

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]

Moreover, 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).

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[0004]

Furthermore, 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 light than epoxy resins but the stability is not yet satisfactory and further improvement is a problem. As a method for solving the problem, there has been known a method of adding a photo-stabilizer (Patent Document 4). However, although light resistance is improved by the addition of the photo-stabilizer, the resins are deteriorated by heat and the like generated from the LED chip.

Related Art

Patent Document

[0005]

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-2009-275206

Summary of the Invention

Problems to Be Solved by the Invention

[0006]

An object of the invention is to provide a novel curable resin composition that affords a cured product excellent in light coloration resistance, thermal coloration resistance and corrosive gas resistance.

Means for Solving the Problems

[0007]

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.

(1) A curable resin composition, comprising:

an organopolysiloxane (A);

a polyhydric carboxylic acid (B);

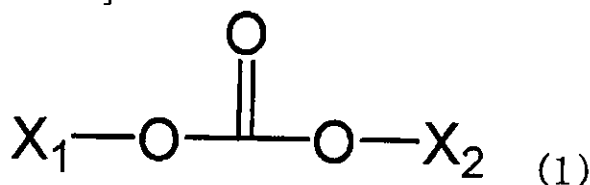
an organometallic salt and/or an organometallic complex (C); and

a photo-stabilizer (D), provided that the organopolysiloxane (A), the polyhydric carboxylic acid (B) and the photo-stabilizer (D) satisfy the following requirements:

Organopolysiloxane (A): an organopolysiloxane having at least a glycidyl group and/or an epoxycyclohexyl group in a molecule thereof;

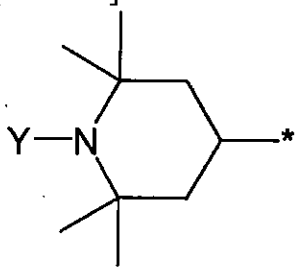
Polyhydric carboxylic acid (B): one having at least two carboxyl groups and having an aliphatic hydrocarbon group as a main skeleton; and

Photo-stabilizer (D): a compound represented by a structural formula (1):
[Chem. 1]



wherein X_1 and X_2 are a hydrogen atom, an alkyl group having 1 to 50 carbon atoms, an aralkyl group, an aryl group, an aryl group having an alkyl group having 1 to 20 carbon atoms, an alkoxy group or a structural formula (2), and at least one of X_1 and X_2 is the structural formula (2):

10 [Chem. 2]



(2)

wherein in formula (2), the structural formula (2) is bonded to the oxygen atom of the structural formula (1) at the sign *; and

Y represents a hydrogen atom, an alkyl group having 1 to 50 carbon atoms, an aryl group or an alkoxy group.

(2) The curable resin composition as described in the above item (1), comprising:

a compound of the structural formula (1) in which Y in the structural formula (2) is an alkoxy group having 1 to 20 carbon atoms.

(3) The curable resin composition as described in the above item (1) or (2), wherein the organometallic salt and/or the organometallic complex (C) is a zinc salt of a phosphate ester or phosphoric acid and/or a zinc complex having the acid or ester as a ligand.

(4) The curable resin composition as described in any one of the above items (1) to (3),

wherein X_1 and X_2 in the structural formula (1) are both the structural formulae (2) and Y in the structural formula (2) is $-\text{OC}_{11}\text{H}_{23}$.

(5) The curable resin composition as described in any one of the above items (1) to (4), comprising:

an acid anhydride.

(6) The curable resin composition as described in any one of the above items (1)

to (5),

wherein the polyhydric carboxylic acid (B) is a compound obtained by reacting a bifunctional to hexafunctional polyhydric alcohol having 5 or more carbon atoms with a saturated aliphatic cyclic acid anhydride.

(7) The curable resin composition as described in any one of the above items (1) to (6), comprising:

an antioxidant.

(8) A cured product, which is obtained by curing the curable resin composition as described in any one of the above items (1) to (7).

Effects of the Invention

[0008]

Since the curable resin composition of the invention is excellent in corrosive gas resistance, thermal coloration resistance and light coloration resistance, the composition is extremely useful as particularly an adhering material and an encapsulating material for optical semiconductors (LED products etc.) to be used in living environment, for example, illumination, among optical materials.

Embodiments for Carrying Out the Invention

[0009]

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

The curable resin composition of the invention comprises an organopolysiloxane (A), a polyhydric carboxylic acid (B), an organometallic salt and/or an organometallic complex (C) and a photo-stabilizer (D).

The organopolysiloxane (A) uses an organopolysiloxane having a glycidyl group and/or an epoxycyclohexyl group in the molecule thereof.

The organopolysiloxane is characterized in that it is an organopolysiloxane having at least a glycidyl group and/or an epoxycyclohexyl group in the molecule thereof, and the organopolysiloxane is obtained by a sol-gel reaction using as a raw material a trialkoxysilane having a glycidyl group or an epoxycyclohexyl group.

Specifically, there may be mentioned silsesquoxane-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.

In the invention, the structure 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 chain

silicone segment and the aforementioned silsesquioxane structure in one molecule is particularly preferred (hereinafter referred to as block-type siloxane compound (E)).

[0010]

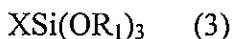
The block-type siloxane compound (E) is not a compound having repeating units linearly as in usual block copolymers but has a three-dimensionally spreading reticular structure in which a silsesquioxane structure is a core and a chain silicone segment is extended and bonded to the next silsesquioxane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

[0011]

The block-type siloxane compound (E) can be, for example, produced using an alkoxysilane (a) represented by the general formula (3) and a silicone oil (b) represented by the general formula (4) as raw materials and, according to need, an alkoxysilane (c) represented by the general formula (5) can be used as a raw material. The chain silicone segment of the block-type siloxane compound (E) is formed from the silicone oil (b) and the three-dimensional reticular silsesquioxane segment is formed from the alkoxysilane (a) (and the alkoxysilane (c) used according to need). The following will explain individual raw materials in detail.

[0012]

The alkoxysilane (a) is represented by the following general formula (3):



As X in the general formula (3) is not particularly limited as long as it is an organic group containing a glycidyl group and/or an epoxycyclohexyl group. Examples thereof include alkyl groups having 1 to 4 carbon atoms substituted with a glycidoxy group, such as β -glycidoxyethyl, γ -glycidoxypropyl and γ -glycidoxybutyl, a glycidyl group, alkyl groups having 1 to 5 carbon atoms substituted with a cyclohexyl group 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 cyclohexyl group 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.

[0013]

A plurality of R_1 groups present in the general formula (3) 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 R₁ 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.

[0014]

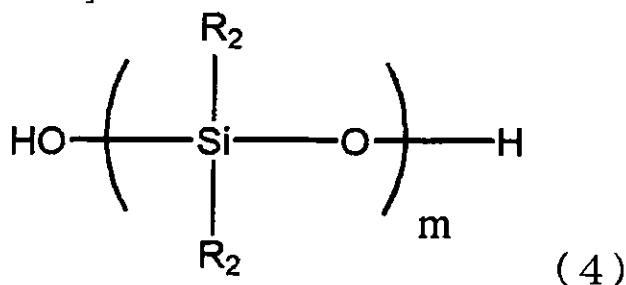
Preferable specific examples of the alkoxysilane (a) include β-glycidoxyethyltrimethoxysilane, β-glycidoxyethyltriethoxysilane, γ-glycidoxypropyltrimethoxysilane, γ-glycidoxypropyltriethoxysilane, β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, β-(3,4-epoxycyclohexyl)ethyltriethoxysilane, and the like. Particularly, β-(3,4-epoxycyclohexyl)ethyltriethoxysilane is preferred. These alkoxysilanes (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.

[0015]

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 (4).

[0016]

[Chem. 3]



[0017]

In the general formula (4), a plurality of R₂ 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. Further, m represents the number of repeating units.

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 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, from the viewpoints 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, R₂ 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.

[0018]

The number m of repeating units in the compound of the general formula (4) 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.

[0019]

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 weight-average molecular weight of 300 to 10,000 are preferred and further, in consideration of compatibility at the preparation of the composition, those having a weight-average molecular weight of 300 to 5,000 are more preferred, those having a weight-average 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

Used solvent: THF (tetrahydrofuran)

Detector: RI (differential refractometry detector)

[0020]

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 block-type siloxane compound (E) is too low and it is not suitable as an optical

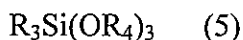
semiconductor encapsulating agent in some cases. When the kinematic viscosity is more than 200 cSt, the viscosity of the block-type siloxane compound (E) increases and a trouble on workability tends to occur, so that the cases are not preferred.

[0021]

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 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 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, 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, YF-3800, YF-3804, 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.

[0022]

The following will describe the alkoxysilane (c) in detail. The alkoxysilane (c) has a structure of the following general formula (5):



R_3 in the general formula (5) represents a methyl group or a phenyl group.

[0023]

A plurality of R_4 groups present in the general formula (5) represent each a linear, branched or cyclic alkyl group having 1 to 10 carbon atoms and may be the same or different from each other. 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, R_4 is preferably a methyl group or an ethyl group.

[0024]

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

[0025]

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 (E), 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 product.

[0026]

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

[0027]

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) (the alkoxysilane (a) and the alkoxysilane (c) in the case where the the alkoxysilane (c) is used in combination 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 (E) becomes too hard and thus the objective low elastic modulus properties decrease.

[0028]

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

[0029]

The production process of the block-type siloxane compound (E) preferably includes the following production steps represented by the following (1) and (2):

Production step (1): a step of performing dealcoholization condensation of a silanol-terminated silicone oil with a silicon compound having an alkoxy group,

Production step (2): a step of adding water to perform hydrolytic condensation between the alkoxy groups of the silicon compound having an alkoxy group.

The production steps (1) and (2) may be performed in any order as long as the steps are included.

[0030]

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

<Production process (a)>

A process for producing the block-type siloxane compound (E), wherein
first, as the production step (1), 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) used according to
need) that is a silicon compound having an alkoxy group, and

subsequently, as the production step (2), a step of adding water to the alkoxysilane
(a) (and the alkoxysilane (c) used 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 (1) to carry out the hydrolytic condensation reaction between the
alkoxy groups is performed.

<Production process (b)>

A process for producing the block-type siloxane compound (E), wherein
first, as the production step (2), a step of obtaining a silsesquioxane (e) having an
alkoxy group in the molecule is performed by carrying out the hydrolytic condensation
reaction between the alkoxy groups of the alkoxysilane (a) (and the alkoxysilane (c) used
according to need) that is a silicon compound having an alkoxy group by adding water, and

subsequently, as the production step (1), a step of reacting the silicone oil (b)
having a silanol group at the terminal with the silsesquioxane (e) to carry out the
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 (E), wherein
first, as the production step (1), the silicone oil terminal is modified with an
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) used
according to need) that is a silicon compound having an alkoxy group to form an
alkoxysilane-modified compound (d), and then, as the production step (2), the hydrolytic
condensation reaction between the alkoxy groups of the remaining alkoxysilane (a) (and
the alkoxysilane (c)) and the alkoxysilane-modified compound (d) is carried out in one pot
by adding water to a reaction system.

[0031]

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
performed in the reverse order contrarily to the aforementioned production process (c), that

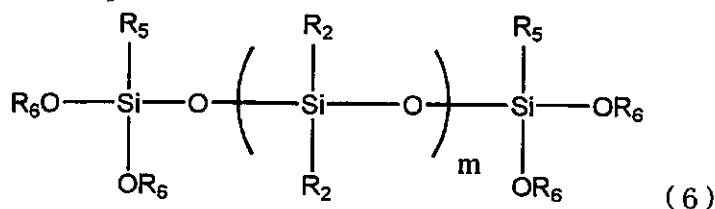
is, the production step (1) is performed after the production step (2) as in the case of (b), there is a high possibility that the silsesquioxane oligomer having an alkoxy group formed in the production step (2) and the silicone oil (b) do not solve each other, the dealcoholization condensation polymerization does not proceed in the following

production step (1), and thus the unreacted silicone oil remains. On the other hand, when a process of performing the production step (2) in one pot after the production step (1) 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 the low-molecular-weight alkoxysilane, which does not undergo the condensation reaction between the alkoxysilanes, 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 (1) is referred to as first-stage reaction and the production step (2) 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 (1)), the dealcoholization condensation of the silicone oil (b) with the alkoxysilane (a) (and the alkoxysilane (c) used 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 (d) is considered to be present as a structure represented by the following formula (6).

[0032]

[Chem. 4]



[0033]

In the formula (6), R₂ and m have the same meanings as described above and R₅ represents the above X or the above R₃, and R₆ represents R₁ in the case where R₅ is the above X or represents R₄ in the case where R₅ is the above R₃.

[0034]

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) used 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 and a ratio of 3.0 equivalents or more is more preferred.

[0035]

After the first-stage reaction is finished, the second-stage reaction (production step (2)) of adding water to perform the hydrolytic condensation between the alkoxy groups is performed without further treatment. Further, in the second-stage reaction, reactions (I) to (III) shown below take place.

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

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

(III) A condensation reaction between the alkoxy groups of the alkoxy silane-modified compound (d) obtained in the first-stage reaction and a partially condensed compound of the alkoxy silane (a) (and the alkoxy silane (c) used 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.

[0036]

The production of the block-type siloxane compound (E) 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 the compounds showing acidity (acid 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 the compounds showing basicity (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 alkoxy silane (a) (and the alkoxy silane (c) used according to need) in the reaction system.

As a method for adding the catalyst, it is directly added or the catalyst 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 alkoxy silane (a) (the alkoxy silane (c) used according to need) occurs unilaterally and the silsesquioxane oligomer formed therefrom and the silicone oil (b) do not solve each other and become turbid.

[0037]

The production of the block-type siloxane compound (E) 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 alkoxy silane (a) (the alkoxy silane (c) used according to need), the silicone oil (b), and the alkoxy silane-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; hydrocarbons 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 alkoxy silane (a) (and the alkoxy silane (c) used 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 steps.

[0038]

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

and isopropyl butanoate; hydrocarbons such as hexane, cyclohexane, toluene and xylene; and the like.

[0039]

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 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 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 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 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.

[0040]

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

[0041]

After the reaction is completed or quenched, the product can be purified by conventional separation and purification methods such as 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.

[0042]

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.

[0043]

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

[0044]

The appearance of the block-type siloxane compound (E) 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

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)

[0045]

Moreover, the epoxy equivalent (measured by the method described in JIS K-7236) of the block-type siloxane compound (E) 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.

[0046]

The viscosity (E-type viscometer, measured at 25°C) of the block-type siloxane compound (E) 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.

[0047]

The ratio of the silicon atom bonded to three oxygen atoms, which is derived from the silsesquioxane in the block-type siloxane compound (E), 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.

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 (E).

[0048]

The polyhydric carboxylic acid (B) is a compound characterized in that it has at least two carboxyl groups and has an aliphatic hydrocarbon group as a main skeleton. In the invention, the polyhydric carboxylic acid includes not only a polyhydric carboxylic acid compound having a single structure but also a mixture of a plurality of compounds in which the positions of the substituents are different or the substituents are different, i.e., a polyhydric carboxylic acid composition. In the invention, they are collectively referred to as polyhydric carboxylic acid.

As the polyhydric carboxylic acid (B), particularly, a bifunctional to hexafunctional carboxylic acid is preferred. Since strong influence of solidification is observed when the number of carbon atoms in the polyhydric carboxylic acid (B) is small and workability as an encapsulating material decreases, a compound obtained by the

reaction of a bifunctional to hexafunctional polyhydric alcohol having 5 or more carbon atoms with an acid anhydride is preferred. When the number of carbon atoms is 5 or more, good workability as an encapsulating material can be secured. Furthermore, from the viewpoint of durability, also for improving heat resistance, a polycarboxylic acid in which the acid anhydride is a saturated aliphatic cyclic acid anhydride is preferred.

[0049]

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, 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, from the viewpoint of imparting heat resistance and light resistance and maintaining a high illuminance retention ratio, 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, methylnadidic 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, methylhexahydrophthalic anhydride and cyclohexane-1,2,4-tricarboxylic-1,2-anhydride are preferred owing to high transparency.

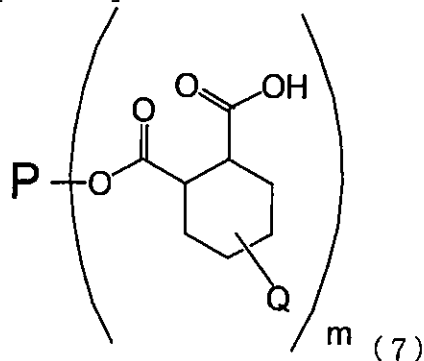
The conditions for the addition reaction are not particularly designated. As one specific reaction condition, there may be mentioned a method of reacting the acid anhydride with the polyhydric alcohol at 40 to 150°C under conditions of no catalyst and no solvent, heating them, and, after completion of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

[0050]

As the thus obtained polycarboxylic acid, particularly preferred is a compound represented by the following formula (7):

[0051]

[Chem. 5]



wherein a plurality of Q's present represents at least one of a hydrogen atom, a methyl group and a carboxyl group; P is a linear, branched or cyclic aliphatic group having 2 to 20 carbon atoms derived from the aforementioned polyhydric alcohol; m is the number of functional groups of the polyhydric alcohol and is preferably an integer of 2 to 6.

[0052]

The curable resin composition of the invention preferably contains an acid anhydride. It becomes possible to arbitrarily control the viscosity as a curing agent by the incorporation of the acid anhydride.

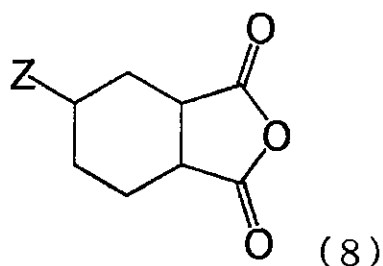
As the acid anhydride, specifically, there may be mentioned acid anhydrides such as phthalic anhydride, trimellitic anhydride, pyromellitic anhydride, maleic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, methylnadic anhydride, nadic anhydride, hexahydrophthalic anhydride, 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-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-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 (8):

[0053]

[Chem. 6]



wherein Z represents at least one selected from a hydrogen atom, a methyl group and a carboxyl group,

are preferred. Of these, methylhexahydrophthalic anhydride and cyclohexane-1,2,4-tricarboxylic-1,2-anhydride are preferred owing to high transparency.

[0054]

The polyhydric carboxylic acid (B) and the acid anhydride are preferably used in combination and, in the case where they are used in combination, the ratio thereof to be used is preferably in the following range.

$$W1/(W1+W2) = 0.05 \text{ to } 0.65$$

Here, W1 represents part(s) by weight of the polyhydric carboxylic acid (B) blended and W2 represents part(s) by weight of the acid anhydride blended. The range of $W1/(W1+W2)$ is preferably 0.05 to 0.65, further preferably 0.10 to 0.65, and particularly preferably 0.3 to 0.6. When the ratio is less than 0.05, there is a strong tendency that vaporization of the acid anhydride increases at curing, so that the case is not preferred. When the ratio exceeds 0.65, the viscosity becomes high and handling becomes difficult. In the case where the acid anhydride is not incorporated (except the case where a small amount remains), the form becomes a solid or nearly a solid or crystals, so that no problem arises.

In the case where the polyhydric carboxylic acid (B) and the acid anhydride are used in combination, a method of producing the polyhydric carboxylic acid (B) in an excess of the acid anhydride at the production of the acid to prepare a mixture of the polyhydric carboxylic acid (B) and the acid anhydride is also preferred from the viewpoint of convenience of the operation.

[0055]

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

Metals of the organometallic salt and/or the organometallic complex (C) include aluminum, manganese, iron, cobalt, nickel, copper, zinc, zirconium, tin, lead and the like.

Examples of the organometallic salt and/or the organometallic complex (C) include aluminum 2-ethylhexanoate, manganese 2-ethylhexanoate, iron 2-ethylhexanoate, cobalt 2-ethylhexanoate, nickel 2-ethylhexanoate, copper 2-ethylhexanoate, zinc 2-ethylhexanoate, zirconium 2-ethylhexanoate, tin 2-ethylhexanoate, lead 2-ethylhexanoate, aluminum naphthenate, manganese naphthenate, iron naphthenate, cobalt naphthenate,

nickel naphthenate, copper naphthenate, zinc naphthenate, zirconium naphthenate, tin naphthenate, lead naphthenate, aluminum stearate, manganese stearate, iron stearate, cobalt stearate, nickel stearate, copper stearate, zinc stearate, zirconium stearate, tin stearate, lead stearate, zinc undecylenate, zinc laurate, zinc behenate, zinc 12-hydroxystearate, zinc montanate, zinc myristate, zinc palmitate, zinc naphthenate, zinc hexoate, zinc octylate, aluminum-acetylacetone complex, manganese-acetylacetone complex, iron-acetylacetone complex, cobalt-acetylacetone complex, nickel-acetylacetone complex, copper-acetylacetone complex, zinc-acetylacetone complex, zinc complex of (2-ethylhexyl) phosphate, zirconium-acetylacetone complex, tin-acetylacetone complex, lead-acetylacetone complex, and the like.

Here, from the viewpoint of imparting corrosive gas resistance, the zinc salt and/or the zinc complex are preferred. Specifically, zinc 2-ethylhexanoate, a zinc complex of (2-ethylhexyl) phosphate and/or a salt thereof, zinc stearate, zinc undecylenate, zinc laurate, zinc behenate, zinc 12-hydroxystearate, zinc montanate, zinc myristate, zinc palmitate, zinc naphthanate, zinc hexoate and zinc octylate are preferred.

Moreover, particularly from the viewpoint of compatibility, zinc 2-ethylhexanoate, a zinc complex of (2-ethylhexyl) phosphate and/or a salt thereof, zinc stearate, zinc undecylenate are more preferred and, when transparency is considered, zinc 2-ethylhexanoate and a zinc complex of (2-ethylhexyl) phosphate and/or a salt thereof are particularly preferred.

As such zinc carboxylates, as commercially available products, Zn-St, Zn-ST 602, Zn-St NZ, ZS-3, ZS-6, ZS-8, ZS-7, ZS-10, ZS-5, ZS-14, ZS-16 (manufactured by Nitto Kasei Kogyo K.K.), XK-614 (manufactured by King Industries Inc.), 18% Octope Zn, 12% Octope Zn, 8% Octope Zn (manufactured by Hope Chemical Co., Ltd.), and as zinc phosphate esters and/or zinc phosphate, LBT-2000B (manufactured by SC Organic Chemical Co., Ltd.), XC-9206 (manufactured by King Industries Inc.) may be mentioned.

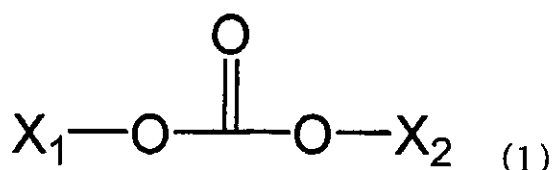
[0056]

Here, the ratio of the organometallic salt and/or the organometallic 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 organopolysiloxane (A) in terms of a weight ratio. Moreover, particularly preferred is 0.1 to 2% by weight.

[0057]

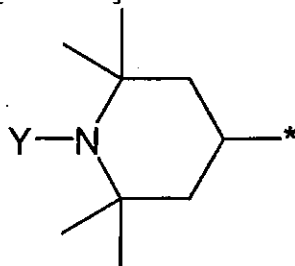
The curable resin composition of the invention contains a photo-stabilizer (D). The photo-stabilizer (D) is preferably a compound represented by the following general formula (1):

[Chem. 7]



wherein X_1 and X_2 are the same or different, and are a hydrogen atom, an alkyl group having 1 to 50 carbon atoms, an aralkyl group, an aryl group, an aryl group having an alkyl group having 1 to 20 carbon atoms, an alkoxy group or a structural formula (2), and at least one of X_1 and X_2 is the structural formula (2):

[Chem. 8]



(2)

wherein the structural formula (2) is bonded to the oxygen atom of the formula (1) at the sign * and Y represents a hydrogen atom, an alkyl group having 1 to 50 carbon atoms, an aryl group and an alkoxy group.

Suitable specific examples of the compound represented by the general formula (1) include bis(2,2,6,6-tetramethylpiperidin-4-yl) carbonate wherein the structural formula (2) where Y is a hydrogen atom is X_1 and X_2 , bis(1,2,2,6,6-pentamethylpiperidin-4-yl) carbonate wherein the structural formula (2) where Y is a methyl group is X_1 and X_2 , bis(2,2,6,6-tetramethyl-propoxypiperidin-4-yl) carbonate wherein the structural formula (2) where Y is a propoxy group is X_1 and X_2 , bis(1-undecanoxo-2,2,6,6-tetramethylpiperidin-4-yl) carbonate wherein the structural formula (2) where Y is an undecyloxy group is X_1 and X_2 , 1,2,2,6,6-pentamethylpiperidin-4-yl tert-pentylcarbonoperoxyate wherein the structural formula (2) where Y is a methyl group is X_1 and a tert-pentyloxy group is X_2 , and the like. As a particularly preferred compound, there may be mentioned bis(1-undecanoxo-2,2,6,6-tetramethylpiperidin-4-yl) carbonate wherein the structural formula (2) where Y is an undecyloxy group is X_1 and X_2 .

[0058]

Here, the ratio of the photo-stabilizer (D) is 0.005 to 5% by weight, more preferably 0.01 to 4% by weight, and further 0.1 to 2% by weight relative to the organopolysiloxane (A) in terms of a weight ratio.

When the ratio of the photo-stabilizer (D) is less than 0.005% by weight relative to the organopolysiloxane (A), an effect of improving light resistance is insufficient. On the other hand, when the ratio is more than 5% by weight, the resin cured product is colored to invite a decrease in illuminance, so that the case is not preferred.

[0059]

The photo-stabilizer (D) can remarkably improve the properties of the resin cured product by using it in combination with the organopolysiloxane (A), the polyhydric carboxylic acid (B), the organometallic salt and/or the organometallic complex (C). Particularly, preferred are the zinc salt and/or the zinc complex as the organometallic salt and/or the organometallic complex (C) and bis(1-undecanoxy-2,2,6,6-tetramethylpiperidine-4-yl) carbonate as the photo-stabilizer (D) and it is preferred to use them in combination. This is because, in the case where they are used as such a combination, the cured product is excellent in light resistance and heat resistance and is hardly colored by light and heat, and the product is also excellent in corrosive gas resistance.

[0060]

The photo-stabilizer (D) can be used in combination with the other photo-stabilizer. Examples of usable photo-stabilizer 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, 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-[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-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 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-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-based compounds such as octabenzone; 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 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.

[0061]

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 preferred to incorporate, as a particularly preferable component, a phosphorus-based compound as an antioxidant.

[0062]

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-

phenylphosphonite, tetrakis(2,4-di-tert-butyl-5-methylphenyl)-4,4'-biphenylene
diphosphonite, 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.

[0063]

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.

[0064]

Here, the ratio of the phosphorus-based compound is 0.005 to 5% by weight, more
preferably 0.01 to 4% by weight, 0.1 to 2% by weight relative to the organopolysiloxane
(A) in terms of weight ratio.

[0065]

The curable resin composition of the invention contains the organopolysiloxane
(A) as an epoxy resin, the polyhydric carboxylic acid (B) as a curing agent, the
organometallic salt and/or the organometallic complex (C) as an additive and the photo-
stabilizer (D) as essential components and further the acid anhydride as a curing agent and
the antioxidant as an additive as preferable optional components. They may be also used
in combination with other epoxy resin, curing agent and various additives.

[0066]

In the epoxy resin, the organopolysiloxane (A) can be used singly or in
combination with the other epoxy resin. In the case where they are used in combination,
the ratio of the organopolysiloxane (A) in the whole epoxy resin is preferably 60% by
weight or more, particularly preferably 70% by weight or more.

[0067]

As epoxy resins usable in combination with the organopolysiloxane (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, solid or liquid epoxy resins such as glycidylamine-based epoxy resins, alicyclic epoxy resins, glycidyl ester-based epoxy resins, silsesquioxane-based epoxy resins (epoxy resins having a glycidyl group and/or an 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.

[0068]

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, the combined use with alicyclic epoxy resins is preferred. In the case of the alicyclic epoxy resins, compounds having an epoxycyclohexane structure in the skeleton are preferred, and epoxy resins obtained by oxidation reaction of compounds having a cyclohexane structure are particularly preferred.

As these 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 (1080) 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, trimethylolpropane, trimethylolbutane, 2-hydroxymethyl-1,4-butanediol; tetraols such as pentaerythritol and ditrimethylolpropane; and the like. 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.

[0069]

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

Specific examples of these epoxy resins include ERL-4221, UVR-6105, ERL-4299 (all trade names, all manufactured by Dow Chemical), Celloxide 2021P, Epolead GT401, EHPE3150, EHPE3150CE (all trade names, all manufactured by Daicel Chemical Industries, Co., Ltd.), 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.

[0070]

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), reaction products of acid anhydrides with silicone-based alcohols (reaction products of acid anhydrides such as phthalic anhydride, trimellitic anhydride, pyromellitic anhydride, maleic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, methyladadic anhydride, nadic anhydride, hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, butanetetrahydrophthalic anhydride, bicyclo[2,2,1]heptane-2,3-dicarboxylic anhydride, methylbicyclo[2,2,1]heptane-2,3-dicarboxylic anhydride, and cyclohexane-1,2,4-tricarboxylic-1,2-anhydride with silicone-based alcohols such as carbinol-modified silicones, 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 naphthols, 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.

[0071]

In the curable resin composition of the invention, with regard to the ratio of the curing agent containing the organopolysiloxane (A) and the polyhydric carboxylic acid (B) as essential components, it is preferred to use a curing agent containing, as an essential component, the polyhydric carboxylic acid (B) having the number of functional groups of preferably 0.7 to 1.2 equivalents, particularly preferably 0.75 to 1.10 equivalents relative to 1 equivalent of the epoxy group that the organopolysiloxane (A) has. In the case where the number of functional groups is less than 0.7 equivalent 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.

[0072]

In the curable resin composition of the invention, since the organometallic salt and/or the organometallic complex (C) as an essential component directly exhibit an action as a curing catalyst, a curing catalyst may not be added separately but the other curing catalyst may be used in combination. 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, 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 agent to be used is appropriately selected depending on the properties required for the resulting transparent resin composition, such as transparency, the curing rate, and working conditions. The curing catalyst is used in the range of usually 0.001 to 15 parts by weight based on 100 parts by weight of the epoxy resin.

[0073]

To the curable resin composition of the invention, various additives and auxiliary materials to be mentioned below can be added. For example, in the case of providing it as two-part liquids, all of them can be added to any one or both of the organopolysiloxane (A) and the polyhydric carboxylic acid (B) and it is also possible to add them after the organopolysiloxane (A) and the polyhydric carboxylic acid (B) are mixed.

[0074]

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.

[0075]

Furthermore, into the curable resin composition of the invention, a binder resin can be also blended according to needs. 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 curable resin component.

[0076]

To the curable resin composition of the invention, an inorganic filler can be added according to needs. 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.

[0077]

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 particle diameter 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.

[0078]

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 needs. The phosphor has an action of forming a 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.

[0079]

5 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) can be added. Examples of such silica fine powder include Aerosil 50, Aerosil 90, Aerosil 130, Aerosil 200, Aerosil
10 300, 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.

[0080]

15 The curable resin composition of the invention may contain a phenol-based compound as an antioxidant.

[0081]

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-
20 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,
25 triethylene glycol-bis[3-(3-t-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,
30 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]-
35 glycol ester and the like.

[0082]

As the phenol-based compounds, commercially available products can be also

used. The commercially available phenol-based compound is 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.

[0083]

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.

[0084]

In the case where the above phenol-based compound is added, 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.

[0085]

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 curable resin composition of the invention is thoroughly mixed with other 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 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 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.

[0086]

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, a curable resin-cured product containing carbon fiber can be also obtained by RTM method using the liquid composition itself.

[0087]

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 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.

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.

[0088]

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 organopolysiloxane (A), the polyhydric carboxylic acid (B), the organometallic salt and/or the organometallic complex (C) and the photo-stabilizer (D), and, if necessary, an epoxy resin other than the above one, the curing agent, the coupling agent, the antioxidant and additives such as a 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 planetary mixer, a homomixer, a homodisper, a beads mill or the like.

[0089]

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 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.

[0090]

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.

[0091]

As heating conditions, for example, conditions of 80 to 230°C and about 1 minute to 24 hours are preferred. 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.

[0092]

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.

As heating conditions, for example, conditions of 80 to 230°C and about 1 minute to 24 hours are preferred. 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.

[0093]

5 The curable resin composition of the invention can be applied to general uses in which curable 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 cyanate resin compositions for encapsulating materials
10 and substrates, acrylate ester-based resins as curing agents for resists, and additives for other resins and the like.

[0094]

As the adhesives, in addition to adhesives for civil engineering, architecture, automobiles, general office works and medical uses, adhesives for electronic materials may
15 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.

20 [0095]

As the encapsulating agents, there may be mentioned potting, dipping, transfer-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,
25 BGA and CSP (including underfill for reinforcement) and the like.

[0096]

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 passes through
30 the material. More specifically, the following may be mentioned in addition 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
35 liquid display field. Moreover, they may be encapsulating materials, antireflection films, optical correction films, housing materials, protective films of front 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 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, PD (phase change disk), disk substrate materials for optical cards, pick-up lenses, protective films, encapsulating materials, adhesives and the like.

[0097]

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 be taking lenses and finders for video cameras. Furthermore, they may be injection 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, gear parts, corrosion-resistant coatings, switch parts, 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.

[0098]

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)

(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.

The following will describe the invention further in detail with reference to Synthetic Examples and Examples. Incidentally, in the following Synthetic Examples and Examples, "parts" means parts by weight and "%" means % by weight, respectively. Examples

[0099]

Synthetic Example 1

As the first-stage reaction, 114 parts of β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 234 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 18 parts of a 0.5% potassium hydroxide (KOH) methanol solution (0.09 part as the number of part of KOH) were charged into a reaction vessel, and the temperature was elevated with setting the bath temperature at 75°C. After the temperature elevation, a reaction was carried out under reflux for 8 hours.

As the second-stage reaction, after 305 parts of methanol was additionally added, 86.4 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 at 75°C for 8 hours. After the reaction was finished, neutralization was performed with a 5% aqueous sodium dihydrogen phosphate solution and then methanol was recovered by distillation at 80°C. Thereafter, 380 parts of methyl isobutyl ketone (MIBK) was added and washing with water was repeated three times. Then, 303 parts of an organopolysiloxane compound (A-1) having a reactive functional group was obtained by removing the solvent at 100°C under reduced pressure from the organic phase. Epoxy equivalent of the obtained compound was 677 g/eq, weight-average molecular weight was 2200, and the appearance was colorless and transparent.

[0100]

Synthetic Example 2

As the first-stage reaction, 257 parts of β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 505 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 (0.2 part as the number of part of KOH) were charged into a reaction vessel, and the temperature was elevated with setting the bath temperature at 75°C. After the temperature elevation, a reaction was carried out under reflux for 8 hours.

As the second-stage reaction, after 510 parts of methanol was additionally added, 130 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 at 75°C for 8 hours. After the reaction was finished, neutralization was performed with a 5% aqueous sodium dihydrogen phosphate solution and then methanol was recovered by distillation at 80°C. Thereafter, 704 parts of methyl isobutyl ketone (MIBK) was added and washing with water was repeated three times. Then, 663 parts of an organopolysiloxane compound (A-2) having a reactive functional group was obtained by removing the solvent at 100°C under reduced pressure from the organic phase. Epoxy equivalent of the obtained compound was 659 g/eq, weight-average molecular weight was 2370, and the appearance was colorless and transparent.

[0101]

Synthetic Example 3

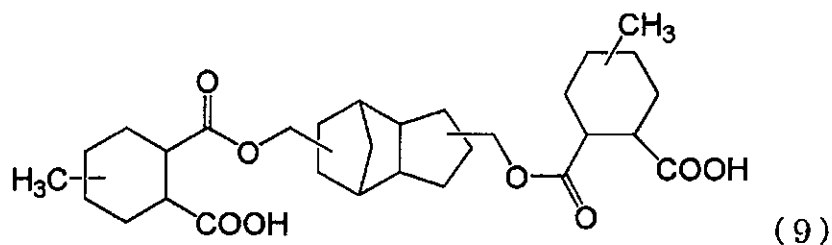
Into a flask fitted with a stirrer, a reflux condenser and a stirring apparatus were added 20 parts of tricyclodecanedimethanol and 100 parts of methylhexahydrophthalic anhydride (RIKACID MH, manufactured by New Japan Chemical Co., Ltd., hereinafter referred to as acid anhydride (H-1)) while performing nitrogen purging. After a reaction

was carried out at 40°C for 3 hours, heating and stirring were performed at 70°C for 1 hour (disappearance (1 area % or less) of tricyclodecanedimethanol was confirmed by GPC) to obtain 120 parts of a curing agent composition (T-1) containing a polyhydric carboxylic acid (B-1) and the acid anhydride (H-1). The obtained one was a colorless liquid resin and, with regard to purity by GPC, the polyhydric carboxylic acid (B-1; the following formula (9)) was 55 area % and methylhexahydrophthalic anhydride was 45 area %. Moreover, functional group equivalent was 201 g/eq.

Formula (9)

[0102]

[Chem. 9]



[0103]

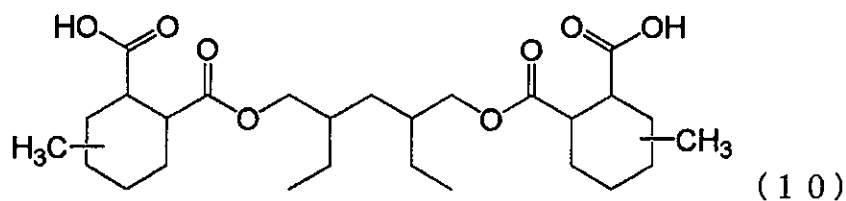
Synthetic Example 4

Into a flask fitted with a stirrer, a reflux condenser and a stirring apparatus were added 20 parts of 2,4-diethylpentanediol and 100 parts of the acid anhydride (H-1) while performing nitrogen purging. After a reaction was carried out at 40°C for 3 hours, heating and stirring were performed at 70°C for 1 hour (disappearance (1 area % or less) of 2,4-diethylpentanediol was confirmed by GPC) to obtain 120 parts of a curing agent composition (T-2) containing a polyhydric carboxylic acid (B-2) and the acid anhydride (H-1). The obtained one was a colorless liquid resin and, with regard to purity by GPC, the polyhydric carboxylic acid (B-2; the following formula (10)) was 50 area % and the acid anhydride (H-1) was 50 area %. Moreover, functional group equivalent was 201 g/eq.

Formula (10)

[0104]

[Chem. 10]



[0105]

Example 1 and Comparative Examples 1, 2

Using the organopolysiloxane compound (A-1) obtained in Synthetic Example 1 as an epoxy resin, a curing agent composition (T-1) obtained in Synthetic Example 3 as a

curing agent (ratio of the organopolysiloxane (A) to the curing agent composition (B) was 1:0.8 in terms of functional group equivalent), a zinc salt (zinc complex) (XC-9206 manufactured by Kusumoto Chemicals, Ltd., hereinafter referred to as C-1) as an organometallic complex, bis(1-undecanoxy-2,2,6,6-tetramethylpiperidin-4-yl) carbonate (ADEKA STAB LA-81 manufactured by Adeka Corporation, hereinafter referred to as D-1), bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate (TINUVIN 770DF manufactured by Ciba Japan, hereinafter referred to as D-2) or bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl) (TINUVIN 123 manufactured by Ciba Japan, hereinafter referred to as D-3) as a photo-stabilizer, and 4,4'-butylidenebis(3-methyl-6-tert-butylphenyl-di-tridecyl phosphite) (ADEKA STAB 260 manufactured by Adeka Corporation, hereinafter referred to as E-1) as a phosphorus-based compound of an antioxidant, they were blended in blending ratios (part(s) by weight) shown in the following Table 1 and defoaming was performed for 20 minutes to obtain curable resin compositions of the invention or for comparison.

[0106]

Example 2 and Comparative Examples 3, 4

Using the organopolysiloxane compound (A-2) obtained in Synthetic Example 2 as an epoxy resin, a curing agent composition (T-2) obtained in Synthetic Example 4 as a curing agent (ratio of the organopolysiloxane (A) to the curing agent composition (B) was 1:0.8 in terms of functional group equivalent), a zinc salt (zinc complex) (18% Octope Zn manufactured by Hope Chemical Co., Ltd., hereinafter referred to as C-2) as an organometallic complex, bis(1-undecanoxy-2,2,6,6-tetramethylpiperidin-4-yl) carbonate (ADEKA STAB LA-81 manufactured by Adeka Corporation, hereinafter referred to as D-1), bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate (TINUVIN 770DF manufactured by Ciba Japan, hereinafter referred to as D-2) or bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl) (TINUVIN 123 manufactured by Ciba Japan, hereinafter referred to as D-3) as a photo-stabilizer, they were blended in blending ratios (part(s) by weight) shown in the following Table 2 and defoaming was performed for 20 minutes to obtain curable resin compositions of the invention or for comparison.

[0107]

(Thermal durability transmittance test)

Each of the obtained curable resin compositions were gently injected into a mold for test piece and the injected material was cured under conditions of 150°C×3 hours after pre-curing at 120°C×1 hour to obtain a cured product for test. For the obtained cured products, thermal durability transmittance test was performed under conditions described below to conduct evaluation (the results are shown in the following Tables 1 and 2).

Measurement conditions

Test conditions: standing in an oven at 180°C for 72 hr

Size of test piece: thickness of 0.8 mm

Evaluation conditions: transmittance at 400 nm was measured on a spectrophotometer and a change ratio thereof was calculated.

[0108]

5 [Table 1]

			Example 1	Comparative Example 1	Comparative Example 2
Composition	Organopolysiloxane	A-1	100	100	100
	Curing agent composition	T-1	24	24	24
	Organometallic salt and/or organometallic complex	C-1	0.5	0.5	0.5
	Photo-stabilizer	D-1	0.25		
		D-2		0.25	
		D-3			0.25
	Antioxidant	E-1	0.25	0.25	0.25
Physical property when cured	Transmittance @ 400 nm	Initial	91.6	91.5	91.6
		After standing at high temperature	77.5	73.3	60.6

[0109]

[Table 2]

			Example 2	Comparative Example 3	Comparative Example 4
Composition	Organopolysiloxane	A-2	100	100	100
	Curing agent composition	T-2	24	24	24
	Organometallic salt and/or organometallic complex	C-2	0.3	0.3	0.3
	Photo-stabilizer	D-1	0.25		
		D-2		0.25	
		D-3			0.25
Physical property when cured	Transmittance @ 400 nm	Initial	91.5	91.4	90.1
		After standing at high temperature	78.7	68.6	64.0

10

[0110]

From Examples 1 to 2 and Comparative Examples 1 to 4, it is understood that the curable resin composition of the invention is excellent in thermal coloration resistance (thermal durability transmittance test).

15

[0111]

(LED lighting test)

Using each of the obtained curable resin compositions, it was filled into a syringe

and injected into a surface-mounted LED package 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. 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. For the lighting test, a lighting test at 60 mA that was twice the specified current 30 mA was performed (acceleration test).

As for measurement, an illuminance retention ratio before and after lighting for 1000 hours was measured using an integrating sphere and an average value of three samples was recorded. Detailed conditions are shown below (results are shown in Table 3).

Detailed conditions for lighting

Emission wavelength: 465 nm

Driving method: constant current method, 60 mA (specified current of the emission element was 30 mA)

Driving environment: 85°C, 85%

[0112]

[Table 3]

			Example 1	Comparative Example 1	Comparative Example 2
Composition	Organopolysiloxane	A-1	100	100	100
	Curing agent composition	T-1	24	24	24
	Organometallic salt and/or organometallic complex	C-1	0.5	0.5	0.5
	Photo-stabilizer	D-1	0.25		
		D-2		0.25	
		D-3			0.25
	Antioxidant	E-1	0.25	0.25	0.25
LED lighting test illuminance retention ratio (%)			82	0	52

[0113]

From Example 1 and Comparative Examples 1 to 2, it is understood that the curable resin composition of the invention is excellent in the illuminance retention ratio.

[0114]

Comparative Examples 5, 6

Using the organopolysiloxane compound (A-1) or (A-2) obtained in Synthetic Example 1 or 2 as an epoxy resin, (T-1) or (T-2) as a curing agent, the zinc salt (zinc complex) (C-1), (C-2), or a quaternary phosphonium salt (Hishicallin PX4MP manufactured by Nippon Chemical Industrial Co., Ltd., hereinafter referred to as (C-3)) as an organometallic complex, (D-1) as a photo-stabilizer, and (E-1) as an antioxidant, they were blended in blending ratios (part(s) by weight) shown in the following Table 4 and

defoaming was performed for 20 minutes to obtain curable resin compositions of the invention or for comparison.

[0115]

(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 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. 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 the following Table 4).

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 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 resistance.

The observation was performed by taking out the package after 10 hours.

Evaluation was as follows: a package exhibiting no color change was evaluated as ○, and a package blackened was evaluated as ×.

[0116]

[Table 4]

			Example 1	Example 2	Comparative Example 5	Comparative Example 6
Composition	Organopolysiloxane	A-1	100		100	
		A-2		100		100
	Curing agent composition	T-1	24		24	
		T-2		24		24
	Organometallic salt and/or organometallic complex	C-1	0.5			
		C-2		0.3		
		C-3			0.5	0.3
	Photo-stabilizer	D-1	0.25	0.25	0.25	0.25
	Antioxidant	E-1	0.25		0.25	
Sulfuration test			○	○	×	×

[0117]

From Examples 1 to 2 and Comparative Examples 5 to 6, the curable resin composition of the invention is excellent in corrosive gas resistance.

[0118]

5 Comparative Examples 7, 8

Using the organopolysiloxane compound (A-1) or (A-2) obtained in Synthetic Example 1 or 2 as an epoxy resin, (T-1) or (T-2) as a curing agent, the zinc salt (zinc complex) (C-1) or (C-2) as an organometallic complex, (D-1) as a photo-stabilizer, and (E-1) as an antioxidant, they were blended in blending ratios (part(s) by weight) shown in the following Table 5 and defoaming was performed for 20 minutes to obtain curable resin compositions of the invention or for comparison.

[0119]

(Light durability transmittance test)

Each of the obtained curable resin compositions was gently injected into a mold for test piece and the injected material was cured under conditions of 150°C×3 hours after pre-curing at 120°C×1 hour to obtain a cured product for test. For the obtained cured products, light durability transmittance test was performed under the conditions described below to conduct evaluation (the results are shown in the following Table 5).

Measurement conditions

20 Tester: Super UV Tester (Iwasaki Electric Co., Ltd.)

Test conditions: 60 mW/cm².nm, 200 hr

Size of test piece: thickness of 0.8 mm

Evaluation conditions: transmittance at 400 nm was measured on a spectrophotometer and a change ratio thereof was calculated.

25 [0120]

[Table 5]

			Example 1	Example 2	Comparative Example 7	Comparative Example 8
Composition	Organopolysiloxane	A-1	100		100	
		A-2		100		100
	Curing agent composition	T-1	24		24	
		T-2		24		24
	Organometallic salt and/or organometallic complex	C-1	0.5		0.5	
		C-2		0.3		0.3
	Photo-stabilizer	D-1	0.25	0.25		
Physical property when cured	Antioxidant		E-1	0.25	0.25	
	Transmittance @ 400 nm	Initial	91.7	91.5	91.8	91.7
		After irradiation	90.3	90.9	86.5	85.4

[0121]

From Examples 1 to 2 and Comparative Examples 7 to 8, it is understood that the curable resin composition of the invention is excellent in light coloration resistance

[0122]

5 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. 2010-133745 filed on June 11, 2010, and the entire contents of which 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 organopolysiloxane (A);

5 a polyhydric carboxylic acid (B);

an organometallic salt and/or an organometallic complex (C); and

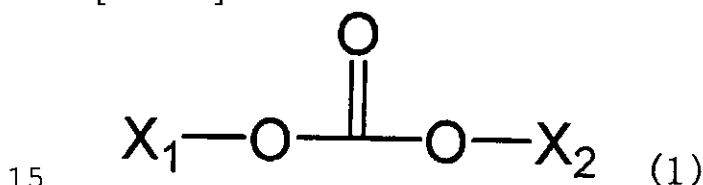
a photo-stabilizer (D), provided that the organopolysiloxane (A), the polyhydric carboxylic acid (B) and the photo-stabilizer (D) satisfy the following requirements:

10 Organopolysiloxane (A): an organopolysiloxane having at least a glycidyl group and/or an epoxycyclohexyl group in a molecule thereof;

Polyhydric carboxylic acid (B): one having at least two carboxyl groups and having an aliphatic hydrocarbon group as a main skeleton; and

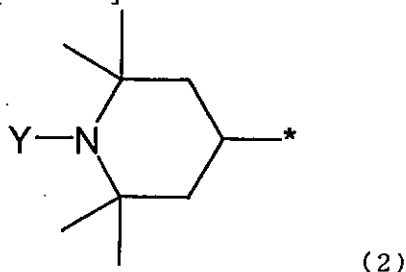
Photo-stabilizer (D): a compound represented by a structural formula (1):

[Chem. 1]



wherein X_1 and X_2 are a hydrogen atom, an alkyl group having 1 to 50 carbon atoms, an aralkyl group, an aryl group, an aryl group having an alkyl group having 1 to 20 carbon atoms, an alkoxy group or a structural formula (2), and at least one of X_1 and X_2 is the structural formula (2):

20 [Chem. 2]



wherein in formula (2), the structural formula (2) is bonded to the oxygen atom of the structural formula (1) at the sign *; and

25 Y represents a hydrogen atom, an alkyl group having 1 to 50 carbon atoms, an aryl group or an alkoxy group.

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

a compound of the structural formula (1) in which Y in the structural formula (2) is an alkoxy group having 1 to 20 carbon atoms.

30

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

wherein the organometallic salt and/or the organometallic complex (C) is a zinc salt and/or a zinc complex.

5 [Claim 4] The curable resin composition according to any one of claims 1 to 3,
wherein X_1 and X_2 in the structural formula (1) are both the structural formulae (2)
and Y in the structural formula (2) is $-OC_{11}H_{23}$.

[Claim 5] The curable resin composition according to any one of claims 1 to 4,
comprising:

10 an acid anhydride.

[Claim 6] The curable resin composition according to any one of claims 1 to 5,
wherein the polyhydric carboxylic acid (B) is a compound obtained by reacting a
bifunctional to hexafunctional polyhydric alcohol having 5 or more carbon atoms with a
15 saturated aliphatic cyclic acid anhydride.

[Claim 7] The curable resin composition according to any one of claims 1 to 6,
comprising:

20 an antioxidant.

[Claim 8] A cured product, which is obtained by curing the curable resin
composition according to any one of claims 1 to 7.