DESCRIPTION

Title of Invention: CURABLE RESIN COMPOSITION AND CURED PRODUCT THEREOF

Technical Field

[0001]

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

Background Art

[0002]

Such resins are exemplified by Patent Document 1. Hitherto, as an encapsulating material for optical semiconductor elements of LED products and the like, epoxy resin compositions for example those resins disclosed in Patent Document 2 and Patent Document 3, 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 epoxy resins as representatives, which are excellent in balance of thermal resistance, transparency, and mechanical strength.

However, as a result of the advancement of shortening of emission wavelength of LED products (480 nm 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.

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 thereof as LED encapsulating materials have been performed (Patent Documents 4 and 5).

[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 6).

Related Art

Patent Document

[0004]

Patent Document 1: US 4365052

Patent Document 2: US 2003/0071366

Patent Document 3: JP 2004292706

Patent Document 4: JP-A-9-213997

Patent Document 5: Japanese Patent No. 3618238

Patent Document 6: WO/2005-100445

Patent Document 7: JP S6377929

Patent Document 8: JP S59182583

Patent Document 9: JP H05226700

Patent Document 10: JP 2006290998

Patent Document 11: JP-A-2007-324256

Patent Document 12: JP-A-2000-174347

Summary of the Invention

Problems that the Invention is to Solve

[0005]

Epoxy resins have good transparency and are used for sealing luminescent elements (for example Patent Document 7) and possess good corrosion resistance (for example Patent Document 8). Nevertheless, they such systems tend to suffer durability problems. 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 resins (Patent Document 6 and Patent Document 9).

In general, it is known that resins to which the siloxane skeleton has been introduced are more stable against heat and light than epoxy resins. For example better yellowing resistance has been found with certain cyclosiloxane derivatives as described in Patent Document 10.

Therefore, in the case of application thereof to an encapsulating material for LED products, from the viewpoint of coloration on an LED chip, it is said that the resins are more excellent in durability than epoxy resins. However, the resins to which the siloxane skeleton has been introduced are inferior in gas permeation resistance to epoxy resins. Therefore, in the case where a silicone resin or a silicone-modified epoxy resin is used as an LED encapsulating material, there arises a problem that deterioration and coloration of interior constituent members occur, although the coloration on the LED chip is not a

problem. Particularly, in the case where the resin is used in living environment, various compounds are floating therein and the permeation of such compounds into the inside triggers off the occurrence of a trouble. For example, in the case where the resin is used in illumination uses, a silver component (silver plating is performed for increasing reflectance) plated on a metal lead frame that is a constituent member in an LED package is discolored or blackened by the permeation of gases in the environment through the encapsulating material of LED and finally, performance as an LED product is lowered (Patent Documents 11 and 12).

[0006]

In order to solve the problem of the gas permeation resistance, Patent Documents 11 and 12 use a method of coverage with a gas permeation-resistant protecting agent, a method of covering a metal part with an inorganic material, or the like. However, there is a problem that steps increase and productivity becomes worse.

[0007]

The present invention is devised in consideration of the above background art and an object thereof is to provide a curable resin composition that affords a cured product capable of satisfying various physical properties to be required for electric and electronic material uses, particularly as an optical semiconductor encapsulating material, especially to provide a curable resin composition that affords a cured product excellent in resistance against corrosive gases and the like in the environment and optical properties such as thermal coloration resistance and light extraction efficiency.

Means for Solving the Problems

[0008]

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

Namely, the present invention relates to:

(1)

A curable resin composition comprising an organopolysiloxane (A) and a zinc salt and/or zinc complex (C) as essential components, wherein the organopolysiloxane (A) satisfies the following requirement,

Organopolysiloxane (A):

an epoxy resin having at least a glycidyl group and/or an epoxycyclohexyl group in the molecule thereof.

(2)

The curable resin composition according to (1) described above, wherein the zinc salt and/or zinc complex (C) is one selected from the group consisting of zinc salts of one or more acids selected from phosphoric esters and phosphoric acid and zinc complexes having said acid and zinc salt as ligands.

(3)

The curable resin composition according to (1) described above, wherein the zinc salt and/or zinc complex (C) is at least one selected from the group consisting of zinc salts of carboxylic acids having 1 to 30 carbon atoms and zinc complexes having said acid and zinc salt as ligands.

(4)

The curable resin composition according to any one of (1) to (3) described above, which comprises a polycarboxylic acid (B) having at least two carboxyl groups and having an aliphatic hydrocarbon group as the main skeleton.

(5)

The curable resin composition according to (4) described above, wherein the polycarboxylic 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.

(6)

The curable resin composition according to any one of (1) to (5) described above, which comprises an acid anhydride.

(7)

The curable resin composition according to any one of (1) to (6) described above, which comprises a hindered amine photo-stabilizer and/or a phosphorus-containing antioxidant.

(8)

A cured product obtained by curing the curable resin composition according to any one of (1) to (7) described above.

Effects of the Invention

[0009]

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

Embodiments for Carrying Out the Invention

[0010]

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

The epoxy resin composition of the present invention comprises an organopolysiloxane (A) and a zinc salt and/or zinc complex (C) as essential components.

The organopolysiloxane (A) is characterized in that it is an epoxy resin 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 silsesquioxane-type organopolysiloxanes having a three-dimensionally spreading reticular structure, described in JP-A-2004-256609, JP-A-2004-346144, WO2004/072150, JP-A-2006-8747, WO2006/003990, JP-A-2006-104248, WO2007/135909, JP-A-2004-10849, JP-A-2004-359933, WO2005/100445, JP-A-2008-174640, and the like.

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

body having a silicone segment and the aforementioned silsesquioxane structure obtained by the sol-gel reaction in one molecule is particularly preferred (hereinafter referred to as block-type siloxane compound (A1)).

[0011]

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

[0012]

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

[0013]

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

$$XSi(OR_2)_3 \quad (1)$$

wherein X represents an organic group having a glycidyl group and/or an epoxycyclohexyl group and R_2 groups to be plurally present 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.

[0014]

X in the general formula (1) is not particularly limited as long as it is an organic group having a glycidyl group and/or an epoxycyclohexyl group. Examples thereof include glycidoxy-substituted alkyl groups having 1 to 4 carbon atoms such as β-glycidoxyethyl, γ-glycidoxypropyl and γ-glycidoxybutyl, a glycidyl group, alkyl groups having 1 to 5 carbon atoms substituted with a cycloalkyl group having an oxirane group and having 5 to 8 carbon atoms, 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, alkyl groups having 1 to 3 carbon atoms substituted

with a cycloalkyl group having an epoxy group and having 5 to 8 carbon atoms, 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.

Here, in the case where an alkoxy silane compound in which X is a glycidyl group and an alkoxy silane compound in which X is an epoxycyclohexyl group are used in combination, it is preferred to use the alkoxy silane compound in which X is an epoxycyclohexyl group in an amount of 80% or more based on the total amount of the alkoxy silane compounds (a).

[0015]

R^2 groups to be plurally present in the general formula (1) 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, a methyl group or an ethyl group is preferred and particularly, a methyl group is preferred.

[0016]

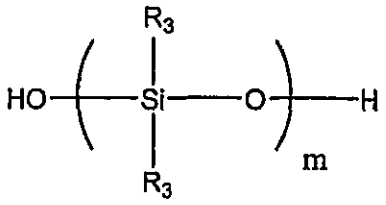
Preferable specific examples of the alkoxysilane (a) include β-glycidoxyethyltrimethoxysilane, β-glycidoxyethyltriethoxysilane, γ-glycidoxypropyltrimethoxysilane, γ-glycidoxypropyltriethoxysilane, β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, β-(3,4-epoxycyclohexyl)ethyltriethoxysilane, and the like.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

[0017]

The silicone oil (b) is a linear silicone oil having a silanol group at the end, which has a structure represented by the following formula (2):

[0018]

[Chem 1]



(2)

[0019]

wherein R_3 groups to be plurally present represent each 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, and may be the same or different from each other; and m represents the number of repeating units.

In the general formula (2), R_3 groups to be plurally present represent each 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, and may be the same or different from each other.

As the alkyl group having 1 to 10 carbon atoms, there may be mentioned 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 amino 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 and heat resistance, a methyl group, an ethyl group, an n-propyl group and a cyclohexyl group are preferred.

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

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

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

[0020]

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

[0021]

With regard to the weight-average molecular weight (Mw) 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 chromatograph (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 linear 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, the compound has a severe layer separated structure, so that transparency becomes worse for use in optical materials and thus it becomes difficult to use it. In the present invention, as the molecular weight of the silicone oil (b), using GPC, the weight-average molecular weight (Mw) can be 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 refractometer detector)

[0022]

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

[0023]

As preferable specific examples as the silicone oil (b), the following product names can be mentioned. Examples thereof include PRX-413 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, TSR-160, YR-3370, YF-3800, XF-3905, YF-3057, YF-3807, YF-3802, YF-3897, YF-3804, and XF-3905 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, PRX-413, BY16-873, X-21-5841, KF-9701, XC96-723, YF-3800, YF-3804, 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.

[0024]

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

$$R_4(OR_5)_3 \quad (3)$$

wherein R_4 represents a methyl group or a phenyl group; R_5 groups to be plurally present 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.

[0025]

R_5 groups to be plurally present in the general formula (3) 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_5 is preferably a methyl group or an ethyl group.

[0026]

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

[0027]

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

[0028]

In the case where the alkoxysilane (c) is used, 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 (c). When the content of (c) is more than 70% by mol, crosslinking density of the cured product decreases and mechanical strength lowers, so that the case is not preferred.

[0029]

As the reaction ratio of the alkoxysilane (a), the silicone oil (b) and the alkoxysilane (c), the reaction is preferably carried out with the equivalent value of the alkoxy group in the alkoxysilane (a) (and the alkoxysilane (c) used according to need)

being 1.5 to 200, preferably 2 to 200, particularly preferably 2 to 100 relative to 1 equivalent of the silanol group in the silicone oil (b).

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

[0030]

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

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

Production step (i): a step of performing dealcoholization condensation of the silanol-ended silicone oil (b) with the alkoxysilane (a) having an alkoxy group (and the alkoxysilane (c) used according to need),

Production step (ii): a step of performing hydrolytic condensation between the alkoxy groups of the alkoxysilane (a) (and the alkoxysilane (c) used according to need) with adding water.

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

[0031]

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

<Production process (a)>

The process includes:

first, as the production step (i), a step of obtaining an alkoxysilane-modified compound (d) is performed by modifying the silicon oil end with an alkoxysilane through a dealcoholization condensation reaction of the silicone oil (b) having a silanol group at the end 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 (ii), a step of carrying out the hydrolytic condensation reaction between the alkoxy groups by 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 (i) is performed to produce the block-type siloxane compound (A1).

<Production process (b)>

The process includes:

first, as the production step (i), a step of obtaining a silsesquioxane (e) is performed by carrying out the hydrolytic condensation reaction between the alkoxy groups

by adding water to the alkoxysilane (a) (and the alkoxysilane (c) used according to need), and

subsequently, as the production step (ii), a step of carrying out the dealcoholization condensation reaction of the alkoxy group remaining in the silsesquioxane structure with a silanol group through the reaction of the silicone oil (b) with the silsesquioxane (e) is performed to produce the block-type siloxane compound (A1).

<Production process (c)>

The process includes:

first, as the production step (i), the silicone oil end is modified with an alkoxysilane by the dealcoholization condensation reaction of the silicone oil (b) having a silanol group at the end 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 subsequently, as the production step (ii), the block-type siloxane compound (A1) is produced by carrying out the hydrolytic condensation reaction between the alkoxy groups of the remaining alkoxysilane (a) (and the alkoxysilane (c) used according to need) and the alkoxysilane-modified compound (d).

[0032]

In the present 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.

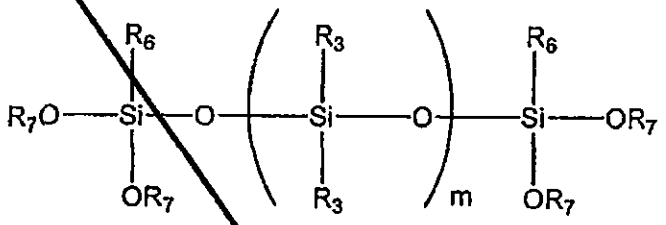
The following will more specifically describe the production process (c).

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 (i) is performed after the production step (ii), there is a high possibility that the silsesquioxane oligomer having an alkoxy group formed in the production step (ii) is not soluble with the silicone oil (b), the dealcoholization condensation polymerization does not proceed in the following production step (i), and thus the silicone oil remains. On the other hand, when a process of performing the production step (ii) in one pot after the production step (i) is used as in the case of the production process (c), the problem that the compounds are not soluble each other and the reaction does not proceed can be avoided since the compatibility of the silicone oil (b) with the alkoxysilane (a) and the alkoxysilane (c) is relatively high. Furthermore, since unreacted low-molecular-weight alkoxysilane is present a large amount relative to the silanol group, the process is also preferred from the viewpoint of reactivity. In the case of performing the steps in one pot, first in the production step (i), 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 end of the silicone oil with an alkoxysilyl, thereby obtaining the alkoxysilane-modified compound (d). Since water is not added in

the production step (i), 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 (4):

[0033]

[Chem 2]



(4)

[0034]

wherein R_3 and m have the same meanings as described above and R_6 groups to be plurally present each independently represent the above X or the above R_4, and R_7 represents the above R_2 in the case where R_6 bonded to the silicon the same as the silicon to which $-OR_7$ is bonded is the above X or represents the above R_5 in the case where R_6 bonded to the silicon the same as the silicon to which $-OR_7$ is bonded is the above R_4.

[0035]

In the production step (i), when the alkoxy group is reacted in a ratio of less than 1 equivalent relative to 1 equivalent of the silanol group, the alkoxy group is not present at the time when the production step (i) is finished, so that the production step (ii) cannot be started. Moreover, when the reaction is carried out using 1 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 production step (i) 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 regulating the reaction, a ratio of 2 equivalents or more is preferred and a ratio of 3 equivalents or more is more preferred.

[0036]

After the production step (i) is finished, the second-stage reaction of performing the hydrolytic condensation between the alkoxy groups (production step (ii)) is performed with adding water without further treatment.

In the production step (ii), reactions (I) to (III) shown below take place.

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

(II) A condensation reaction between the alkoxy groups of the alkoxysilane-modified compound (d) obtained in the production step (i) and the alkoxysilane (a) (and the alkoxysilane (c) used according to need).

(III) A condensation reaction between the alkoxy groups of the alkoxysilane-modified compound (d) obtained in the production step (i) and a partially condensed compound of the alkoxysilane (a) (and the alkoxysilane (c) used according to need) obtained in (I).

In the production step (ii), the above reactions occur in a multiple manner and the formation of the silsesquioxane segment and further the condensation thereof with the linear silicone segment derived from the silicone oil are simultaneously take place.

[0037]

The production of the block-type siloxane compound (A1) can be performed with no catalyst but, since the reaction proceeds only slowly with no catalyst, it is preferred to perform the production in the presence of a catalyst from the viewpoint of shortening the reaction time. As usable catalyst, any compounds can be used as long as they are compounds showing acidity or basicity. Examples of acidic catalysts include inorganic acids such as hydrochloric acid, sulfuric acid and nitric acid and organic acids such as formic acid, acetic acid and oxalic acid. Moreover, as examples of basic catalysts, use can be made of inorganic bases including alkali metal hydroxides such as sodium hydroxide, potassium hydroxide, lithium hydroxide and cesium hydroxide, alkali metal carbonate salts such as sodium carbonate, potassium carbonate, sodium hydrogen carbonate and potassium hydrogen carbonate, and the like; organic bases such as ammonia, triethylamine, diethylenetriamine, n-butylamine, dimethylaminoethanol, triethanolamine and tetramethylammonium hydroxide. Of these, particularly in view of easy removal of the catalyst from the product, inorganic bases are preferred and particularly, sodium hydroxide and potassium hydroxide are preferred. The amount of the catalyst to be added is usually 0.001 to 7.5% by weight, preferably 0.01 to 5% by weight based on the total weight of the alkoxysilane (a) (and the alkoxysilane (c) 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 alkoxysilane (a) (and the alkoxysilane (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.

[0038]

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

[0039]

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; alkanes such as hexane, cyclohexane, toluene and xylene; and the like.

[0040]

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 easy.

[0041]

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 products manufactured by Toshin Chemicals Co., Ltd.; and GALLEON EARTH, MIZUKAACE as products manufactured by Mizusawa Industrial Chemicals, Ltd.; and the like. Examples of the active carbon include CL-H, Y-10S, Y-10SF as products manufactured by Ajinomoto Fine-Techno Co., Ltd.; S, Y, FC, DP, SA1000, K, A, KA, M, CW130BR, CW130AR, GM130A as products manufactured by Futamura Chemical Co., Ltd.; and the like. Examples of the zeolite include Molecular Sieves 3A, 4A, 5A, 13X as products 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 products manufactured by Kyowa Chemical Industry Co., Ltd.; Amberlyst 15JWET, 15DRY, 16WET, 31WET, A21, Amberlite IRA400JCI, IRA403BLCI, IRA404JCI as products manufactured by Rohm and Haas Company; Dowex 66, HCR-S, HCR-W2, MAC-3 as products 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.

[0042]

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.

[0043]

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.

[0044]

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

[0045]

The appearance of the block-type siloxane compound (A1) thus obtained is usually a colorless and transparent liquid having fluidity at 25°C. Moreover, the molecular weight thereof is preferably 800 to 20,000, more preferably 1,000 to 10,000, and particularly preferably 1,500 to 6,000 as weight-average molecular weight measured by GPC. When the weight-average molecular weight is less than 800, there is a concern that heat resistance decreases. When it is more than 20,000, viscosity increases and thus workability is adversely affected. The molecular weight can be controlled by the equivalent ratio of the alkoxysilane (a) (and the alkoxysilane (c) used according to need) to the silicone oil (b), the molecular weight of the silicone oil (b), the amount of water added at the reaction, the reaction time, and the reaction temperature.

The above 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 refractometer detector)

[0046]

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

[0047]

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

[0048]

The ratio of the silicon atom bonded to three oxygen atoms, which is derived from the silsesquioxane in the block-type siloxane compound (A1), to the whole silicon atoms is preferably 5 to 50% by mol, more preferably 8 to 30% by mol, and particularly preferably 10 to 20% by mol. When the ratio of the silicon atom bonded to three oxygen atoms, which is derived from the silsesquioxane, is less than 5% by mol, the cured product tends to become too soft as a characteristic feature of a linear 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. Thus, the cases are not preferred.

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

[0049]

The curable resin composition of the present invention contains the polycarboxylic acid (B) as a preferable component.

The polycarboxylic 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 present invention, the polycarboxylic acid includes not only a polycarboxylic acid 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 polycarboxylic acid composition. In the present invention, they are collectively referred to as polycarboxylic acid.

[0050]

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

The difunctional to hexafunctional polyhydric alcohol is not particularly limited as long as it 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.

[0051]

Particularly preferable polyhydric 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, polyhydric 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.

[0052]

As the acid 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, cyclohexane-1,3,4-tricarboxylic-3,4-anhydride and the like are preferred. Of these, methylhexahydrophthalic anhydride and cyclohexane-1,3,4-tricarboxylic-3,4-anhydride are preferred.

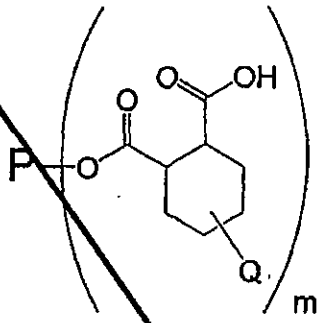
The conditions for the addition reaction are not particularly designated. As one specific reaction condition, there may be mentioned a method of reacting the acid anhydride with the polyhydric alcohol at 40 to 150°C under conditions of no catalyst and no solvent, heating them, and, after completion of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

[0053]

As the thus obtained polycarboxylic acid, particularly preferred is a compound represented by the following formula (5):

[0054]

[Chem 3]



(5)

[0055]

wherein Q to be plurally 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 derived from the aforementioned polyhydric alcohol; m is the number of functional groups of the polyhydric alcohol (number of the alcohol groups) and is preferably an integer of 2 to 6.

[0056]

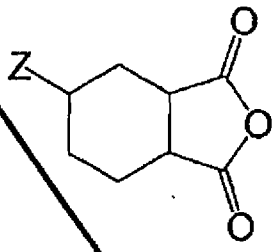
The curable resin composition of the present invention preferably contains an acid anhydride. As the acid anhydride, specifically, there may be mentioned acid anhydrides such as phthalic anhydride, trimellitic anhydride, pyromellitic anhydride, maleic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic 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-1,3,4-tricarboxylic-3,4-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-1,3,4-tricarboxylic-3,4-anhydride are preferred.

Furthermore, of the acid anhydrides, hexahydrophthalic anhydride, methylhexahydrophthalic anhydride and cyclohexane-1,3,4-tricarboxylic-3,4-anhydride, which are represented by the following formula (6):

[0057]

[Chem 4]



(6)

[0058]

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-1,3,4-tricarboxylic-3,4-anhydride are preferred.

[0059]

In the case where the curable resin composition of the present invention contains the acid anhydride, the amount thereof to be used is determined by the ratio thereof to the polycarboxylic acid (B) and is preferably in the range of the following equation.

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

wherein W1 represents part(s) by weight of the polycarboxylic acid (B) blended and W2 represents part(s) by weight of the acid anhydride.

In the above, the range of W1/(W1+W2) is more 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 of the polycarboxylic acid (B) becomes a solid or nearly a solid or crystals at ordinary temperature, so that no problem arises.

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

[0060]

The curable resin composition of the present invention contains the zinc salt and/or zinc complex (C) as an essential component. The zinc salt and/or zinc complex (C) contribute as a curing accelerator of the epoxy resin and the curing agent in the present invention.

The zinc salt and/or zinc complex are not particularly limited as long as it is a salt and/or a complex containing a zinc ion as a central element but it preferably has at lest one acid selected from carboxylic acids having an alkyl groups having 1 to 30 carbon atoms, phosphate esters and phosphoric acid as a counter ion and/or a ligand. In the present invention, particularly, zinc carboxylate compounds and zinc phosphate esters are preferred and particularly in view of compatibility, the zinc carboxylate compounds are preferred.

As the alkyl groups in the above, there may be mentioned a methyl group, an isopropyl group, a butyl group, a 2-ethylhexyl group, an octyl group, an isodecyl group, an isostearyl group, a decanyl group, a cetyl group, an undecylene group and the like.

[0061]

As the zinc carboxylate compounds, at least one selected from the group consisting of zinc salts of carboxylic acids having 1 to 30 carbon atoms and zinc complexes having carboxylic acids having 1 to 30 carbon atoms and zinc salts as ligands can be used. In the zinc carboxylate compounds, the carboxylic acids having 1 to 30 carbon atoms are preferably those of an alkyl group having a linear branched structure or an alkyl group having a functional group such as olefin, further preferably those having 3 to 30 carbon atoms. Of these, particularly, those having 5 to 20 carbon atoms are preferred. They are preferred in view of compatibility. In the case where the number of carbon atoms is too large (the case where the number of carbon atoms exceeds 30) or where the compounds do not have any branched structure or structure of a functional group such as olefin or the like, the compatibility with resins is bad, so that the case is not preferred.

Specifically, there may be mentioned zinc 2-ethylhexylate, zinc isostearate, zinc undecylenate and the like.

[0062]

As the phosphate ester compounds, at least one selected from the group consisting of zinc salts of phosphate esters and zinc complexes having phosphate esters and the zinc salts as ligands can be used. Moreover, the phosphate ester compound may also contain phosphoric acid derived from the phosphate ester as a counter ion and/or a ligand.

As especially preferred phosphate ester compounds in the present invention, zinc salts and/or zinc complexes of phosphate esters (monoalkyl ester compounds, dialkyl ester compounds, trialkyl ester compounds or mixtures thereof) are preferred, and a plurality of phosphate ester compounds may be incorporated. Specifically, in the molar ratios (using purity on gas chromatography as a substitute but there is a difference in sensitivity since trimethylsilylation is necessary) of the monoalkyl ester compound, dialkyl ester compound and trialkyl ester compound of the phosphate esters incorporated in the phosphate ester

compound, the amount of the monoester compound present is preferably 50 area % or more at the stage where a trimethylsilylation treatment is finished.

Such zinc salts and/or zinc complexes of zinc phosphate esters are obtained, for example, by reacting phosphate esters with, for example, zinc carbonate, zinc hydroxide or the like (patent Document EP699708).

As the phosphate esters, 2-ethylhexyl phosphate, stearyl phosphate and the like are preferred.

[0063]

As details of such zinc salts and/or zinc complexes of phosphate esters, the ratio of the phosphorus atom to the zinc atom (P/Zn) is preferably 1.2 to 2.3 and more preferably 1.3 to 2.0. Particularly preferred is 1.4 to 1.9. Namely, in the particularly preferred embodiment, the phosphate ester (or phosphoric acid derived from the phosphate ester) is 2.0 mol or less relative to 1 mol of the zinc ion, and preferred are those having not a simple ion structure but a structure where some molecules precipitate through ionic bonds (or coordinate bonds). The zinc salts and/or zinc complexes can be also obtained, for example, by the procedure described in JP-T-2003-51495.

[0064]

As such compounds, as commercially available products, there may be mentioned Zn-St, Zn-St 602, Zn-St NZ, ZS-3, ZS-6, ZS-8, 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.), as zinc carboxylates, and LBT-2000B (manufactured by SC Organic Chemical Co., Ltd.), XC-9206 (manufactured by King Industries Inc.), as zinc phosphate esters and/or zinc phosphate.

[0065]

In the curable resin composition of the present invention, with regard to the ratio of the organopolysiloxane (A) to the zinc salt and/or the zinc complex (C), the zinc salt and/or the zinc complex (C) is in a ratio of 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.

[0066]

In the case where the curable resin composition of the present invention is used as an optical material, particularly an optical semiconductor encapsulating agent, as a particularly preferable component, it is preferred to incorporate a hindered amine compound as a photo-stabilizer and a phosphorus-based compound as an antioxidant. In the present invention, particularly, it is preferred to incorporate a hindered amine compound and, if necessary, it is preferred to incorporate a phosphorus-based compound.

Examples of the above amine compound include hindered amine-based compounds such as tetrakis(1,2,2,6,6-pentamethyl-4-piperidyl)=1,2,3,4-butanetetracarboxylate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)=1,2,3,4-butanetetracarboxylate, a mixed esterified product of 1,2,3,4-butanetetracarboxylic acid with 1,2,2,6,6-pentamethyl-4-piperidinol and 3,9-bis(2-hydroxy-1,1-dimethylethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane, decanedioic acid bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate, bis(1-undecanoxy-2,2,6,6-tetramethylpiperidin-4-yl) carbonate, 2,2,6,6-tetramethyl-4-piperidyl methacrylate, bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate, 4-benzoyloxy-2,2,6,6-tetramethylpiperidine, 1-[2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]ethyl]-4-[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-benzenedicarboxyamide and N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl).

[0067]

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

Examples thereof include TINUVIN 765, TINUVIN 770DF, TINUVIN 144, TINUVIN 123, TINUVIN 622LD, TINUVIN 152, CHIMASSORB 944 as products manufactured by Ciba Specialty Chemicals; LA-52, LA-57, LA-62, LA-63P, LA-77Y, LA-81, LA-82, LA-87 as products manufactured by Adeka Corporation; and the like.

[0068]

In the curable resin composition of the present invention, the amount of the photostabilizer to be used is 0.005 to 5% by weight, more preferably 0.01 to 4% by weight, 0.1 to 2% by weight based on the organopolysiloxane (A) in terms of weight ratio.

[0069]

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(2,4-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 diphosphonite, tetrakis(2,4-di-tert-butylphenyl)-4,3'-biphenylene diphosphonite, tetrakis(2,4-di-tert-butylphenyl)-3,3'-biphenylene diphosphonite, tetrakis(2,6-di-tert-butylphenyl)-4,4'-biphenylene diphosphonite, tetrakis(2,6-di-tert-butylphenyl)-4,3'-biphenylene diphosphonite, tetrakis(2,6-di-tert-butylphenyl)-3,3'-biphenylene diphosphonite, bis(2,4-di-tert-butylphenyl)-4-phenyl-phenylphosphonite, bis(2,4-di-tert-butylphenyl)-3-phenyl-phenylphosphonite, bis(2,6-di-n-butylphenyl)-3-phenyl-phenylphosphonite, bis(2,6-di-tert-butylphenyl)-4-phenyl-phenylphosphonite, 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.

[0070]

As the above phosphorus-based compounds, commercially available products can be also used.

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.

[0071]

In the curable resin composition of the present invention, the amount of the phosphorus-based compound to be used is 0.005 to 5% by weight, more preferably 0.01 to 4% by weight, 0.1 to 2% by weight based on the organopolysiloxane (A) in terms of weight ratio.

[0072]

The curable resin composition of the present invention contains the organopolysiloxane (A) as an epoxy resin and the zinc salt and/or the zinc complex (C) as a curing accelerator as essential components and further the polycarboxylic acid (B) and the acid anhydride as curing agents and the hindered amine-based photo-stabilizer and the phosphorus-containing antioxidant as additives as preferable optional components. They may be also used in combination with other epoxy resin, curing agent, and various additives.

[0073]

In the epoxy resin component, in the case where the organopolysiloxane (A) is used in combination with the other epoxy resin, 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.

[0074]

As epoxy resins usable in combination with the organopolysiloxane (A), there may be mentioned solid or liquid epoxy resins including 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 bisphenol A, bisphenol S, thiodiphenol, fluorene bisphenol, terpene diphenol, 4,4'-biphenol, 2,2'-biphenol, 3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'-diol, hydroquinone, resorcin, naphthalenediol, tris-(4-hydroxyphenyl)methane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, polycondensates of phenols (phenol, alkyl-substituted phenols, naphthol, alkyl-substituted naphthaols, dihydroxybenzene, dihydroxynaphthalene, etc.) with formaldehyde, acetaldehyde, bezaldehyde, p-hydroxybenzaldehyde, o-hydroxybenzaldehyde, p-hydroxyacetophenone, o-hydroxyacetophenone, dicyclopentadiene, furfural, 4,4'-bis(chloromethyl)-1,1'-biphenyl, 4,4'-bis(methoxymethyl)-1,1'-biphenyl, 1,4-bis(chloromethyl)benzene, 1,4-bis(methoxymethyl)benzene or the like and modified compounds thereof, halogenated bisphenols such as tetrabromobisphenol A, glycidyl etherified compounds derived from alcohols, alicyclic epoxy resins, glycidylamine-based epoxy resins, glycidyl ester-based epoxy resins 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.

[0075]

Particularly, it is mainly purposed that the curable resin composition of the present invention is used in optical uses. In the case where the composition is used in optical uses, the combined use of alicyclic epoxy resins is preferred. In the case of the alicyclic epoxy resins, compounds having an epoxycyclohexnae structure in the skeleton are preferred, and epoxy resins obtained by oxidation reaction of compounds having a cyclohexene structure are particularly preferred.

As these 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, trimethylolethane, trimethylolpropane, trimethylolbutane, 2-hydroxymethyl-1,4-butanediol; tetraols such as pentaerythritol; 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.

Further, as the other epoxy resins, there may be mentioned epoxy resins obtained by epoxidation of acetal compounds through the oxidation reaction, the acetal compounds being obtained by the acetalization reaction of cyclohexenealdehyde derivatives with alcohol compounds.

[0076]

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.

[0077]

The curing agent component in the present invention is not particularly limited but it is desirable to use the polycarboxylic acid compound (B) singly or in combination with

the acid anhydride and also 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 polycarboxylic 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 other 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, 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-1,3,4-tricarboxylic-3,4-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 naphthaols, dihydroxybenzene, dihydroxynaphthalene, etc.) with formaldehyde, acetaldehyde, bezaldehyde, p-hydroxybenzaldehyde, o-hydroxybenzaldehyde, p-hydroxyacetophenone, o-hydroxyacetophenone, dicyclopentadiene, furfural, 4,4'-bis(chloromethyl)-1,1'-biphenyl, 4,4'-bis(methoxymethyl)-1,1'-biphenyl, 1,4'-bis(chloromethyl)benzene, 1,4'-bis(methoxymethyl)benzene or the like and modified compounds thereof, halogenated bisphenols such as tetrabromobisphenol A, condensates of terpenes with phenols), others (imidazole, trifluoroborane-amine complexes, guanidine derivatives, etc.) and the like but they are not limited thereto. They may be used singly or two or more thereof may be used.

[0078]

In the curable resin composition of the present invention, the ratio of the curing agent component to the epoxy resin is preferably 0.7 to 1.2 equivalents and particularly preferably 0.75 to 1.1 equivalents relative to 1 equivalent of the epoxy group of the epoxy resin component.

In the case where the ratio 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.

[0079]

In the curable resin composition of the present invention, since the zinc salt and/or the zinc complex (C) as an essential component exhibit an action as a curing catalyst as they are, 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 these imidazoles with polycarboxylic 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-diazabicyclo[5.4.0]undecene-7 and salts thereof with tetraphenylborate, phenol novolak and the like, salts with the above polycarboxylic acids or phosphinic acids, ammonium salts such as tetrabutylammonium bromide, cetyltrimethylammonium bromide and trioctylmethylammonium bromide, phosphines and phosphonium compounds such as tripheylphosphine, tri(toluyl)phosphine, 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, working conditions. The curing accelerator is used in the range of usually 0.001 to 15 parts by weight based on 100 parts by weight of the epoxy resin.

[0080]

To the curable resin composition of the present invention, the following various additives and auxiliary materials can be added.

In the curable resin composition of the present 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-phosphaphenathrene-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 resins = 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 materials are adversely affected.

[0081]

Furthermore, into the curable resin composition of the present 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 material 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 epoxy resin component and the curing agent component.

[0082]

To the curable resin composition of the present 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 or beads obtained by forming them into spherical shape and the like but the filler is not limited thereto. They 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 present invention. Furthermore, to the curable resin composition of the present 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.

[0083]

In the case where the curable resin composition of the present invention is used as an optical material, particularly an optical semiconductor encapsulating agent, it is possible to reinforce the mechanical strength or 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.

[0084]

In the case where the curable resin composition of the present 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 yellow light resulting from wavelength conversion. 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 $YAlO_3$:Ce, $Y_3Al_5O_{12}$:Ce, $Y_4Al_2O_9$:Ce, Y_2O_2S:Eu, $Sr_5(PO_4)_3Cl$:Eu, (SrEu)O·Al_2O_3 and the like are exemplified. As the particle diameter of such phosphors, those having a known particle diameter 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 organic components such as the organopolysiloxane (A).

[0085]

In the case where the curable resin composition of the present 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 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.

[0086]

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

Specific examples of the phenol compound include 2,6-di-tert-butyl-4-methylphenol, n-octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, tetrakis[methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]methane, 2,4-di-tert-butyl-6-methylphenol, 1,6-hexanediol-bis-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-isocyanurate, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, pentaerythrityl-tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 3,9-bis-[2-[3-(3-tert-butyl-4-hydroxy-5-methylphenyl)-propionyloxy}-1,1-dimethylethyl]-2,4,8,10-tetraoxaspiro[5,5]undecane, triethylene glycol-bis[3-(3-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, 4,4'-thiobis(3-methyl-6-tert-butylphenol), 4,4'-butylidenebis(3-methyl-6-tert-butylphenol), 2-tert-butyl-4-methylphenol, 2,4-di-tert-butylphenol, 2,4-di-tert-pentylphenol, 4,4'-thiobis(3-methyl-6-tert-butylphenol), 4,4'-butylidenebis(3-methyl-6-tert-butylphenol), bis[3,3-bis-(4'-hydroxy-3'-tert-butylphenyl)butanoic acid]-glycol ester, 2,4-di-tert-butylphenol, 2,4-di-tert-pentylphenol, 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate, bis[3,3-bis-(4'-hydroxy-3'-tert-butylphenyl)butanoic acid]-glycol ester and the like.

[0087]

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

Examples thereof include IRGANOX 1010, IRGANOX 1035, IRGANOX 1076, IRGANOX 1135, IRGANOX 245, IRGANOX 259, IRGANOX 295, IRGANOX 3114 IRGANOX 1098, IRGANOX 1520L as products 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 products manufactured by Adeka Corporation, Sumilizer GA-80, Sumilizer MDP-S, Sumilizer BBM-S, Sumilizer GM, Sumilizer GS(F), Sumilizer GP as products manufactured by Sumitomo Chemical Co., Ltd., and the like.

[0088]

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 products manufactured by Ciba Specialty Chemicals, and the like.

[0089]

In the case where the above phenol-based compound is added, the amount thereof to be blended is not particularly limited and it can be added in an amount of 0.005 to 5.0% by weight in the curable resin composition of the present invention.

[0090]

The curable resin composition of the present invention is obtained by mixing individual components homogeneously. The curable resin composition of the present 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 can be obtained by thoroughly mixing the epoxy resin component, the curing agent component, and the zinc salt and/or zinc complex (C) using an extruder, a kneader, a roll, a planetary mixer, or the like according to need until a homogeneous state is achieved. In the case where the obtained curable resin composition is liquid, the cured product can be formed by potting or casting the composition, impregnating a substrate therewith, or injecting the curable resin composition into a mold, and then curing it by heating or, in the case where the composition is solid, the cured product can be formed by injecting it into a mold after melting or molding it using a transfer molding machine or the like and further curing it by heating.

Incidentally, the other curing accelerator, amine compound, phosphorus-containing compound, phenol compound, binder resin, inorganic filler and the like which are optional components may be added and mixed in the above mixing step. 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 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.

[0091]

Moreover, a cured product of the curable resin composition of the present invention can be formed by dissolving the curable resin composition of the present invention in a solvent such as toluene, xylene, acetone, methyl ethyl ketone, methyl isobutyl ketone, dimethylformamide, dimethylacetamide or N-methylpyrrolidone to transform 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 at this time 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 present invention and the solvent. Moreover, an epoxy resin cured product containing carbon fiber can be also obtained by RTM (Resin Transfer Molding) method using the liquid composition itself.

[0092]

Furthermore, the curable resin composition of the present invention can be also used as a film-type composition for encapsulation. As a method of obtaining such a film-type resin composition, there may be mentioned a method of transforming the curable resin composition of the present invention into the varnish of the curable resin composition as mentioned above, applying it on a release film, removing the solvent under heating, and then performing transformation into B-stage. Thereby, the film-type composition for encapsulation can be obtained as 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.

[0093]

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

In the case where the curable resin composition of the present invention is used as an encapsulating material or die-bonding material for optical semiconductors such as a highly luminous white LED, the curable resin composition is prepared by thoroughly mixing the epoxy resin, the curing agent, the coupling agent, the antioxidant, and additives such as the photo-stabilizer. As a mixing method, they are mixed at normal 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. The obtained curable resin composition can be used as the encapsulating material or both of the die-bonding material and the encapsulating material.

[0094]

The optical semiconductor element such as the 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 flame, 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. On the other hand, the periphery of such a semiconductor chip is encapsulated with an encapsulating material such as an epoxy resin. The encapsulating material is used for protecting the semiconductor chip from heat and moisture and playing a role of lens function.

The curable resin composition of the present 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 present invention as both of the die-bonding material and the encapsulating material.

[0095]

As a method of adhering the semiconductor chip to the substrate using the curable resin composition of the present invention, there may be mentioned a method of placing the semiconductor chip on the curable resin composition of the present invention and performing heat curing after the curable resin composition is applied on the substrate by a dispenser, potting, or screen printing. By such a method, the semiconductor chip can be adhered to the substrate. For heating, a method of hot-air circulation, infrared ray, high frequency wave or the like can be employed.

[0096]

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.

[0097]

As a molding method of the encapsulating material, an injection method where 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 where 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.

[0098]

Uses of the curable resin composition of the present invention are not limited to the above uses and can be applied to general uses in which thermosetting resins such as

epoxy resins are used. For example, there may be mentioned adhesives, paints, coating agents, molding materials (including sheets, films, FRP and the like), insulating materials (including printed boards, electric wire coverings, etc.), encapsulating agents, and also additives for other resins such as cyanate resin compositions for encapsulating materials and substrates and acrylate ester-based resins as curing agents for resists, and the like.

[0099]

As the adhesives, in addition to adhesives for civil engineering, architecture, automobiles, general office works and medical uses, adhesives for electronic materials may be mentioned. Of these, as the adhesives for electronic materials, there may be mentioned interlayer adhesives of multilayer substrates such as build-up substrates, die-bonding agents, semiconductor adhesives such as underfill, underfill for BGA reinforcement, anisotropic conductive films (ACF), adhesives for mounting such as anisotropic conductive pastes (ACP) and the like.

[0100]

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

[0101]

The cured product obtained in the present 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 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 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.

[0102]

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 circuit, they may be resist materials for microlithography for LSI or ultra LSI materials. In the automobile/transport aircraft fields, lamp reflectors for automobiles, baring 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 photoreflective 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.

[0103]

As the other uses of the optical material, there may be mentioned general uses where curable resin compositions are used. For example, there may be mentioned adhesives, paints, coating agents, molding materials (including sheets, films, FRP and the like), insulating materials (including printed boards, electric wire coverings, etc.), encapsulating agents, and also additives for other resins and the like.

Examples

[0104]

The following will describe the present invention further in detail with reference to Synthetic Examples and Examples. Incidentally, the present invention is not limited to these Synthetic Examples and Examples. Moreover, in the following Synthetic Examples and Examples, "parts" means parts by weight and "%" means % by weight, respectively. Incidentally, individual physical property values in Examples were measured by the following methods.

(1) Molecular weight: weight-average molecular weight as a value in terms of polystyrene measured under the following conditions was calculated 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 refractometer 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.

[0105]

Synthetic Example 1

As the production step (i), 106 parts of β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 234 parts of a silanol-ended 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 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 production step (ii), after 305 parts of methanol was 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, 300 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 718 g/eq, weight-average molecular weight was 2200, and the appearance was colorless and transparent.

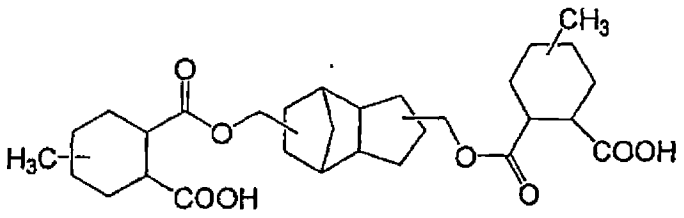
[0106]

Synthetic Example 2

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 polycarboxylic acid (B-1) and the acid anhydride (H-1). The obtained curing agent composition (T-1) was a colorless liquid resin and, with regard to purity by GPC, the polycarboxylic acid (B-1; the following formula (7)) was 55 area % and the acid anhydride (H-1) was 45 area %. Moreover, functional group equivalent was 201 g/eq. Furthermore, viscosity at 25°C was 18,900 mPa.s (E-type viscometer).

[0107]

[Chem 5]



(7)

[0108]

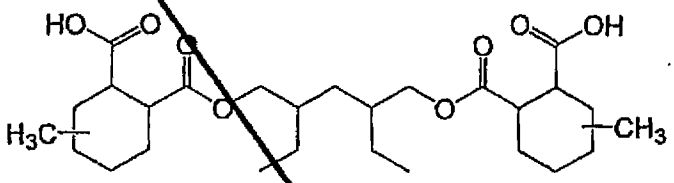
Synthetic Example 3

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 polycarboxylic acid (B-2) and the acid anhydride (H-1). The obtained curing agent composition (T-2) was a colorless liquid resin and, with regard to purity by GPC, the polycarboxylic acid (B-2; the following formula (8)) was 50 area % and the acid anhydride (H-1) was 50 area %. Moreover, functional group equivalent was 201 g/eq. Furthermore, viscosity at 25°C was 16,200 mPa.s (E-type viscometer).

[0109]

[Chem 6]



(8)

[0110]

Synthetic Example 4

As the production step (i), 296 parts of β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 595 parts of a silanol-ended 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 production step (ii), after 510 parts of methanol was 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, 697 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 598 g/eq, weight-average molecular weight was 2370, and the appearance was colorless and transparent.

[0111]

Synthetic Example 5

Into a flask fitted with a stirrer, a reflux condenser and a stirring apparatus were added 12 parts of tricyclodecanedimethanol, 18 parts of 2,4-diethyl-1,5-pentanediol and 155 parts of methylhexahydrophthalic anhydride (RIKACID MH, manufactured by New Japan Chemical Co., Ltd., corresponding to the acid anhydride (H-1)) and 15 parts of 1,3,4-cyclohexanetricarboxylic-3,4-anhydride (H-TMAn, manufactured by Mitsubishi Gas Chemical Co., Inc., hereinafter referred to as acid anhydride (H-2)) 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 the raw material alcohol was confirmed by GPC) to obtain 200 parts of a curing agent composition (T-3) containing polycarboxylic acids (B-1) (B-2) and the acid anhydrides (H-1) (H-2). The obtained curing agent composition (T-3) was a colorless liquid resin and, with regard to purity by GPC, the polycarboxylic acids (B-1) (B-2) was 52 area % and the acid anhydrides (H-1) (H-2) was 48 area %. Moreover, functional group equivalent was 190 g/eq. Furthermore, viscosity at 25°C was 15,500 mPa.s (E-type viscometer).

[0112]

Synthetic Example 6

As the production step (i), 44 parts of β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 158 parts of a silanol-ended 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 11.2 parts of a 0.5% potassium hydroxide (KOH) methanol solution (0.056 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 production step (ii), after 157 parts of methanol was added, 19.3 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, 177 parts of methyl isobutyl ketone (MIBK) was added and washing with water was repeated three times. Then, 178 parts of an organopolysiloxane compound (A-3) 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 1020 g/eq, weight-average molecular weight was 2100, and the appearance was colorless and transparent.

[0113]

Examples 1, 2, 3, 4 and Comparative Examples 1, 2, 3

Using the organopolysiloxane compound (A-1) obtained in Synthetic Example 1 as an epoxy resin, a curing agent composition (T-1), (T-2) obtained in Synthetic Examples 2, 3 as a curing agent (ratio of the organopolysiloxane (A) to the curing agent composition (T-1), (T-2) was 1:1 in terms of functional group equivalent), a propylene glycol solution of a zinc complex of phosphoric acid 2-ethylhexane ester (phosphoric acid:monoester compound:diester compound:triester compound = 3.5:68.2:26.5:1.8, however, since a trimethylsilylation treatment was performed, sensitivity was different and thus the weight ratio is not accurate; hereinafter referred to as zinc salt and/or zinc complex (C-1)) (phosphorus:zinc = 1.7:1 measured by ICP emission spectrochemical analysis, in accordance with JIS K 0166) (produced in accordance with JP-T-2003-51495, hereinafter referred to as (C-1)) as a zinc salt and/or zinc complex, a quaternary phosphonium salt (Hishicallin PX4MP manufactured by Nippon Chemical Industrial Co., Ltd., hereinafter referred to as catalyst (I-1)) as a curing accelerator, bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate (TINUVIN 770DF manufactured by Ciba Japan, hereinafter referred to as (L-1)) as an additive, and 4,4'-butylidenebis(3-methyl-6-tert-butylphenyl-di-tridecyl phosphite) (ADEKA STAB 260 manufactured by Adeka Corporation, hereinafter referred to as (M-1)) as a phosphorus-based compound, they were blended in blending ratios shown in the following Table 1 and defoaming was performed for 20 minutes to obtain curable resin compositions of the present invention or for comparison.

[0114]

The obtained curable resin compositions were gently injected into a mold for test piece and the injected materials were cured under conditions of 150°C×1 hour after pre-curing at 120°C×3 hours to obtain various cured products for test. For the obtained cured products, with regard to tests for hardness and thermal durability transmittance test, evaluation was performed under conditions described below. The results are also shown in the following Table 1.

[0115]

(Hardness)

Shore A

It was measured in accordance with JIS K 7215 "Test Method for Durometer Hardness of Plastics".

[0116]

(Thermal durability transmittance test)

Conditions for heat resistance test: a test piece was allowed to stand in an oven at 150°C for 96 hours

Size of test piece: thickness of 1 mm

Evaluation conditions: transmittance at 400 nm was measured by a spectrophotometer and a change ratio (retention ratio) thereof was calculated.

[0117]

(LED lighting test)

After each of the curable resin compositions obtained in Examples and Comparative Example was subjected to vacuum defoaming for 20 minutes, it was filled into a syringe and injected into a surface-mounted LED on which an emission element having an emission wavelength of 465 nm had been mounted, using a precise injection apparatus. Thereafter, an LED for lighting test was obtained by curing under prescribed curing conditions (at 110°C for 2 hours and further at 150°C for 3 hours). For the lighting test, a lighting test at 60 mA that was twice the specified current (constant current drive, specified current of 30 mA) was performed and initial illuminance was measured.

[0118]

[Table 1]

	Item			Example 1	Example 2	Comparative Example 1
Composition	Epoxy resin	Organopolysiloxane	A-1	10.0	10.0	10.0
	Curing agent	Curing agent composition	T-1	2.8	2.8	2.8
			T-2			
	Curing accelerator	Zinc salt (zinc complex)	C-1	0.01	0.03	
		Quaternary phosphonium salt	I-1			0.01
	Additive	Photo-stabilizer	L-1	0.03	0.03	0.03
		Phosphorus-based compound	M-1	0.03	0.03	0.03
Physical property when cured	Hardness test	Shore A		97	97	98
	Thermal durability transmittance test	Retention ratio (400 nm)	%	98.3%	98.6%	97.7%
	LED lighting test	Initial illuminance	mW	9577	9597	8183

	Item			Example 3	Comparative Example 2	
Composition	Epoxy resin	Organopolysiloxane	A-1	10.0	10.0	
	Curing agent	Curing agent composition	T-1			
			T-2	2.8	2.8	
	Curing accelerator	Zinc salt (zinc complex)	C-1	0.03		
		Quaternary phosphonium salt	I-1		0.03	
	Additive	Photo-stabilizer	L-1			
		Phosphorus-based compound	M-1			
Physical property when cured	Hardness test	Shore A		90	90	
	Thermal durability transmittance test	Retention ratio (400 nm)	%	95.1%	82.1%	
	LED lighting test	Initial illuminance	mW	7737	4993	

	Item			Example 4	Comparative Example 3	
Composition	Epoxy resin	Organopolysiloxane	A-1	10.0	10.0	
	Curing agent	Curing agent composition	T-1			
			T-2	2.8	2.8	
	Curing accelerator	Zinc salt (zinc complex)	C-1	0.01		
		Quaternary phosphonium salt	I-1		0.01	
	Additive	Photo-stabilizer	L-1	0.05	0.05	
		Phosphorus-based compound	M-1	0.05	0.05	
Physical property when cured	Hardness test	Shore A		93	92	
	Thermal durability transmittance test	Retention ratio (400 nm)	%	97.5%	95.3%	
	LED lighting test	Initial illuminance	mW	9037	9030	

[0119]

Examples 5, 6 and Comparative Example 4

Using the organopolysiloxane compound (A-2) obtained in Synthetic Example 2 as an epoxy resin, a curing agent composition (T-1) obtained in Synthetic Example 2 as a curing agent (ratio of the organopolysiloxane (A) to the curing agent composition (T-1) was 1:0.8 in terms of functional group equivalent), the zinc salt and/or zinc complex (C-1) as a curing accelerator, the catalyst (I-1), and the additives (L-1) (M-1), they were blended in blending ratios shown in the following Table 2 and defoaming was performed for 20 minutes to obtain curable resin compositions of the present invention or for comparison.

[0120]

The obtained curable resin compositions were gently injected into a mold for test piece and the injected materials were cured under conditions of 150°C×1 hour after pre-curing at 120°C×3 hours to obtain various cured products for test. For the obtained cured products, with regard to the following tests for heat resistance property test, hardness and thermal durability transmittance test, evaluation was performed under conditions described below. The results are also shown in the following Table 2.

[0121]

(Heat resistance property test)

Measurement conditions

Dynamic viscoelasticity measuring instrument: DMA-2980 manufactured by TA-instruments

Measurement temperature range: -30°C to 280°C

Temperature elevation rate: 2°C/minute

Test piece size: an article cut into a size of 5 mm×50 mm was used (thickness of about 800 μm).

Analytical conditions

Tg: a peak point of Tan-δ at DMA measurement was taken as Tg.

30°C elastic modulus: elastic modulus at 30°C was measured.

[0122]

(Hardness test)

Shore A

It was measured in accordance with JIS K 7215 "Test Method for Durometer Hardness of Plastics".

[0123]

(Transmittance test)

Size of test piece: thickness of 1 mm

Evaluation conditions: transmittance at 400 nm was measured by a spectrophotometer.

[0124]

Furthermore, 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 (inner diameter of 4.4 mm, outer wall height of 1.25 mm) on which a chip having a central emission wavelength of 465 nm had been mounted, using a precise injection apparatus. The injected article 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 (corrosive gas permeation test). The results are also shown in Table 2.

[0125]

(Corrosive gas permeation test)

Measurement Conditions

Corrosive gas: a 20% by weight 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 bottle and, under a tightly closed situation with capping the wide-mouthed 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 every hour and the LED package requiring longer color change time is judged to be more excellent in resistance to corrosive gas. The observation was performed by taking out the package after 1 hour, after 2 hours, after 3 hours, and after 4 hours. Evaluation was as follows: a package exhibiting no discoloration was evaluated as O, a package colored into light brown to brown was evaluated as ×, and a package completely blackened was evaluated as ××.

[0126]

[Table 2]

	Item			Example 5	Example 6	Comparative Example 4
Composition	Epoxy resin	Organopolysiloxane	A-2	10.0	10.0	10.0
	Curing agent	Curing agent composition	T-1	2.7	2.7	2.7
	Curing accelerator	Zinc salt (zinc complex)	C-1	0.01	0.10	
		Quaternary phosphonium salt	I-1			0.01
	Additive	Photo-stabilizer	L-1	0.02	0.02	0.02
		Phosphorus-based compound	M-1	0.02	0.02	0.02
Physical property when cured	Heat resistance property test	Tg	°C	55.3	61.7	55.3
		30° elastic modulus	MPa	269	469	280
	Hardness test	Shore A		94	95	96
	Transmittance measurement	Initial transmittance	%	91.6	91.8	91.7
	Corrosive gas permeation test	Exposure time	1h	O	O	O
			2h	O	O	O
			3h	O	O	×
			4h	O	O	×

[0127]

From Examples 1 to 4 and Comparative Examples 1 to 3, the curable resin composition of the present invention is excellent in heat coloring resistance (heat-resistant transmittance test) and affords a curable product having a good light extraction efficiency (LED lighting test), so that it is realized that the composition is excellent in optical properties.

From Examples 5 and 6 and Comparative Example 4, it becomes obvious that the curable resin composition of the present invention affords a curable product excellent in gas permeation resistance (corrosive gas permeation test) and thus the composition is useful in the fields where the optical property is necessary, like a semiconductor chip and LED which are susceptible to external environment.

[0128]

Examples 7 to 12 and Comparative Examples 5 to 9

Using each of the organopolysiloxane compounds (A-1), (A-2), (A-3) obtained in Synthetic Examples 1, 4, 6 as an epoxy resin, a curing agent composition (T-1) or (T-2) obtained in Synthetic Example 2 or 3 as a curing agent (ratio of the organopolysiloxane (A) to the curing agent composition (T-1) or (T-2) was 1:0.8 in terms of functional group equivalent), zinc 2-ethylhexanoate (C-2), zinc undecylenate (C-3), zinc 2-ethylhexanoate (containing an imidazole compound, XK-614 manufactured by King Industry, hereinafter referred to as (C-4)) as a zinc salt and/or zinc complex, a quaternary phosphonium salt (Hishicallin PX-4ET manufactured by Nippon Chemical Industrial Co., Ltd., hereinafter

referred to as catalyst (I-2)) as a curing accelerator, an imidazole compound (2E4MZ manufactured by Shikoku Chemicals Corporation, hereinafter referred to as catalyst (I-3)), and bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate (TINUVIN 770DF manufactured by Ciba Japan, hereinafter referred to as (L-1)) as an additive, they were blended in blending ratios shown in the following Tables 3 and 4 and defoaming was performed for 20 minutes to obtain curable resin compositions of the present invention or for comparison.

[0129]

The obtained curable resin compositions were gently injected into a mold for test piece and the injected materials were cured under conditions of 140°C×5 hours after pre-curing at 110°C×2 hours to obtain various cured products for test. For the obtained cured products, corrosive gas permeation test was performed (the test method and the like are the same as described above except that observation is performed after 1 hour, after 2 hours, after 3 hours, after 6 hours and after 10 hours). The results are also shown in the following Tables 3 and 4.

[0130]

	C-4			0.07			
aternary phosphonium salt	I-2					0.07	
Imidazole compound	I-3						0.07
Photo-stabilizer	L-1	0.01	0.01	0.01	0.01	0.01	0.01
Exposure time	1h	O	O	O	O	O	O
	2h	O	O	O	O	O	O
	3h	O	O	O	O	O	O
	6h	O	O	O	×	×	×
	10h	O	O	O	××	××	××

nc complex)	C-3	0.06		0.06		
	C-4					
aternary phosphonium salt	I-2				0.06	0.06
Imidazole compound	I-3					
Photo-stabilizer	L-1					
Exposure time	1h	O	O	O	O	O
	2h	O	O	O	O	×
	3h	O	O	O	O	×
	6h	O	O	O	×	××
	10h	O	O	×	××	××

[0132]

Examples 13, 14

Using the organopolysiloxane compound (A-3) obtained in Synthetic Example 6 as an epoxy resin, a curing agent composition (T-3) obtained in Synthetic Example 5 as a curing agent (ratio of the organopolysiloxane (A) to the curing agent composition (T-3) was 1:0.8 in terms of functional group equivalent), the zinc salt and/or zinc complex (C-1), (C-2) as a curing accelerator, a hindered amine compound (LA-81 manufactured by Adeka Corporation, hereinafter referred to as (L-2)) as an additive and a phosphorus compound (ADEKA 260 manufactured by Adeka Corporation, hereinafter referred to as (L-3)), they were blended in blending ratios shown in the following Table 5 and defoaming was performed for 20 minutes to obtain curable resin compositions of the present invention or for comparison.

[0133]

(Corrosive gas permeation test)

The obtained curable resin compositions were gently injected into a mold for test piece and the injected materials were cured under conditions of 150°C×3 hours after pre-curing at 120°C×1 hour to obtain various cured products for test. For the obtained cured products, corrosive gas permeation test was performed (the test method and the like are the same as described above). The results are also shown in the following Table 5.

[0134]

(LED lighting test)

After each of the obtained curable resin compositions was filled into a syringe and injected into a surface-mounted LED (SMD type 5 mmϕ, specified current of 20 mA) on which an emission element having an emission wavelength of 465 nm had been mounted, using a precise injection apparatus. Thereafter, an LED for lighting test was obtained by curing under prescribed curing conditions (at 120°C for 1 hour and further at 150°C for 3 hours). For the lighting test, a lighting test at 230 mA that was more than 20 mA as the specified current to a large extent was performed. Detailed conditions were shown below. As a measurement item, illuminance before and after lighting for 40 hours was measured using an integrating sphere and a retention ratio of illuminance of the LED for test was calculated. The results are shown in Table 5.

Detailed conditions for lighting

Emission wavelength: 465 nm

Driving method: constant current method, 230 mA (specified current of the emission element was 20 mA), three LEDs were lighted simultaneously in series

Driving environment: lighting in a wet-heat chamber at 25°C, 65%

Evaluation: Illuminance and illuminance retention ratios after 20 hours and 40 hours were measured, respectively.

[0135]

[Table 5]

	Item			Example 13	Example 14
Composition	Epoxy resin	Organopolysiloxane	A-3	10.2	10.2
	Curing agent	Curing agent composition	T-3	1.5	1.5
	Zinc salt (zinc complex)		C-1	0.05	
			C-2		0.03
	Additive	Photo-stabilizer	L-2	0.02	0.02
		Phosphorus compound	L-3	0.02	0.02
Physical property when cured	Corrosive gas permeation test	Exposure time	10h	O	O
	Lighting test (230 mA)	Illuminance (μW) / illuminance retention ratio (%)	0h(ref)	9900	9900
			20h	9950	10100
				100%	102%
			40h	8400	10200
				85%	103%

[0136]

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. 2009-271469 filed on November 30, 2009, and the contents are incorporated herein by reference. Also, all the references cited herein are incorporated as a whole.

Claims

[Claim 1]

A curable resin composition comprising an organopolysiloxane (A) and a zinc salt and/or zinc complex (C) as essential components, wherein the organopolysiloxane (A) satisfies the following requirement,

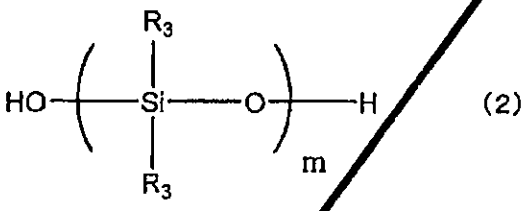
Organopolysiloxane (A):

ablock-type siloxane compound that is produced by reacting an alkoxysilane compound (a) represented by the following general formula (1) and a silicone oil (b) represented by the following general formula (2), and thereafter performing hydrolytic condensation betweenalkoxy groups of the alkoxysilane compound (a), or

ablock-type siloxane compound that is produced by reacting an alkoxysilane compound (a) represented by the following general formula (1), a silicone oil (b) represented by the following general formula (2) and an alkoxysilane compound (c) represented by the following general formula (3), and thereafter performing hydrolytic condensation betweenalkoxy groups of the alkoxysilane compound (a) and the alkoxysilane compound (c):

$XSi(OR_2)_3$ (1)

wherein X represents an organic group having a glycidyl group and/or an epoxycyclohexyl group and R_2groups to be plurally present 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;



(2)

wherein R_3groups to be plurally present represent each 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, and may be the same or different from each other; and m represents the number of repeating units; and

$R_4Si(OR_5)_3$ (3)

wherein R_4 represents a methyl group or a phenyl group; R_5groups to be plurally present 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.

[Claim 2]

The curable resin composition according to claim 1, which further comprises apolycarboxylic acid (B).

[Claim 3]

The curable resin composition according to claim 1 or 2, wherein the zinc salt and/or zinc complex (C) is one selected from the group consisting of zinc salts of one or more acids selected from phosphoric esters and phosphoric acid and zinc complexes having said acid and zinc salt as ligands.

[Claim 4]

The curable resin composition according to claim 1 or 2, wherein the zinc salt and/or zinc complex (C) is at least one selected from the group consisting of zinc salts of carboxylic acids having 1 to 30 carbon atoms and zinc complexes having said acid and zinc salt as ligands.

[Claim 5]

The curable resin composition according to any one of claims 2 to 4, wherein the polycarboxylic acid (B) has at least two carboxyl groups and has an aliphatic hydrocarbon group as the main skeleton.

[Claim 6]

The curable resin composition according to claim 5, wherein the polycarboxylic acid (B) is a compound obtained by reacting a bifunctional to hexafunctionalpolyhydric alcohol having 5 or more carbon atoms with a saturated aliphatic cyclic acid anhydride.

[Claim 7]

The curable resin composition according to any one of claims 1 to 6, which comprises an acid anhydride.

[Claim 8]

The curable resin composition according to any one of claims 1 to 7, which comprises a hindered amine photo-stabilizer and/or a phosphorus-containing antioxidant.

[Claim 9]

A cured product obtained by curing the curable resin composition according to any one of claims 1 to 8.

DESCRIPTION

Title of Invention: CURABLE RESIN COMPOSITION AND CURED PRODUCT THEREOF

Technical Field

[0001]

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

Background Art

[0002]

Such resins are exemplified by Patent Document 1. Hitherto, as an encapsulating material for optical semiconductor elements of LED products, epoxy resin compositions for example those resins disclosed in Patent Document 2 and Patent Document 3, 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 epoxy resins as representatives, which are excellent in balance of thermal resistance, transparency, and mechanical strength.

However, as a result of the advancement of shortening of emission wavelength of LED products (480 nm 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.

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 thereof as LED encapsulating materials have been performed (Patent Documents 4 and 5).

[0003]

Moreover, since brightness has been further heightened for illumination, backlight for TV sets 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 6).

Related Art

Patent Document

[0004]

Patent Document 1: US 4365052

Patent Document 2: US 2003/0071366

Patent Document 3: JP 2004292706

Patent Document 4: JP-A-9-213997

Patent Document 5: Japanese Patent No. 3618238

Patent Document 6: WO/2005-100445

Patent Document 7: JP S6377929

Patent Document 8: JP S59182583

Patent Document 9: JP H05226700

Patent Document 10: JP 2006290998

Patent Document 11: JP-A-2007-324256

Patent Document 12: JP-A-2000-174347

Summary of the Invention

Problems that the Invention is to Solve

[0005]

Epoxy resins have good transparency and are used for sealing luminescent elements (for example Patent Document 7) and possess good corrosion resistance (for example Patent Document 8). Nevertheless, they such systems tend to suffer durability problems. 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 and silicone-modified epoxy resins as representatives, are used as encapsulating resins (Patent Document 6 and Patent Document 9).

In general, it is known that resins to which the siloxane skeleton has been introduced are more stable against heat and light than epoxy resins. For example better yellowing resistance has been found with certain cyclosiloxane derivatives as described in Patent Document 10.

Therefore, in the case of application thereof to an encapsulating material for LED products, from the viewpoint of coloration on an LED chip, it is said that the resins are more excellent in durability than epoxy resins. However, the resins to which the siloxane skeleton has been introduced are inferior in gas permeation resistance to epoxy resins. Therefore, in the case where a silicone resin or a silicone-modified epoxy resin is used as an LED encapsulating material, there arises a problem that deterioration and coloration of interior constituent members occur, although the coloration on the LED chip is not a

problem. Particularly, in the case where the resin is used in living environment, various compounds are floating therein and the permeation of such compounds into the inside triggers off the occurrence of a trouble. For example, in the case where the resin is used in illumination uses, a silver component (silver plating is performed for increasing reflectance) plated on a metal lead frame that is a constituent member in an LED package is discolored or blackened by the permeation of gases in the environment through the encapsulating material of LED and finally, performance as an LED product is lowered (Patent Documents 11 and 12).

[0006]

In order to solve the problem of the gas permeation resistance, Patent Documents 11 and 12 use a method of coverage with a gas permeation-resistant protecting agent, a method of covering a metal part with an inorganic material. However, there is a problem that steps increase and productivity becomes worse.

[0007]

The present invention is devised in consideration of the above background art and an object thereof is to provide a curable resin composition that affords a cured product capable of satisfying various physical properties to be required for electric and electronic material uses, particularly as an optical semiconductor encapsulating material, especially to provide a curable resin composition that affords a cured product excellent in resistance against corrosive gases in the environment and optical properties such as thermal coloration resistance and light extraction efficiency.

Means for Solving the Problems

[0008]

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

Namely, the present invention relates to:

(1)

A curable resin composition comprising an organopolysiloxane (A) and a zinc salt and/or zinc complex (C) as essential components, wherein the organopolysiloxane (A) satisfies the following requirement,

Organopolysiloxane (A):

an epoxy resin having at least a glycidyl group and/or an epoxycyclohexyl group in the molecule thereof.

(2)

The curable resin composition according to (1) described above, wherein the zinc salt and/or zinc complex (C) is one selected from the group consisting of zinc salts of one or more acids selected from phosphoric esters and phosphoric acid and zinc complexes having said acid and zinc salt as ligands.

(3)

The curable resin composition according to (1) described above, wherein the zinc salt and/or zinc complex (C) is at least one selected from the group consisting of zinc salts of carboxylic acids having 1 to 30 carbon atoms and zinc complexes having said acid and zinc salt as ligands.

(4)

The curable resin composition according to any one of (1) to (3) described above, which comprises a polycarboxylic acid (B) having at least two carboxyl groups and having an aliphatic hydrocarbon group as the main skeleton.

(5)

The curable resin composition according to (4) described above, wherein the polycarboxylic 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.

(6)

The curable resin composition according to any one of (1) to (5) described above, which comprises an acid anhydride.

(7)

The curable resin composition according to any one of (1) to (6) described above, which comprises a hindered amine photo-stabilizer and/or a phosphorus-containing antioxidant.

(8)

A cured product obtained by curing the curable resin composition according to any one of (1) to (7) described above.

Effects of the Invention

[0009]

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

Embodiments for Carrying Out the Invention

[0010]

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

The epoxy resin composition of the present invention comprises an organopolysiloxane (A) and a zinc salt and/or zinc complex (C) as essential components.

The organopolysiloxane (A) is characterized in that it is an epoxy resin 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 silsesquioxane-type organopolysiloxanes having a three-dimensionally spreading reticular structure, described in JP-A-2004-256609, JP-A-2004-346144, WO2004/072150, JP-A-2006-8747, WO2006/003990, JP-A-2006-104248, WO2007/135909, JP-A-2004-10849, JP-A-2004-359933, WO2005/100445 and JP-A-2008-174640.

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

body having a silicone segment and the aforementioned silsesquioxane structure obtained by the sol-gel reaction in one molecule is particularly preferred (hereinafter referred to as block-type siloxane compound (A1)).

[0011]

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

[0012]

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

[0013]

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

$$XSi(OR_2)_3 \quad (1)$$

wherein X represents an organic group having a glycidyl group and/or an epoxycyclohexyl group and R_2 groups to be plurally present 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.

[0014]

X in the general formula (1) is not particularly limited as long as it is an organic group having a glycidyl group and/or an epoxycyclohexyl group. Examples thereof include glycidoxy-substituted alkyl groups having 1 to 4 carbon atoms such as β-glycidoxyethyl, γ-glycidoxypropyl and γ-glycidoxybutyl, a glycidyl group, alkyl groups having 1 to 5 carbon atoms substituted with a cycloalkyl group having an oxirane group and having 5 to 8 carbon atoms, 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, alkyl groups having 1 to 3 carbon atoms substituted

with a cycloalkyl group having an epoxy group and having 5 to 8 carbon atoms, 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.

Here, in the case where an alkoxy silane compound in which X is a glycidyl group and an alkoxy silane compound in which X is an epoxycyclohexyl group are used in combination, it is preferred to use the alkoxy silane compound in which X is an epoxycyclohexyl group in an amount of 80% or more based on the total amount of the alkoxy silane compounds (a).

[0015]

R^2 groups to be plurally present in the general formula (1) 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~~,~~ and a cyclohexyl group. 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.

[0016]

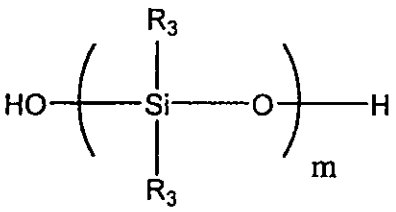
Preferable specific examples of the alkoxysilane (a) include β-glycidoxyethyltrimethoxysilane, β-glycidoxyethyltriethoxysilane, γ-glycidoxypropyltrimethoxysilane, γ-glycidoxypropyltriethoxysilane, β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane~~,~~ and β-(3,4-epoxycyclohexyl)ethyltriethoxysilane. Particularly,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

[0017]

The silicone oil (b) is a linear silicone oil having a silanol group at the end, which has a structure represented by the following formula (2):

[0018]

[Chem 1]



(2)

[0019]

wherein R_3 groups to be plurally present represent each 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, and may be the same or different from each other; and m represents the number of repeating units.

In the general formula (2), R_3 groups to be plurally present represent each 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, and may be the same or different from each other.

As the alkyl group having 1 to 10 carbon atoms, there may be mentioned 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 amino group, an n-hexyl group, a cyclopentyl group, a cyclohexyl group, an octyl group, a 2-ethylhexyl group, a nonyl group and a decyl group. Of these, from the viewpoints of light resistance and heat resistance, a methyl group, an ethyl group, an n-propyl 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 and a xylyl group.

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

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

[0020]

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

[0021]

With regard to the weight-average molecular weight (Mw) 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 chromatograph (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 linear 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, the compound has a severe layer separated structure, so that transparency becomes worse for use in optical materials and thus it becomes difficult to use it. In the present invention, as the molecular weight of the silicone oil (b), using GPC, the weight-average molecular weight (Mw) can be 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 refractometer detector)

[0022]

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

[0023]

As preferable specific examples as the silicone oil (b), the following product names can be mentioned. Examples thereof include PRX-413 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, TSR-160, YR-3370, YF-3800, XF-3905, YF-3057, YF-3807, YF-3802, YF-3897, YF-3804, and XF-3905 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. Of the above ones, from the viewpoints of the molecular weight and the kinematic viscosity, PRX-413, BY16-873, X-21-5841, KF-9701, XC96-723, YF-3800, YF-3804, 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.

[0024]

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

$$R_4(OR_5)_3 \quad (3)$$

wherein R_4 represents a methyl group or a phenyl group; R_5 groups to be plurally present 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.

[0025]

R_5 groups to be plurally present in the general formula (3) 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 and a cyclohexyl group. From the viewpoints of reaction conditions such as compatibility and reactivity, R_5 is preferably a methyl group or an ethyl group.

[0026]

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

[0027]

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

[0028]

In the case where the alkoxysilane (c) is used, 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 (c). When the content of (c) is more than 70% by mol, crosslinking density of the cured product decreases and mechanical strength lowers, so that the case is not preferred.

[0029]

As the reaction ratio of the alkoxysilane (a), the silicone oil (b) and the alkoxysilane (c), the reaction is preferably carried out with the equivalent value of the alkoxy group in the alkoxysilane (a) (and the alkoxysilane (c) used according to need)

being 1.5 to 200, preferably 2 to 200, particularly preferably 2 to 100 relative to 1 equivalent of the silanol group in the silicone oil (b).

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

[0030]

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

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

Production step (i): a step of performing dealcoholization condensation of the silanol-ended silicone oil (b) with the alkoxysilane (a) having an alkoxy group (and the alkoxysilane (c) used according to need),

Production step (ii): a step of performing hydrolytic condensation between the alkoxy groups of the alkoxysilane (a) (and the alkoxysilane (c) used according to need) with adding water.

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

[0031]

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

<Production process (a)>

The process includes:

first, as the production step (i), a step of obtaining an alkoxysilane-modified compound (d) is performed by modifying the silicon oil end with an alkoxysilane through a dealcoholization condensation reaction of the silicone oil (b) having a silanol group at the end 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 (ii), a step of carrying out the hydrolytic condensation reaction between the alkoxy groups by 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 (i) is performed to produce the block-type siloxane compound (A1).

<Production process (b)>

The process includes:

first, as the production step (i), a step of obtaining a silsesquioxane (e) is performed by carrying out the hydrolytic condensation reaction between the alkoxy groups

by adding water to the alkoxysilane (a) (and the alkoxysilane (c) used according to need), and

subsequently, as the production step (ii), a step of carrying out the dealcoholization condensation reaction of the alkoxy group remaining in the silsesquioxane structure with a silanol group through the reaction of the silicone oil (b) with the silsesquioxane (e) is performed to produce the block-type siloxane compound (A1).

<Production process (c)>

The process includes:

first, as the production step (i), the silicone oil end is modified with an alkoxysilane by the dealcoholization condensation reaction of the silicone oil (b) having a silanol group at the end 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 subsequently, as the production step (ii), the block-type siloxane compound (A1) is produced by carrying out the hydrolytic condensation reaction between the alkoxy groups of the remaining alkoxysilane (a) (and the alkoxysilane (c) used according to need) and the alkoxysilane-modified compound (d).

[0032]

In the present 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.

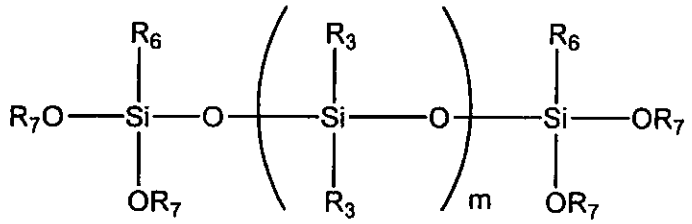
The following will more specifically describe the production process (c).

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 (i) is performed after the production step (ii), there is a high possibility that the silsesquioxane oligomer having an alkoxy group formed in the production step (ii) is not soluble with the silicone oil (b), the dealcoholization condensation polymerization does not proceed in the following production step (i), and thus the silicone oil remains. On the other hand, when a process of performing the production step (ii) in one pot after the production step (i) is used as in the case of the production process (c), the problem that the compounds are not soluble each other and the reaction does not proceed can be avoided since the compatibility of the silicone oil (b) with the alkoxysilane (a) and the alkoxysilane (c) is relatively high. Furthermore, since unreacted low-molecular-weight alkoxysilane is present a large amount relative to the silanol group, the process is also preferred from the viewpoint of reactivity. In the case of performing the steps in one pot, first in the production step (i), 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 end of the silicone oil with an alkoxysilyl, thereby obtaining the alkoxysilane-modified compound (d). Since water is not added in

the production step (i), 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 (4):

[0033]

[Chem 2]



(4)

[0034]

wherein R_3 and m have the same meanings as described above and R_6 groups to be plurally present each independently represent the above X or the above R_4, and R_7 represents the above R_2 in the case where R_6 bonded to the silicon the same as the silicon to which $-OR_7$ is bonded is the above X or represents the above R_5 in the case where R_6 bonded to the silicon the same as the silicon to which $-OR_7$ is bonded is the above R_4.

[0035]

In the production step (i), when the alkoxy group is reacted in a ratio of less than 1 equivalent relative to 1 equivalent of the silanol group, the alkoxy group is not present at the time when the production step (i) is finished, so that the production step (ii) cannot be started. Moreover, when the reaction is carried out using 1 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 production step (i) 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 regulating the reaction, a ratio of 2 equivalents or more is preferred and a ratio of 3 equivalents or more is more preferred.

[0036]

After the production step (i) is finished, the second-stage reaction of performing the hydrolytic condensation between the alkoxy groups (production step (ii)) is performed with adding water without further treatment.

In the production step (ii), reactions (I) to (III) shown below take place.

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

(II) A condensation reaction between the alkoxy groups of the alkoxysilane-modified compound (d) obtained in the production step (i) and the alkoxysilane (a) (and the alkoxysilane (c) used according to need).

(III) A condensation reaction between the alkoxy groups of the alkoxysilane-modified compound (d) obtained in the production step (i) and a partially condensed compound of the alkoxysilane (a) (and the alkoxysilane (c) used according to need) obtained in (I).

In the production step (ii), the above reactions occur in a multiple manner and the formation of the silsesquioxane segment and further the condensation thereof with the linear silicone segment derived from the silicone oil are simultaneously take place.

[0037]

The production of the block-type siloxane compound (A1) can be performed with no catalyst but, since the reaction proceeds only slowly with no catalyst, it is preferred to perform the production in the presence of a catalyst from the viewpoint of shortening the reaction time. As usable catalyst, any compounds can be used as long as they are compounds showing acidity or basicity. Examples of acidic catalysts include inorganic acids such as hydrochloric acid, sulfuric acid and nitric acid and organic acids such as formic acid, acetic acid and oxalic acid. Moreover, as examples of basic catalysts, use can be made of inorganic bases including alkali metal hydroxides such as sodium hydroxide, potassium hydroxide, lithium hydroxide and cesium hydroxide, alkali metal carbonate salts such as sodium carbonate, potassium carbonate, sodium hydrogen carbonate and potassium hydrogen carbonate;-organic bases such as ammonia, triethylamine, diethylenetriamine, n-butylamine, dimethylaminoethanol, triethanolamine and tetramethylammonium hydroxide. Of these, particularly in view of easy removal of the catalyst from the product, inorganic bases are preferred and particularly, sodium hydroxide and potassium hydroxide are preferred. The amount of the catalyst to be added is usually 0.001 to 7.5% by weight, preferably 0.01 to 5% by weight based on the total weight of the alkoxysilane (a) (and the alkoxysilane (c) 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. 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 may result in a possibility that the condensation of the alkoxysilane (a) (and the alkoxysilane (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.

[0038]

The production of the block-type siloxane compound (A1) can be performed without any solvent or in a solvent. Moreover, a solvent can be added in the middle of

the production step. The solvent to be used is not particularly limited as long as it is a solvent capable of dissolving the alkoxysilane (a), the alkoxysilane (c), the silicone oil (b), and the alkoxysilane-modified compound (d). Examples of the solvent include aprotic polar solvents such as dimethylformamide, dimethylacetamide and tetrahydrofuran, ketones such as methyl ethyl ketone, methyl isobutyl ketone and cyclopentanone; esters such as ethyl acetate, butyl acetate, ethyl lactate and isopropyl butanoate; alcohols such as methanol, ethanol, propanol and butanol; alkanes such as hexane, cyclohexane, toluene and xylene. In the present invention, from the viewpoint of reaction regulation, the reaction in an alcohol is preferred and methanol or ethanol is more preferred. The amount of the solvent to be used is not particularly limited as long as the amount is in the range where the reaction smoothly proceeds but the solvent is usually used in an amount of 0 to 900 parts by weight based on 100 parts of the total weight of the compounds of the alkoxysilane (a) (and the alkoxysilane (c) 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.

[0039]

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; alkanes such as hexane, cyclohexane, toluene and xylene.

[0040]

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;-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-with which pH adjustment to around neutral is easy.

[0041]

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

After the adsorbent is added to a reaction solution and treatments such as stirring and heating 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.

[0042]

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 and extraction. These purification methods may be performed singly or two or more thereof may be performed in combination.

[0043]

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.

[0044]

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

[0045]

The appearance of the block-type siloxane compound (A1) thus obtained is usually a colorless and transparent liquid having fluidity at 25°C. Moreover, the molecular weight thereof is preferably 800 to 20,000, more preferably 1,000 to 10,000, and particularly preferably 1,500 to 6,000 as weight-average molecular weight measured by GPC. When the weight-average molecular weight is less than 800, there is a concern that heat resistance decreases. When it is more than 20,000, viscosity increases and thus workability is adversely affected. The molecular weight can be controlled by the equivalent ratio of the alkoxysilane (a) (and the alkoxysilane (c) used according to need) to the silicone oil (b), the molecular weight of the silicone oil (b), the amount of water added at the reaction, the reaction time, and the reaction temperature.

The above 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 refractometer detector)

[0046]

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

[0047]

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

20,000 mPa.s, the viscosity is too high and the composition is sometimes poor in workability.

[0048]

The ratio of the silicon atom bonded to three oxygen atoms, which is derived from the silsesquioxane in the block-type siloxane compound (A1), to the whole silicon atoms is preferably 5 to 50% by mol, more preferably 8 to 30% by mol, and particularly preferably 10 to 20% by mol. When the ratio of the silicon atom bonded to three oxygen atoms, which is derived from the silsesquioxane, is less than 5% by mol, the cured product tends to become too soft as a characteristic feature of a linear 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. Thus, the cases are not preferred.

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

[0049]

The curable resin composition of the present invention contains the polycarboxylic acid (B) as a preferable component.

The polycarboxylic 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 present invention, the polycarboxylic acid includes not only a polycarboxylic acid 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 polycarboxylic acid composition. In the present invention, they are collectively referred to as polycarboxylic acid.

[0050]

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

The difunctional to hexafunctional polyhydric alcohol is not particularly limited as long as it 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.

[0051]

Particularly preferable polyhydric 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, polyhydric 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.

[0052]

As the acid 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, cyclohexane-1,3,4-tricarboxylic-3 and 4-anhydride are preferred. Of these, methylhexahydrophthalic anhydride and cyclohexane-1,3,4-tricarboxylic-3,4-anhydride are preferred.

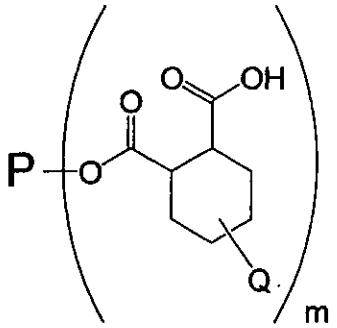
The conditions for the addition reaction are not particularly designated. As one specific reaction condition, there may be mentioned a method of reacting the acid anhydride with the polyhydric alcohol at 40 to 150°C under conditions of no catalyst and no solvent, heating them, and, after completion of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

[0053]

As the thus obtained polycarboxylic acid, particularly preferred is a compound represented by the following formula (5):

[0054]

[Chem 3]



(5)

[0055]

wherein Q to be plurally 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 derived from the

aforementioned polyhydric alcohol; m is the number of functional groups of the polyhydric alcohol (number of the alcohol groups) and is preferably an integer of 2 to 6.

[0056]

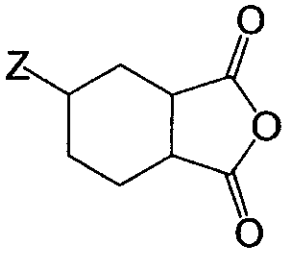
The curable resin composition of the present invention preferably contains an acid anhydride. As the acid anhydride, specifically, there may be mentioned acid anhydrides such as phthalic anhydride, trimellitic anhydride, pyromellitic anhydride, maleic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic 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-1,3,4-tricarboxylic-3,4-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-1,3,4-tricarboxylic-3,4-anhydride are preferred.

Furthermore, of the acid anhydrides, hexahydrophthalic anhydride, methylhexahydrophthalic anhydride and cyclohexane-1,3,4-tricarboxylic-3,4-anhydride, which are represented by the following formula (6):

[0057]

[Chem 4]



(6)

[0058]

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-1,3,4-tricarboxylic-3,4-anhydride are preferred.

[0059]

In the case where the curable resin composition of the present invention contains the acid anhydride, the amount thereof to be used is determined by the ratio thereof to the polycarboxylic acid (B) and is preferably in the range of the following equation.

$W1/(W1+W2) = 0.05$ to 0.65

wherein W1 represents part(s) by weight of the polycarboxylic acid (B) blended and W2 represents part(s) by weight of the acid anhydride.

In the above, the range of W1/(W1+W2) is more 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 of the polycarboxylic acid (B) becomes a solid or nearly a solid or crystals at ordinary temperature, so that no problem arises.

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

[0060]

The curable resin composition of the present invention contains the zinc salt and/or zinc complex (C) as an essential component. The zinc salt and/or zinc complex (C) contribute as a curing accelerator of the epoxy resin and the curing agent in the present invention.

The zinc salt and/or zinc complex are not particularly limited as long as it is a salt and/or a complex containing a zinc ion as a central element but it preferably has at lest one acid selected from carboxylic acids having an alkyl groups having 1 to 30 carbon atoms, phosphate esters and phosphoric acid as a counter ion and/or a ligand. In the present invention, particularly, zinc carboxylate compounds and zinc phosphate esters are preferred and particularly in view of compatibility, the zinc carboxylate compounds are preferred.

As the alkyl groups in the above, there may be mentioned a methyl group, an isopropyl group, a butyl group, a 2-ethylhexyl group, an octyl group, an isodecyl group, an isostearyl group, a decanyl group, a cetyl group, and an undecylene group.

[0061]

As the zinc carboxylate compounds, at least one selected from the group consisting of zinc salts of carboxylic acids having 1 to 30 carbon atoms and zinc complexes having carboxylic acids having 1 to 30 carbon atoms and zinc salts as ligands can be used. In the zinc carboxylate compounds, the carboxylic acids having 1 to 30 carbon atoms are preferably those of an alkyl group having a linear branched structure or an alkyl group having a functional group such as olefin, further preferably those having 3 to 30 carbon atoms. Of these, particularly, those having 5 to 20 carbon atoms are preferred. They are preferred in view of compatibility. In the case where the number of

carbon atoms is too large (the case where the number of carbon atoms exceeds 30) or where the compounds do not have any branched structure or structure of a functional group such as olefin, the compatibility with resins is bad, so that the case is not preferred.

Specifically, there may be mentioned zinc 2-ethylhexylate, zinc isostearate, and zinc undecylenate.

[0062]

As the phosphate ester compounds, at least one selected from the group consisting of zinc salts of phosphate esters and zinc complexes having phosphate esters and the zinc salts as ligands can be used. Moreover, the phosphate ester compound may also contain phosphoric acid derived from the phosphate ester as a counter ion and/or a ligand.

As especially preferred phosphate ester compounds in the present invention, zinc salts and/or zinc complexes of phosphate esters (monoalkyl ester compounds, dialkyl ester compounds, trialkyl ester compounds or mixtures thereof) are preferred, and a plurality of phosphate ester compounds may be incorporated. Specifically, in the molar ratios (using purity on gas chromatography as a substitute but there is a difference in sensitivity since trimethylsilylation is necessary) of the monoalkyl ester compound, dialkyl ester compound and trialkyl ester compound of the phosphate esters incorporated in the phosphate ester compound, the amount of the monoester compound present is preferably 50 area % or more at the stage where a trimethylsilylation treatment is finished.

Such zinc salts and/or zinc complexes of zinc phosphate esters are obtained, for example, by reacting phosphate esters with, for example, zinc carbonate or zinc hydroxide (patent Document EP699708).

As the phosphate esters, 2-ethylhexyl phosphate and stearyl phosphate are preferred.

[0063]

As details of such zinc salts and/or zinc complexes of phosphate esters, the ratio of the phosphorus atom to the zinc atom (P/Zn) is preferably 1.2 to 2.3 and more preferably 1.3 to 2.0. Particularly preferred is 1.4 to 1.9. Namely, in the particularly preferred embodiment, the phosphate ester (or phosphoric acid derived from the phosphate ester) is 2.0 mol or less relative to 1 mol of the zinc ion, and preferred are those having not a simple ion structure but a structure where some molecules precipitate through ionic bonds (or coordinate bonds). The zinc salts and/or zinc complexes can be also obtained, for example, by the procedure described in JP-T-2003-51495.

[0064]

As such compounds, as commercially available products, there may be mentioned Zn-St, Zn-St 602, Zn-St NZ, ZS-3, ZS-6, ZS-8, 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.), as zinc carboxylates, and LBT-2000B (manufactured by SC Organic Chemical Co., Ltd.), XC-9206 (manufactured by King Industries Inc.), as zinc phosphate esters and/or zinc phosphate.

[0065]

In the curable resin composition of the present invention, with regard to the ratio of the organopolysiloxane (A) to the zinc salt and/or the zinc complex (C), the zinc salt and/or the zinc complex (C) is in a ratio of 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.

[0066]

In the case where the curable resin composition of the present invention is used as an optical material, particularly an optical semiconductor encapsulating agent, as a particularly preferable component, it is preferred to incorporate a hindered amine compound as a photo-stabilizer and a phosphorus-based compound as an antioxidant. In the present invention, particularly, it is preferred to incorporate a hindered amine compound and, if necessary, it is preferred to incorporate a phosphorus-based compound.

Examples of the above amine compound include hindered amine-based compounds such as tetrakis(1,2,2,6,6-pentamethyl-4-piperidyl)=1,2,3,4-butanetetracarboxylate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)=1,2,3,4-butanetetracarboxylate, a mixed esterified product of 1,2,3,4-butanetetracarboxylic acid with 1,2,2,6,6-pentamethyl-4-piperidinol and 3,9-bis(2-hydroxy-1,1-dimethylethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane, decanedioic acid bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate, bis(1-undecanoxy-2,2,6,6-tetramethylpiperidin-4-yl) carbonate, 2,2,6,6-tetramethyl-4-piperidyl methacrylate, bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate, 4-benzoyloxy-2,2,6,6-tetramethylpiperidine, 1-[2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]ethyl]-4-[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-benzenedicarboxyamide and N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl).

[0067]

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

Examples thereof include TINUVIN 765, TINUVIN 770DF, TINUVIN 144, TINUVIN 123, TINUVIN 622LD, TINUVIN 152, CHIMASSORB 944 as products manufactured by Ciba Specialty Chemicals; LA-52, LA-57, LA-62, LA-63P, LA-77Y, LA-81, LA-82 and LA-87 as products manufactured by Adeka Corporation.

[0068]

In the curable resin composition of the present invention, the amount of the photo-stabilizer to be used is 0.005 to 5% by weight, more preferably 0.01 to 4% by weight, 0.1 to 2% by weight based on the organopolysiloxane (A) in terms of weight ratio.

[0069]

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(2,4-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 diphosphonite, tetrakis(2,4-di-tert-butylphenyl)-4,3'-biphenylene diphosphonite, tetrakis(2,4-di-tert-butylphenyl)-3,3'-biphenylene diphosphonite, tetrakis(2,6-di-tert-butylphenyl)-4,4'-biphenylene diphosphonite, tetrakis(2,6-di-tert-butylphenyl)-4,3'-biphenylene diphosphonite, tetrakis(2,6-di-tert-butylphenyl)-3,3'-biphenylene diphosphonite, bis(2,4-di-tert-butylphenyl)-4-phenyl-phenylphosphonite, bis(2,4-di-tert-butylphenyl)-3-phenyl-phenylphosphonite, bis(2,6-di-n-butylphenyl)-3-phenyl-phenylphosphonite, bis(2,6-di-tert-

butylphenyl)-4-phenyl-phenylphosphonite, 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, and diisopropyl phosphate.

[0070]

As the above phosphorus-based compounds, commercially available products can be also used.

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.

[0071]

In the curable resin composition of the present invention, the amount of the phosphorus-based compound to be used is 0.005 to 5% by weight, more preferably 0.01 to 4% by weight, 0.1 to 2% by weight based on the organopolysiloxane (A) in terms of weight ratio.

[0072]

The curable resin composition of the present invention contains the organopolysiloxane (A) as an epoxy resin and the zinc salt and/or the zinc complex (C) as a curing accelerator as essential components and further the polycarboxylic acid (B) and the acid anhydride as curing agents and the hindered amine-based photo-stabilizer and the phosphorus-containing antioxidant as additives as preferable optional components. They may be also used in combination with other epoxy resin, curing agent, and various additives.

[0073]

In the epoxy resin component, in the case where the organopolysiloxane (A) is used in combination with the other epoxy resin, 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.

[0074]

As epoxy resins usable in combination with the organopolysiloxane (A), there may be mentioned solid or liquid epoxy resins including novolak-type epoxy resins, bisphenol A-type epoxy resins, biphenyl-type epoxy resins, triphenylmethane-type epoxy resins and phenolaralkyl-type epoxy resins. Specifically, there may be mentioned 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 and modified compounds thereof, halogenated bisphenols such as tetrabromobisphenol A, glycidyl etherified compounds derived from alcohols, alicyclic epoxy resins, glycidylamine-based epoxy resins, and glycidyl ester-based epoxy resins. They may be used singly or two or more thereof may be used in combination.

[0075]

Particularly, it is mainly purposed that the curable resin composition of the present invention is used in optical uses. In the case where the composition is used in optical uses, the combined use of alicyclic epoxy resins is preferred. In the case of the alicyclic epoxy resins, compounds having an epoxycyclohexnae structure in the skeleton are preferred, and epoxy resins obtained by oxidation reaction of compounds having a cyclohexene structure are particularly preferred.

As these 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) and Tetrahedron Letter p.4475 (1080)), or the Tishchenko reaction of cyclohexenealdehyde (procedures described in JP-A-2003-170059 and JP-A-2004-262871), or further the ester-exchange reaction of cyclohexenecarboxylate esters (procedures described in JP-A-2006-052187).

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

Further, as the other epoxy resins, there may be mentioned epoxy resins obtained by epoxidation of acetal compounds through the oxidation reaction, the acetal compounds

being obtained by the acetalization reaction of cyclohexenealdehyde derivatives with alcohol compounds.

[0076]

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.) and dicyclopentadiene diepoxide (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.

[0077]

The curing agent component in the present invention is not particularly limited but it is desirable to use the polycarboxylic acid compound (B) singly or in combination with the acid anhydride and also 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 polycarboxylic 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 other curing agent usable in combination include amine-based compounds, acid anhydride-based compounds, amide-based compounds, phenol-based compounds and carboxylic acid-based compounds. 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), 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, 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-1,3,4-tricarboxylic-3,4-anhydride with silicone-based alcohols such as carbinol-modified silicones), polyhydric phenols (bisphenol A, bisphenol F, bisphenol S, fluorene bisphenol, terpene diphenol, 4,4'-biphenol, 2,2'-biphenol, 3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'-diol, hydroquinone, resorcin, naphthalenediol, tris-(4-hydroxyphenyl)methane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, polycondensates of phenols (phenol, alkyl-substituted phenols, naphthol, alkyl-substituted naphthaols, dihydroxybenzene, dihydroxynaphthalene, etc.) with formaldehyde, acetaldehyde, bezaldehyde, p-hydroxybenzaldehyde, o-hydroxybenzaldehyde, p-hydroxyacetophenone, o-hydroxyacetophenone, dicyclopentadiene, furfural, 4,4'-bis(chloromethyl)-1,1'-biphenyl, 4,4'-bis(methoxymethyl)-

1,1'-biphenyl, 1,4'-bis(chloromethyl)benzene, 1,4'-bis(methoxymethyl)benzene and modified compounds thereof, halogenated bisphenols such as tetrabromobisphenol A, condensates of terpenes with phenols) and others (imidazole, trifluoroborane-amine complexes, guanidine derivatives, etc.). They may be used singly or two or more thereof may be used.

[0078]

In the curable resin composition of the present invention, the ratio of the curing agent component to the epoxy resin is preferably 0.7 to 1.2 equivalents and particularly preferably 0.75 to 1.1 equivalents relative to 1 equivalent of the epoxy group of the epoxy resin component.

In the case where the ratio 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.

[0079]

In the curable resin composition of the present invention, since the zinc salt and/or the zinc complex (C) as an essential component exhibit an action as a curing catalyst as they are, 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 these imidazoles with polycarboxylic 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-diazabicyclo[5.4.0]undecene-7 and salts thereof with tetraphenylborate, phenol novolak, salts with the above polycarboxylic acids or phosphinic acids, ammonium salts such as tetrabutylammonium bromide, cetyltrimethylammonium bromide and trioctylmethylammonium bromide, phosphines and phosphonium compounds such as tripheylphosphine, tri(toluyl)phosphine, tetraphenylphosphonium bromide and tetraphenylphosphonium tetraphenylborate, phenols such as 2,4,6-trisaminomethylphenol, amine adducts, metal compounds such as tin octylate, and microcapsulated curing accelerators obtained by microcapsulation of these curing accelerators. 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, working conditions. The curing accelerator is used in the range of usually 0.001 to 15 parts by weight based on 100 parts by weight of the epoxy resin.

[0080]

To the curable resin composition of the present invention, the following various additives and auxiliary materials can be added.

In the curable resin composition of the present 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-phosphaphenathrene-10-oxide; phosphorus-containing epoxy compounds obtained by reacting an epoxy resin with active hydrogen of the phosphanes and red phosphorus. 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 resins = 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 materials are adversely affected.

[0081]

Furthermore, into the curable resin composition of the present 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 and silicone resins.The amount of the binder resin to be blended is preferably in the range where flame retardancy and heat resistance of the cured material 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 epoxy resin component and the curing agent component.

[0082]

To the curable resin composition of the present 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 or beads obtained by forming them into spherzical shape. They 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 present invention. Furthermore, to the curable resin composition of the present 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.

[0083]

In the case where the curable resin composition of the present invention is used as an optical material, particularly an optical semiconductor encapsulating agent, it is possible to reinforce the mechanical strength 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.

[0084]

In the case where the curable resin composition of the present 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 yellow light resulting from wavelength conversion. 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 and orthosilicate salts 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 $YAlO_3$:Ce, $Y_3Al_5O_{12}$:Ce, $Y_4Al_2O_9$:Ce, Y_2O_2S:Eu, $Sr_5(PO_4)_3Cl$:Eu and $(SrEu)O{\cdot}Al_2O_3$ are exemplified. As the particle diameter of such phosphors, those having a known particle diameter 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 organic components such as the organopolysiloxane (A).

[0085]

In the case where the curable resin composition of the present 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 300, Aerosil 380, Aerosil OX50, Aerosil TT600, Aerosil R972, Aerosil R974, Aerosil R202, Aerosil R812, Aerosil R812S, Aerosil R805, RY200 and RX200 (manufactured by Nippon Aerosil Co., Ltd.).

[0086]

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

Specific examples of the phenol compound include 2,6-di-tert-butyl-4-methylphenol, n-octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, tetrakis[methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]methane, 2,4-di-tert-butyl-6-methylphenol, 1,6-hexanediol-bis-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-isocyanurate, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, pentaerythrityl-tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 3,9-bis-[2-[3-(3-tert-butyl-4-hydroxy-5-methylphenyl)-propionyloxy}-1,1-dimethylethyl]-2,4,8,10-tetraoxaspiro[5,5]undecane, triethylene glycol-bis[3-(3-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, 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 and bis[3,3-bis-(4'-hydroxy-3'-tert-butylphenyl)butanoic acid]-glycol ester.

[0087]

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

Examples thereof include IRGANOX 1010, IRGANOX 1035, IRGANOX 1076, IRGANOX 1135, IRGANOX 245, IRGANOX 259, IRGANOX 295, IRGANOX 3114 IRGANOX 1098, IRGANOX 1520L as products 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 products manufactured by Adeka Corporation, Sumilizer GA-80, Sumilizer MDP-S, Sumilizer BBM-S, Sumilizer

GM, Sumilizer GS(F) and Sumilizer GP as products manufactured by Sumitomo Chemical Co., Ltd.

[0088]

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 and CHIMASSORB 119FL as products manufactured by Ciba Specialty Chemicals.

[0089]

In the case where the above phenol-based compound is added, the amount thereof to be blended is not particularly limited and it can be added in an amount of 0.005 to 5.0% by weight in the curable resin composition of the present invention.

[0090]

The curable resin composition of the present invention is obtained by mixing individual components homogeneously. The curable resin composition of the present 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 can be obtained by thoroughly mixing the epoxy resin component, the curing agent component, and the zinc salt and/or zinc complex (C) using an extruder, a kneader, a roll or a planetary mixer according to need until a homogeneous state is achieved. In the case where the obtained curable resin composition is liquid, the cured product can be formed by potting or casting the composition, impregnating a substrate therewith, or injecting the curable resin composition into a mold, and then curing it by heating or, in the case where the composition is solid, the cured product can be formed by injecting it into a mold after melting or molding it using a transfer molding machine and further curing it by heating.

Incidentally, the other curing accelerator, amine compound, phosphorus-containing compound, phenol compound, binder resin and inorganic filler which are optional components may be added and mixed in the above mixing step. 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 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.

[0091]

Moreover, a cured product of the curable resin composition of the present invention can be formed by dissolving the curable resin composition of the present invention in a solvent such as toluene, xylene, acetone, methyl ethyl ketone, methyl

isobutyl ketone, dimethylformamide, dimethylacetamide or N-methylpyrrolidone to transform 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 at this time 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 present invention and the solvent. Moreover, an epoxy resin cured product containing carbon fiber can be also obtained by RTM (Resin Transfer Molding) method using the liquid composition itself.

[0092]

Furthermore, the curable resin composition of the present invention can be also used as a film-type composition for encapsulation. As a method of obtaining such a film-type resin composition, there may be mentioned a method of transforming the curable resin composition of the present invention into the varnish of the curable resin composition as mentioned above, applying it on a release film, removing the solvent under heating, and then performing transformation into B-stage. Thereby, the film-type composition for encapsulation can be obtained as a sheet-shaped adhesive agent. The sheet-shaped adhesive agent can be used as an interlayer insulating layer in multilayer substrates and en bloc film encapsulation of optical semiconductors.

[0093]

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

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

[0094]

The optical semiconductor element such as the 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 or ZnO, to a lead flame, 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. On the other hand, the periphery of such a semiconductor chip is encapsulated with an encapsulating material such as an epoxy resin. The encapsulating material is used for protecting the semiconductor chip from heat and moisture and playing a role of lens function.

The curable resin composition of the present 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 present invention as both of the die-bonding material and the encapsulating material.

[0095]

As a method of adhering the semiconductor chip to the substrate using the curable resin composition of the present invention, there may be mentioned a method of placing the semiconductor chip on the curable resin composition of the present invention and performing heat curing after the curable resin composition is applied on the substrate by a dispenser, potting, or screen printing. By such a method, the semiconductor chip can be adhered to the substrate. For heating, a method of hot-air circulation, infrared ray or high frequency wave can be employed.

[0096]

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.

[0097]

As a molding method of the encapsulating material, an injection method where 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 where 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 or injection molding may be mentioned.

For heating, a method of hot-air circulation, infrared ray or high frequency wave 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.

[0098]

Uses of the curable resin composition of the present invention are not limited to the above uses and can be applied to general uses in which thermosetting resins such as epoxy resins are used. For example, there may be mentioned adhesives, paints, coating agents, molding materials (including sheets, films and FRP), insulating materials (including printed boards, electric wire coverings, etc.), encapsulating agents, and also additives for other resins such as cyanate resin compositions for encapsulating materials and substrates and acrylate ester-based resins as curing agents for resists.

[0099]

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

[0100]

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

[0101]

The cured product obtained in the present 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 the material. More specifically, the following may be mentioned in addition to LED encapsulating materials of lamp type and SMD type. 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 in the 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 and adhesives.

[0102]

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 and adhesives for projection television sets. They may be lens materials, encapsulating materials, adhesives and films for optical sensing devices. In the optical parts field, they may be fiber materials, lenses, optical waveguides, encapsulating materials for elements and adhesives in the periphery of optical switches in the optical communication system. They may be optical fiber materials, ferrules, encapsulating materials and adhesives 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 and adhesives. They may be substrate materials, fiber materials, encapsulating materials for elements and adhesives in the periphery of optical electronic integrated circuits (OEIC). In the optical fiber field, they may be illumination lamps/light guides for decoration display, sensors in industrial uses, displays/signs, and optical fibers for communication infrastructure and for domestic digital device connection. In the peripheral materials for semiconductor integrated circuit, they may be resist materials for microlithography for LSI or ultra LSI materials. In the automobile/transport aircraft fields, lamp reflectors for automobiles, baring 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 photoreflective 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 and adhesives.

[0103]

As the other uses of the optical material, there may be mentioned general uses where curable resin compositions are used. For example, there may be mentioned adhesives, paints, coating agents, molding materials (including sheets, films and FRP), insulating materials (including printed boards, electric wire coverings, etc.), encapsulating agents, and also additives for other resins.

Examples

[0104]

The following will describe the present invention further in detail with reference to Synthetic Examples and Examples. Incidentally, the present invention is not limited to these Synthetic Examples and Examples. Moreover, in the following Synthetic Examples and Examples, "parts" means parts by weight and "%" means % by weight, respectively. Incidentally, individual physical property values in Examples were measured by the following methods.

(1) Molecular weight: weight-average molecular weight as a value in terms of polystyrene measured under the following conditions was calculated 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 refractometer 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.

[0105]

Synthetic Example 1

As the production step (i), 106 parts of β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 234 parts of a silanol-ended 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 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 production step (ii), after 305 parts of methanol was 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, 300 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 718 g/eq, weight-average molecular weight was 2200, and the appearance was colorless and transparent.

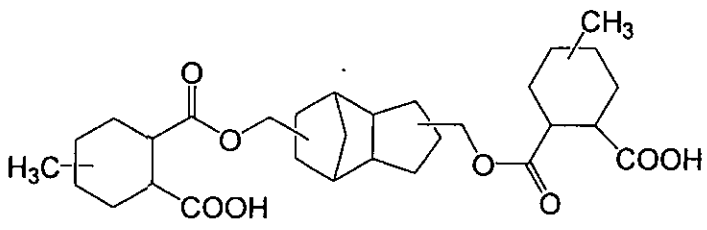
[0106]

Synthetic Example 2

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 polycarboxylic acid (B-1) and the acid anhydride (H-1). The obtained curing agent composition (T-1) was a colorless liquid resin and, with regard to purity by GPC, the polycarboxylic acid (B-1; the following formula (7)) was 55 area % and the acid anhydride (H-1) was 45 area %. Moreover, functional group equivalent was 201 g/eq. Furthermore, viscosity at 25°C was 18,900 mPa.s (E-type viscometer).

[0107]

[Chem 5]



(7)

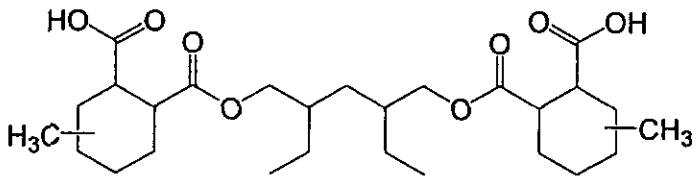
[0108]

Synthetic Example 3

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 polycarboxylic acid (B-2) and the acid anhydride (H-1). The obtained curing agent composition (T-2) was a colorless liquid resin and, with regard to purity by GPC, the polycarboxylic acid (B-2; the following formula (8)) was 50 area % and the acid anhydride (H-1) was 50 area %. Moreover, functional group equivalent was 201 g/eq. Furthermore, viscosity at 25°C was 16,200 mPa.s (E-type viscometer).

[0109]

[Chem 6]



(8)

[0110]

Synthetic Example 4

As the production step (i), 296 parts of β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 505 parts of a silanol-ended 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 production step (ii), after 510 parts of methanol was 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, 697 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 598 g/eq, weight-average molecular weight was 2370, and the appearance was colorless and transparent.

[0111]

Synthetic Example 5

Into a flask fitted with a stirrer, a reflux condenser and a stirring apparatus were added 12 parts of tricyclodecanedimethanol, 18 parts of 2,4-diethyl-1,5-pentanediol and 155 parts of methylhexahydrophthalic anhydride (RIKACID MH, manufactured by New Japan Chemical Co., Ltd., corresponding to the acid anhydride (H-1)) and 15 parts of 1,3,4-cyclohexanetricarboxylic-3,4-anhydride (H-TMAn, manufactured by Mitsubishi Gas Chemical Co., Inc., hereinafter referred to as acid anhydride (H-2)) 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 the raw material alcohol was confirmed by GPC) to obtain 200 parts of a curing agent composition (T-3) containing polycarboxylic acids (B-1) (B-2) and the acid anhydrides (H-1) (H-2). The obtained curing agent composition (T-3) was a colorless liquid resin and, with regard to purity by GPC, the polycarboxylic acids (B-1) (B-2) was 52 area % and the acid anhydrides (H-1) (H-2) was 48 area %. Moreover, functional group equivalent was 190 g/eq. Furthermore, viscosity at 25°C was 15,500 mPa.s (E-type viscometer).

[0112]

Synthetic Example 6

As the production step (i), 44 parts of β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 153 parts of a silanol-ended 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 11.2 parts of a 0.5% potassium hydroxide (KOH) methanol solution (0.056 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 production step (ii), after 157 parts of methanol was added, 19.3 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, 177 parts of methyl isobutyl ketone (MIBK) was added and washing with water was repeated three times. Then, 178 parts of an organopolysiloxane compound (A-3) 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 1020 g/eq,

weight-average molecular weight was 2100, and the appearance was colorless and transparent.

[0113]

Examples 1, 2, 3, 4 and Comparative Examples 1, 2, 3

Using the organopolysiloxane compound (A-1) obtained in Synthetic Example 1 as an epoxy resin, a curing agent composition (T-1), (T-2) obtained in Synthetic Examples 2, 3 as a curing agent (ratio of the organopolysiloxane (A) to the curing agent composition (T-1), (T-2) was 1:1 in terms of functional group equivalent), a propylene glycol solution of a zinc complex of phosphoric acid 2-ethylhexane ester (phosphoric acid:monoester compound:diester compound:triester compound = 3.5:68.2:26.5:1.8, however, since a trimethylsilylation treatment was performed, sensitivity was different and thus the weight ratio is not accurate; hereinafter referred to as zinc salt and/or zinc complex (C-1)) (phosphorus:zinc = 1.7:1 measured by ICP emission spectrochemical analysis, in accordance with JIS K 0166) (produced in accordance with JP-T-2003-51495, hereinafter referred to as (C-1)) as a zinc salt and/or zinc complex, a quaternary phosphonium salt (Hishicallin PX4MP manufactured by Nippon Chemical Industrial Co., Ltd., hereinafter referred to as catalyst (I-1)) as a curing accelerator, bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate (TINUVIN 770DF manufactured by Ciba Japan, hereinafter referred to as (L-1)) as an additive, and 4,4'-butylidenebis(3-methyl-6-tert-butylphenyl-di-tridecyl phosphite) (ADEKA STAB 260 manufactured by Adeka Corporation, hereinafter referred to as (M-1)) as a phosphorus-based compound, they were blended in blending ratios shown in the following Table 1 and defoaming was performed for 20 minutes to obtain curable resin compositions of the present invention or for comparison.

[0114]

The obtained curable resin compositions were gently injected into a mold for test piece and the injected materials were cured under conditions of 150°C×1 hour after pre-curing at 120°C×3 hours to obtain various cured products for test. For the obtained cured products, with regard to tests for hardness and thermal durability transmittance test, evaluation was performed under conditions described below. The results are also shown in the following Table 1.

[0115]

(Hardness)

Shore A

It was measured in accordance with JIS K 7215 "Test Method for Durometer Hardness of Plastics".

[0116]

(Thermal durability transmittance test)

Conditions for heat resistance test: a test piece was allowed to stand in an oven at 150°C for 96 hours

Size of test piece: thickness of 1 mm

Evaluation conditions: transmittance at 400 nm was measured by a spectrophotometer and a change ratio (retention ratio) thereof was calculated.

[0117]

(LED lighting test)

After each of the curable resin compositions obtained in Examples and Comparative Example was subjected to vacuum defoaming for 20 minutes, it was filled into a syringe and injected into a surface-mounted LED on which an emission element having an emission wavelength of 465 nm had been mounted, using a precise injection apparatus. Thereafter, an LED for lighting test was obtained by curing under prescribed curing conditions (at 110°C for 2 hours and further at 150°C for 3 hours). For the lighting test, a lighting test at 60 mA that was twice the specified current (constant current drive, specified current of 30 mA) was performed and initial illuminance was measured.

[0118]

[Table 1]

	Item			Example 1	Example 2	Comparative Example 1
Composition	Epoxy resin	Organopolysiloxane	A-1	10.0	10.0	10.0
	Curing agent	Curing agent composition	T-1	2.8	2.8	2.8
			T-2			
	Curing accelerator	Zinc salt (zinc complex)	C-1	0.01	0.03	
		Quaternary phosphonium salt	I-1			0.01
	Additive	Photo-stabilizer	L-1	0.03	0.03	0.03
		Phosphorus-based compound	M-1	0.03	0.03	0.03
Physical property when cured	Hardness test	Shore A		97	97	98
	Thermal durability transmittance test	Retention ratio (400 nm)	%	98.3%	98.6%	97.7%
	LED lighting test	Initial illuminance	mW	9577	9597	8183

	Item			Example 3	Comparative Example 2	
Composition	Epoxy resin	Organopolysiloxane	A-1	10.0	10.0	
	Curing agent	Curing agent composition	T-1			
			T-2	2.8	2.8	
	Curing accelerator	Zinc salt (zinc complex)	C-1	0.03		
		Quaternary phosphonium salt	I-1		0.03	
	Additive	Photo-stabilizer	L-1			
		Phosphorus-based compound	M-1			
Physical property when cured	Hardness test	Shore A		90	90	
	Thermal durability transmittance test	Retention ratio (400 nm)	%	95.1%	82.1%	
	LED lighting test	Initial illuminance	mW	7737	4993	

	Item			Example 4	Comparative Example 3	
Composition	Epoxy resin	Organopolysiloxane	A-1	10.0	10.0	
	Curing agent	Curing agent composition	T-1			
			T-2	2.8	2.8	
	Curing accelerator	Zinc salt (zinc complex)	C-1	0.01		
		Quaternary phosphonium salt	I-1		0.01	
	Additive	Photo-stabilizer	L-1	0.05	0.05	
		Phosphorus-based compound	M-1	0.05	0.05	
Physical property when cured	Hardness test	Shore A		93	92	
	Thermal durability transmittance test	Retention ratio (400 nm)	%	97.5%	95.3%	
	LED lighting test	Initial illuminance	mW	9037	9030	

[0119]

Examples 5, 6 and Comparative Example 4

Using the organopolysiloxane compound (A-2) obtained in Synthetic Example 2 as an epoxy resin, a curing agent composition (T-1) obtained in Synthetic Example 2 as a curing agent (ratio of the organopolysiloxane (A) to the curing agent composition (T-1) was 1:0.8 in terms of functional group equivalent), the zinc salt and/or zinc complex (C-1) as a curing accelerator, the catalyst (I-1), and the additives (L-1) (M-1), they were blended in blending ratios shown in the following Table 2 and defoaming was performed for 20 minutes to obtain curable resin compositions of the present invention or for comparison.

[0120]

The obtained curable resin compositions were gently injected into a mold for test piece and the injected materials were cured under conditions of 150°C×1 hour after pre-curing at 120°C×3 hours to obtain various cured products for test. For the obtained cured products, with regard to the following tests for heat resistance property test, hardness and thermal durability transmittance test, evaluation was performed under conditions described below. The results are also shown in the following Table 2.

[0121]

(Heat resistance property test)

Measurement conditions

Dynamic viscoelasticity measuring instrument: DMA-2980 manufactured by TA-instruments

Measurement temperature range: -30°C to 280°C

Temperature elevation rate: 2°C/minute

Test piece size: an article cut into a size of 5 mm×50 mm was used (thickness of about 800 μm).

Analytical conditions

Tg: a peak point of Tan-δ at DMA measurement was taken as Tg.

30°C elastic modulus: elastic modulus at 30°C was measured.

[0122]

(Hardness test)

Shore A

It was measured in accordance with JIS K 7215 "Test Method for Durometer Hardness of Plastics".

[0123]

(Transmittance test)

Size of test piece: thickness of 1 mm

Evaluation conditions: transmittance at 400 nm was measured by a spectrophotometer.

[0124]

Furthermore, 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 (inner diameter of 4.4 mm, outer wall height of 1.25 mm) on which a chip having a central emission wavelength of 465 nm had been mounted, using a precise injection apparatus. The injected article 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 (corrosive gas permeation test). The results are also shown in Table 2.

[0125]

(Corrosive gas permeation test)

Measurement Conditions

Corrosive gas: a 20% by weight 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 bottle and, under a tightly closed situation with capping the wide-mouthed 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 every hour and the LED package requiring longer color change time is judged to be more excellent in resistance to corrosive gas. The observation was performed by taking out the package after 1 hour, after 2 hours, after 3 hours, and after 4 hours. Evaluation was as follows: a package exhibiting no discoloration was evaluated as O, a package colored into light brown to brown was evaluated as ×, and a package completely blackened was evaluated as ××.

[0126]

[Table 2]

	Item			Example 5	Example 6	Comparative Example 4
Composition	Epoxy resin	Organopolysiloxane	A-2	10.0	10.0	10.0
	Curing agent	Curing agent composition	T-1	2.7	2.7	2.7
	Curing accelerator	Zinc salt (zinc complex)	C-1	0.01	0.10	
		Quaternary phosphonium salt	I-1			0.01
	Additive	Photo-stabilizer	L-1	0.02	0.02	0.02
		Phosphorus-based compound	M-1	0.02	0.02	0.02
Physical property when cured	Heat resistance property test	Tg	°C	55.3	61.7	55.3
		30° elastic modulus	MPa	269	469	280
	Hardness test	Shore A		94	95	96
	Transmittance measurement	Initial transmittance	%	91.6	91.8	91.7
	Corrosive gas permeation test	Exposure time	1h	O	O	O
			2h	O	O	O
			3h	O	O	×
			4h	O	O	×

[0127]

From Examples 1 to 4 and Comparative Examples 1 to 3, the curable resin composition of the present invention is excellent in heat coloring resistance (heat-resistant transmittance test) and affords a curable product having a good light extraction efficiency (LED lighting test), so that it is realized that the composition is excellent in optical properties.

From Examples 5 and 6 and Comparative Example 4, it becomes obvious that the curable resin composition of the present invention affords a curable product excellent in gas permeation resistance (corrosive gas permeation test) and thus the composition is useful in the fields where the optical property is necessary, like a semiconductor chip and LED which are susceptible to external environment.

[0128]

Examples 7 to 12 and Comparative Examples 5 to 9

Using each of the organopolysiloxane compounds (A-1), (A-2), (A-3) obtained in Synthetic Examples 1, 4, 6 as an epoxy resin, a curing agent composition (T-1) or (T-2) obtained in Synthetic Example 2 or 3 as a curing agent (ratio of the organopolysiloxane (A) to the curing agent composition (T-1) or (T-2) was 1:0.8 in terms of functional group equivalent), zinc 2-ethylhexanoate (C-2), zinc undecylenate (C-3), zinc 2-ethylhexanoate (containing an imidazole compound, XK-614 manufactured by King Industry, hereinafter referred to as (C-4)) as a zinc salt and/or zinc complex, a quaternary phosphonium salt (Hishicallin PX-4ET manufactured by Nippon Chemical Industrial Co., Ltd., hereinafter

referred to as catalyst (I-2)) as a curing accelerator, an imidazole compound (2E4MZ manufactured by Shikoku Chemicals Corporation, hereinafter referred to as catalyst (I-3)), and bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate (TINUVIN 770DF manufactured by Ciba Japan, hereinafter referred to as (L-1)) as an additive, they were blended in blending ratios shown in the following Tables 3 and 4 and defoaming was performed for 20 minutes to obtain curable resin compositions of the present invention or for comparison.

[0129]

The obtained curable resin compositions were gently injected into a mold for test piece and the injected materials were cured under conditions of 140°C×5 hours after pre-curing at 110°C×3 hours to obtain various cured products for test. For the obtained cured products, corrosive gas permeation test was performed (the test method are the same as described above except that observation is performed after 1 hour, after 2 hours, after 3 hours, after 6 hours and after 10 hours). The results are also shown in the following Tables 3 and 4.

[0130]

aternary phosphonium salt	I-2					0.07	
Imidazole compound	I-3						0.07
Photo-stabilizer	L-1	0.01	0.01	0.01	0.01	0.01	0.01
Exposure time	1h	O	O	O	O	O	O
	2h	O	O	O	O	O	O
	3h	O	O	O	O	O	O
	6h	O	O	O	×	×	×
	10h	O	O	O	××	××	××

[0131]

[Table 4]

Item	Item			Example 10	Example 11	Example 12	Comparative Example 8	Comparative Example 9
Composition	Epoxy resin	Organopolysiloxane	A-1					
		Organopolysiloxane	A-2	6.0		6.0	6.0	6.0
		Organopolysiloxane	A-3		10.2			
	Curing agent	Curing agent composition	T-1	1.6	1.6		1.6	
		Curing agent composition	T-2					
		Acid anhydride	H-1			1.3		1.3
	Zinc salt (zinc complex)		C-2		0.06			
			C-3	0.06		0.06		
			C-4					
	Curing accelerator	Quaternary phosphonium salt	I-2				0.06	0.06
		Imidazole compound	I-3					
	Additive	Photo-stabilizer	L-1					
Physical property when cured	Corrosive gas permeation test	Exposure time	1h	O	O	O	O	O
			2h	O	O	O	O	×
			3h	O	O	O	O	×
			6h	O	O	O	×	××
			10h	O	O	×	××	××

[0132]

Examples 13, 14

Using the organopolysiloxane compound (A-3) obtained in Synthetic Example 6 as an epoxy resin, a curing agent composition (T-3) obtained in Synthetic Example 5 as a curing agent (ratio of the organopolysiloxane (A) to the curing agent composition (T-3) was 1:0.8 in terms of functional group equivalent), the zinc salt and/or zinc complex (C-1), (C-2) as a curing accelerator, a hindered amine compound (LA-81 manufactured by Adeka Corporation, hereinafter referred to as (L-2)) as an additive and a phosphorus compound (ADEKA 260 manufactured by Adeka Corporation, hereinafter referred to as (L-3)), they were blended in blending ratios shown in the following Table 5 and defoaming was performed for 20 minutes to obtain curable resin compositions of the present invention or for comparison.

[0133]

(Corrosive gas permeation test)

The obtained curable resin compositions were gently injected into a mold for test piece and the injected materials were cured under conditions of 150°C×3 hours after pre-curing at 120°C×1 hour to obtain various cured products for test. For the obtained cured products, corrosive gas permeation test was performed (the test method is the same as described above). The results are also shown in the following Table 5.

[0134]

(LED lighting test)

After each of the obtained curable resin compositions was filled into a syringe and injected into a surface-mounted LED (SMD type 5 mmϕ, specified current of 20 mA) on which an emission element having an emission wavelength of 465 nm had been mounted, using a precise injection apparatus. Thereafter, an LED for lighting test was obtained by curing under prescribed curing conditions (at 120°C for 1 hour and further at 150°C for 3 hours). For the lighting test, a lighting test at 230 mA that was more than 20 mA as the specified current to a large extent was performed. Detailed conditions were shown below. As a measurement item, illuminance before and after lighting for 40 hours was measured using an integrating sphere and a retention ratio of illuminance of the LED for test was calculated. The results are shown in Table 5.

Detailed conditions for lighting

Emission wavelength: 465 nm

Driving method: constant current method, 230 mA (specified current of the emission element was 20 mA), three LEDs were lighted simultaneously in series

Driving environment: lighting in a wet-heat chamber at 25°C, 65%

Evaluation: Illuminance and illuminance retention ratios after 20 hours and 40 hours were measured, respectively.

[0135]

[Table 5]

	Item			Example 13	Example 14
Composition	Epoxy resin	Organopolysiloxane	A-3	10.2	10.2
	Curing agent	Curing agent composition	T-3	1.5	1.5
	Zinc salt (zinc complex)		C-1	0.05	
			C-2		0.03
	Additive	Photo-stabilizer	L-2	0.02	0.02
		Phosphorus compound	L-3	0.02	0.02
Physical property when cured	Corrosive gas permeation test	Exposure time	10h	O	O
	Lighting test (230 mA)	Illuminance (μW) / illuminance retention ratio (%)	0h(ref)	9900	9900
			20h	9950	10100
				100%	102%
			40h	8400	10200
				85%	103%

[0136]

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. 2009-271469 filed on November 30, 2009, and the contents are incorporated herein by reference. Also, all the references cited herein are incorporated as a whole.

Claims

[Claim 1]

A curable resin composition comprising an organopolysiloxane (A) and a zinc salt and/or zinc complex (C) as essential components, wherein the organopolysiloxane (A) satisfies the following requirement,

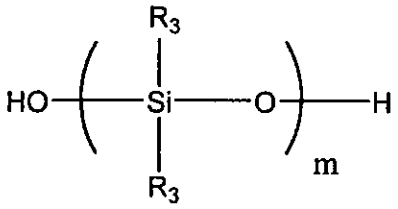
Organopolysiloxane (A):

a block-type siloxane compound that is produced by reacting an alkoxysilane compound (a) represented by the following general formula (1) and a silicone oil (b) represented by the following general formula (2), and thereafter performing hydrolytic condensation between alkoxy groups of the alkoxysilane compound (a), or

a block-type siloxane compound that is produced by reacting an alkoxysilane compound (a) represented by the following general formula (1), a silicone oil (b) represented by the following general formula (2) and an alkoxysilane compound (c) represented by the following general formula (3), and thereafter performing hydrolytic condensation between alkoxy groups of the alkoxysilane compound (a) and the alkoxysilane compound (c):

$XSi(OR_2)_3$ (1)

wherein X represents an organic group having a glycidyl group and/or an epoxycyclohexyl group and R_2 groups to be plurally present 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;



(2)

wherein R_3 groups to be plurally present represent each 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, and may be the same or different from each other; and m represents the number of repeating units and represents 3 to 200 as an average value; and

$R_4Si(OR_5)_3$ (3)

wherein R_4 represents a methyl group or a phenyl group; R_5 groups to be plurally present 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, and

wherein the block-type siloxane compound has a molecular weight of 800 to 20,000 as weight-average molecular weight measured by GPC.

[Claim 2]

The curable resin composition according to claim 1,

wherein in the hydrolytic condensation between the alkoxy groups of the alkoxysilane compound (a), reactions (I) to (III) shown below take place:

(I) a condensation reaction between the alkoxy groups of the alkoxysilane compound (a) remaining in a system;

(II) a condensation reaction between alkoxy groups of: an alkoxysilane-modified compound (d) obtained in the reaction of the alkoxysilane compound (a) and the silicone oil (b); and the alkoxysilane compound (a); and

(III) a condensation reaction between alkoxy groups of: an alkoxysilane-modified compound (d) obtained in the reaction of the alkoxysilane compound (a) and the silicone oil (b); and a partially condensed compound of the alkoxysilane compound (a) obtained in (I), and

wherein in the hydrolytic condensation between the alkoxy groups of the alkoxysilane compound (a) and the alkoxysilane compound (c), reactions (I)' to (III)' shown below take place:

(I)' a condensation reaction between the alkoxy groups of the alkoxysilane compound (a) and the alkoxysilane compound (c) remaining in a system;

(II)' a condensation reaction between alkoxy groups of: an alkoxysilane-modified compound (d) obtained in the reaction of the alkoxysilane compound (a), the silicone oil (b) and the alkoxysilane compound (c); the alkoxysilane compound (a); and the alkoxysilane compound (c); and

(III)' a condensation reaction between alkoxy groups of: an alkoxysilane-modified compound (d) obtained in the reaction of the alkoxysilane compound (a), the silicone oil (b) and the alkoxysilane compound (c); and a partially condensed compound of the alkoxysilane compound (a) and the alkoxysilane compound (c) obtained in (I)'.

[Claim 3]

The curable resin composition according to claim 1 or 2, which further comprises a polycarboxylic acid (B) having at least two carboxyl groups and having an aliphatic hydrocarbon group as the main skeleton.

[Claim 4]

The curable resin composition according to any one of claims 1 to 3, wherein the zinc salt and/or zinc complex (C) is one selected from the group consisting of zinc salts of one or more acids selected from phosphoric esters and phosphoric acid and zinc complexes having said acid and zinc salt.

[Claim 5]

The curable resin composition according to any one of claims 1 to 3, wherein the zinc salt and/or zinc complex (C) is at least one selected from the group consisting of zinc

salts of carboxylic acids having 1 to 30 carbon atoms and zinc complexes having said acid and zinc salt.

[Claim 6]

The curable resin composition according to any one of claims 3 to 5, wherein the polycarboxylic 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.

[Claim 7]

The curable resin composition according to any one of claims 1 to 6, which comprises an acid anhydride.

[Claim 8]

The curable resin composition according to any one of claims 1 to 7, which comprises a hindered amine photo-stabilizer and/or a phosphorus-containing antioxidant.

[Claim 9]

A cured product obtained by curing the curable resin composition according to any one of claims 1 to 8.