

DESCRIPTION

Title of the Invention: EPOXY RESIN COMPOSITION

5 Technical Field

[0001]

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

10

Background Art

[0002]

Hitherto, as an encapsulating material for optical semiconductor elements of LED products and the like, epoxy resin compositions have been adopted in view of balance between performance and economic efficiency. Particularly, 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, have been widely used.

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

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

[0003]

30 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, it has been pointed out a problem that coloration has occurred on the LED chip and finally illuminance as the LED products has decreased, and also a problem still remains in view of durability (Patent Document 3).

Background Art Documents

Patent Documents

[0004]

5 Patent Document 1: JP-A-9-213997

Patent Document 2: Japanese Patent No. 3618238

Patent Document 3: JP-T-2005-100445

Summary of the Invention

10 Problems that the Invention is to Solve

[0005]

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-
15 modified epoxy resins and the like as representatives, are used as encapsulating resins (Patent Document 3).

In general, it is known that resins to which the siloxane skeleton has been introduced are more stable against heat and light than epoxy resins. Therefore, in the case of application thereof to encapsulating materials for LED products, from the
20 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, a problem that deterioration and coloration of interior
25 constituent members occurs, 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 problem that a silver component (silver plating is
30 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 arises.

In the market, an epoxy resin composition containing a siloxane structure,
35 which has no problem in the above gas permeability resistance has been desired.

Means for Solving the Problems

[0006]

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) An epoxy resin composition comprising an organopolysiloxane (A) and a polycarboxylic acid (B),
wherein the organopolysiloxane (A) and the polycarboxylic acid (B) satisfy the following requirements:
organopolysiloxane (A):
an epoxy resin having at least a glycidyl group and/or an epoxycyclohexyl group in the molecule thereof and
polycarboxylic acid (B):
a polycarboxylic acid having two or more carboxyl groups and having an aliphatic hydrocarbon group as the main skeleton.
- (2) The epoxy resin composition according to the above (1), which contains an acid anhydride (C).
- (3) The epoxy resin composition according to the above (1) or (2),
wherein the polycarboxylic acid 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.
- (4) A cured product obtained by curing the epoxy resin composition according to any one of the above (1), (2), and (3).
- (5) An optical semiconductor device comprising an optical semiconductor element and the cured product according to the above (4).

Effect of the Invention

[0007]

Since the epoxy resin composition of the present invention is excellent in corrosive gas resistance, 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.

Best mode for Carrying Out the Invention

[0008]

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

5 The epoxy resin composition of the present invention comprises an organopolysiloxane (A) and a polycarboxylic acid (B) as essential components.

Feature of the organopolysiloxane (A) is 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.
10 Specific examples thereof include 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.

15 Although the structure of the organopolysiloxane is not particularly limited, 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
20 preferable (hereinafter referred to as block-type siloxane compound (D)).

[0009]

The block-type siloxane compound (D) is not a compound having repeating units in a linear chain as in usual block copolymers but has a three-dimensionally spreading reticular structure in which a silsesquioxane structure is a
25 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.

[0010]

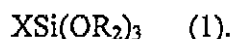
30 The block-type siloxane compound (D) can be, for example, produced using an alkoxysilane compound (a) represented by the formula (1) and a silicone oil (b) represented by the formula (2) as raw materials, as described below. According to need, an alkoxysilane compound (c) represented by the formula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

need). The following will explain individual raw materials in detail.

[0011]

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

5



X in the formula (1) is not particularly limited as long as it is an organic group having an epoxy 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 preferable, and particularly, a β -(3,4-epoxycyclohexyl)ethyl group is preferable.

20

[0012]

R_2 in the formula (1) represents a linear, branched, or cyclic alkyl group having 1 to 10 carbon atoms. Examples thereof include a methyl group, an ethyl group, an n-propyl group, an i-propyl group, an n-butyl group, an i-butyl group, a tert-butyl group, an n-pentyl group, an n-hexyl group, a cyclopentyl group, a cyclohexyl group, and the like. From the viewpoints of reaction conditions such as compatibility and reactivity, a methyl group or an ethyl group is preferred and particularly, a methyl group is preferable.

25

[0013]

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

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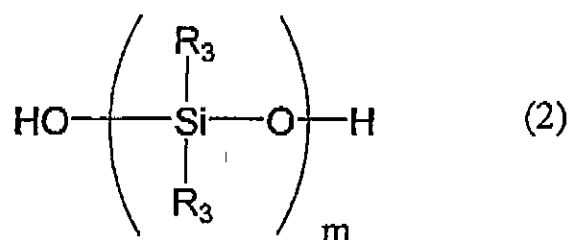
be mentioned below.

[0014]

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):

5

[0015]



[0016]

wherein m represents the number of repeating units.

10

R₃ groups which are plurally present may be the same or different from each other and represent an alkyl group having 1 to 10 carbon atoms, an aryl group having 6 to 14 carbon atoms, or an alkenyl group having 2 to 10 carbon atoms.

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

20

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.

25

From the viewpoints of light resistance and heat resistance, it is preferable that R₃ is a methyl group, a phenyl group, a cyclohexyl group, or an n-propyl group and it is particularly preferable that R₃ is a methyl group or a phenyl group.

[0017]

30

The number m in the compound of the formula (2) represents from 3 to 200 as an average value and is preferably from 3 to 100, more preferably from 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 preferable.

[0018]

5 With regard to the weight-average molecular weight (Mw) of the silicone oil (b), a weight-average molecular weight ranging from 300 to 18,000 (a value measured by gel permeation chromatography (GPC)) are preferable. Of these, in consideration of elastic modulus at low temperature, those having a weight-average molecular weight of 300 to 10,000 are preferable, further, in consideration of
10 compatibility at the preparation of the composition, those having a weight-average molecular weight of 300 to 5,000 are more preferable, and those having a weight-average molecular weight of 500 to 3,000 are particularly preferable. 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
15 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
20 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.

25 Column temperature: 40°C

Used solvent: THF (tetrahydrofuran)

Detector: RI (refractive index detector)

[0019]

The kinematic viscosity of the silicone oil (b) is preferably in the range of
30 from 10 to 200 cSt, more preferably from 30 to 90 cSt. When it is less than 10 cSt, the viscosity of the block-type siloxane compound (D) becomes 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 (D) increases and a trouble on workability tends to occur, so that the cases
35 are not preferable. Here, the kinematic viscosity means a value measured in accordance with JIS Z 8809 using Ubbelohde's viscometer.

[0020]

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

[0021]

The following will describe the alkoxysilane (c), which is used according to need, in detail. The alkoxysilane (c) has a structure of the following formula (3):
20
$$R_4(OR_5)_3 \quad (3)$$
 wherein R_4 represents a methyl group or a phenyl group.

[0022]

R_5 in the formula (3) represents a linear, branched, or cyclic alkyl group having 1 to 10 carbon atoms. Examples thereof include a methyl group, an ethyl
25 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, it is preferable that R_5 is a methyl group or an ethyl group.

[0023]

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

[0024]

35 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 (D), the compatibility at the formation of the composition, and the heat resistance, light resistance, low moisture permeability, low gas permeability, and the like of the cured product.

[0025]

5 In the case where the alkoxysilane (c) is used, the alkoxysilane (c) is used in the range of preferably from 5 to 70% by mol, further preferably from 5 to 50% by mol, and particularly preferably from 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
10 that the case is not preferable.

[0026]

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)
15 of from 1.5 to 200, preferably from 2 to 200, particularly preferably from 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 (D) becomes too hard and thus the objective low elastic modulus properties decrease.

20 [0027]

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

The production process of the block-type siloxane compound (D) preferably includes the following production steps represented by the following (i) and
25 (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)),

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

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

[0028]

As preferable production processes, specifically, the following three kinds
35 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) with the alkoxysilane (a) (and the alkoxysilane (c)), 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)) 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 (D).

<Production process (b)>

The process includes:

first, as the production step (ii), 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)), and

subsequently, as the production step (i), 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 (D).

<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) with the alkoxysilane (a) (and the alkoxysilane (c)) to form an alkoxysilane-modified compound (d), subsequently, water is added into the system and, as the production step (ii), the block-type siloxane compound (D) is produced in one pot by carrying out the hydrolytic condensation reaction between the alkoxy groups of the remaining alkoxysilane (a) (and the alkoxysilane (c)) and the alkoxysilane-modified compound (d).

[0029]

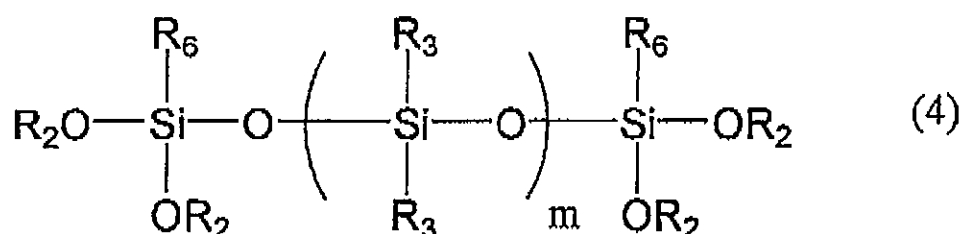
In the present invention, from the viewpoint of shortening the production steps, it is preferable to use the aforementioned production process (c) in which the reactions are sequentially carried out in one pot.

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), namely, 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
 5 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
 10 (b) with the alkoxysilanes (a) and (c) is relatively high. Furthermore, since unreacted low-molecular-weight alkoxysilane is present in a large amount relative to the silanol group, the process is also preferable from the viewpoint of reactivity. In the case of performing the steps in one pot, firstly in the production step (i), the dealcoholization condensation of the silicone oil (b) with the alkoxysilane (a) (and the alkoxysilane (c))
 15 is performed to modify the end of the silicone oil with an alkoxysilyl to obtain 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)
 20 is considered to be present as a structure represented by the following formula (4):

[0030]



[0031]

25 wherein R_2 , R_3 and m have the same meanings as described above and R_6 represents the above X or R_4 .

[0032]

In the production step (i), when the alkoxy group is reacted in a ratio of less than 1.0 equivalent relative to 1 equivalent of the silanol group, the alkoxy group
 30 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 1.0 to 1.5 equivalents of the alkoxy group, two or more alkoxy groups in the alkoxy silane (a) (and the alkoxy silane (c)) 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.

- 5 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 2.0 equivalents or more is preferable.

[0033]

- 10 After finishing the production step (i), the hydrolytic condensation between the alkoxy groups is performed with adding water without further treatment (production step (ii)). Furthermore, in the production step (ii), reactions (I) to (III) shown below take place.

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

- 15 (II) A condensation reaction between the alkoxy groups of the alkoxy silane-modified compound (d) obtained in the production step (i) and the alkoxy silane (a) (and the alkoxy silane (c)).

- (III) A condensation reaction between the alkoxy groups of the alkoxy silane-modified compound (d) obtained in the production step (i) and a partially condensed compound of the alkoxy silane (a) (and the alkoxy silane (c)) formed in (I).

20 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.

- 25 [0034]

- Although the production of the block-type siloxane compound (D) can be performed with no catalyst, since the reaction proceeds only slowly with no catalyst, it is preferable to perform the production in the presence of a catalyst from the viewpoint of shortening the reaction time. As usable catalysts, 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 basic catalysts, 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 can be used. Of these, particularly in view of easy removal of the catalyst from the product, inorganic bases are preferable and particularly, sodium hydroxide and potassium hydroxide are
5 preferable. The amount of the catalyst to be added is usually from 0.001 to 7.5% by weight, preferably from 0.01 to 5% by weight based on the total weight of the alkoxysilane (a) (and the alkoxysilane (c)) 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
10 preferable 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)) occurs unilaterally and the silsesquioxane oligomer formed therefrom and the silicone oil (b) do not solve
15 each other and become turbid.

[0035]

The production of the block-type siloxane compound (D) can be performed without any solvent or in a solvent. Moreover, a solvent can be added during the production step. The solvent to be used is not particularly limited as long
20 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
25 butanoate; alcohols such as methanol, ethanol, propanol and butanol; hydrocarbons 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 preferable and methanol or ethanol is more preferable. Although the amount of the solvent to be used is not particularly limited as long as the amount is in the range
30 wherein the reaction smoothly proceeds, 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 from 20 to 160°C, preferably from 40 to 140°C, and particularly preferably
35 from 50 to 150°C. The reaction time is usually from 1 to 40 hours, preferably from 5 to 30 hours in each production steps.

[0036]

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 preferable to add a solvent separable from water depending on the kind of the solvent used. Examples of preferable solvents may include ketones such as methyl ethyl ketone, methyl isobutyl ketone and cyclopentanone; esters such as ethyl acetate, butyl acetate, ethyl lactate and isopropyl butanoate; hydrocarbons such as hexane, cyclohexane, toluene and xylene; and the like.

[0037]

In the reaction, although the removal of the catalyst may be performed by washing with water alone, since the reaction is carried out under either condition of an acidic condition and a basic condition, it is preferable to perform washing with water after quenching of the reaction by a neutralization reaction or remove an adsorbent by filtration after adsorption of the catalyst 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, 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 can be used. Of these, particularly in view of easy removal from the product, inorganic bases or inorganic acids are preferable and phosphate salts and the like with which pH adjustment to around neutral is easy are further preferable.

[0038]

Examples of the adsorbent include activated clay, active carbon, zeolite, inorganic/organic synthetic absorbents, ion-exchange resins and the like. As specific examples, the following products are 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 addition of the adsorbent 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.

[0039]

After completion of the reaction or quenching, 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. The purification methods may be performed singly or two or more thereof may be performed in combination.

[0040]

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

[0041]

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

[0042]

The appearance of the block-type siloxane compound (D) thus obtained is usually a colorless and transparent liquid having fluidity at 25°C. Moreover, the molecular weight thereof is preferably from 800 to 20,000, more preferably from 1,000

to 10,000, and particularly preferably from 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)) 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 weight-average molecular weight is weight-average molecular weight (Mw) in terms of polystyrene measured under the following conditions using GPC.

10 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

15 Used solvent: THF (tetrahydrofuran)

Detector: RI (refractive index detector)

[0043]

Moreover, the epoxy equivalent (measured by the method described in JIS K-7236) of the block-type siloxane compound (D) is preferably from 300 to 1,600 g/eq, more preferably from 400 to 1,000 g/eq., and particularly from 450 to 900 g/eq.

20 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 which is not preferable.

25 [0044]

The viscosity (E-type viscometer, measured at 25°C) of the block-type siloxane compound (D) is preferably from 50 to 20,000 mPa.s, more preferably from 500 to 10,000 mPa.s, and particularly preferably from 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.

30 [0045]

The ratio of the silicon atom bonded to three oxygen atoms, which is derived from the silsesquioxane in the block-type siloxane compound (D), to the whole silicon atoms is preferably from 5 to 50% by mol, more preferably from 8 to

35

30% by mol, and particularly preferably from 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 which is not preferable. In this connection, the ratio can be determined by an equivalent ratio of the alkoxysilane (a) (and the alkoxysilane (c)) to the silicone oil (b).

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

[0046]

Feature of the polycarboxylic acid (B) is that it has at least two or more carboxyl groups and has an aliphatic hydrocarbon group as a main skeleton.

As the polycarboxylic acid (B), a difunctional to hexafunctional carboxylic acid is preferable, 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 preferable. Furthermore, a polycarboxylic acid in which the acid anhydride is a saturated aliphatic cyclic acid anhydride is preferable.

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

[0047]

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

norbornenediol are more preferable.

[0048]

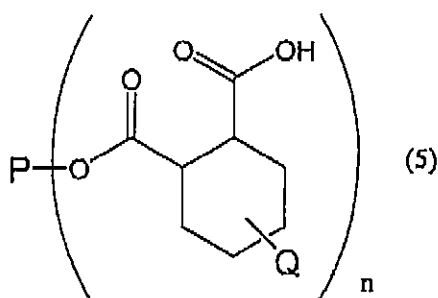
As the acid anhydride, methyltetrahydrophthalic anhydride, methylnad-
ic anhydride, nadic anhydride, hexahydrophthalic anhydride, methylhexahydrophthalic
anhydride, butanetetracarboxylic anhydride, bicyclo[2,2,1]heptane-2,3-dicarboxylic
anhydride, methylbicyclo[2,2,1]heptane-2,3-dicarboxylic anhydride, cyclohexane-
1,3,4-tricarboxylic-3,4-anhydride and the like are preferable. Of these,
methylhexahydrophthalic anhydride and cyclohexane-1,3,4-tricarboxylic-3,4-
anhydride are preferable.

The conditions for the addition reaction are not particularly designated.
As one specific reaction condition, 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 is mentioned. However, the conditions are not limited to the
reaction condition.

[0049]

As the polycarboxylic acid (B), a compound represented by the following
formula (5):

[0050]



wherein Q which is plurally present is at least one of a hydrogen atom, a methyl group
and a carboxyl group; P is a linear, branched, or cyclic aliphatic group having 2 to 20
carbon atoms, which is derived from the aforementioned polyhydric alcohol; n is the
number of valency of the polyhydric alcohol is particularly preferable.

[0051]

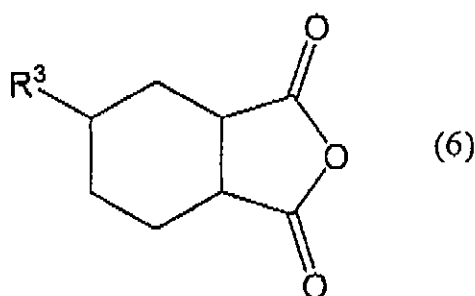
The epoxy resin composition of the present invention preferably contains
an acid anhydride (C). Examples of the acid anhydride (C) specifically include acid
anhydrides such as phthalic anhydride, trimellitic anhydride, pyromellitic anhydride,
maleic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic 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 preferable.

Hexahydrophthalic anhydride, methylhexahydrophthalic anhydride and cyclohexane-1,3,4-tricarboxylic-3,4-anhydride, which are represented by the following formula (6):

[0052]



wherein R^3 represents at least one selected from a hydrogen atom, a methyl group and a carboxyl group, are particularly preferable. Of these, methylhexahydrophthalic anhydride and cyclohexane-1,3,4-tricarboxylic-3,4-anhydride are preferable.

[0053]

In the case wherein the acid anhydride (C) is used, the ratio thereof to be used to the polycarboxylic acid (B) is preferably in the following range.

$$W1/(W1+W2) = 0.05 \text{ to } 0.70$$

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

W2 represents part(s) by weight of the acid anhydride blended. The range of

$W1/(W1+W2)$ is more preferably from 0.05 to 0.60, further preferably from 0.10 to

0.55, and particularly preferably from 0.15 to 0.4. 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 preferable. When the ratio exceeds 0.70, the viscosity becomes

high and handling becomes difficult.

[0054]

The epoxy resin composition of the present invention contains the organopolysiloxane (A) as an epoxy resin and the polycarboxylic acid (B) as a curing agent as essential components and further the acid anhydride (C) as an optional
5 component. Furthermore, the other epoxy resin, and the other curing agent may be included.

[0055]

In the case where the other epoxy resin is used in combination, it is preferable that the ratio of the epoxy resin of the present invention in the whole epoxy
10 resin is 60% by weight or more and it is particularly preferable that the epoxy resin of the present invention in the whole epoxy resin is 70% by weight or more.

[0056]

Examples of usable other epoxy resins include novolak-type epoxy resins, bisphenol A-type epoxy resins, biphenyl-type epoxy resins, triphenylmethane-type
15 epoxy resins, phenolalkyl-type epoxy resins and the like. Specifically, solid or liquid epoxy resins such as 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-
20 substituted phenols, naphthol, alkyl-substituted naphthols, dihydroxybenzene, dihydroxynaphthalene, *etc.*) with formaldehyde, acetaldehyde, bezaldehyde, p-hydroxybenzaldehyde, o-hydroxybenzaldehyde, p-hydroxyacetophenone, o-hydroxyacetophenone, dicyclopentadiene, furfural, 4,4'-bis(chloromethyl)-1,1'-biphenyl, 4,4'-bis(methoxymethyl)-1,1'-biphenyl, 1,4-bis(chloromethyl)benzene, 1,4-
25 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, and glycidyl ester-based epoxy resins are mentioned. However, the epoxy resins are not limited thereto. They may be used singly or two or more thereof may be used in
30 combination.

[0057]

Particularly, it is mainly purposed that the epoxy 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 thereof with alicyclic epoxy resins is preferable. In
35 the case of the alicyclic epoxy resins, compounds having an epoxycyclohexane

structure in the skeleton are preferable, and epoxy resins obtained by oxidation reaction of compounds having a cyclohexene structure are particularly preferable.

Examples of the epoxy resins include those obtained by oxidation of compounds that can be produced by the esterification reaction of
5 cyclohexenecarboxylic acid with alcohols or the esterification reaction of cyclohexenemethanol with carboxylic acids (procedures described in Tetrahedron vol. 36 p.2409 (1980), Tetrahedron Letter p.4475 (1980) and the like), or the Tishchenko reaction of cyclohexenealdehyde (procedures described in JP-A-2003-170059, JP-A-2004-262871 and the like), or further the ester-exchange reaction of
10 cyclohexenecarboxylate esters (procedures described in JP-A-2006-052187 and the like).

Although the alcohols are not particularly limited as long as they are compounds having an alcoholic hydroxyl group, examples thereof include diols such as ethylene glycol, propylene glycol, 1,3-propanediol, 1,2-butanediol, 1,4-butanediol,
15 1,5-pentanediol, 1,6-hexanediol, cyclohexanedimethanol, 2,4-diethylpentanediol, 2-ethyl-2-butyl-1,3-propanediol, neopentyl glycol, tricyclodecanedimethanol and norbornenediol; triols such as glycerin, trimethylolpropane, trimethylolbutane, and 2-hydroxymethyl-1,4-butanediol; tetraols such as pentaerythritol and ditrimethylolpropane; and the like. Although examples of the
20 carboxylic acids include oxalic acid, maleic acid, fumaric acid, phthalic acid, isophthalic acid, adipic acid, cyclohexanedicarboxylic acid and the like, the acids are not limited thereto.

[0058]

Furthermore, acetal compounds obtained by the acetalization reaction of
25 cyclohexenealdehyde derivatives with alcohol compounds are described.

Although specific examples of the 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
30 they are not limited thereto (Reference Literature: Sosetsu Epokisi Jyushi Kiso-hen I p76-85).

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

[0059]

35 As the curing agent component, in the case of the combined use with the other curing agent, it is preferable that the ratio of the total weight of the

polycarboxylic acid compound (B) and the acid anhydride (C) in the whole curing agent is 30% by weight or more and it is particularly preferable that the ratio of the total weight of the polycarboxylic acid compound (B) and the acid anhydride (C) in the whole curing agent 40% by weight or more.

- 5 Examples of the other curing agent 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
10 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, methyl nadic
15 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,
20 bisphenol S, fluorene bisphenol, terpene diphenol, 4,4'-biphenol, 2,2'-biphenol, 3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'-diol, hydroquinone, resorcin, naphthalenediol, tris-(4-hydroxyphenyl)methane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, polycondensates of phenols (phenol, alkyl-substituted phenols, naphthol, alkyl-substituted naphthols, dihydroxybenzene, dihydroxynaphthalene, *etc.*) with
25 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
30 bisphenols such as tetrabromobisphenol A, condensates of terpenes with phenols), others (imidazole, trifluoroborane-amine complexes, guanidine derivatives, *etc.*) and the like. However, they are not limited thereto. They may be used singly or two or more thereof may be used.

[0060]

- 35 In the epoxy resin composition of the present invention, the blending ratio of the curing agent component to the epoxy resin is preferably 0.7 to 1.2 equivalents

relative to 1 equivalent of the epoxy group of the total epoxy resins. 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 it is cured are not obtained in both cases.

5 [0061]

In the epoxy resin composition of the present invention, a curing catalyst may be used together with the curing agent. Specific examples of usable curing accelerators include various imidazoles such as 2-methylimidazole, 2-phenylimidazole, 2-undecylimidazole, 2-heptadecylimidazole, 2-phenyl-4-methylimidazole, 1-benzyl-2-phenylimidazole, 1-benzyl-2-methylimidazole, 1-cyanoethyl-2-methylimidazole, 1-cyanoethyl-2-phenylimidazole, 1-cyanoethyl-2-undecylimidazole, 2,4-diamino-6(2'-methylimidazole(1'))ethyl-s-triazine, 2,4-diamino-6(2'-undecylimidazole(1'))ethyl-s-triazine, 2,4-diamino-6(2'-ethyl, 4-methylimidazole(1'))ethyl-s-triazine, 2,4-diamino-6(2'-methylimidazole(1'))ethyl-s-triazine-isocyanuric acid adduct, 2:3 adduct of 2-methylimidazole isocyanuric acid, 2-phenylimidazole isocyanuric acid adduct, 2-phenyl-3,5-dihydroxymethylimidazole, 2-phenyl-4-hydroxymethyl-5-methylimidazole and 1-cyanoethyl-2-phenyl-3,5-dicyanoethoxymethylimidazole, and salts of the imidazoles with polycarboxylic acids such as phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, pyromellitic acid, naphthalenedicarboxylic acid, maleic acid and oxalic acid, amides such as dicyandiamide, diaza compounds such as 1,8-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 triphenylphosphine, tri(toluy)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 catalysts obtained by microcapsulation of these curing catalysts, and the like. The curing catalyst to be used is appropriately selected depending on the properties required for the resulting transparent resin composition, such as transparency, a curing rate, and working conditions. The curing catalyst is used in the range of usually 0.001 to 15 parts by weight based on 100 parts by weight of the epoxy resin.

[0062]

35 In the epoxy resin composition of the present invention, it is also possible to include a phosphorus-containing compound as a flame retardancy-imparting

component. The phosphorus-containing compound may be reaction type one or addition type one. Specific examples of the phosphorus-containing compound include phosphate esters such as trimethyl phosphate, triethyl phosphate, tricresyl phosphate, trixylylenyl phosphate, cresyl diphenyl phosphate, cresyl-2,6-dixylylenyl phosphate, 1,3-phenylenebis(dixylylenyl phosphate), 1,4-phenylenebis(dixylylenyl phosphate) and 4,4'-biphenyl(dixylylenyl phosphate); phosphanes such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide and 10(2,5-dihydroxyphenyl)-10H-9-oxa-10-phosphaphenanthrene-10-oxide; phosphorus-containing epoxy compounds obtained by reacting an epoxy resin with active hydrogen of the phosphanes, red phosphorus and the like. The phosphate esters, the phosphanes, or phosphorus-containing epoxy compounds are preferable, and 1,3-phenylenebis(dixylylenyl phosphate), 1,4-phenylenebis(dixylylenyl phosphate), 4,4'-biphenyl(dixylylenyl phosphate) or a phosphorus-containing epoxy compound is particularly preferable. The content of the phosphorus-containing compound is preferably as follows:
phosphorus-containing compound/total epoxy resins = 0.1 to 0.6 (weight ratio).
When the content is 0.1 or less, 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 products are adversely affected.

[0063]

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

[0064]

To the epoxy resin composition of the present invention, an inorganic filler can be added according to need. Although examples of the inorganic filler include 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, the filler is not limited thereto. The fillers may be used singly or two or more thereof may be used. With regard to the content of the inorganic filler, an

amount of from 0 to 95% by weight is used in the epoxy resin composition of the present invention. Furthermore, to the epoxy 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.

[0065]

In the case where the epoxy 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 preferable 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.

[0066]

In the case where the epoxy 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 need. 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 dispersion the phosphor in the epoxy 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, examples thereof include phosphors such as YAG phosphors, TAG phosphors, orthosilicate phosphors, thiogallate phosphors, and sulfide phosphors, and $\text{YAlO}_3\text{:Ce}$, $\text{Y}_3\text{Al}_5\text{O}_{12}\text{:Ce}$, $\text{Y}_4\text{Al}_2\text{O}_9\text{:Ce}$, $\text{Y}_2\text{O}_2\text{S:Eu}$, $\text{Sr}_5(\text{PO}_4)_3\text{Cl:Eu}$, $(\text{SrEu})\text{O}\cdot\text{Al}_2\text{O}_3$ and the like. As the particle diameter of such phosphors, although those having a known particle diameter in this field are used, the average particle diameter is preferably from 1 to 250 μm and particularly preferably from 2 to 50 μm . In the case of using these phosphors, the amount of them to be added is from 1 to 80 parts by weight and preferably from 5 to 60 parts by weight based on 100 parts by weight of the resin component.

[0067]

In the case where the epoxy 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.

[0068]

The epoxy resin composition of the present invention as an optical material, particularly an optical semiconductor encapsulating agent, for the purpose of coloring prevention, possibly include an amine compound as a photo-stabilizer and a phosphorus-based compound and a phenol compound as an antioxidant.

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-undecanoxo-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-piperidiny-methacrylate, bis(1,2,2,6,6-pentamethyl-4-piperidiny) [[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]methyl]butylmalonate, decanedioic acid bis(2,2,6,6-tetramethyl-1(octyloxy)-4-piperidiny) 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-piperidiny)-dodecyl ester/tetradecyl ester, N-acetyl-

3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidiny)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 acidm, [(4-methoxyphenyl)-methylene]-bis(1,2,2,6,6-pentamethyl-4-piperidiny) ester, higher fatty acid esters of 2,2,6,6-tetramethyl-4-piperidinol, 1,3-benzenedicarboxamide and N,N'-bis(2,2,6,6-tetramethyl-4-piperidiny); benzophenone-based compounds such as octabenzene; benzotriazole-based compounds such as 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol, 2-(2-hydroxy-5-methylphenyl)benzotriazole, 2-[2-hydroxy-3-(3,4,5,6-tetrahydrophthalimido-metyl)-5-methylphenyl]benzotriazole, 2-(3-tert-butyl-2-hydroxy-5-methylphenyl)-5-chlorobenzotriazole, 2-(2-hydroxy-3,5-di-tert-pentylphenyl)benzotriazole, a reaction product of methyl 3-(3-(2H-benzotriazol-2-yl)-5-tert-butyl-4-hydroxyphenyl)propionate with polyethylene glycol, and 2-(2H-benzotriazol-2-yl)-6-dodecyl-4-methylphenol; benzoate-based compounds such as 2,4-di-tert-butylphenyl-3,5-di-tert-butyl-4-hydroxybenzoate; triazine-based compounds such as 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-[(hexyl)oxy]phenol; and the like.

Hindered amine-based compounds are particularly preferable.

[0069]

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

Commercially available amine-based compounds are not particularly limited and examples thereof include TINUVIN 765, TINUVIN 770DF, TINUVIN 144, TINUVIN 123, TINUVIN 622LD, TINUVIN 152, CHIMASSORB 944 as 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.

[0070]

The phosphorus-based compound is not particularly limited and examples thereof include 1,1,3-tris(2-methyl-4-ditridecylphosphite-5-tert-butylphenyl)butane, distearyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl) pentaerythritol diphosphite, phenylbisphenol A pentaerythritol diphosphite, dicyclohexyl pentaerythritol diphosphite, tris(diethylphenyl) phosphite, tris(di-isopropylphenyl) phosphite, tris(di-n-butylphenyl) phosphite, tris(2,4-di-tert-butylphenyl) phosphite, tris(2,6-di-tert-butylphenyl) phosphite, tris(2,6-di-tert-butylphenyl) phosphite, 2,2'-methylenebis(4,6-di-tert-butylphenyl) (2,4-di-tert-butylphenyl) phosphite, 2,2'-methylenebis(4,6-di-tert-

butylphenyl) (2-tert-butyl-4-methylphenyl) phosphite, 2,2'-methylenebis(4-methyl-6-tert-butylphenyl) (2-tert-butyl-4-methylphenyl) phosphite, 2,2'-ethylidenebis(4-methyl-6-tert-butylphenyl) (2-tert-butyl-4-methylphenyl) phosphite, tetrakis(2,4-di-tert-butylphenyl)-4,4'-biphenylene 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-phenylphenylphosphonite, bis(2,4-di-tert-butylphenyl)-3-phenylphenylphosphonite, bis(2,6-di-n-butylphenyl)-3-phenylphenylphosphonite, bis(2,6-di-tert-butylphenyl)-4-phenylphenylphosphonite, bis(2,6-di-tert-butylphenyl)-3-phenylphenylphosphonite, 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.

[0071]

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

The commercially available products are not particularly limited and for example, as those manufactured by Adeka Corporation include 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, ADEKA STAB TPP and the like.

[0072]

The phenol compound is not particularly limited and examples thereof include 2,6-di-tert-butyl-4-methylphenol, n-octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, tetrakis[methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]methane, 2,4-di-tert-butyl-6-methylphenol, 1,6-hexanediol-bis-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-isocyanurate, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, pentaerythritol-tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 3,9-bis-[2-[3-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionyloxy]-1,1-dimethylethyl]-2,4,8,10-tetraoxaspiro[5,5]undecane, triethylene glycol-bis[3-(3-tert-butyl-5-methyl-4-hydroxyphenyl)propionate], 2,2'-butylidenebis(4,6-

di-tert-butylphenol), 4,4'-butylidenebis(3-methyl-6-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 2,2'-methylenebis(4-ethyl-6-tert-butylphenol), 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenol acrylate, 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate, 4,4'-thiobis(3-methyl-6-tert-butylphenol), 4,4'-butylidenebis(3-methyl-6-tert-butylphenol), 2-tert-butyl-4-methylphenol, 2,4-di-tert-butylphenol, 2,4-di-tert-pentylphenol, 4,4'-thiobis(3-methyl-6-tert-butylphenol), 4,4'-butylidenebis(3-methyl-6-tert-butylphenol), bis[3,3-bis-(4'-hydroxy-3'-tert-butylphenyl)butanoic acid]-glycol ester, 2,4-di-tert-butylphenol, 2,4-di-tert-pentylphenol, 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate, bis[3,3-bis-(4'-hydroxy-3'-tert-butylphenyl)butanoic acid]-glycol ester and the like.

[0073]

As the phenol-based compounds, commercially available products can be also used. The commercially available phenol-based compound is not particularly limited and examples thereof include IRGANOX 1010, IRGANOX 1035, IRGANOX 1076, IRGANOX 1135, IRGANOX 245, IRGANOX 259, IRGANOX 295, IRGANOX 3114 IRGANOX 1098, IRGANOX 1520L as 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.

[0074]

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.

[0075]

It is preferable to include at least one of the above phosphorus-based compound, amine compound, and phenol-based compound. The amount thereof to be blended is not particularly limited and it can be included in an amount of 0.005 to 5.0% by weight based on the epoxy resin composition of the present invention.

[0076]

The epoxy resin composition of the present invention is obtained by mixing individual components homogeneously. The epoxy 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 epoxy resin
5 composition can be obtained by thoroughly mixing the epoxy resin component, the curing agent component, and, if necessary, the curing accelerator, the phosphorus-containing compound, the binder resin, the inorganic filler, the blending agents, and the like 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 epoxy
10 resin composition is liquid, the cured product can be formed by potting or casting the composition, impregnating a substrate therewith, or injecting the epoxy resin composition into a mold, and then curing it by heating. Moreover, in the case where the epoxy resin 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
15 and further curing it by heating. The curing temperature and time are 80 to 200°C and 2 to 10 hours. As the curing method, although it is possible to harden it at once at high temperature, 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,
20 it is preferable to elevate the temperature with dividing the temperature elevation step into from 2 to 8 stages, more preferably from 2 to 4 stages.

[0077]

Moreover, a cured product of the epoxy resin composition of the present invention can be formed by dissolving the epoxy resin composition of the present
25 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
30 resulting prepreg to hot pressing. The solvent at the time is used in an amount of usually from 10 to 70% by weight, preferably from 15 to 70% by weight in the mixture of the epoxy resin composition of the present invention and the solvent. Moreover, an epoxy resin cured product containing carbon fiber can be also obtained by RTM method using the liquid composition itself.

35 [0078]

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

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

[0079]

In the case where the epoxy 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 epoxy resin composition is prepared by thoroughly mixing the epoxy resin, the curing agent, the coupling agent, the antioxidant, and additives such as the photo-stabilizer and used as the encapsulating material or both of the die-bonding material and the encapsulating material. 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.

[0080]

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 frame, a heat sink or a package using an adhesive (die-bonding material). There is a type where a wire such as a gold wire is connected for conducting an electric current. The semiconductor chip is encapsulated with an encapsulating material such as an epoxy resin for protecting the semiconductor chip from heat and moisture and playing a role of lens function. The epoxy 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 epoxy resin composition of the present invention as both of the die-bonding material and the encapsulating material.

[0081]

As a method of adhering the semiconductor chip to the substrate using the epoxy resin composition of the present invention, there may be mentioned a method of placing the semiconductor chip on the epoxy resin composition of the present invention and performing heat curing after applying the epoxy resin composition 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.

[0082]

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

[0083]

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

Examples of an injection method include a dispenser, a transfer molding, injection molding or the like.

For heating, a method of hot-air circulation, infrared ray, high frequency wave or the like can be used. As heating conditions, for example, conditions of from 80 to 230°C and about from 1 minute to 24 hours are preferable. For the purpose of reducing internal stress to be generated in heat curing, for example, pre-cure can be performed at from 80 to 120°C for from 30 minutes to 5 hours and then after-cure can be performed under conditions of from 120 to 180°C and from 30 minutes to 10 hours.

[0084]

Furthermore, there may be mentioned 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.

[0085]

Examples of the adhesives include, in addition to adhesives for civil
5 engineering, architecture, automobiles, general office works and medical uses,
adhesives for electronic materials. 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 and the like,
underfill for BGA reinforcement, anisotropic conductive films (ACF), adhesives for
10 mounting such as anisotropic conductive pastes (ACP) and the like.

[0086]

Examples of the encapsulating materials include 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,
15 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.

[0087]

The cured product obtained in the present invention can be used in various
uses including optical parts materials. The optical materials means general materials
20 to be used in uses wherein light such as visible light, infrared ray, ultraviolet ray, X-ray
or laser passes through the materials. 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, phase plates, viewing
25 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
30 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, phase plate, viewing angle
correction films, adhesives and polarizer protective films in plasma address liquid
crystal (PALC) displays; protective films of front glass, front glass substituting
35 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.

5 [0088]

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

10 the like for projection television. 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,

15 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,

20 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, bearing retainers, gear parts, corrosion-resistant coatings, switch parts, headlamps, parts in engines, electrical components, various interior and exterior equipments, driving engines, brake oil tanks, rustproof steel plates for automobiles, interior panels, interior materials, protective/bonding wire harness, fuel hoses,

30 automobile lamps and glass substitutes. Moreover, they may be double-glazed 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, they may be

35 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.

5 [0089]

Examples of the encapsulating materials include 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 BGA and CSP (including underfill for reinforcement) and the like.

[0090]

Examples of the other uses of the optical material include general uses wherein epoxy resin compositions are used. For example, they may be adhesives, paints, coating agents, molding materials (including sheets, films, FRP and the like),
15 insulating materials (including printed boards, electric wire coverings, etc.), encapsulating agents, and also additives for other resins and the like. 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
20 mentioned interlayer adhesives of multilayer substrates such as build-up substrates, die-bonding agents, semiconductor adhesives such as underfill and the like, underfill for BGA reinforcement, anisotropic conductive films (ACF), adhesives for mounting such as anisotropic conductive pastes (ACP) and the like.

25 Examples

[0091]

The following will describe the present invention further in detail with reference to Synthetic Examples and Examples. In this connection, the present invention is not limited to these Synthetic Examples and Examples. In the
30 Description, parts, %, ratios, and the like are all on the basis of weight without specific annotation. 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 GPC method.

35 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)

5 Detector: RI (refractive index detector)

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

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

[0092]

10 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 1,700 (value measured on GPC) (silanol equivalent of 850, calculated as a half of the weight-average molecular weight measured using GPC), and 18 parts of a 0.5% potassium hydroxide (KOH) methanol solution 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 addition of 305 parts of methanol, 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 completion of the reaction, 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 for 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 729 g/eq; weight-average molecular weight was 2,200; and the appearance was colorless and transparent.

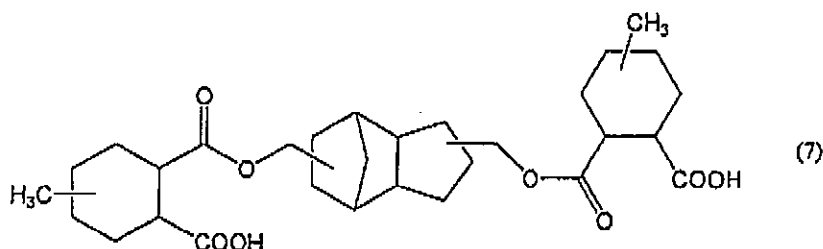
30 [0093]

Synthetic Example 2

In a flask equipped with a stirrer, a reflux condenser and a stirring apparatus, 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 (C-1)) were added with performing nitrogen purging. After carrying out a reaction at 40°C for 3 hours,

heating and stirring were performed at 70°C for 1 hour and disappearance (1 area % or less) of tricyclodecanedimethanol was confirmed by GPC.) to obtain 120 parts of a curing agent composition (H-1) containing a polycarboxylic acid (B-1) and the acid anhydride (C-1). The obtained one 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 methylhexahydrophthalic anhydride was 45 area %. Moreover, functional group equivalent was 201 g/eq.

[0094]

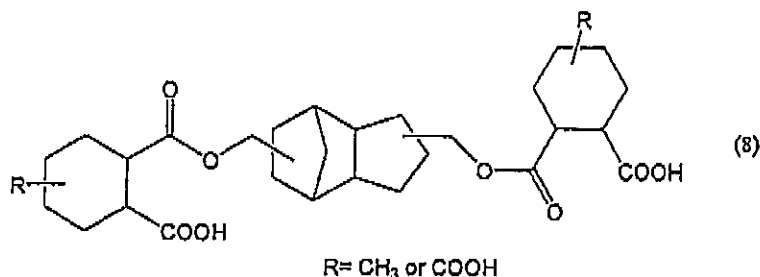


[0095]

Synthetic Example 3

In a flask equipped with a stirrer, a reflux condenser and a stirring apparatus, 15 parts of tricyclodecanedimethanol, 70 parts of the acid anhydride (C-1), and 15 parts of cyclohexane-1,2,4-tricarboxylic-1,2-anhydride (H-TMA_n, manufactured by Mitsubishi Gas Chemical Co., Inc., hereinafter referred to as acid anhydride (C-2)) were added with performing nitrogen purging. After carrying out a reaction 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 100 parts of a curing agent composition (H-2) containing a polycarboxylic acid (B-2) and the acid anhydride (C-2). The obtained one was a colorless liquid resin and, with regard to purity by GPC, the polycarboxylic acid (B-2; the following formula (8)) was 37 area %; the acid anhydride (C-2) was 11 area %; and the acid anhydride (C-1) was 52 area %. Moreover, functional group equivalent was 171 g/eq.

[0096]



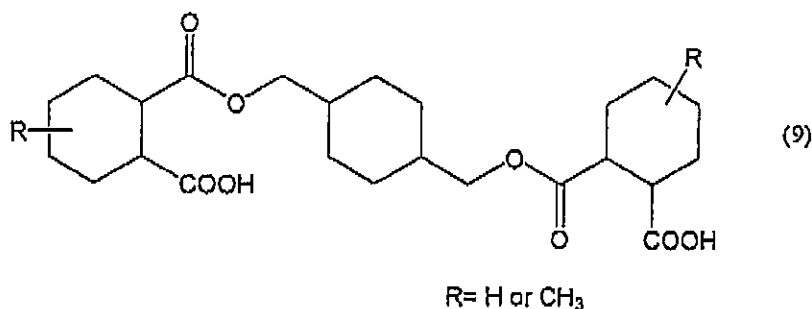
[0097]

Synthetic Example 4

In a flask equipped with a stirrer, a reflux condenser and a stirring apparatus, 20 parts of 1,4-cyclohexanedimethanol and 100 parts of a mixture of methylhexahydrophthalic anhydride and hexahydrophthalic anhydride (RIKACID MH-700, manufactured by New Japan Chemical Co., Ltd., hereinafter referred to as acid anhydride C-3) were added with performing nitrogen purging. After carrying out a reaction at 40°C for 3 hours, heating and stirring were performed at 70°C for 1 hour (disappearance (1 area % or less) of 1,4-cyclohexanedimethanol was confirmed by GPC) to obtain 120 parts of a curing agent composition (H-3) containing a polycarboxylic acid (B-3) and the acid anhydride (C-3). The obtained one was a colorless liquid resin and, with regard to purity by GPC, the polycarboxylic acid (B-3; the following formula (9)) was 57 area % and the acid anhydride (C-3) was 43 area %.

Moreover, functional group equivalent was 200 g/eq.

[0098]



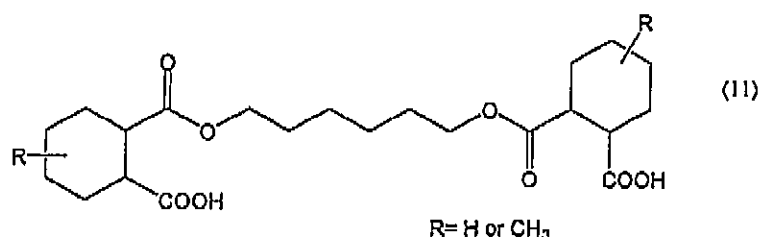
[0099]

Synthetic Example 5

In a flask equipped with a stirrer, a reflux condenser and a stirring apparatus, 20 parts of 1,6-hexanediol and 100 parts of the acid anhydride (C-3) were added with performing nitrogen purging. After carrying out a reaction at 40°C for 3 hours, heating and stirring were performed at 70°C for 1 hour (disappearance (1

area % or less) of 1,6-hexanediol was confirmed by GPC) to obtain 120 parts of a curing agent composition (H-4) containing a polycarboxylic acid (B-4) and the acid anhydride (C-3). The obtained one was a colorless liquid resin and, with regard to purity by GPC, the polycarboxylic acid (B-4; the following formula (11)) was 65 area % and the acid anhydride (C-3) was 35 area %. Moreover, functional group equivalent was 200 g/eq.

[0100]

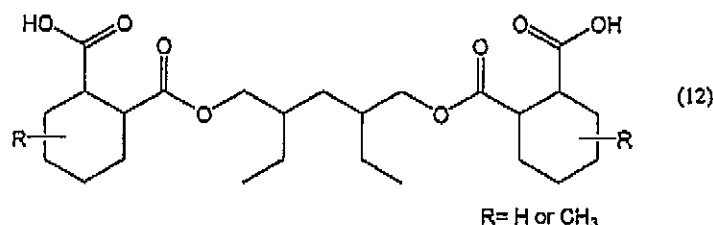


[0101]

Synthetic Example 6

Into a flask equipped with a stirrer, a reflux condenser and a stirring apparatus, 20 parts of 2,4-diethylpentanediol and 100 parts of the acid anhydride (C-3) were added with performing nitrogen purging. After carrying out a reaction 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 (H-5) containing a polycarboxylic acid (B-5) and the acid anhydride (C-3). The obtained one was a colorless liquid resin and, with regard to purity by GPC, the polycarboxylic acid (B-5; the following formula (12)) was 50 area % and the acid anhydride (C-3) was 50 area %. Moreover, functional group equivalent was 201 g/eq.

[0102]



[0103]

Examples 1, 2, 3, 4, 5, and Comparative Example 1

Using the organopolysiloxane compound (A-1) obtained in Synthetic Example 1 as an epoxy resin, a curing agent composition (H-1), (H-2), (H-3), (H-4) (H-5) obtained in Synthetic Examples 2, 3, 4, 5, 6 as a curing agent for Examples, an acid anhydride (C-3) as a curing agent for Comparative Example, and a curing accelerator (Hishicallin PX4MP manufactured by Nippon Chemical Industrial Co., Ltd., hereinafter referred to as catalyst I-1) as a curing accelerator, they were blended in blending ratios shown in the following Table 1 and defoaming was performed for 20 minutes to obtain epoxy resin compositions of the present invention or for comparison.

[0104]

(Corrosive gas permeation test)

Using the obtained epoxy resin compositions, it was filled into a syringe and injected into a surface-mounted LED package having 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. The results are shown in Table 1.

[0105]

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 which is present inside the LED package to black (called blackening) was observed and the LED package requiring longer color change time is judged to be more excellent in corrosive gas resistance.

The observation was performed by taking out the package after 10 minutes, after 30 minutes, after 1 hour, and after 2 hours. Evaluation was as follows:

a package exhibiting no discoloration was evaluated as ○, a package colored into light brown to brown was evaluated as ×, and a package completely blackened was evaluated as ××.

[0106]

5 [Table 1]

			Examples					Comparative Example
			1	2	3	4	5	1
Composition	Epoxy resin	A-1	7.3	7.3	7.3	7.3	7.3	7.3
	Curing agent	H-1	2.0					
		H-2		1.7				
		H-3			2.0			
		H-4				2.0		
		H-5					2.0	
		C-3						1.7
	Curing catalyst	I-1	0.04	0.04	0.04	0.04	0.04	0.04
Discoloration time of lead frame		10 minutes	○	○	○	○	○	○
		30 minutes	○	○	○	○	○	×
		1 hour	○	○	○	○	○	×
		2 hours	○	○	○	○	○	××

[0107]

From the above results, it becomes obvious that the epoxy resin composition of the present invention (composition containing the organopolysiloxane compound and the polycarboxylic acid) does not discolor the silver plating of the lead frame as compared with the epoxy resin composition of Comparative Example (containing the siloxane compound and the acid anhydride). Therefore, the composition of the present invention is excellent in corrosive gas resistance.

[0108]

While the present 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. 2009-256810 filed on November 10, 2009, and the whole contents are incorporated by reference. Also, all the references cited herein are incorporated herein by reference as a whole.

Claims

1. An epoxy resin composition comprising an organopolysiloxane (A)
and a polycarboxylic acid (B),
5 wherein
the organopolysiloxane (A) is an epoxy resin having at least a glycidyl
group and/or an epoxycyclohexyl group in the molecule thereof and
the polycarboxylic acid (B) is a polycarboxylic acid having at least two or
more carboxyl groups and having an aliphatic hydrocarbon group as the main skeleton.
10
2. The epoxy resin composition according to claim 1, which contains an
acid anhydride (C).
3. The epoxy resin composition according to claim 1 or 2, wherein the
15 polycarboxylic acid 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.
4. A cured product obtained by curing the epoxy resin composition
20 according to any one of claims 1 to 3.
5. An optical semiconductor device comprising an optical
semiconductor element and the cured product according to claim 4.