoint of shortening the production steps, it is preferred to use the aforementioned production process (c) in which the reactions are sequentially carried out in one pot.

The following will more specifically describe the production process (c).

In the case where the reactions are carried out in one pot, when the steps are
 10 performed in the reverse order contrarily to the aforementioned production process (c), that is, the production step (i) is performed after the production step (ii), there is a high possibility that the silsesquioxane oligomer having an alkoxy group formed in the production step (ii) and the silicone oil (b) do not solve each other, the dealcoholization condensation polymerization does not proceed in the following production step (i), and
 15 thus the silicone oil remains. On the other hand, when a process of performing the production step (ii) in one pot after the production step (i) is used as in the case of the production process (c), since the compatibility of the silicone oil (b) with the alkoxysilane (a) and the alkoxysilane (c) is relatively high, the problem that the compounds do not solve each other and the reaction does not proceed can be avoided. Furthermore, since
 20 unreacted low-molecular-weight alkoxysilane is present in a large amount relative to the silanol group, the process is also preferred from the viewpoint of reactivity. When the production step (i) is referred to as first-stage reaction and the production step (ii) is referred to as second-stage reaction in the case of performing the steps in one pot, first, in the first-stage reaction (production step (i)), the dealcoholization condensation of the
 25 silicone oil (b) with the alkoxysilane (a) (and the alkoxysilane (c) to be added according to need) is performed to modify the terminal of the silicone oil with alkoxysilyl, thereby obtaining the alkoxysilane-modified compound (d). Since water is not added in the first-stage reaction, the hydrolytic condensation between the alkoxy groups does not occur and, in the case where the reaction is carried out using 3 equivalents or more of the alkoxy group relative to 1 equivalent of the silanol group, the alkoxysilane-modified compound
 30 (d) is considered to be present as a structure represented by the following formula (4).

[0040]

[Chem. 2]



[0041]

In the formula (4), R_3 and m have the same meanings as described above and R_6 represents the above X or R_4 , and R_7 represents R_2 in the case where R_6 is the above X or represents R_5 in the case where R_6 is the above R_4 .

[0042]

In the first-stage reaction, when the alkoxy group is reacted in a ratio of less than 1.0 equivalent relative to 1 equivalent of the silanol group, the alkoxy group is not present at the time when the first-stage reaction is finished, so that the second-stage reaction cannot be started. Moreover, when the reaction is carried out using 1.0 to 1.5 equivalents of the alkoxy group, two or more alkoxy groups in the alkoxysilane (a) (and the alkoxysilane (c) to be added according to need) are to be reacted with the silanol group in the silicone oil (b), so that a product having exceedingly high molecular weight is obtained and gelation occurs at the time when the first-stage reaction is finished. Therefore, it is necessary to react the alkoxy group in a ratio of 1.5 equivalents or more relative to 1 equivalent of the silanol group. From the viewpoint of reaction regulation, a ratio of 2.0 equivalents or more is preferred.

[0043]

After the first-stage reaction is finished, the second-stage reaction (production step (ii)) of adding water to perform the hydrolytic condensation between the alkoxy groups is performed without further treatment. Furthermore, in the second-stage reaction, reactions (I) to (III) shown below take place.

(I) A condensation reaction between the alkoxy groups of the alkoxysilane (a) (and the alkoxysilane (c) to be added according to need) remaining in the system.

(II) A condensation reaction between the alkoxy groups of the alkoxysilane-modified compound (d) obtained in the first-stage reaction and the alkoxysilane (a) (and the alkoxysilane (c) to be added according to need).

(III) A condensation reaction between the alkoxy groups of the alkoxysilane-modified compound (d) obtained in the first-stage reaction and a partially condensed compound of the alkoxysilane (a) (and the alkoxysilane (c) to be added according to need) obtained in (I).

In the second-stage reaction, the above reactions occur in a multiple manner and the formation of the silsesquioxane segment and further the condensation thereof with the chain silicone segment derived from the silicone oil are simultaneously take place.

[0044]

The production of the block-type siloxane compound (A1) can be performed with no catalyst but, since the reaction proceeds only slowly with no catalyst, it is preferred to perform the production in the presence of a catalyst from the viewpoint of shortening the reaction time. As usable catalyst, any compounds can be used as long as they are

compounds showing acidity or basicity. Examples of acidic catalysts include inorganic acids such as hydrochloric acid, sulfuric acid and nitric acid and organic acids such as formic acid, acetic acid and oxalic acid. Moreover, as examples of basic catalysts, use can be made of inorganic bases including alkali metal hydroxides such as sodium hydroxide, potassium hydroxide, lithium hydroxide and cesium hydroxide, alkali metal carbonate salts such as sodium carbonate, potassium carbonate, sodium hydrogen carbonate and potassium hydrogen carbonate, and the like; organic bases such as ammonia, triethylamine, diethylenetriamine, n-butylamine, dimethylaminoethanol, triethanolamine and tetramethylammonium hydroxide. Of these, particularly in view of easy removal of the catalyst from the product, inorganic bases are preferred and particularly, sodium hydroxide and potassium hydroxide are preferred. The amount of the catalyst to be added is usually 0.001 to 7.5% by weight, preferably 0.01 to 5% by weight based on the total weight of the alkoxysilane (a) (and the alkoxysilane (c) to be added according to need) in the reaction system.

As a method for adding the catalyst, it is directly added or is used in a state that it is dissolved in a soluble solvent or the like. Of these, it is preferred to add the catalyst in a state that it is previously dissolved in an alcohol such as methanol, ethanol, propanol or butanol. On this occasion, the addition as an aqueous solution using water or the like may result in a possibility that the condensation of the alkoxysilane (a) (the alkoxysilane (c) to be added according to need) occurs unilaterally as described above and the silsesquioxane oligomer formed therefrom and the silicone oil (b) do not solve each other and become turbid.

[0045]

The production of the block-type siloxane compound (A1) can be performed without any solvent or in a solvent. Moreover, a solvent can be added in the middle of the production step. The solvent to be used is not particularly limited as long as it is a solvent capable of dissolving the alkoxysilane (a), the alkoxysilane (c), the silicone oil (b) and the alkoxysilane-modified compound (d). Examples of the solvent include aprotic polar solvents such as dimethylformamide, dimethylacetamide and tetrahydrofuran, ketones such as methyl ethyl ketone, methyl isobutyl ketone and cyclopentanone; esters such as ethyl acetate, butyl acetate, ethyl lactate and isopropyl butanoate; alcohols such as methanol, ethanol, propanol and butanol; alkanes such as hexane, cyclohexane, toluene and xylene; and the like. In the invention, from the viewpoint of reaction regulation, the reaction in an alcohol is preferred and methanol or ethanol is more preferred. The amount of the solvent to be used is not particularly limited as long as the amount is in the range where the reaction smoothly proceeds but the solvent is usually used in an amount of 0 to 900 parts by weight based on 100 parts of the total weight of the compounds of the alkoxysilane (a) (and the alkoxysilane (c) to be added according to need) and the silicone

oil (b). The reaction temperature varies depending on the amount of the catalyst but is usually 20 to 160°C, preferably 40 to 140°C, and particularly preferably 50 to 150°C. The reaction time is usually 1 to 40 hours, preferably 5 to 30 hours in each production step.

[0046]

5 After completion of the reaction, the catalyst is removed by quenching and/or washing with water according to need. In the case of performing washing with water, it is preferred to add a solvent separable from water depending on the kind of the solvent used. Examples of preferable solvents may include ketones such as methyl ethyl ketone, methyl isobutyl ketone and cyclopentanone; esters such as ethyl acetate, butyl acetate, ethyl lactate
10 and isopropyl butanoate; hydrocarbons such as hexane, cyclohexane, toluene and xylene; and the like.

[0047]

In the reaction, the removal of the catalyst may be performed by washing with water alone but, since the reaction is carried out under either condition of an acidic
15 condition and a basic condition, it is preferred to perform washing with water after the reaction is quenched by a neutralization reaction or remove an adsorbent by filtration after the catalyst is adsorbed using the adsorbent.

For the neutralization reaction, any compound showing acidity or basicity can be used. Examples of the compound showing acidity include inorganic acids such as
20 hydrochloric acid, sulfuric acid and nitric acid and organic acids such as formic acid, acetic acid and oxalic acid. As examples of the compound showing basicity, use can be made of inorganic bases including alkali metal hydroxides such as sodium hydroxide, potassium hydroxide, lithium hydroxide and cesium hydroxide, alkali metal carbonate salts such as sodium carbonate, potassium carbonate, sodium hydrogen carbonate and potassium
25 hydrogen carbonate, phosphate salts such as phosphoric acid, sodium dihydrogen phosphate, disodium hydrogen phosphate, trisodium phosphate, polyphosphoric acid and sodium tripolyphosphate, and the like; organic bases such as ammonia, triethylamine, diethylenetriamine, n-butylamine, dimethylaminoethanol, triethanolamine and tetramethylammonium hydroxide. Of these, particularly in view of easy removal from
30 the product, inorganic bases or inorganic acids are preferred and further preferred are phosphate salts and the like with which pH adjustment to around neutral is easier.

[0048]

As the adsorbent, activated clay, active carbon, zeolite, inorganic/organic synthetic absorbents, ion-exchange resins and the like may be exemplified. As specific examples,
35 the following products may be mentioned.

Examples of the activated clay include Activated Clay SA35, SA1, T, R-15, E, Nikkanite G-36, G-153, G-168 as those manufactured by Toshin Chemicals Co., Ltd.; and GALLEON EARTH, MIZUKAACE as those manufactured by Mizusawa Industrial

Chemicals, Ltd.; and the like. Examples of the active carbon include CL-H, Y-10S, Y-10SF as those manufactured by Ajinomoto Fine-Techno Co., Ltd.; S, Y, FC, DP, SA1000, K, A, KA, M, CW130BR, CW130AR, GM130A as those manufactured by Futamura Chemical Co., Ltd.; and the like. Examples of the zeolite include Molecular Sieves 3A, 4A, 5A, 13X as those manufactured by Union Showa K.K.; and the like. Examples of the synthetic adsorbents include Kyoward 100, 200, 300, 400, 500, 600, 700, 1000, 2000 as those manufactured by Kyowa Chemical Industry Co., Ltd.; Amberlyst 15JWET, 15DRY, 16WET, 31WET, A21, Amberlite IRA400JCI, IRA403BLCI, IRA404JCI as those manufactured by Rohm and Haas Company; Dowex 66, HCR-S, HCR-W2, MAC-3 as those manufactured by Dow Chemical Company; and the like.

After the adsorbent is added to a reaction solution and treatments such as stirring, heating and the like are performed to adsorb the catalyst, the adsorbent is filtrated and further the residue is washed with water, whereby the catalyst and the adsorbent can be removed.

[0049]

After the reaction is completed or quenched, the product can be purified by conventional separation and purification methods, besides washing with water and filtration. Examples of the purification methods include column chromatography, concentration under reduced pressure, distillation, extraction and the like. These purification methods may be performed singly or two or more thereof may be performed in combination.

[0050]

In the case where the reaction is carried out using a solvent miscible with water as a reaction solvent, it is preferred to perform washing with water using a solvent separable from water after the reaction solvent miscible with water is removed from the system by distillation or concentration under reduced pressure after quenching.

[0051]

After washing with water, the block-type siloxane compound (A1) can be obtained by removing the solvent through concentration under reduced pressure or the like.

[0052]

The appearance of the block-type siloxane compound (A1) thus obtained is usually a colorless and transparent liquid having fluidity at 25°C. Moreover, the molecular weight thereof is preferably 800 to 20,000, more preferably 1,000 to 10,000, and particularly preferably 1,500 to 6,000 as weight-average molecular weight measured by GPC. When the weight-average molecular weight is less than 800, there is a concern that heat resistance decreases. When it is more than 20,000, viscosity increases and thus workability is adversely affected.

The weight-average molecular weight is weight-average molecular weight (Mw)

in terms of polystyrene measured under the following conditions using GPC (gel permeation chromatography).

Various conditions for GPC

Manufacturer: Shimadzu Corporation

5 Column: guard column SHODEX GPC LF-G LF-804 (3 columns)

Flow rate: 1.0 ml/min.

Column temperature: 40°C

Used solvent: THF (tetrahydrofuran)

Detector: RI (differential refractometry detector)

10 [0053]

Moreover, the epoxy equivalent (measured by the method described in JIS K-7236) of the block-type siloxane compound (A1) is preferably 300 to 1,600 g/eq, more preferably 400 to 1,000 g/eq., and particularly 450 to 900 g/eq. When the epoxy equivalent is less than 300 g/eq, the cured product thereof is hard and the elastic modulus tends to be too high. When the epoxy equivalent is more than 1,600 g/eq, the mechanical properties of the cured product tend to become worse. Thus, the cases are not preferred.

[0054]

The viscosity (E-type viscometer, measured at 25°C) of the block-type siloxane compound (A1) is preferably 50 to 20,000 mPa·s, more preferably 500 to 10,000 mPa·s, and particularly preferably 800 to 5,000 mPa·s. When the viscosity is less than 50 mPa·s, the viscosity is too low and there is a concern that the composition is not suitable for uses as an optical semiconductor encapsulating material. When the viscosity is more than 20,000 mPa·s, the viscosity is too high and the composition is sometimes poor in workability.

25 [0055]

The ratio of the silicon atom bonded to three oxygen atoms, which is derived from the silsesquioxane in the block-type siloxane compound (A1), to the whole silicon atoms is preferably 5 to 50% by mol, more preferably 8 to 30% by mol, and particularly preferably 10 to 20% by mol. When the ratio of the silicon atom bonded to three oxygen atoms, which is derived from the silsesquioxane, to the whole silicon atoms is less than 5% by mol, the cured product tends to become too soft as a characteristic feature of a chain silicone segment and thus there is a concern that the cured product has surface tackiness and is easily scratched. Moreover, when the ratio is more than 50% by mol, the cured product becomes too hard as a characteristic feature of the silsesquioxane segment and the case is not preferred.

35 The ratio of the silicon atoms present can be determined by ^1H NMR, ^{29}Si NMR, elemental analysis and the like of the block-type siloxane compound (A1).

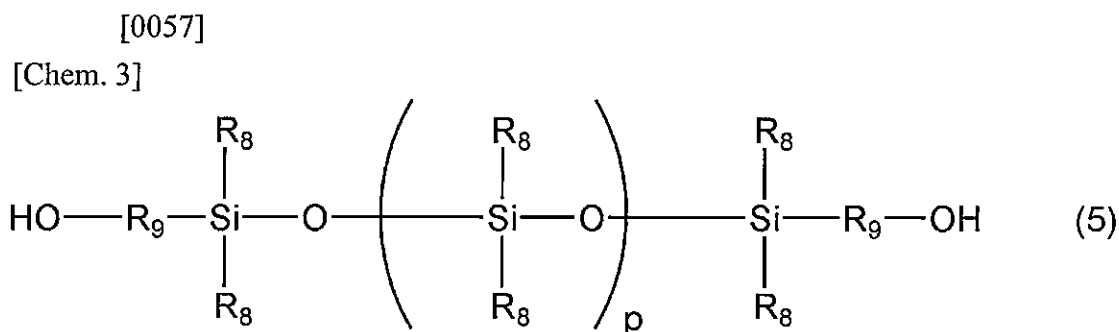
[0056]

The following will describe the polyhydric carboxylic acid (B).

The polyhydric carboxylic acid (B) in the invention is a polyhydric carboxylic acid having at least two carboxyl groups and having a siloxane skeleton as a main skeleton, preferably has a linear polysiloxane structure and is a skeleton having carboxylic acids at both terminals. More preferably, the polyhydric carboxylic acid is a compound obtained by the reaction of a carbinol-modified compound having a linear polysiloxane structure with an acid anhydride. Retention of liquefaction of the curing agent and control of viscosity are facilitated by the presence of the siloxane structure and thus workability becomes satisfactory in the case of the use as an encapsulating agent.

The polyhydric carboxylic acid to be used in the invention is preferably one produced by the reaction of the silicone compound (f) with the acid anhydride (g) having one or more carboxylic anhydride groups in the molecule.

The silicone compound (f) is preferably a compound represented by the following formula (5):



wherein in formula (5), R_9 represents an alkylene group having 1 to 10 total carbon atoms, R_8 represents a methyl group or a phenyl group, and p represents 1 to 100 as an average value.

[0058]

In the formula (5), specific examples of R_9 include alkylene groups such as methylene, ethylene, propylene, isopropylene, butylene, isobutylene, pentylene, isopentylene, hexylene, heptylene and octylene, an ethoxyethylene group, a propoxyethylene group, a propoxypropylene group, an ethoxypropylene group, and the like. Particularly preferred are a propoxyethylene group and an ethoxypropylene group.

[0059]

Next, R_8 represents a methyl group or a phenyl group and may be the same or different. In order that the polyhydric carboxylic acid (B) obtained by addition reaction of the silicone compound (f) with the acid anhydride (g) is liquid at room temperature, the methyl group is preferred as compared with the phenyl group.

[0060]

In the formula (5), p is 1 to 100 as an average value, preferably is 2 to 80, and more preferably 5 to 30.

[0061]

As the silicone compound (f) represented by the formula (5), for example, silicone-based compounds having alcoholic hydroxyl groups at both terminals may be mentioned. Specific examples thereof include X-22-160AS, KF6001, KF6002 and
5 KF6003 (all manufactured by Shin-Etsu Chemical Co., Ltd.); BY16-201, BY16-004 and SF8427 (all manufactured by Dow Corning Toray Co.); XF42-B0970 and XF42-C3294 (all manufactured by Momentive Performance Materials Japan Inc.); and the like that are both terminals carbinol-modified silicone oils, and all of them are commercially available. These modified silicone oils having alcoholic hydroxyl groups at both terminals may be
10 used singly or two or more thereof may be used in combination. Of these, X-22-160AS, KF6001, KF6002, BY16-201 and XF42-B0970 are preferred.

[0062]

The acid anhydride (g) is sufficiently a compound having one or more carboxylic anhydride groups in the molecule. Examples thereof include saturated aliphatic
15 carboxylic anhydrides such as succinic anhydride, methylsuccinic anhydride, ethylsuccinic anhydride, 2,3-butanedicarboxylic anhydride, 2,4-pentanedicarboxylic anhydride, 3,5-heptanedicarboxylic anhydride and 1,2,3,4-butanetetracarboxylic dianhydride; unsaturated aliphatic carboxylic anhydrides such as maleic anhydride and dodecylsuccinic anhydride; cyclic saturated aliphatic carboxylic anhydrides such as hexahydrophthalic anhydride,
20 methylhexahydrophthalic anhydride, 1,3-cyclohexanedicarboxylic anhydride, norbornane-2,3-dicarboxylic anhydride, methylnorbornane-2,3-dicarboxylic anhydride, nadic anhydride, methylnadic anhydride, bicyclo[2,2,2]octane-2,3-dicarboxylic anhydride, 1,2,4-cyclohexanetricarboxylic-1,2-anhydride, 1,2,3,4-cyclobutanetetracarboxylic dianhydride, 1,2,3,4-cyclopentanetetracarboxylic dianhydride and 1,2,4,5-cyclohexanetetracarboxylic
25 dianhydride; cyclic unsaturated aliphatic carboxylic anhydrides such as tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, nadic anhydride, methylnadic anhydride, 4,5-dimethyl-4-cyclohexene-1,2-dicarboxylic anhydride and bicyclo[2,2,2]-5-octene-2,3-dicarboxylic anhydride; aromatic carboxylic anhydrides such as phthalic anhydride, isophthalic anhydride, terephthalic anhydride, trimellitic anhydride and pyromellitic
30 anhydride, and the like. In addition, polycarboxylic acid compounds having a saturated aliphatic carboxylic anhydride, a cyclic saturated carboxylic anhydride and a cyclic unsaturated carboxylic anhydride in the same compound, such as 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride, 4-(2,5-dioxotetrahydrofuran-3-yl)-1,2,3,4-tetrahydronaphthalene-1,2-dicarboxylic anhydride and
35 the like may be also mentioned.

The acid anhydrides (g) can be used singly or two or more thereof can be used in combination. Of these, cyclic saturated aliphatic acid anhydrides are preferred and particularly, hexahydrophthalic anhydride, methylhexahydrophthalic anhydride,

norbornane-2,3-dicarboxylic anhydride, methylnorbornane-2,3-dicarboxylic anhydride, 1,2,4-cyclohexanetricarboxylic-1,2-anhydride and 1,2,3,4-butanetetracarboxylic dianhydride are preferred. The reason for the preference is that the polyhydric carboxylic acid (B) obtained therefrom is liquid at room temperature and transparency of the crude product obtained by curing the polyhydric carboxylic acid (B) and the epoxy resin (A) is excellent.

Of these, methylhexahydrophthalic anhydride and 1,2,4-cyclohexanetricarboxylic-1,2-anhydride are further preferred and methylhexahydrophthalic anhydride is particularly preferred.

[0063]

The reaction of the silicone compound (f) with the acid anhydride (g) can be also carried out in a solvent or with no solvent. The solvent is not particularly limited as long as it is a solvent which does not react with the silicone compound (f) represented by the formula (5) and the acid anhydride (g). Examples of usable solvent include aprotic polar solvents such as dimethylformamide, dimethylacetamide dimethylsulfoxide, tetrahydrofuran and acetonitrile, ketones such as methyl ethyl ketone, cyclopentanone and methyl isobutyl ketone; aromatic hydrocarbons such as toluene and xylene; and the like. Of these, the aromatic hydrocarbons and the ketones are preferred. These solvents may be used singly or two or more thereof may be used in combination. The amount of the solvent to be used is not particularly limited but the solvent is preferably used in an amount of usually 0.1 to 300 parts by weight based on 100 parts of the total weight of the silicone compound (f) and the acid anhydride (g).

[0064]

A catalyst may be used in the reaction and examples of usable catalyst include acidic compounds such as hydrochloric acid, sulfuric acid, methanesulfonic acid, trifluoromethanesulfonic acid, p-toluenesulfonic acid, nitric acid, trifluoroacetic acid and trichloroacetic acid; metal hydroxides such as sodium hydroxide, potassium hydroxide, calcium hydroxide and magnesium hydroxide; amine compounds such as triethylamine, tripropylamine and tributylamine; heterocyclic compounds such as pyridine, dimethylaminopyridine, 1,8-diazabicyclo[5.4.0]undec-7-ene, imidazole, triazole and tetrazole; quaternary ammonium salts such as tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, trimethylethylammonium hydroxide, trimethylpropylammonium hydroxide, trimethylbutylammonium hydroxide, trimethylcetyl ammonium hydroxide, trioctylmethylammonium hydroxide, tetramethylammonium chloride, tetramethylammonium bromide, tetramethylammonium iodide, tetramethylammonium acetate and trioctylmethylammonium acetate; and the like. These catalysts may be used singly or two or more thereof may be used in combination. Of these, triethylamine,

pyridine and dimethylaminopyridine are preferred.

[0065]

The amount of the catalyst to be used is not particularly limited but the catalyst is preferably used in an amount of usually 0.1 to 100 parts by weight based on 100 parts of the total weight of the silicone compound (f) represented by the formula (5) and the acid anhydride (g), according to need.

[0066]

The reaction temperature in the reaction is usually 80 to 180°C, preferably 110 to 140°C. Moreover, the reaction time is usually 1 to 12 hours. Mw (weight-average molecular weight) of the reaction product can be measured by GPC (gel permeation chromatography). After the reaction is finished, an objective polyhydric carboxylic acid can be obtained by stopping heating and, in the case where a solvent is used, removing the solvent under reduced pressure. Mw (weight-average molecular weight) of the obtained polyhydric carboxylic acid can be similarly confirmed by GPC.

As the polyhydric carboxylic acid (B) in the invention, besides the reaction product of the aforementioned silicone compound (f) and the acid anhydride (g), other polyhydric carboxylic acid can be also used in combination.

As the other polyhydric carboxylic acid usable in combination, particularly a bifunctional to hexafunctional carboxylic acid is preferred and a compound obtained by the reaction of a bifunctional to hexafunctional polyhydric alcohol having 5 or more carbon atoms with an acid anhydride is more preferred. Furthermore, a polycarboxylic acid in which the acid anhydride is a cyclic saturated aliphatic acid anhydride is preferred.

The bifunctional to hexafunctional polyhydric alcohol is not particularly limited as long as the alcohol is a compound having an alcoholic hydroxyl group but there may be mentioned diols such as ethylene glycol, propylene glycol, 1,3-propanediol, 1,2-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, cyclohexanedimethanol, 2,4-diethylpentanediol, 2-ethyl-2-butyl-1,3-propanediol, neopentyl glycol, tricyclodecanedimethanol and norbornenediol; triols such as glycerin, trimethylolethane, trimethylolpropane, trimethylolbutane and 2-hydroxymethyl-1,4-butanediol; tetraols such as pentaerythritol and ditrimethylolpropane; hexaols such as dipentaerythritol; and the like.

Particularly preferable alcohols are alcohols having 5 or more carbon atoms and particularly, compounds such as 1,6-hexanediol, 1,4-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, 1,2-cyclohexanedimethanol, 2,4-diethylpentanediol, 2-ethyl-2-butyl-1,3-propanediol, neopentyl glycol, tricyclodecanedimethanol and norbornenediol are preferred. Of these, alcohols having a branched chain structure or a cyclic structure, such as 2-ethyl-2-butyl-1,3-propanediol, neopentyl glycol, 2,4-diethylpentanediol, 1,4-cyclohexanedimethanol, tricyclodecanedimethanol and norbornenediol are more preferred.

As the acid anhydride, methyltetrahydrophthalic anhydride, methyladnic

anhydride, nadic anhydride, hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, butanetetracarboxylic anhydride, bicyclo[2,2,1]heptane-2,3-dicarboxylic anhydride, methylbicyclo[2,2,1]heptane-2,3-dicarboxylic anhydride, cyclohexane-1,2,4-tricarboxylic-1,2-anhydride and the like are preferred. Of these,

5 methylhexahydrophthalic anhydride and cyclohexane-1,2,4-tricarboxylic-1,2-anhydride are preferred.

The conditions for the addition reaction are not particularly limited. As one specific reaction condition, there may be mentioned a method of reacting the acid anhydride with the polyhydric alcohol at 40 to 150°C under conditions of no catalyst and
10 no solvent, heating them, and, after completion of the reaction, taking out the product without further treatment.

[0067]

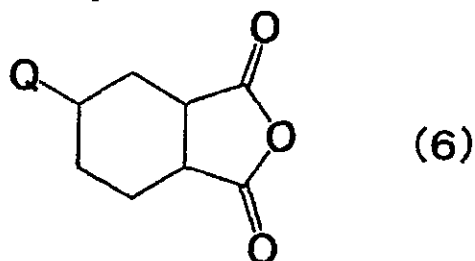
The curable resin composition of the invention may contain an acid anhydride. As the acid anhydride, specifically, there may be mentioned acid anhydrides such as
15 phthalic anhydride, trimellitic anhydride, pyromellitic anhydride, maleic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, methylnadic anhydride, nadic anhydride, hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, butanetetracarboxylic anhydride, bicyclo[2,2,1]heptane-2,3-dicarboxylic anhydride, methylbicyclo[2,2,1]heptane-2,3-dicarboxylic anhydride and cyclohexane-1,2,4-
20 tricarboxylic-1,2-anhydride.

Particularly, methyltetrahydrophthalic anhydride, methylnadic anhydride, nadic anhydride, hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, butanetetracarboxylic anhydride, bicyclo[2,2,1]heptane-2,3-dicarboxylic anhydride, methylbicyclo[2,2,1]heptane-2,3-dicarboxylic anhydride and cyclohexane-1,2,4-
25 tricarboxylic-1,2-anhydride are preferred.

Particularly preferably, hexahydrophthalic anhydride, methylhexahydrophthalic anhydride and cyclohexane-1,2,4-tricarboxylic-1,2-anhydride, which are represented by the following formula (6):

[0068]

30 [Chem. 4]



are preferred. Of these, methylhexahydrophthalic anhydride and cyclohexane-1,2,4-tricarboxylic-1,2-anhydride are preferred.

[0070]

The curable resin composition of the invention contains the zinc salt and/or the zinc complex (C).

The zinc salt and/or the zinc complex is a salt and/or complex containing a zinc ion as a central element and preferably, there may be mentioned compounds having an ion of a carboxylic acid, a phosphate ester or a phosphoric acid as a counter and/or a ligand, such as zinc carboxylates, zinc phosphates and zinc phosphate esters.

As the zinc carboxylates, zinc carboxylates having 1 to 30 carbon atoms may be mentioned and there may be mentioned 2-ethylhexylic acid, octylic acid, isodecylic acid, stearic acid, isostearic acid, hydroxystearic acid, undecylenic acid, behenic acid, undecanoic acid, decanoic acid and the like.

In the invention, carboxylic acids having 3 to 20 carbon atoms are particularly preferred and more preferred are those having 5 to 15 carbon atoms.

As zinc phosphates and zinc phosphate esters, zinc salts and/or zinc complexes of phosphoric acid or phosphate esters (monoester compounds, diester compounds, triester compounds or mixtures thereof) having 1 to 30 carbon atoms are preferred, and specific examples of alkyls of the esters include methyl, isopropyl, butyl, 2-ethylhexyl, octyl, isodecyl, isostearyl, decanyl, cetyl and the like.

[0071]

In the invention, particularly preferred are phosphate esters having 3 to 15 carbon atoms. The ester compounds may be a mixture or a single substance but a main component thereof is preferably a phosphate monoester compound. Particularly, in the molar ratios (using purity on gas chromatography as a substitute but there is a difference in sensitivity since trimethylsilylation is necessary) of the monoester compound, diester compound and triester compound contained in the phosphate ester, the amount of the monoester compound present is preferably 50 area % or more at the stage where a trimethylsilylation treatment is finished.

Such phosphate ester compounds can be obtained by esterifying alcohols with phosphorus pentoxide, phosphorus oxychloride, phosphorus trichloride or the like as a phosphorylating agent. Also, these phosphates are obtained, for example, by the reaction with zinc carbonate, zinc hydroxide or the like (patent Document EP699708).

[0072]

As details of such zinc salts and/or zinc complexes of phosphate esters, the ratio of the phosphorus atom to the zinc atom (P/Zn) is preferably 1.2 to 2.3 and more preferably 1.3 to 2.0. Particularly preferred is 1.4 to 1.9. Namely, in the particularly preferred embodiment, the phosphate ester (or phosphoric acid) is 2.0 mol or less relative to 1 mol of the zinc ion, and preferred are those having not a simple ion structure but a structure where some molecules participate through ionic bonds (or coordinate bonds).

[0073]

Here, the ratio of the zinc salt and/or zinc complex (C) is 0.01 to 8% by weight, more preferably 0.05 to 5% by weight, and further 0.1 to 4% by weight relative to the epoxy resin (A) in terms of a weight ratio. Moreover, particularly preferred is 0.1 to 2% by weight.

[0074]

As the curing agent, it is possible to use the polyhydric carboxylic acid (B) singly or in combination with the acid anhydride and further, it is also possible to use them in combination with the other curing agent. In the case of the combined use, the ratio of the total weight of the polyhydric carboxylic acid compound (B) and the acid anhydride in the whole curing agent is preferably 30% by weight or more and particularly preferably 40% by weight or more.

Examples of the curing agent usable in combination include amine-based compounds, acid anhydride-based compounds, amide-based compounds, phenol-based compounds, carboxylic acid-based compounds and the like. Specific examples of usable curing agent include amines and polyamide compounds (diaminodiphenylmethane, diethylenetriamine, triethylenetetramine, diaminodiphenyl sulfone, isophoronediamine, dicyandiamide, polyamide resins synthesized from dimer of linolenic acid and ethylenediamine, and the like), polyhydric phenols (bisphenol A, bisphenol F, bisphenol S, fluorene bisphenol, terpene diphenol, 4,4'-biphenol, 2,2'-biphenol, 3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'-diol, hydroquinone, resorcin, naphthalenediol, tris-(4-hydroxyphenyl)methane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, polycondensates of phenols (phenol, alkyl-substituted phenols, naphthol, alkyl-substituted naphthaols, dihydroxybenzene, dihydroxynaphthalene, etc.) with formaldehyde, acetaldehyde, bezaldehyde, p-hydroxybenzaldehyde, o-hydroxybenzaldehyde, p-hydroxyacetophenone, o-hydroxyacetophenone, dicyclopentadiene, furfural, 4,4'-bis(chloromethyl)-1,1'-biphenyl, 4,4'-bis(methoxymethyl)-1,1'-biphenyl, 1,4'-bis(chloromethyl)benzene, 1,4'-bis(methoxymethyl)benzene or the like and modified compounds thereof, halogenated bisphenols such as tetrabromobisphenol A, condensates of terpenes with phenols), others (imidazole, trifluoroborane-amine complexes, guanidine derivatives, etc.) and the like but they are not limited thereto.

They may be used singly or two or more thereof may be used.

[0075]

In the curable resin composition of the invention, with regard to the ratio of the epoxy resin and the curing agent to be blended, it is preferred to use the curing agent of preferably 0.7 to 1.2 equivalents relative to 1 equivalent of the epoxy group of the whole epoxy resin. In the case where it is less than 0.7 equivalents or is more than 1.2 equivalents relative to 1 equivalent of the epoxy group, there is a concern that curing is insufficient and good physical properties when cured are not obtained in both cases.

[0076]

In the curable resin composition of the invention, a curing catalyst can be used in combination with the curing agent. Examples of usable curing accelerators include various imidazoles such as 2-methylimidazole, 2-phenylimidazole, 2-undecylimidazole, 2-heptadecylimidazole, 2-phenyl-4-methylimidazole, 1-benzyl-2-phenylimidazole, 1-benzyl-2-methylimidazole, 1-cyanoethyl-2-methylimidazole, 1-cyanoethyl-2-phenylimidazole, 1-cyanoethyl-2-undecylimidazole, 2,4-diamino-6(2'-methylimidazole(1'))ethyl-s-triazine, 2,4-diamino-6(2'-undecylimidazole(1'))ethyl-s-triazine, 2,4-diamino-6(2'-ethyl, 4-methylimidazole(1'))ethyl-s-triazine, 2,4-diamino-6(2'-methylimidazole(1'))ethyl-s-triazine-isocyanuric acid adduct, 2:3 adduct of 2-methylimidazole isocyanuric acid, 2-phenylimidazole isocyanuric acid adduct, 2-phenyl-3,5-dihydroxymethylimidazole, 2-phenyl-4-hydroxymethyl-5-methylimidazole and 1-cyanoethyl-2-phenyl-3,5-dicyanoethoxymethylimidazole, and salts of the imidazoles with polyhydric carboxylic acids such as phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, pyromellitic acid, naphthalenedicarboxylic acid, maleic acid and oxalic acid, amides such as dicyandiamide, diaza compounds such as 1,8-diaza-bicyclo(5.4.0)undecene-7 and salts such as tetraphenylborate, phenol novolak thereof, salts with the above polyhydric carboxylic acids or phosphinic acids, ammonium salts such as tetrabutylammonium bromide, cetyltrimethylammonium bromide and trioctylmethylammonium bromide, phosphines and phosphonium compounds such as triphenylphosphine, tri(toluy)lphosphine, tetraphenylphosphonium bromide and tetraphenylphosphonium tetraphenylborate, phenols such as 2,4,6-trisaminomethylphenol, amine adducts, metal compounds such as tin octylate and the like, and microcapsulated curing accelerators obtained by microcapsulation of these curing accelerators, and the like. The curing accelerators to be used are appropriately selected depending on the properties required for the resulting transparent resin composition, such as transparency, the curing rate and working conditions. The curing accelerator is used in the range of usually 0.001 to 15 parts by weight based on 100 parts by weight of the epoxy resin.

[0077]

In the curable resin composition of the invention, it is also possible to incorporate a phosphorus-containing compound as a flame retardancy-imparting component. The phosphorus-containing compound may be reaction type one or addition type one. Specific examples of the phosphorus-containing compound include phosphate esters such as trimethyl phosphate, triethyl phosphate, tricresyl phosphate, trixylylenyl phosphate, cresyl diphenyl phosphate, cresyl-2,6-dixylylenyl phosphate, 1,3-phenylenebis(dixylylenyl phosphate), 1,4-phenylenebis(dixylylenyl phosphate) and 4,4'-biphenyl(dixylylenyl phosphate); phosphanes such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide and 10(2,5-dihydroxyphenyl)-10H-9-oxa-10-phosphaphenanthrene-10-oxide; phosphorus-

containing epoxy compounds obtained by reacting an epoxy resin with active hydrogen of the phosphanes, red phosphorus and the like. The phosphate esters, the phosphanes or phosphorus-containing epoxy compounds are preferred, and 1,3-phenylenebis(dixylylenyl phosphate), 1,4-phenylenebis(dixylylenyl phosphate), 4,4'-biphenyl(dixylylenyl phosphate) or a phosphorus-containing epoxy compound is particularly preferred. The content of the phosphorus-containing compound is preferably as follows: phosphorus-containing compound/epoxy resin = 0.1 to 0.6 (weight ratio). When the content is less than 0.1, flame retardancy is insufficient and when the content exceeds 0.6, there is a concern that moisture absorbing properties and dielectric properties of the cured product are adversely affected.

[0078]

Furthermore, into the curable resin composition of the invention, a binder resin can be also blended according to need. As the binder resin, there may be mentioned butyral resins, acetal resins, acrylic resins, epoxy-nylon resins, NBR-phenolic resins, epoxy-NBR resins, polyamide resins, polyimide resins, silicone resins and the like but the resin is not limited thereto. The amount of the binder resin to be blended is preferably in the range where flame retardancy and heat resistance of the cured product are not impaired and is usually 0.05 to 50 parts by weight and preferably 0.05 to 20 parts by weight based on 100 parts by weight of the resin component, according to need.

[0079]

To the curable resin composition of the invention, an inorganic filler can be added according to need. As the inorganic filler, there may be mentioned powders of crystalline silica, fused silica, alumina, zircon, calcium silicate, calcium carbonate, silicon carbide, silicon nitride, boron nitride, zirconia, fosterite, steatite, spinel, titania and talc; beads obtained by forming them into spherical shape; and the like but the filler is not limited thereto. The filler may be used singly or two or more thereof may be used. With regard to the content of the inorganic filler, an amount of 0 to 95% by weight is used in the curable resin composition of the invention. Furthermore, to the curable resin composition of the invention, various blending agents such as a silane-coupling agent, a releasing agent such as stearic acid, palmitic acid, zinc stearate or calcium stearate and a pigment and various thermosetting resins can be added.

[0080]

In the case where the curable resin composition of the invention is used as an optical material, particularly an optical semiconductor encapsulating agent, it is possible to reinforce the mechanical strength and the like without inhibiting transparency by using a filler having a nano-order level as particle diameter of the inorganic filler to be used as described above. As a guideline of the nano-order level, it is preferred to use a filler having an average particle diameter of 500 nm or less, particularly an average particle

diameter of 200 nm or less in view of transparency.

[0081]

In the case where the curable resin composition of the invention is used as an optical material, particularly an optical semiconductor encapsulating agent, a phosphor can be added according to need. The phosphor has an action of forming white light by absorbing a part of blue light emitted from a blue LED element and emitting wavelength-converted yellow light. The optical semiconductor is encapsulated after the phosphor is dispersed in the curable resin composition beforehand. The phosphor is not particularly limited and conventionally known phosphors can be used. Examples thereof include aluminate salts, thiogallate salts, orthosilicate salts and the like of rare earth elements. More specifically, there may be mentioned phosphors such as YAG phosphors, TAG phosphors, orthosilicate phosphors, thiogallate phosphors and sulfide phosphors, and $\text{YAlO}_3\text{:Ce}$, $\text{Y}_3\text{Al}_5\text{O}_{12}\text{:Ce}$, $\text{Y}_4\text{Al}_2\text{O}_9\text{:Ce}$, $\text{Y}_2\text{O}_2\text{S:Eu}$, $\text{Sr}_5(\text{PO}_4)_3\text{Cl:Eu}$, $(\text{SrEu})\text{O}\cdot\text{Al}_2\text{O}_3$ and the like are exemplified. As the particle diameter of such phosphors, those having a particle diameter known in this field are used but the average particle diameter is preferably 1 to 250 μm and particularly preferably 2 to 50 μm . In the case of using these phosphors, the amount of them to be added is 1 to 80 parts by weight and preferably 5 to 60 parts by weight based on 100 parts by weight of the resin components thereof.

[0082]

In the case where the curable resin composition of the invention is used as an optical material, particularly an optical semiconductor encapsulating agent, for the purpose of preventing precipitation of various phosphors in curing, a thixotropy-imparting agent including silica fine powder (also called as aerosil or aerosol) as a representative can be added. Examples of such silica fine powder include Aerosil 50, Aerosil 90, Aerosil 130, Aerosil 200, Aerosil 300, Aerosil 380, Aerosil OX50, Aerosil TT600, Aerosil R972, Aerosil R974, Aerosil R202, Aerosil R812, Aerosil R812S, Aerosil R805, RY200, RX200 (manufactured by Nippon Aerosil Co., Ltd.) and the like.

[0083]

The curable resin composition of the invention, an optical material, particularly an optical semiconductor encapsulating agent, may contain an amine compound as a photostabilizer or a phosphorus-based compound and a phenol-based compound as an antioxidant, for the purpose of coloration prevention.

Examples of the above amine compound include hindered amine-based compounds such as tetrakis(1,2,2,6,6-pentamethyl-4-piperidyl)=1,2,3,4-butanetetracarboxylate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)=1,2,3,4-butanetetracarboxylate, a mixed esterified product of 1,2,3,4-butanetetracarboxylic acid with 1,2,2,6,6-pentamethyl-4-piperidinol and 3,9-bis(2-hydroxy-1,1-dimethylethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane, decanedioic acid bis(2,2,6,6-tetramethyl-4-piperidyl)

sebacate, bis(1-undecanoxy-2,2,6,6-tetramethylpiperidin-4-yl) carbonate, 2,2,6,6-tetramethyl-4-piperidyl methacrylate, bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate, 4-benzoyloxy-2,2,6,6-tetramethylpiperidine, 1-[2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]ethyl]-4-
 5 [3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]-2,2,6,6-tetramethylpiperidine, 1,2,2,6,6-pentamethyl-4-piperidyl-methacrylate, bis(1,2,2,6,6-pentamethyl-4-piperidyl) [[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]methyl]butylmalonate, decanedioic acid bis(2,2,6,6-tetramethyl-1(octyloxy)-4-piperidinyl) ester, a reaction product of 1,1-dimethylethyl hydroperoxide with octane, N,N',N'',N'''-tetrakis-(4,6-bis-(butyl-(N-methyl-
 10 2,2,6,6-tetramethylpiperidin-4-yl)amino)-triazin-2-yl)-4,7-diazadecane-1,10-diamine, a polycondensate of dibutylamine·1,3,5-triazine·N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)-1,6-hexamethylenediamine with N-(2,2,6,6-tetramethyl-4-piperidyl)butylamine, poly[[6-(1,1,3,3-tetramethylbutyl)amino-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidyl)imino]hexamethylene[(2,2,6,6-tetramethyl-4-piperidyl)imino]], a polymerized
 15 product of dimethyl succinate with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinethanol, 2,2,4,4-tetramethyl-20-(β-lauryloxycarbonyl)ethyl-7-oxa-3,20-diazadispiro[5.1.11.2]heneicosan-21-one, β-alanine, N-(2,2,6,6-tetramethyl-4-piperidinyl)-dodecyl ester/tetradecyl ester, N-acetyl-3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidinyl)pyrrolidine-2,5-dione, 2,2,4,4-tetramethyl-7-oxa-3,20-
 20 diazadispiro[5,1,11,2]heneicosan-21-one, 2,2,4,4-tetramethyl-21-oxa-3,20-diazadicyclo[5,1,11,2]heneicosan-20-propanoic acid dodecyl ester/tetradecyl ester, propanedioic acid [(4-methoxyphenyl)-methylene]-bis(1,2,2,6,6-pentamethyl-4-piperidinyl) ester, higher fatty acid esters of 2,2,6,6-tetramethyl-4-piperidinol, 1,3-benzenedicarboxamide and N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl); benzophenone-
 25 based compounds such as octabenzene; benzotriazole-based compounds such as 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol, 2-(2-hydroxy-5-methylphenyl)benzotriazole, 2-[2-hydroxy-3-(3,4,5,6-tetrahydrophthalimido-methyl)-5-methylphenyl]benzotriazole, 2-(3-tert-butyl-2-hydroxy-5-methylphenyl)-5-chlorobenzotriazole, 2-(2-hydroxy-3,5-di-tert-pentylphenyl)benzotriazole, a reaction
 30 product of methyl 3-(3-(2H-benzotriazol-2-yl)-5-tert-butyl-4-hydroxyphenyl)propionate with polyethylene glycol, and 2-(2H-benzotriazol-2-yl)-6-dodecyl-4-methylphenol; benzoate-based ones such as 2,4-di-tert-butylphenyl-3,5-di-tert-butyl-4-hydroxybenzoate; triazine-based compounds such as 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-[(hexyl)oxy]phenol; and the like. Particularly preferred are hindered amine-based
 35 compounds.

[0084]

As amine compounds that is the above photo-stabilizer, commercially available products shown below can be used.

The commercially available amine-based compounds are not particularly limited and examples thereof include TINUVIN 765, TINUVIN 770DF, TINUVIN 144, TINUVIN 123, TINUVIN 622LD, TINUVIN 152, CHIMASSORB 944 as those manufactured by Ciba Specialty Chemicals; LA-52, LA-57, LA-62, LA-63P, LA-77Y, LA-81, LA-82, LA-87 as those manufactured by Adeka Corporation; and the like.

[0085]

The phosphorus-based compound is not particularly limited and examples thereof include 1,1,3-tris(2-methyl-4-ditridecylphosphite-5-tert-butylphenyl)butane, distearyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl) pentaerythritol diphosphite, phenylbisphenol A pentaerythritol diphosphite, dicyclohexyl pentaerythritol diphosphite, tris(diethylphenyl) phosphite, tris(di-isopropylphenyl) phosphite, tris(di-n-butylphenyl) phosphite, tris(2,4-di-tert-butylphenyl) phosphite, tris(2,6-di-tert-butylphenyl) phosphite, tris(2,6-di-tert-butylphenyl) phosphite, 2,2'-methylenebis(4,6-di-tert-butylphenyl) (2,4-di-tert-butylphenyl) phosphite, 2,2'-methylenebis(4,6-di-tert-butylphenyl) (2-tert-butyl-4-methylphenyl) phosphite, 2,2'-methylenebis(4-methyl-6-tert-butylphenyl) (2-tert-butyl-4-methylphenyl) phosphite, 2,2'-ethylidenebis(4-methyl-6-tert-butylphenyl) (2-tert-butyl-4-methylphenyl) phosphite, tetrakis(2,4-di-tert-butylphenyl)-4,4'-biphenylene diphosponite, tetrakis(2,4-di-tert-butylphenyl)-4,3'-biphenylene diphosponite, tetrakis(2,4-di-tert-butylphenyl)-3,3'-biphenylene diphosponite, tetrakis(2,6-di-tert-butylphenyl)-4,4'-biphenylene diphosponite, tetrakis(2,6-di-tert-butylphenyl)-4,3'-biphenylene diphosponite, tetrakis(2,6-di-tert-butylphenyl)-3,3'-biphenylene diphosponite, bis(2,4-di-tert-butylphenyl)-4-phenyl-phenylphosponite, bis(2,4-di-tert-butylphenyl)-3-phenyl-phenylphosponite, bis(2,6-di-n-butylphenyl)-3-phenyl-phenylphosponite, bis(2,6-di-tert-butylphenyl)-4-phenyl-phenylphosponite, bis(2,6-di-tert-butylphenyl)-3-phenyl-phenylphosponite, tetrakis(2,4-di-tert-butyl-5-methylphenyl)-4,4'-biphenylene diphosponite, tributyl phosphate, trimethyl phosphate, tricresyl phosphate, triphenyl phosphate, trichlorophenyl phosphate, triethyl phosphate, diphenyl cresyl phosphate, diphenyl monoorthoxenyl phosphate, tributoxyethyl phosphate, dibutyl phosphate, dioctyl phosphate, diisopropyl phosphate and the like.

[0086]

As the above phosphorus-based compounds, commercially available products can be also used. The commercially available phosphorus-based compounds are not particularly limited and, for example, as those manufactured by Adeka Corporation, there may be mentioned ADEKA STAB PEP-4C, ADEKA STAB PEP-8, ADEKA STAB PEP-24G, ADEKA STAB PEP-36, ADEKA STAB HP-10, ADEKA STAB 2112, ADEKA STAB 260, ADEKA STAB 522A, ADEKA STAB 1178, ADEKA STAB 1500, ADEKA STAB C, ADEKA STAB 135A, ADEKA STAB 3010 and ADEKA STAB TPP.

[0087]

The phenol compound is not particularly limited and examples thereof include 2,6-di-tert-butyl-4-methylphenol, n-octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, tetrakis[methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]methane, 2,4-di-tert-butyl-6-methylphenol, 1,6-hexanediol-bis-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-isocyanurate, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, pentaerythrityl-tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 3,9-bis-[2-[3-(3-tert-butyl-4-hydroxy-5-methylphenyl)-propionyloxy]-1,1-dimethylethyl]-2,4,8,10-tetraoxaspiro[5,5]undecane, triethylene glycol-bis[3-(3-tert-butyl-5-methyl-4-hydroxyphenyl)propionate], 2,2'-butylidenebis(4,6-di-tert-butylphenol), 4,4'-butylidenebis(3-methyl-6-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 2,2'-methylenebis(4-ethyl-6-tert-butylphenol), 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenol acrylate, 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate, 4,4'-thiobis(3-methyl-6-tert-butylphenol), 4,4'-butylidenebis(3-methyl-6-tert-butylphenol), 2-tert-butyl-4-methylphenol, 2,4-di-tert-butylphenol, 2,4-di-tert-pentylphenol, 4,4'-thiobis(3-methyl-6-tert-butylphenol), 4,4'-butylidenebis(3-methyl-6-tert-butylphenol), bis[3,3-bis-(4'-hydroxy-3'-tert-butylphenyl)butanoic acid]-glycol ester, 2,4-di-tert-butylphenol, 2,4-di-tert-pentylphenol, 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate, bis-[3,3-bis-(4'-hydroxy-3'-tert-butylphenyl)-butanoic acid]-glycol ester and the like.

[0088]

As the phenol-based compounds, commercially available products can be also used. The commercially available phenol-based compounds are not particularly limited and examples thereof include IRGANOX 1010, IRGANOX 1035, IRGANOX 1076, IRGANOX 1135, IRGANOX 245, IRGANOX 259, IRGANOX 295, IRGANOX 3114 IRGANOX 1098, IRGANOX 1520L as those manufactured by Ciba Specialty Chemicals, and ADEKA STAB AO-20, ADEKA STAB AO-30, ADEKA STAB AO-40, ADEKA STAB AO-50, ADEKA STAB AO-60, ADEKA STAB AO-70, ADEKA STAB AO-80, ADEKA STAB AO-90, ADEKA STAB AO-330 as those manufactured by Adeka Corporation, Sumilizer GA-80, Sumilizer MDP-S, Sumilizer BBM-S, Sumilizer GM, Sumilizer GS(F), Sumilizer GP as those manufactured by Sumitomo Chemical Co., Ltd., and the like.

[0089]

Besides them, it is possible to use additives commercially available as coloring inhibitors for resins. Examples thereof include TINUVIN 328, TINUVIN 234, TINUVIN 326, TINUVIN 120, TINUVIN 477, TINUVIN 479, CHIMASSORB 2020FDL, CHIMASSORB 119FL as those manufactured by Ciba Specialty Chemicals, and the like.

[0090]

It is preferred to incorporate at least one of the above phosphorus-based compounds, amine compounds and phenol-based compounds. The amount thereof to be blended is not particularly limited and is in the range of 0.005 to 5.0% by weight based on the curable resin composition of the invention.

[0091]

The curable resin composition of the invention is obtained by mixing individual components homogeneously. The curable resin composition of the invention can be easily transformed into a cured product thereof in the same manner as a conventionally known method. For example, the epoxy resin and the curing agent, and, if necessary, the curing accelerator, the phosphorus-containing compound, the binder resin, the inorganic filler and the blending agent are thoroughly mixed using an extruder, a kneader, a roll, a planetary mixer or the like according to need until a homogeneous state is achieved, thereby obtaining a curable resin composition. In the case where the obtained curable resin composition of the invention is liquid, the composition is potted or cast, a substrate is impregnated therewith, or the curable resin composition is injected into a mold, and then curing is performed through heating. Moreover, in the case where the obtained curable resin composition of the invention is solid, there may be mentioned a procedure of injecting it into a mold after melting or molding it using a transfer molding machine or the like and further curing it through heating. The curing temperature and time are 80 to 200°C and 2 to 10 hours. As the curing method, it is possible to harden it at once at high temperature but it is preferred to elevate the temperature stepwise to allow the curing reaction to proceed. Specifically, initial curing is performed between 80°C and 150°C and then after-cure is performed between 100°C and 200°C. As a curing step, it is preferred to elevate the temperature with dividing the temperature elevation into 2 to 8 stages, more preferably 2 to 4 stages.

[0092]

Moreover, a cured product of the curable resin composition of the invention can be formed by dissolving the curable resin composition of the invention in a solvent such as toluene, xylene, acetone, methyl ethyl ketone, methyl isobutyl ketone, dimethylformamide, dimethylacetamide or N-methylpyrrolidone to transform the composition into a varnish of the curable resin composition, impregnating a substrate such as glass fiber, carbon fiber, polyester fiber, polyamide fiber, alumina fiber or paper therewith, drying the impregnated one under heating, and finally subjecting the resulting prepreg to hot pressing. The solvent on this occasion is used in an amount of usually 10 to 70% by weight, preferably 15 to 70% by weight in the mixture of the curable resin composition of the invention and the solvent. Moreover, an epoxy resin-cured product containing carbon fiber can be also obtained by RTM method using the liquid composition itself.

[0093]

Furthermore, the curable resin composition of the invention can be also used as a film-type composition for encapsulation. In the case of obtaining such a film-type resin composition, the curable resin composition of the invention is first applied as the
5 aforementioned varnish on a release film, the solvent is removed under heating, and then transformation into B-stage is performed, thereby forming a sheet-shaped adhesive agent. The sheet-shaped adhesive agent can be used as an interlayer insulating layer in multilayer substrates and the like and en bloc film encapsulation of optical semiconductors.

[0094]

10 The following will explain the case where the curable resin composition of the invention is used as an encapsulating material or die-bonding material for optical semiconductors in detail.

[0095]

15 In the case where the curable resin composition of the invention is used as an encapsulating material or die-bonding material for optical semiconductors such as a highly luminous white LED, the curable resin composition is prepared by thoroughly mixing the epoxy resin, the curing agent, the coupling agent, the antioxidant and additives such as the photo-stabilizer, and is used as the encapsulating material or as both of the die-bonding material and the encapsulating material. As a mixing method, they are mixed at ordinary temperature or elevated temperature using a kneader, a three-roll roller, a universal mixer, a
20 planetary mixer, a homomixer, a homodisper, a beads mill or the like.

[0096]

25 An optical semiconductor element such as a highly luminous white LED is generally formed by adhering a semiconductor chip such as GaAs, GaP, GaAlAs, GaAsP, AlGa, InP, GaN, InN, AlN or InGaN, which has been laminated on a substrate of sapphire, spinel, SiC, Si, ZnO or the like, to a lead frame, a heat sink or a package using an adhesive (die-bonding material). There is a type where a wire such as a gold wire is connected for conducting an electric current. For protecting the semiconductor chip from heat and moisture and playing a role of lens function, the semiconductor chip is encapsulated with an encapsulating material such as an epoxy resin. The curable resin composition of the
30 invention can be used as the encapsulating material or die-bonding material. In view of steps, it is convenient to use the curable resin composition of the invention as both of the die-bonding material and the encapsulating material.

[0097]

35 As a method of adhering the semiconductor chip to the substrate using the curable resin composition of the invention, the semiconductor chip can be adhered by placing the semiconductor chip on the curable resin composition of the invention after the composition is applied on the substrate by a dispenser, potting, or screen printing and then performing

heat curing. For heating, a method of hot-air circulation, infrared ray, high frequency wave or the like can be employed.

[0098]

Heating conditions are preferably, for example, 80 to 230°C and about 1 minute to 24 hours. For the purpose of reducing internal stress to be generated in heat curing, for example, pre-cure can be performed at 80 to 120°C for 30 minutes to 5 hours and then after-cure can be performed under conditions of 120 to 180°C and 30 minutes to 10 hours.

[0099]

As a molding method of the encapsulating material, an injection method wherein the encapsulating material is injected into a mold frame in which the substrate having the semiconductor chip fixed thereon has been inserted and then is heat-cured to achieve molding, a compression molding method wherein the encapsulating material is injected on a mold beforehand, the semiconductor chip fixed on the substrate is immersed therein, heat curing is performed, and then the chip is released from the mold, or the other method has been used.

As an injection method, a dispenser, a transfer molding, injection molding or the like may be mentioned.

For heating, a method of hot-air circulation, infrared ray, high frequency wave or the like can be employed.

Heating conditions are preferably, for example, 80 to 230°C and about 1 minute to 24 hours. For the purpose of reducing internal stress to be generated in heat curing, for example, pre-cure can be performed at 80 to 120°C for 30 minutes to 5 hours and then after-cure can be performed under conditions of 120 to 180°C and 30 minutes to 10 hours.

[0100]

Furthermore, the curable resin composition of the invention can be applied to general uses in which thermosetting resins such as epoxy resins are used. For example, there may be mentioned adhesives, paints, coating agents, molding materials (including sheets, films, FRP and the like), insulating materials (including printed boards, electric wire coverings, etc.), encapsulating agents, and also additives for other resins such as cyanate resin compositions for encapsulating materials and substrates and acrylate ester-based resins as curing agents for resists, and the like.

[0101]

As the adhesives, in addition to adhesives for civil engineering, architecture, automobiles, general office works and medical uses, adhesives for electronic materials may be mentioned. Of these, as the adhesives for electronic materials, there may be mentioned interlayer adhesives of multilayer substrates such as build-up substrates, die-bonding agents, semiconductor adhesives such as underfill, underfill for BGA

reinforcement, anisotropic conductive films (ACF), adhesives for mounting such as anisotropic conductive pastes (ACP), and the like.

[0102]

As the encapsulating agents, there may be mentioned potting, dipping, transfer-
5 mold encapsulation used for condensers, transistors, diodes, light-emitting diodes, IC, LSI and the like, potting encapsulation used for COB, COF, TAB and the like for IC and LSI, underfill for flip chips and the like, encapsulation at mounting of IC packages such as QFP, BGA and CSP (including underfill for reinforcement) and the like.

[0103]

10 The cured product obtained in the invention can be used in various uses including optical parts materials. The optical materials means general materials to be used in uses where light such as visible light, infrared ray, ultraviolet ray, X-ray or laser is allowed to pass through the material. More specifically, the following may be mentioned in addition
15 to LED encapsulating materials of lamp type, SMD type and the like. They may be peripheral materials for liquid crystal displays, including substrate materials, optical waveguides, prism sheets, polarizing plates, retardation films, viewing angle correction films, adhesives, films for liquid crystals such as polarizer protective films and the like in the liquid crystal display field. Moreover, they may be encapsulating materials, antireflection films, optical correction films, housing materials, protective films of front
20 glass, front glass substituting materials and adhesives for color PDP (plasma display) expected as a next-generation flat panel display; mold materials for LED, encapsulating materials for LED, protective films of front glass, front glass substituting materials and adhesives for use in LED displays; substrate materials, optical waveguides, prism sheets, polarizing plates, retardation films, viewing angle correction films, adhesives and polarizer
25 protective films in plasma address liquid crystal (PALC) displays; protective films of front glass, front glass substituting materials and adhesives in organic EL (electroluminescence) displays; and various film substrates, protective films of front glass, front glass substituting materials and adhesives in field emission displays (FED). In the optical recording field, they may be VD (video disk), CD/CD-ROM, CD-R/RW, DVD-R/DVD-RAM, MO/MD,
30 PD (phase change disk), disk substrate materials for optical cards, pick-up lenses, protective films, encapsulating materials, adhesives and the like.

[0104]

In the optical device field, they may be lens materials for still cameras, finder
prisms, target prisms, finder covers and a light-receiving sensor part. Moreover, they may
35 be taking lenses and finders for video cameras. Furthermore, they may be projection lenses, protective films, encapsulating materials, adhesives and the like for projection television sets. They may be lens materials, encapsulating materials, adhesives, films and the like for optical sensing devices. In the optical parts field, they may be fiber materials,

lenses, optical waveguides, encapsulating materials for elements, adhesives and the like in the periphery of optical switches in the optical communication system. They may be optical fiber materials, ferrules, encapsulating materials, adhesives and the like in the periphery of optical connectors. In the optical receiving parts and optical circuit parts, they may be lenses, optical waveguides, encapsulating materials for LED, encapsulating materials for CCD, adhesives and the like. They may be substrate materials, fiber materials, encapsulating materials for elements, adhesives and the like in the periphery of optical electronic integrated circuits (OEIC). In the optical fiber field, they may be illumination lamps/light guides and the like for decoration display, sensors in industrial uses, displays/signs and the like, and optical fibers for communication infrastructure and for domestic digital device connection. In the peripheral materials for semiconductor integrated circuits, they may be resist materials for microlithography for LSI or ultra LSI materials. In the automobile/transport aircraft fields, lamp reflectors for automobiles, bearing retainers, a gear part, corrosion-resistant coatings, a switch part, headlamps, parts in engines, electrical components, various interior and exterior equipments, driving engines, brake oil tanks, rustproof steel plates for automobiles, interior panels, interior materials, protective/bonding wire harness, fuel hoses, automobile lamps and glass substitutes. Moreover, they may be double-grazed glasses for railway vehicles. Furthermore, they may be toughness-imparting agents for aircraft structural materials, engine peripheral members, protective/bonding wire harness and corrosion-resistant coatings. In the architecture field, interior/processing materials, electric covers, sheets, glass intermediate films, glass substitutes and solar battery periphery materials. In agriculture, they may be house-covering films. As next-generation optical/electronic function organic materials, they may be organic EL element peripheral materials, organic photorefractive elements, optical amplification elements that are light-light conversion devices, optical arithmetic elements, substrate materials in the periphery of organic solar batteries, fiber materials, encapsulating materials for elements, adhesives and the like.

[0105]

The following will describe the invention further in detail with reference to Synthetic Examples and Examples. Incidentally, the invention is not limited to these Synthetic Examples and Examples. Here, individual physical property values in Examples were measured by the following methods.

(1) Molecular weight: weight-average molecular weight was calculated as a value in terms of polystyrene measured under the following conditions by gel permeation chromatography (GPC) method.

Various conditions for GPC

Manufacturer: Shimadzu Corporation

Column: guard column SHODEX GPC LF-G LF-804 (3 columns)

Flow rate: 1.0 ml/min.

Column temperature: 40°C

Used solvent: THF (tetrahydrofuran)

Detector: RI (differential refractometry detector)

5 (2) Epoxy equivalent: measured by the method described in JIS K-7236.

(3) Viscosity: measured at 25°C using an E-type viscometer (TV-20) manufactured by Toki Sangyo Co., Ltd.

[0106]

The following will describe the invention further in detail with reference to

10 Synthetic Examples and Examples. Incidentally, in the following Synthetic Examples and Examples, "parts" means parts by weight and "%" means % by weight, respectively. Examples

[0107]

Synthetic Example 1 (20)

15 As step 1, 375 parts of β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 475 parts of a silanol-terminated methylphenylsilicone oil having a weight-average molecular weight of 1700 (value measured on GPC) (silanol equivalent of 850, calculated as a half of the weight-average molecular weight measured using GPC), and 40 parts of a 0.5% potassium hydroxide (KOH) methanol solution were charged into a reaction vessel, and a reaction
20 was carried out under reflux for 8 hours.

As step 2, after 655 parts of methanol was additionally added, 144 parts of a 50% distilled water methanol solution was added dropwise over a period of 60 minutes and a reaction was carried out under reflux for 8 hours. After the reaction was finished, neutralization was performed with a 5% aqueous sodium dihydrogen phosphate solution
25 and then about 90% of methanol was recovered by distillation. Thereafter, 750 parts of methyl isobutyl ketone (MIBK) was added and washing with water was repeated three times. Then, 647 parts of an epoxy resin (A-1) to be used in the invention was obtained by removing the solvent at 100°C under reduced pressure from the obtained organic phase. Epoxy equivalent of the obtained compound was 541 g/eq, weight-average molecular
30 weight was 2100, and the appearance was a colorless and transparent resin in liquid form.

[0108]

Synthetic Example 2 (17)

As step 1, 263 parts of β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 475 parts of a silanol-terminated methylphenylsilicone oil having a weight-average molecular weight of
35 1900 (value measured on GPC) (silanol equivalent of 950, calculated as a half of the weight-average molecular weight measured using GPC), and 40 parts of a 0.5% potassium hydroxide (KOH) methanol solution were charged into a reaction vessel, and a reaction was carried out under reflux for 8 hours.

As step 2, after 655 parts of methanol was additionally added, 115 parts of a 50% distilled water methanol solution was added dropwise over a period of 60 minutes and a reaction was carried out under reflux for 8 hours. After the reaction was finished, neutralization was performed with a 5% aqueous sodium dihydrogen phosphate solution and then about 90% of methanol was recovered by distillation. Thereafter, 750 parts of methyl isobutyl ketone (MIBK) was added and washing with water was repeated three times. Then, 605 parts of an epoxy resin (A-2) to be used in the invention was obtained by removing the solvent at 100°C under reduced pressure from the obtained organic phase. Epoxy equivalent of the obtained compound was 636 g/eq, weight-average molecular weight was 2090, and the appearance was a colorless and transparent resin in liquid form.

[0109]

Synthetic Example 3 (18)

As step 1, 285 parts of β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 475 parts of a silanol-terminated methylphenylsilicone oil having a weight-average molecular weight of 1700 (value measured on GPC) (silanol equivalent of 850, calculated as a half of the weight-average molecular weight measured using GPC), and 40 parts of a 0.5% potassium hydroxide (KOH) methanol solution were charged into a reaction vessel, and a reaction was carried out under reflux for 8 hours.

As step 2, after 655 parts of methanol was additionally added, 123 parts of a 50% distilled water methanol solution was added dropwise over a period of 60 minutes and a reaction was carried out under reflux for 8 hours. After the reaction was finished, neutralization was performed with a 5% aqueous sodium dihydrogen phosphate solution and then about 90% of methanol was recovered by distillation. Thereafter, 750 parts of methyl isobutyl ketone (MIBK) was added and washing with water was repeated three times. Then, 620 parts of an epoxy resin (A-3) to be used in the invention was obtained by removing the solvent at 100°C under reduced pressure from the obtained organic phase. Epoxy equivalent of the obtained compound was 605 g/eq, weight-average molecular weight was 2120, and the appearance was a colorless and transparent resin in liquid form.

[0110]

Synthetic Example 4

Into a flask fitted with a stirrer, a reflux condenser and a stirring apparatus were added 84 parts of methylhexahydrophthalic anhydride (RIKACID MH, manufactured by New Japan Chemical Co., Ltd., hereinafter referred to as acid anhydride H-1) and 239 parts of a carbinol-modified silicone oil (X22-160AS manufactured by Shin-Etsu Chemical Co., Ltd.) while performing nitrogen purging. After a reaction was carried out at 60°C for 2 hours, heating and stirring were performed at 90°C for 3 hours to obtain 323 parts of a polyhydric carboxylic acid (B-1) represented by the following formula (7). The obtained one was a colorless liquid resin and functional group equivalent was 646 g/eq.

[Chem. 5]

rate of 2°C/second and then kept at 150°C for 2 minutes, temperature is further elevated to 260°C at a rate of 2°C/second and, after the temperature is kept for 10 seconds, cooling is performed to room temperature at a rate of 1.3°C/second.

[0114]

5 (Corrosive gas permeation test)

Using each of the obtained curable resin compositions, it was filled into a syringe and injected into a surface-mounted LED package (inner diameter of 4.4 mm, outer wall height of 1.25 mm) 5 mm square as an outer diameter on which a chip having a central emission wavelength of 465 nm had been mounted, using a precise injection apparatus.

10 The injected material was placed into a heating furnace and subjected to a curing treatment at 120°C for 1 hour and further at 150°C for 3 hours to prepare an LED package. The LED package was allowed to stand in a corrosive gas under the following conditions and color change of the silver-plated lead frame part present inside the encapsulation was observed. The results are shown in Table 1.

15 Measurement Conditions

Corrosive gas: a 20% aqueous ammonium sulfide solution (discoloration into black is observed in the case where the sulfur component is reacted with silver)

Contact method: a vessel containing the aqueous ammonium sulfide solution and the LED package were placed together in a wide-mouthed glass bottle and, under a tightly
20 closed situation with capping the wide-mouthed glass bottle, vaporized ammonium sulfide gas was allowed to come into contact with the LED package.

Judgment on corrosion: The time required for discoloring the lead frame present inside the LED package black (called blackening) was observed and an LED package requiring longer time for color change is judged to be more excellent in corrosive gas
25 resistance.

The observation was performed every 1 hour and evaluation was performed until 5 hours. For evaluation, time required for discoloration was evaluated.

[0115]

(LED lighting test)

30 Each of the obtained curable resin compositions was filled into a syringe and injected into a surface-mounted LED (SMD type 5 mmφ, specified current of 30 mA) on which an emission element having an emission wavelength of 465 nm had been mounted, using a precise injection apparatus. Thereafter, an LED for lighting test was obtained by curing under curing conditions at 120°C for 1 hour and further at 150°C for 3 hours. For
35 the lighting test, a lighting test at a current of 230 mA, 220 mA that was more than the specified current 30 mA at large extent was performed. Detailed conditions were shown below. As for a measurement item, illuminance before and after lighting for 40 hours was measured using an integrating sphere and an illuminance retention ratio of the LED for test

was calculated. The results are shown in Table 1.

Detailed conditions for lighting

Emission wavelength: a main emission wavelength 465 nm

- 5 Driving method: constant current method, 220 mA, 230 mA (specified current of the emission element was 30 mA); three LEDs were simultaneously lighted in series.

Driving environment: lighting in a wet heat machine of 85°C, 85%

Evaluation: illuminance retention ratio after 40 hours

[0116]

[Table 1]

			Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2	Comparative Example 3
Composition	Epoxy resin (A)	A-1	10.0			10.0	10.0	
		A-2		10.0				
		A-3			10.0			
	Polyhydric carboxylic acid (B)	B-1	11.9	10.2	10.7		11.9	
		H-1				3.1		
		C-1	0.11	0.11	0.11	0.11		
	Zinc salt/complex (C)	I-1				0.05	0.05	
		J-1	0.02	0.02	0.02	0.02	0.02	
		J-2	0.02	0.02	0.02	0.02	0.02	
	Additive	S-1						0.5
		S-2						10.0
Evaluation results	Concave		○	○	○	△	○	○
	Tackiness		○	○	○	×	○	○
	Corrosive gas permeation test	Discoloration time	>5 hours	>5 hours	>5 hours	>5 hours	2 hours	1 hour
	Reflow crack	Crack number	0/3	0/3	0/3	3/3	1/3	0/3
	Accelerated lighting test (220 mA)	Retention ratio (%) after 40 hours	-	-	101%	-	-	27%
	Accelerated lighting test (230 mA)	Retention ratio (%) after 40 hours	96%	94%	-	-	-	33%

[0117]

As Comparative Example 3, there was used a silicone resin obtained by addition polymerization of an organopolysiloxane (S-1) having at least two alkenyl groups bonding to silicon atoms and an organohydrogenpolysiloxane (S-2) having at least two hydrogen atoms bonding to silicon atoms, which participate in addition polymerization with the alkenyl groups.

The above silicone resins S-1 and S-2 specifically have the following structures.

S-1: an organohydrogenpolysiloxane containing a platinum catalyst in a catalytic amount (0.1% or less) and having phenyl group/methyl group/vinyl group as organo groups in a ratio of 0.4/1/1 in terms of mol.

S-2: an organohydrogenpolysiloxane having a phenyl group, a methyl group and a vinyl group as organo groups in which the ratio of contained phenyl group/methyl group/vinyl group/hydrogen atom in hydrosilyl group is 2/2/1/1 in terms of mol.

Incidentally, in Comparative Example 3, the blending ratio (mass ratio) was S-1/S-2=1/20 and curing conditions were 150°C and 1 hour.

[0118]

From the above results, it is revealed that the curable resin compositions of the invention (compositions containing an epoxy resin (A), a polyhydric carboxylic acid (B) having a silicone skeleton, and a zinc salt and/or a zinc complex (C)) does not discolor silver plating on a lead frame as compared with the curable resin compositions of Comparative Examples, so that the curable resin compositions of the invention are not only excellent in corrosive gas resistance but also excellent in crack resistance. Furthermore, from the results that better illuminance retention ratio is shown in the high-current accelerated lighting test even when compared with a silicone resin, it is understood that the cured products of the compositions of the invention are also excellent in electrical reliability and light-resistant and heat-resistant properties.

[0119]

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

The present application is based on Japanese Patent Application No. 2010-134465 filed on June 11, 2010, and the contents are incorporated herein by reference. Also, all the references cited herein are incorporated as a whole.

Claims

[Claim 1] A curable resin composition, comprising:

an epoxy resin (A);

5 a polyhydric carboxylic acid (B); and

a zinc salt and/or a zinc complex (C) as essential components, provided that the polyhydric carboxylic acid (B) and the zinc salt and/or the zinc complex (C) satisfy the following requirements respectively:

10 Polyhydric carboxylic acid (B): a polyhydric carboxylic acid having at least two carboxyl groups and having a siloxane skeleton as a main skeleton; and

Zinc salt and/or zinc complex (C): a zinc carboxylate, a zinc salt of a phosphate ester or phosphoric acid and/or a zinc complex having the acid or ester as a ligand.

[Claim 2] The curable resin composition according to claim 1,

15 wherein the polyhydric carboxylic acid (B) has a linear polysiloxane structure and has carboxylic acids at both terminals.

[Claim 3] The curable resin composition according to claim 1 or 2,

20 wherein the polyhydric carboxylic acid (B) is a compound obtained by a reaction of a carbinol-modified compound having a linear polysiloxane structure with a cyclic saturated aliphatic acid anhydride.

[Claim 4] The curable resin composition according to any one of claims 1 to 3, comprising:

25 a hindered amine-based photo-stabilizer; and
a phosphorus-containing antioxidant.

[Claim 5] A cured product, which is obtained by curing the curable resin composition according to any one of claims 1 to 4.