

DESCRIPTION

Title of Invention:

CARBOXYLIC ACID COMPOUND AND EPOXY RESIN COMPOSITION
CONTAINING THE SAME

Technical Field

[0001]

The present invention relates to a carboxylic acid compound and a resin composition containing the same. More particularly, it relates to a carboxylic acid compound useful as a raw material or modifier for epoxy resin curing agents, paints, adhesives, molded articles, optical materials, semiconductors, encapsulating resins for optical semiconductors, resins for die-bonding materials of optical semiconductors, polyimide resins, and the like, a plasticizer, a lubricating oil raw material, an intermediate for medicaments and pesticides, a raw material for resins for paints, a resin for toner, and the like, and an epoxy resin composition containing the same.

Background Art

[0002]

Since cured products excellent in adhesiveness, mechanical properties, water resistance, chemical resistance, heat resistance, electric properties, and the like are obtained by curing epoxy resins, the resins have been used in wide range of fields such as paints, adhesives, composite materials, molding materials, casting materials, various coating materials, and resists. As the curing agents for use in the epoxy resins, for example, amine compounds, carboxylic acid compounds, carboxylic anhydrides, phenol compounds, thiol compounds, and the like are mentioned as common ones. Among these curing agents, various carboxylic acid compounds and carboxylic anhydrides have been frequently used in the use applications in the case where high transparency and heat resistance are required for the cured products or in the case where an appropriate usable period of time is needed. Particularly in liquid compositions, it becomes common to use liquid carboxylic anhydrides as the curing agents. Since a carboxylic acid exhibits a strong intermolecular hydrogen bond and not only it crystallizes but also the compatibility to other resins is extremely poor, it is an actual situation that its use is avoided.

[0003]

As resins for encapsulation of optical semiconductors such as LED (Light Emitting Diode), liquid epoxy resin compositions using a bisphenol-type epoxy resin, an alicyclic epoxy resin, or the like have been used since they are excellent in mechanical strength and adhesive force (see Patent Document 1). Recently, LED has been employed

in the fields where high luminance is required, e.g., headlamps for automobiles and lighting uses. Accordingly, UV resistance and heat resistance have been particularly required for the resins for encapsulating optical semiconductors. However, it is difficult to say that the bisphenol-type epoxy resins, the alicyclic epoxy resins, and the like are sufficient in UV resistance and heat resistance, and hence they cannot be used in some cases in the fields where high luminance is required. Thus, as encapsulating materials having high UV resistance and heat resistance, silicone resin encapsulating materials using an organopolysiloxane containing a non-covalent bonding group and an organohydrogenpolysiloxane have been employed (see Patent Document 2). However, the encapsulating materials using such silicone resins are excellent in UV resistance and heat resistance but they have problems that adhesiveness to base materials is low and the encapsulated surface is sticky. In order to solve these problems, encapsulating materials having excellent UV resistance and heat resistance and good adhesiveness are required and have been developed using a condensate of a silicon compound having an epoxy group and a liquid acid anhydride (see Patent Documents 3 and 4). As the acid anhydride for use in such use applications, carboxylic anhydrides such as hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, norbornane-2,3-dicarboxylic anhydride, and methylnorbornane-2,3-dicarboxylic anhydride, and mixtures thereof have been used for the reasons that they are transparent and colorless, liquid at room temperature, easy to handle, and the like. However, most of these carboxylic anhydrides are low-molecular-weight compounds. Therefore, in an epoxy resin composition containing the carboxylic anhydride as a curing agent, vaporization thereof becomes a problem at heat curing. The vaporization of the carboxylic anhydride is not only a problem that insufficient curing of the epoxy resin compositions attributable to the absence of necessary amount of the carboxylic anhydride (curing agent) may occur but also influences on the environment are large, such as adverse influence on the human body owing to its harmfulness, contamination of production lines, and air pollution. Moreover, in this case, since curing becomes insufficient, for example, stickiness owing to remaining unreacted epoxy resin also takes place, so that curing by the carboxylic anhydride which vaporizes at curing is viewed with suspicion also from the functional and environmental viewpoints.

Related Art Document

Patent Document

[0004]

Patent Document 1: JP-A-2003-277473

Patent Document 2: JP-A-2006-299099

Patent Document 3: JP-A-2008-174640

Disclosure of Invention

Technical Problem

5 [0005]

An object of the present invention is to provide a carboxylic acid compound which is liquid at room temperature and excellent in vaporization resistance at high temperature, and, particularly as a curing agent for epoxy resin compositions, is little in volatility during a curing step thereof and affords a colorless and transparent cured product whose surface is not sticky.

Problems to Be Solved by the Invention

[0006]

15 As a result of extensive studies for solving the above-described problems, the present inventors have found that the problems are solved by using a carboxylic acid compound having a silicone skeleton obtained by reacting a silicone-based compound having a specific skeleton with a carboxylic anhydride having a specific skeleton as a curing agent for epoxy resins.

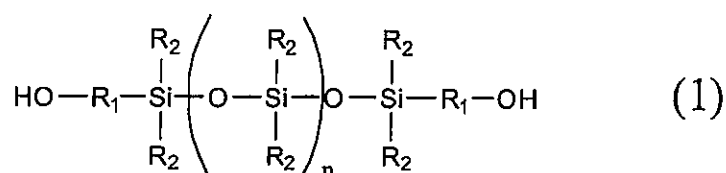
[0007]

20 Namely, the present invention relates to:

(1) A carboxylic acid compound (A) obtainable by an addition reaction of a silicone compound (a) represented by the following formula (1):

[0008]

[Chem. 1]



25

[0009]

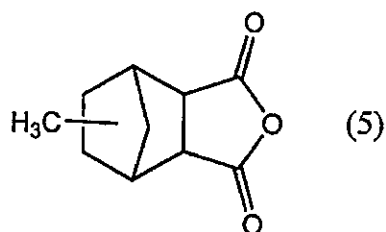
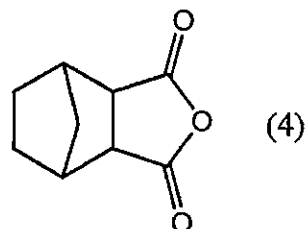
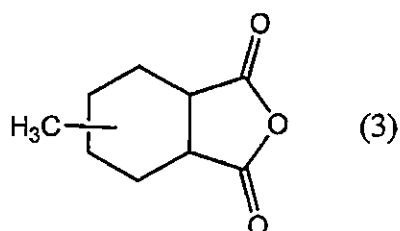
wherein R_1 represents an alkylene group having 1 to 10 carbon atoms in total which may contain an ether group, R_2 represents a methyl group or a phenyl group, and n represents from 1 to 100 as an average value, respectively,

30 with a compound having one or more carboxylic anhydride group in the molecule,

wherein the compound having one or more carboxylic anhydride group in the molecule is at least one selected from compounds (c) represented by the following formulae (3) to (5):

[0010]

[Chem. 2]

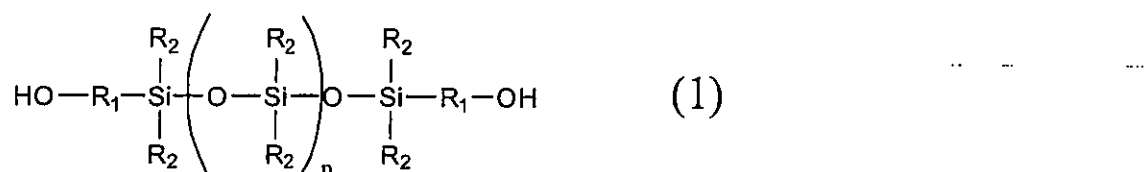


[0011]

- 5 (2) A carboxylic acid compound (A) obtainable by an addition reaction of a silicone compound (a) represented by the following formula (1):

[0012]

[Chem. 3]



10 [0013]

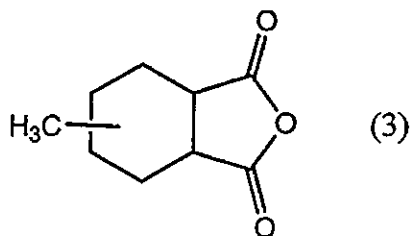
wherein R₁ represents an alkylene group having 1 to 10 carbon atoms in total which may contain an ether group, R₂ represents a methyl group or a phenyl group, and n represents from 1 to 100 as an average value, respectively,

with a compound having one or more carboxylic anhydride group in the molecule,

- 15 wherein the compound having one or more carboxylic anhydride group in the molecule is the compound represented by the formula (3):

[0014]

[Chem. 4]



[0015]

- 5 (3) An epoxy resin curing agent containing the carboxylic acid compound (A) according to the above (1) or (2) and a curing accelerator;
- (4) An epoxy resin composition containing the carboxylic acid compound (A) according to the above (1) or (2) or the epoxy resin curing agent according to claim 3 and an epoxy resin;
- 10 (5) The epoxy resin composition according to the above (4), wherein epoxy equivalent of the epoxy resin is from 400 to 1,500 g/eq. and weight-average molecular weight is from 1,500 to 5,000;
- (6) The epoxy resin composition according to the above (5), wherein use of the epoxy resin composition is an encapsulating material for optical semiconductors;
- 15 (7) The epoxy resin composition according to the above (5), wherein use of the epoxy resin composition is a die-bonding material for optical semiconductors;
- (8) A cured product of the epoxy resin composition according to any one of the above (4) to (7).

20 Effect of the Invention

[0016]

The carboxylic acid compound (A) of the present invention is liquid at room temperature (25°C) and volatility is extremely little in the temperature range which is usually adopted for curing epoxy resins. Furthermore, the carboxylic acid compound (A)

25 is useful as a raw material or modifier for epoxy resin curing agents, paints, adhesives, molded articles, semiconductors, encapsulating resins for optical semiconductors, resins for die-bonding materials of optical semiconductors, polyimide resins, and the like, a plasticizer, a lubricating oil raw material, an intermediate for medicaments and pesticides, a raw material for resins for paints, and a resin for toner. Particularly, the carboxylic acid

30 compound (A) is extremely useful as a curing agent for epoxy resins for encapsulation of optical semiconductors such as a highly luminous white LED because of curing ability toward epoxy resins and high transparency of cured products obtained therefrom.

Best Mode for Carrying Out the Invention

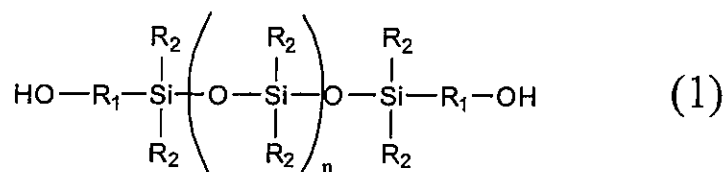
[0017]

The following will describe the present invention in detail.

First, the silicone compound (a) of the present invention represented by the
5 following formula (1) will be described.

[0018]

[Chem. 5]



[0019]

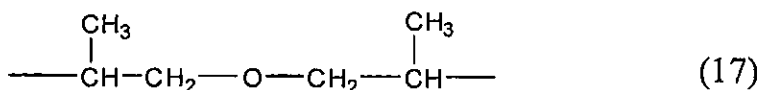
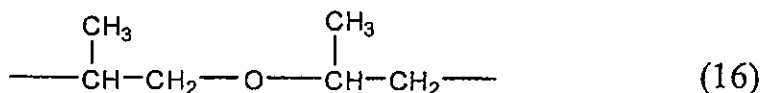
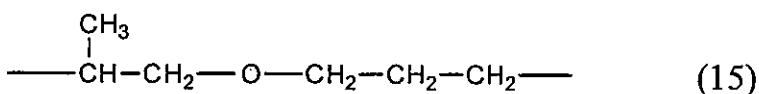
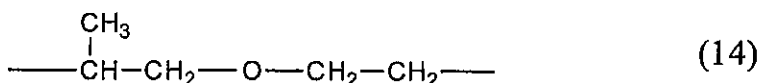
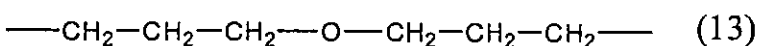
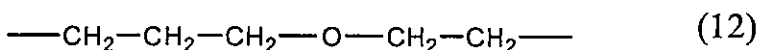
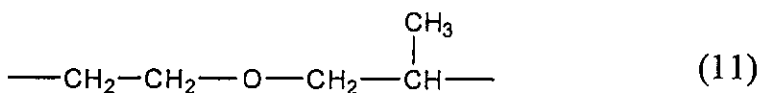
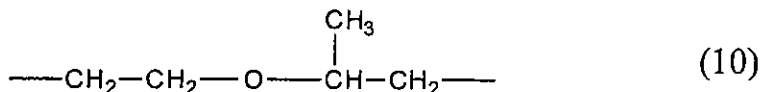
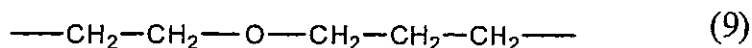
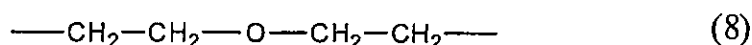
10 wherein R_1 represents an alkylene group having 1 to 10 carbon atoms in total which may contain an ether group, R_2 represents a methyl group or a phenyl group, and n represents from 1 to 100 as an average value, respectively.

[0020]

15 In the formula (1), specific examples of R_1 include alkylene groups such as methylene, ethylene, propylene, isopropylene, butylene, isobutylene, pentylene, isopentylene, hexylene, heptylene, and octylene, alkylene groups interrupted by an ether represented by the following formulae (8) to (17), and the like, and the total number of carbon atoms is from 1 to 10. As particularly preferred one, an alkylene group interrupted by an ether represented by the formula (12) is mentioned. (In the formulae (8)
20 to (17), the carbon atom on the extreme left is a side to which the silicon atom of the formula (1) is bonded)

[0021]

[Chem. 6]



[0022]

In the above formula (1), R₂ represents a methyl group or a phenyl group, and may be the same or different but a methyl group is preferred as compared with a phenyl group for the reason that the carboxylic acid compound (A) is liquid at room temperature.

[0023]

In the formula (1), n represents from 1 to 100 but is preferably from 2 to 80 and more preferably from 5 to 50, as an average value.

[0024]

As the silicone compound (a) represented by the formula (1), for example, silicone-based compounds having alcoholic hydroxyl groups at both ends may be mentioned. Specific examples thereof include X-22-160AS, KF6001, KF6002, KF6003 (all manufactured by Shin-Etsu Chemical Co., Ltd.); BY16-201, BY16-004, SF8427 (all manufactured by Dow Corning Toray Co., Ltd.); XF42-B0970, XF42-C3294 (all manufactured by Momentive Performance Materials Inc.); and the like, which are dual-end carbinol-modified silicone oils, which are all commercially available. These modified silicone oils having alcoholic hydroxyl groups at both ends can be used singly or as a

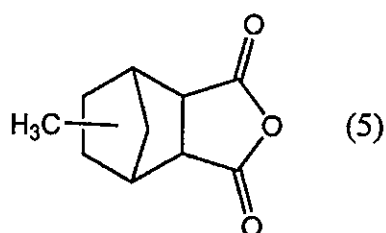
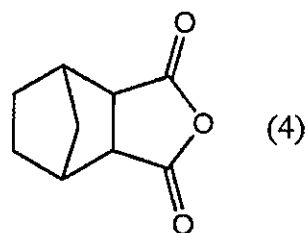
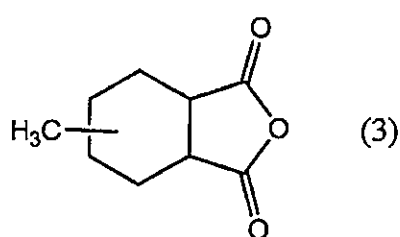
mixture of two or more thereof. Of these, X-22-160AS, KF6001, KF6002, BY16-201, or XF42-B0970 is preferred.

[0025]

The following will describe compounds (c) having a carboxylic anhydride group represented by any of the formulae (3) to (5).

[0026]

[Chem. 7]



[0027]

The compounds represented by the formulae (3) to (5) are methylhexahydrophthalic anhydride, norbornane-2,3-dicarboxylic anhydride, and methylnorbornane-2,3-dicarboxylic anhydride, respectively, and are compounds having a carboxylic anhydride group in the molecule. The carboxylic anhydride group undergoes a ring-opening addition reaction with a functional group having an active hydrogen, such as an alcoholic hydroxyl group, a phenolic hydroxyl group, an amino group, a carboxyl group, or a silanol group to form an ester bond, an amide group, or the like, while it forms a free carboxylic acid through ring-opening of the acid anhydride group.

The carboxylic acid compound (A) of the present invention is an adduct of the silicone compound (a) with at least one selected from the compounds (c) represented by the formulae (3) to (5). The carboxylic acid compound (A) can be obtained by the addition reaction of the carboxylic anhydride group of the compounds (c) represented by the formulae (3) to (5) with the alcoholic hydroxyl group of the silicone compound (a).

In the addition reaction, for the purpose of controlling molecular weight and viscosity of the carboxylic acid compound (A), the addition reaction can be also carried out with using a compound (b) having one or more carboxylic anhydride groups in the

molecule in combination with the compound (c) having a carboxylic anhydride represented by any of the formulae (3) to (5).

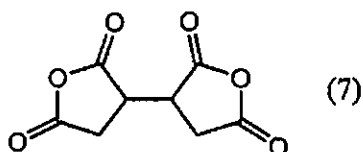
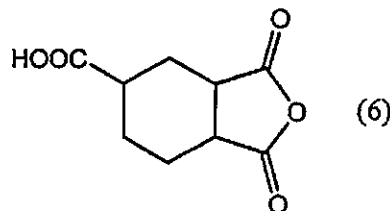
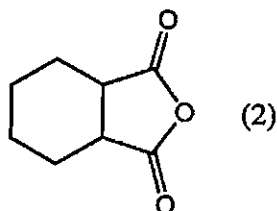
[0028]

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

In the case where the compound (b) having one or more carboxylic anhydride groups in the molecule is used in combination with the compounds (c) represented by the formulae (3) to (5), the compound (b) can be used as a mixture of one or more thereof other than the compounds (c). Of the compounds (b), since the carboxylic acid compound (A) is liquid at room temperature and the cured product obtained by curing the carboxylic acid compound (A) and the epoxy resin is excellent in transparency, hexahydrophthalic anhydride, 1,2,4-cyclohexanetricarboxylic-1,2-anhydride, and 1,2,3,4-butanetetracarboxylic dianhydride represented by the following formulae (2), (6), and (7) are preferred.

[0029]

[Chem. 8]



[0030]

5 In the case where the compound (b) is used, the compound (b) is desirably in an amount of 5 to 80 mol%, more preferably 10 to 78 mol% in the total amount of the compound (b) and the compound (c).

10 The reaction of the silicone compound (a) with the compound (c) (and the compound (b), if necessary) can be carried out in a solvent or with no solvent. The solvent may be used without limitation as far as it is a solvent which does not react with the silicone compound (a) represented by the formula (1) and the compound (c) (and the compound (b), if necessary). Examples of usable solvents include aprotic polar solvents such as dimethylformamide, dimethylacetamide, dimethyl sulfoxide, tetrahydrofuran, acetonitrile, methyl ethyl ketone, cyclopentanone, and methyl isobutyl ketone; aromatic
15 hydrocarbons such as toluene and xylene; and the like. Of these, the aromatic hydrocarbons are preferred. These solvents may be used singly or as a mixture of one or more thereof. The amount of the solvent to be used is not particularly limited but it is usually preferred to use it in an amount of 0.1 to 300 parts by weight based on 100 parts by weight of the total weight of the silicone compound (a) and the compounds (c) represented
20 by the formulae (3) to (5) (and the compound (b), if necessary).

[0031]

 In the reaction, a catalyst may be used. Examples of usable catalysts include acidic compounds such as hydrochloric acid, sulfuric acid, methanesulfonic acid, trifluoromethanesulfonic acid, p-toluenesulfonic acid, nitric acid, trifluoroacetic acid, and
25 trichloroacetic acid; metal hydroxides such as sodium hydroxide, potassium hydroxide, calcium hydroxide, and magnesium hydroxide; amine compounds such as triethylamine, tripropylamine, and tributylamine; heterocyclic compounds such as pyridine, dimethylaminopyridine, 1,8-diazabicyclo[5.4.0]undec-7-ene, imidazole, triazole, and tetrazole; quaternary ammonium salts such as tetramethylammonium hydroxide,

tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, trimethylethylammonium hydroxide, trimethylpropylammonium hydroxide, trimethylbutylammonium hydroxide, trimethylcetylammmonium hydroxide, trioctylmethylammonium hydroxide, tetramethylammonium chloride, 5 tetramethylammonium bromide, tetramethylammonium iodide, tetramethylammonium acetate, and trioctylmethylammonium acetate. These catalysts may be used singly or as a mixture of two or more thereof. Of these, triethylamine, pyridine, and dimethylaminopyridine are preferred.

[0032]

10 The amount of the catalyst to be used is not particularly limited but it is usually preferred to use it in an amount of 0.1 to 100 parts by weight based on 100 parts by weight of the total weight of the silicone compound (a) and the compounds (c) represented by the formulae (3) to (5) (and the compound (b), if necessary), according to needs.

[0033]

15 The reaction temperature in the reaction is usually from 80 to 180°C, and preferably from 110 to 140°C. Moreover, the reaction time is usually from 1 to 12 hours. Mw (weight-average molecular weight) of the reaction product can be measured by GPC (gel permeation chromatography). When the reaction is finished, heating is stopped and, in the case where the solvent is used, the solvent is removed under reduced pressure to 20 obtain an objective carboxylic compound. Mw (weight-average molecular weight) of the resulting carboxylic acid compound can be similarly confirmed by GPC.

[0034]

The carboxylic acid compound (A) of the present invention has a specific structure, is liquid at room temperature (25°C), and volatility in the temperature range 25 usually adopted for curing epoxy resins is extremely little.

Additionally, since the carboxylic acid compound (A) is excellent in transparency, it is useful as a raw material or modifier for epoxy resin curing agents, paints, adhesives, molded articles, semiconductors, encapsulating resins for optical semiconductors, resins for die-bonding materials of optical semiconductors, polyimide resins, and the like, a 30 plasticizer, a lubricating oil raw material, an intermediate for medicaments and pesticides, a raw material for paint resins, and a resin for toner. Particularly, in the case where it is used as a curing agent for epoxy resins, it is excellent in curing ability and transparency of the cured product thereof is excellent, so that it is extremely useful as a curing agent for epoxy resins for use in optical semiconductor encapsulation such as a highly luminous 35 white LED.

[0035]

The carboxylic acid compound (A) of the present invention can be used singly as a curing agent for epoxy resins but the use of the carboxylic acid compound (A) in

combination with a curing accelerator as a curing agent for epoxy resins is also a preferred embodiment. As the curing accelerator to be mixed in the carboxylic acid compound (A), any one can be used as far as it has the ability to accelerate the curing reaction of an epoxy group with a carboxylic acid and a carboxylic anhydride. Examples of usable curing
5 accelerators include ammonium salt-based curing accelerators, phosphonium salt-based curing accelerators, imidazole-based curing accelerators, amine-based curing accelerators, phosphine-based curing accelerators, phosphite-based curing accelerators, Lewis acid-based curing accelerators, and the like.

[0036]

10 Of these, for the use application of the curing agent for epoxy resin composition for use in encapsulation of optical semiconductors such as a highly luminous white LED, owing to excellent transparency, ammonium salt-based curing accelerators and phosphonium salt-based curing accelerators are particularly superior. Examples of the ammonium salt-based curing accelerators include tetramethylammonium hydroxide,
15 tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, trimethylethylammonium hydroxide, trimethylpropylammonium hydroxide, trimethylbutylammonium hydroxide, trimethylcetylammmonium hydroxide, trioctylmethylammonium hydroxide, tetramethylammonium chloride, tetramethylammonium bromide, tetramethylammonium iodide, tetramethylammonium acetate, trioctylmethylammonium acetate, and the like. Examples of the phosphonium
20 salt-based curing accelerators include ethyltriphenylphosphonium bromide, tetraphenylphosphonium tetraphenylborate, methyltributylphosphonium dimethylphosphate, methyltributylphosphonium diethylphosphate, and the like. These curing accelerators may be used singly or as a mixture of two or more thereof. Of these
25 curing accelerators, trimethylcetylammmonium hydroxide and methyltributylphosphonium dimethylphosphate are preferred.

[0037]

For other general use applications, in addition to the above ammonium salt-based curing accelerators and phosphonium salt-based curing accelerators, imidazole-based
30 curing accelerators, amine-based curing accelerators, phosphine-based curing accelerators, phosphite-based curing accelerators, Lewis acid-based curing accelerators, and the like can be used.

[0038]

35 Examples of the imidazole-based curing accelerators include 2-methylimidazole, 2-ethyl-4-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, 2,3-dihydro-1H-pyrrolo-[1,2-a]benzimidazole, 2,4-

diamino-6(2'-methyylimidazole(1'))ethyl-s-triazine, 2,4-diamino-6(2'-undecylimidazole(1'))ethyl-s-triazine, 2,4-diamino-6(2'-ethyl, 4-methyylimidazole(1'))ethyl-s-triazine, 2,4-diamino-6(2'-methyylimidazole(1'))ethyl-s-triazine-isocyanuric acid adduct, 2:3 adduct of 2-methyylimidazole isocyanuric acid, 2-phenylimidazole isocyanuric acid
5 adduct, 2-phenyl-3,5-dihydroxymethyylimidazole, 2-phenyl-4-methyl-5-hydroxymethyylimidazole or 1-cyanoethyl-2-phenyl-3,5-dicyanoethoxymethyylimidazole, and the like.

[0039]

Examples of the amine-based curing accelerators include triethylamine,
10 tripropylamine, tributylamine, and the like.

Examples of the heterocyclic compound-based curing accelerators include pyridine, dimethylaminopyridine, 1,8-diazabicyclo[5.4.0]undec-7-ene, imidazole, triazole, tetrazole, and the like.

Examples of the phosphine-based curing accelerators include triethylphosphine,
15 tributylphosphine, triphenylphosphine, and the like.

Examples of the phosphite-based curing accelerators include trimethylphosphite, triethylphosphite, and the like.

Examples of the Lewis acid-based curing accelerators include BF₃ monoethylamine, BF₃ diethylamine, BF₃ triethylamine, BF₃ benzylamine, BF₃ aniline, BF₃
20 piperadine, BF₃ piperidine, PF₅ ethylamine, PF₅ butylamine, PF₅ laurylamine, PF₅ benzylamine, AsF₅ laurylamine, and the like. These curing accelerators may be used singly or as a mixture of two or more thereof.

[0040]

The above each curing accelerator can be added in an amount of 0.1 to 10 parts by
25 weight based on 100 parts by weight of the carboxylic acid compound (A) of the present invention.

[0041]

The epoxy resin composition of the present invention contains the carboxylic acid compound (A) and an epoxy resin, as well as a curing accelerator, various additives and the
30 like according to needs.

Examples of epoxy resins usable here include epoxy resins which are glycidyl etherified products of phenol compounds, epoxy resins which are glycidyl etherified products of various novolak resins, alicyclic epoxy resins, aliphatic epoxy resins, heterocyclic epoxy resins, glycidyl ester-based epoxy resins, glycidylamine-based epoxy
35 resins, epoxy resins obtained by glycidylation of halogenated phenols, condensates of silicon compounds having an epoxy group with the other silicon compounds, copolymers of polymerizable unsaturated compounds having an epoxy group with the other polymerizable unsaturated compounds, and the like.

[0042]

Examples of the epoxy resins which are glycidyl etherified products of phenol compounds include 2-[4-(2,3-epoxypropoxy)phenyl]-2-[4-[1,1-bis[4-(2,3-hydroxy)phenyl]ethyl]phenyl]propane, bisphenol A, bisphenol F, bisphenol S, 4,4'-
5 biphenol, tetramethylbisphenol A, dimethylbisphenol A, tetramethylbisphenol F, dimethylbisphenol F, tetramethylbisphenol S, dimethylbisphenol S, tetramethyl-4,4'-biphenol, dimethyl-4,4'-biphenol, 1-(4-hydroxyphenyl)-2-[4-(1,1-bis-(4-hydroxyphenyl)ethyl)phenyl]propane, 2,2'-methylene-bis(4-methyl-6-tert-butylphenol), 4,4'-butylidene-bis(3-methyl-6-tert-butylphenol), trishydroxyphenylmethane, resorcinol,
10 hydroquinone, pyrogallol, fluoroglycinol, phenols having a diisopropylidene skeleton, phenols having a fluorene skeleton such as 1,1-di-4-hydroxyphenylfluorene, epoxy resins which are glycidyl etherified products of polyphenol compounds, such as phenolated polybutadienes, and the like.

[0043]

15 Examples of the epoxy resins which are glycidyl etherified products of various novolak resins include glycidyl etherified products of various novolak resins such as novolak resins using various phenols such as phenol, cresols, ethylphenols, butylphenols, and octylphenols, bisphenols such as bisphenol A, bisphenol F, and bisphenol S, and naphthols as starting materials; xylylene skeleton-containing phenol novolak resins;
20 dicyclopentadiene skeleton-containing phenol novolak resins; biphenyl skeleton-containing phenol novolak resins; and fluorene skeleton-containing phenol novolak resins, and the like.

[0044]

25 Examples of the alicyclic epoxy resins include alicyclic epoxy resins having an aliphatic ring-skeleton, such as 3,4-epoxycyclohexylmethyl-(3,4-epoxy)-cyclohexylcarboxylate and bis(3,4-epoxycyclohexylmethyl) adipate.

Examples of the aliphatic epoxy resins include glycidyl ethers of polyhydric alcohols such as 1,4-butanediol, 1,6-hexanediol, polyethylene glycol, and pentaerythritol.

30 Examples of the heterocyclic epoxy resins include heterocyclic epoxy resins having a heterocycle such as an isocyanurate ring or a hydantoin ring.

Examples of the glycidyl ester-based epoxy resins include epoxy resins composed of carboxylic acid esters such as hexahydrophthalic acid diglycidyl ester.

Examples of the glycidylamine-based epoxy resins include epoxy resins obtained by glycidylation of amines such as aniline and toluidine.

35 Examples of the epoxy resins obtained by glycidylation of halogenated phenols include epoxy resins obtained by glycidylation of halogenated phenols such as brominated bisphenol A, brominated bisphenol F, brominated bisphenol S, brominated phenol novolak, brominated cresol novolak, chlorinated bisphenol S, and chlorinated bisphenol A.

[0045]

The condensates of silicon compounds having an epoxy group with the other silicon compounds mean hydrolytic condensates of alkoxysilane compounds having an epoxy group with alkoxysilanes having methyl group(s) and/or phenyl group(s),
5 condensates of alkoxysilane compounds having an epoxy group with polydimethylsiloxane having a silanol group or polydimethyldiphenylsiloxanes having a silanol group, or condensate compounds obtained using them in combination. Examples of the alkoxysilane compounds having an epoxy group include 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltriethoxysilane, 3-
10 glycidoxypropyltrimethoxysilane, 3-glycidoxypropylmethyldimethoxysilane, and the like. As the polydimethylsiloxane having a silanol group and the polydimethyldiphenylsiloxanes having a silanol group, examples of commercially available products include X-21-5841, KF-9701 (manufactured by Shin-Etsu Chemical Co., Ltd.), BY16-873, PRX413 (manufactured by Dow Corning Toray Co., Ltd.), XC96-
15 723, YF3804, YF3800, XF3905, YF3057 (Momentive Performance Materials Inc.), DMS-S12, DMS-S14, DMS-S15, DMS-S21, DMS-S27, DMS-S31 (manufactured by Gelest Inc.), and the like.

The copolymers of polymerizable unsaturated compounds having an epoxy group with the other polymerizable unsaturated compounds include Ma Proof G-0115S, idem G-
20 0130S, idem G-0250S, idem G-1010S, G-0150M, idem G-2050M (manufactured by NOF Corporation) and the like. Examples of the polymerizable unsaturated compounds having an epoxy group include glycidyl acrylate, glycidyl methacrylate, 4-vinyl-1-cyclohexene-1,2-epoxide, and the like. Moreover, examples of the other polymerizable unsaturated compounds include methyl (meth)acrylate, ether (meth)acrylate, benzyl (meth)acrylate,
25 cyclohexyl (meth)acrylate, styrene, vinylcyclohexane, and the like. These epoxy resins may be used singly or as a mixture of two or more thereof.

[0046]

In the case where the epoxy resin composition of the present invention is used in the use application of optical semiconductor encapsulating materials, among the epoxy
30 resins, those having an epoxy equivalent (measured by the method described in JIS K-7236) of 400 to 1,500 g/eq. are preferred, and those having an epoxy equivalent of 450 to 1,100 g/eq. are further preferred. When the epoxy equivalent is less than 400 g/eq., the cured product is too hard and fractures such as cracks tend to be generated. When the equivalent is larger than 1,500 g/eq., there is a tendency that stickiness on the surface is
35 generated.

Moreover, the weight-average molecular weight is preferably from 1,500 to 10,000 and more preferably from 1,800 to 5,000. When the weight-average molecular weight is less than 1,500, the toughness of the cured product tend to be inferior and, for example,

there is a concern that fractures such as cracks may be generated in a thermo cycle test. When the weight-average molecular weight is larger than 10,000, the viscosity is high and workability tends to be inferior.

5 Among the epoxy resins having the epoxy equivalent and the weight-average molecular weight as mentioned above, from the viewpoints of transparency, heat-resistant transparency, light-resistant transparency, thermal cycle resistance, and the like, condensates of silicon compounds having an epoxy group with the other silicone compounds are further preferred.

10 In this regard, the weight-average molecular weight means weight-average molecular weight (Mw) in terms of polystyrenes, which is measured under the following conditions using GPC (gel permeation chromatography).

Various conditions for GPC

Manufacturer: Shimadzu Corporation

Columns: Guard Column SHODEX GPC LF-G LF-804 (three columns)

15 Flow rate: 1.0 ml/min.

Column temperature: 40°C

Solvent used: THF (tetrahydrofuran)

Detector: RI (differential refractometer detector)

[0047]

20 The contents of the above individual components in the epoxy resin composition of the present invention are from 5 to 95 parts by weight, preferably from 20 to 80 parts by weight of the carboxylic acid compound (A) obtained by addition reaction of the silicon compound (a) represented by the formula (1) of the present invention with the compounds represented by the formulae (3) to (5) (and the compound (b) having a carboxylic
25 anhydride group, if necessary), from 5 to 95 parts by weight, preferably from 20 to 80 parts by weight of the epoxy resin as mentioned above, and from 0.005 to 10 parts by weight, preferably from 0.05 to 5 parts by weight of the curing accelerator according to needs.

[0048]

30 The epoxy resin composition of the present invention is obtained by homogeneously mixing the above individual components at normal temperature or under elevated temperature. For example, the composition is prepared by sufficiently mixing them to be homogeneous using an extruder, a kneader, three-roll roller, a universal mixer, a planetary mixer, a homomixer, a homodisper, a beads mill, or the like and, if necessary, performing a filtration treatment through a SUS mesh or the like.

35 [0049]

In the epoxy resin curing agent and the epoxy resin composition of the present invention, the other epoxy resin curing agent can be used in combination.

Examples of the epoxy resin curing agent usable in combination include polybasic carboxylic acids, carboxylic anhydrides, phenols, hydrazines, mercaptans, and the like.

[0050]

5 The polybasic carboxylic acids include aliphatic polybasic carboxylic acids, cyclic aliphatic polybasic carboxylic acids, aromatic polybasic carboxylic acids, heterocyclic polybasic carboxylic acids, and the like.

10 Examples of the aliphatic polybasic carboxylic acids include oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, 1,2,3-propanetricarboxylic acid, 1,2,3,4-butanetetracarboxylic acid, and the like.

15 Examples of the cyclic aliphatic polybasic carboxylic acids include hexahydrophthalic acid, 1,3-adamantanedicarboxylic acid, 1,3-adamantanedicarboxylic acid, tetrahydrophthalic acid, 2,3-norbornenedicarboxylic acid, 1,2,4-cyclohexanetricarboxylic acid, 1,3,5-cyclohexanetricarboxylic acid, 1,2,3-cyclohexanetricarboxylic acid, 1,2,4,6-cyclohexanetetracarboxylic acid, and the like.

20 Examples of the aromatic polybasic carboxylic acids include phthalic acid, isophthalic acid, terephthalic acid, 1,2-naphthalenedicarboxylic acid, 1,4-naphthalenedicarboxylic acid, 1,8-naphthalenedicarboxylic acid, 2,3-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 9,10-anthracenedicarboxylic acid, 4,4'-benzophenonedicarboxylic acid, 2,2'-biphenyldicarboxylic acid, 3,3'-biphenyldicarboxylic acid, 4,4'-biphenyldicarboxylic acid, 3,3'-biphenyletherdicarboxylic acid, 4,4'-biphenyletherdicarboxylic acid, 4,4'-binaphthyldicarboxylic acid, hemimellitic acid, trimellitic acid, trimesic acid, 1,2,4-naphthalenetetracarboxylic acid, 2,5,7-naphthalenetetracarboxylic acid, mellophanic acid, 25 prehnitic acid, pyromellitic acid, 3,3',4,4'-benzophenonetetracarboxylic acid, 2,2',3,3'-benzophenonetetracarboxylic acid, 2,3,3',4'-benzophenonetetracarboxylic acid, 3,3',4,4'-biphenyltetracarboxylic acid, 2,2',3,3'-biphenyltetracarboxylic acid, 2,3,3',4'-biphenyltetracarboxylic acid, 4,4'-oxydiphthalic acid, 3,3',4,4'-diphenylmethanetetracarboxylic acid, 1,4,5,8-naphthalenetetracarboxylic acid, 1,2,5,6-30 naphthalenetetracarboxylic acid, 2,3,6,7-naphthalenetetracarboxylic acid, anthracenetetracarboxylic acid, and the like.

Examples of the heterocyclic polybasic carboxylic acids include tris(2-carboxyethyl) isocyanurate, tris(3-carboxypropyl) isocyanurate, and the like.

[0051]

35 The carboxylic anhydrides include aliphatic carboxylic anhydrides, cyclic aliphatic carboxylic anhydrides, aromatic carboxylic anhydrides, and the like.

Examples of the aliphatic carboxylic anhydrides include succinic anhydride, methylsuccinic anhydride, ethylsuccinic anhydride, 2,3-butanedicarboxylic anhydride, 2,4-

pentanedicarboxylic anhydride, 3,5-heptanedicarboxylic anhydride, 1,2,3,4-butanetetracarboxylic dianhydride, maleic anhydride, dodecylsuccinic anhydride, and the like.

5 The cyclic aliphatic carboxylic anhydrides include hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, 1,3-cyclohexanedicarboxylic anhydride, hydrogenated nadic anhydride, hydrogenated methylnadic anhydride, bicyclo[2.2.2]octane-2,3-dicarboxylic anhydride, 1,2,4-cyclohexanetricarboxylic-1,2-anhydride, 1,2,3,4-cyclobutanetetracarboxylic dianhydride, 1,2,3,4-cyclopentanetetracarboxylic dianhydride, 1,2,4,5-cyclohexanetetracarboxylic dianhydride, tetrahydrophthalic anhydride, 10 methyltetrahydrophthalic anhydride, nadic anhydride, methylnadic anhydride, 4,5-dimethyl-4-cyclohexene-1,2-dicarboxylic anhydride, bicyclo[2,2,2]-5-octene-2,3-dicarboxylic anhydride, and the like

15 Examples of the aromatic carboxylic anhydrides include phthalic anhydride, isophthalic anhydride, terephthalic anhydride, trimellitic anhydride, pyromellitic anhydride, and the like.

In addition, compounds having an aliphatic carboxylic anhydride and a cyclic aliphatic carboxylic anhydride in the same molecule, such as 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride and 4-(2,5-dioxotetrahydrofuran-3-yl)-1,2,3,4-tetrahydronaphthalene-1,2-dicarboxylic anhydride, and the like are included.

20 [0052]

Examples of the phenols include bisphenol A, bisphenol F, bisphenol S, 4,4'-biphenol, tetramethylbisphenol A, dimethylbisphenol A, tetramethylbisphenol F, dimethylbisphenol F, tetramethylbisphenol S, dimethylbisphenol S, tetramethyl-4,4'-biphenol, dimethyl-4,4'-biphenylphenol, 1-(4-hydroxyphenyl)-2-[4-(1,1-bis-(4-hydroxyphenyl)ethyl)phenyl]propane, 2,2'-methylene-bis(4-methyl-6-tert-butylphenol), 25 4,4'-butylidene-bis(3-methyl-6-tert-butylphenol), trishydroxyphenylmethane, resorcinol, hydroquinone, pyrogallol, phenols having a diisopropylidene skeleton; phenols having a fluorene skeleton, such as 1,1-di-4-hydroxyphenylfluorene; novolak resins using various phenols such as phenolated polybutadiene, phenol, cresols, ethylphenols, butylphenols, octylphenols, bisphenol A, bisphenol F, bisphenol S, and naphthols as raw materials; 30 various novolak resins such as xylylene skeleton-containing phenol novolak resins, dicyclopentadiene skeleton-containing phenol novolak resins, biphenyl skeleton-containing phenol novolak resins, fluorene skeleton-containing phenol novolak resins, and furan skeleton-containing phenol novolak resins, and the like.

35 [0053]

Examples of the hydrazines include isophthalodihydrazide, adipodihydrazide, sebacodihydrazide, decanediodihydrazide, 2,6-naphthalenedicarbodihydrazide, and the like.

[0054]

Examples of the mercaptans include trimethylolpropane tris(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptopropionate), dipentaerythritol hexakis(3-mercaptopropionate), tris[(3-mercaptopropionyloxy)-ethane], isocyanurate 1,4-bis(3-mercaptobutyryloxy)butane, pentaerythritol tetrakis(3-mercaptobutyrate), 1,3,5-tris(3-mercaptobutyloxyethyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione, and the like.

[0055]

These epoxy resin curing agents may be used singly or as a mixture of two or more thereof. In the case where the carboxylic acid compound (A) of the present invention is used in combination with the other curing agent as mentioned above, the amount to be used is adjusted so that the ratio of the carboxylic acid compound (A) in the total curing agents is 50% by weight or more and preferably 80% by weight or more.

[0056]

Next, if necessary, a coupling agent, a phosphor, an inorganic filler, highly thermally conductive fine particles, a phosphorus compound filler as a flame retardant, a binder resin, and the like can be added to the epoxy resin composition of the present invention.

Examples of usable coupling agents include silane-based coupling agents such as 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropylmethyldimethoxysilane, 3-glycidoxypropylmethyldimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, N-(2-aminoethyl) 3-aminopropylmethyldimethoxysilane, N-(2-aminoethyl) 3-aminopropylmethyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-mercaptopropyltrimethoxysilane, vinyltrimethoxysilane, N-(2-(vinylbenzylamino)ethyl) 3-aminopropyltrimethoxysilane hydrochloride, 3-methacryloxypropyltrimethoxysilane, 3-chloropropylmethyldimethoxysilane, and 3-chloropropyltrimethoxysilane; titanium-based coupling agents such as isopropyl (N-ethylaminoethylamino)titanate, isopropyl triisostearoyltitanate, titanium di(dioctylpyrophosphate)oxyacetate, tetraisopropyl di(dioctylphosphite)titanate, and neoalkoxy tri(p-N-(β -aminoethyl)aminophenyl) titanate; zirconium or aluminum-based coupling agents such as Zr-acetylacetonate, Zr-methacrylate, Zr-propionate, neoalkoxy dizirconate, neoalkoxytrisneodecanoyl zirconate, neoalkoxytris(dodecanoyl)benzenesulfonyl zirconate, neoalkoxytris(ethylenediaminoethyl) zirconate, neoalkoxytris(m-aminophenyl) zirconate, ammonium zirconium carbonate, Al-acetylacetonate, Al-methacrylate, and Al-propionate; and the like.

These coupling agents may be used singly or as a mixture of two or more thereof.

Improvement of adhesiveness with the base material and improvement of hardness of the cured products are expectable by the use of the coupling agent. The coupling agent may be contained usually in an amount of 0.05 to 20 parts by weight and preferably 0.1 to 10 parts by weight in the epoxy resin composition of the present invention according to needs.

[0057]

The usable phosphors include phosphors such as YAG phosphors, TAG phosphors, orthosilicate phosphors, thiogallate phosphors, and sulfide phosphors. Fluorescent properties can be imparted to the epoxy resin composition by adding the phosphor.

5

[0058]

Examples of usable inorganic fillers 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. By adding the inorganic filler, it is possible to impart heat resistance and light resistance or control the viscosity or the like. With regard to the content of the inorganic filler, an amount of 0 to 90 parts by weight is used in the epoxy resin composition of the present invention.

10

[0059]

Examples of usable highly thermo-conductive fine particles include particles of metals such as gold, silver, copper, iron, nickel, tin, aluminum, cobalt, and indium and alloys thereof, metal oxides such as aluminum oxide, magnesium oxide, and titanium oxide, metal nitrides such as boron nitride and aluminum nitride, carbon compounds such as graphite, diamond, and carbon black, metal-coated particles obtained by coating resin particles with a metal layer, and the like. By adding the highly thermo-conductive fine particles, thermo-conductivity of the epoxy resin composition can be improved.

15

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[0060]

Usable phosphorus-containing compounds may be reaction type ones or addition type ones. Examples of the phosphorus-containing compounds include phosphate esters such as trimethyl phosphate, triethyl phosphate, tricresyl phosphate, trixylenyl phosphate, cresyl diphenyl phosphate, cresyl-2,6-dixylenyl phosphate, 1,3-phenylenebis(dixylenyl phosphate), 1,4-phenylenebis(dixylenyl phosphate), and 4,4'-biphenyl(dixylenylphosphate); phosphanes such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide and 10(2,5-dihydroxyphenyl)-10H-9-oxa-10-phosphaphenanthrene-10-oxide; phosphorus-containing epoxy compounds obtained by reacting an epoxy resin with active hydrogen of the phosphanes, red phosphorus, and the like. The phosphate esters, the phosphanes, or phosphorus-containing epoxy compounds are preferred and 1,3-phenylenebis(dixylylenyl phosphate), 1,4-phenylenebis(dixylenyl phosphate), 4,4'-biphenyl(dixylenyl phosphate), or a phosphorus-containing epoxy compound is preferred. The content of the phosphorus-containing compound is preferably as follows: phosphorus-containing compound/epoxy resin = 0.1 to 0.6 (weight ratio). When the content is less than 0.1, flame retardancy is insufficient and when the content exceeds 0.6, there is a concern that moisture absorbing properties and dielectric properties of the cured products are adversely affected.

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[0061]

Usable binder resins 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 but are not limited thereto. The binder resin is usually
5 contained in an amount of 0.05 to 50 parts by weight and preferably 0.05 to 20 parts by weight in the epoxy resin composition of the present invention, according to needs.

[0062]

Furthermore, additives such as a releasing agent such as stearic acid, palmitic acid, zinc stearate, or calcium stearate, a colorant such as a dye or a pigment, an antioxidant, a
10 photo-stabilizer, a moisture resistance improver, a thixotropy-imparting agent, a defoaming agent, a tackifier, an impact resistance improver, an ion-trapping agent, an antistatic agent, a lubricant, a leveling agent, a surface tension-lowering agent, a defoaming agent, a precipitation inhibitor, a surfactant, and a UV absorber, various thermosetting resins, and other various resins can be added to the curable resin composition of the present invention.
15 These are added to the epoxy resin composition of the present invention by a method known per se.

[0063]

The epoxy resin composition of the present invention can be used as a varnish or ink after mixed with a solvent according to needs. Any solvent can be used as far as it
20 has a high solubilizing property toward individual components of the carboxylic acid compound (A) of the present invention, an epoxy resin, a curing accelerator, and other additives and is not reactive therewith. Specific examples thereof include alcohols such as methanol, ethanol, propanol, and butanol; glycol ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether,
25 propylene glycol monomethyl ether, 3-methoxybutanol, and 3-methyl-3-methoxybutanol; alkylene glycol ether acetates such as ethylene glycol monoethyl ether acetate, ethylene glycol monobutyl ether acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, 3-methoxybutyl acetate, 3-methyl-3-methoxybutyl acetate, and ethyl ethoxypropionate; aromatic hydrocarbons such as benzene, toluene, and xylene;
30 ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, cyclopentanone, and 4-hydroxy-4-methyl-2-pentanone; esters such as methyl acetate, ethyl acetate, propyl acetate, butyl acetate, methyl 2-hydroxy-2-methylpropionate, ethyl 2-hydroxy-2-methylpropionate, methyl hydroxyacetate, ethyl hydroxyacetate, butyl hydroxyacetate, methyl lactate, ethyl lactate, butyl lactate, methyl 3-hydroxypropionate,
35 ethyl 3-hydroxypropionate, propyl 3-hydroxypropionate, butyl 3-hydroxypropionate, propyl 2-hydroxy-3-methylbutanate, ethyl methoxyacetate, propyl methoxyacetate, methyl ethoxyacetate, ethyl ethoxyacetate, propyl ethoxyacetate, butyl ethoxyacetate, methyl 2-methoxypropionate, ethyl 2-methoxypropionate, propyl 2-methoxypropionate, butyl 2-

methoxypropionate, methyl 2-ethoxypropionate, ethyl 2-ethoxypropionate, propyl 2-ethoxypropionate, butyl 2-ethoxypropionate, methyl 3-methoxypropionate, ethyl 3-methoxypropionate, propyl 3-methoxypropionate, butyl 3-methoxypropionate, methyl 3-ethoxypropionate, ethyl 3-ethoxypropionate, propyl 3-ethoxypropionate, and butyl 3-ethoxypropionate; ethers such as diethyl ether and tetrahydrofuran; and the like. In addition, as aprotic polar solvents, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, acetonitrile, and the like can be used.

These solvents are contained usually in an amount of 2 to 90 parts by weight in the epoxy resin composition of the present invention, according needs. In the case where the composition is formed into a varnish or ink using a solvent, the epoxy resin composition of the present invention may be subjected to microfiltration using a filter of 0.05 to 2 μm according to needs.

[0064]

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

[0065]

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 carboxylic acid compound (A) of the present invention with an epoxy resin and also other additives such as a curing agent, a curing accelerator, a coupling material, an antioxidant, and a photo-stabilizer and is used as an encapsulating material or as both of a die-bonding material and an encapsulating agent. 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.

[0066]

The optical semiconductor element such as the highly luminous white LED is 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. In order to protect the semiconductor chip from heat and moisture and play a role of lens function, the semiconductor chip is encapsulated with an encapsulating material such as an epoxy resin. 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.

[0067]

As a method of adhering the semiconductor chip to the substrate using the epoxy resin composition of the present invention, after the epoxy resin composition of the present invention is applied by a dispenser, potting, or screen printing, the semiconductor chip is placed thereon and heat curing is performed, whereby the semiconductor chip can be adhered. For heating, a method of hot-air circulation, infrared ray, high frequency wave, or the like can be employed.

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

[0068]

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

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

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

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

[0069]

The carboxylic acid compound (A) of the present invention has a specific structure, is liquid at room temperature (25°C), and is excellent in curing ability to cure epoxy resins, and volatility in the temperature range usually adopted for curing epoxy resins is extremely little. The epoxy resin composition containing the carboxylic acid compound (A) of the present invention can be used in various use applications including optical parts materials in which conventional epoxy resin compositions are used.

The optical materials means materials to be used in use applications where light such as visible light, infrared ray, ultraviolet ray, X-ray, or laser passes through the material. More specifically, the following may be mentioned in addition to optical semiconductor encapsulating materials of lamp type, SMD type, and the like and optical

semiconductor die-bonding materials. They may be peripheral materials for liquid crystal display, including substrate materials, optical waveguides, prism sheets, polarizing plates, retardation films, viewing angle correction films, adhesives, films for liquid crystals such as polarizer protective films, and the like in the liquid display field. Moreover, they may be encapsulating materials, antireflection films, optical correction films, housing materials, protective films of front glass, front glass substituting materials, adhesives for color PDP (plasma display) expected as a next-generation flat panel display; mold materials for LED, encapsulating materials for LED, protective films of front glass, front glass substituting materials, and adhesives for use in LED displays; substrate materials, optical waveguides, prism sheets, polarizing plates, retardation films, viewing angle correction films, adhesives, and polarizer protective films in plasma address liquid crystal (PALC) displays; protective films of front glass, front glass substituting materials, and adhesives in organic EL (electroluminescence) displays; and various film substrates, protective films of front glass, front glass substituting materials, and adhesives in field emission displays (FED). In the optical recording field, they may be VD (video disk), CD/CD-ROM, CD-R/RW, DVD-R/DVD-RAM, MO/MD, PD (phase change disk), disk substrate materials for optical cards, pick-up lenses, protective films, encapsulating materials, adhesives, and the like.

[0070]

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

engines, electrical components, driving engines, brake oil tanks, rustproof steel plates for automobiles, interior panels, interior materials, protective/bonding wire harness, fuel hoses, automobile lamps, and glass substitutes. Moreover, they may be double-grazed glasses for railway vehicles. Furthermore, they may be toughness-imparting agents for aircraft structural materials, engine peripheral members, protective/bonding wire harness, and corrosion-resistant coatings. In the architecture field, interior/processing materials, electric covers, sheets, glass intermediate films, glass substitutes, and solar battery periphery materials. In agriculture, they may be house-covering films. As the next-generation optical/electronic function organic materials, they may be organic EL element peripheral materials, organic photoreflexive elements, photoamplification elements that are light-light conversion devices, photo-operating elements, substrate materials in the periphery of organic solar battery, fiber materials, encapsulating materials for elements, adhesives, and the like.

[0071]

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 (underfill for reinforcement), and the like.

[0072]

As other use applications of the optical materials, there may be mentioned general use applications where epoxy resin compositions are used. For example, there may be mentioned adhesives, paints, coatings, molding materials (including sheets, films, FRP, and the like), insulating materials (including printed boards, electric wire coverings), 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 mentioned interlayer adhesives of multilayer substrates such as build-up substrates, die-bonding agents, semiconductor adhesives such as underfill, underfill for BGA reinforcement, anisotropic conductive films (ACF), adhesives for mounting such as anisotropic conductive pastes (ACP), and the like. Particularly, the optical materials are extremely excellent as curing agents of epoxy resins for encapsulation of optical semiconductors such as highly luminous white LED since cured products obtained therefrom are excellent in transparency. As the other use applications, the optical materials are useful as raw materials and modifying agents of polyimide resins and the like, plasticizers, raw materials for lubricant oils, isocyanate resin compositions for substrates, additives for other resins, raw materials for resins for paints, resins for toners, and intermediates for medicaments and pesticides.

Examples

[0073]

The following will describe the present invention in more detail with reference to
5 Examples but the present invention is not limited to these Examples. In the following, "parts" means parts by weight and "%" means % by weight. Moreover, measurement methods for tests in Examples are as follows.

[0074]

Epoxy equivalent: It was measured by the method described in JIS K-7236.

10 Acid value: It was measured using an AT-610 type potentiometric titration apparatus of Kyoto Electronics Manufacturing Co. Ltd. Specifically, a measurement sample was dissolved in methyl ethyl ketone or ethanol and was titrated with a 0.1 mol/L aqueous sodium hydroxide solution.

Viscosity: It was measured at 25°C using an E-type viscometer.

15 Weight-average-molecular weight: It was measured using a GPC (gel permeation chromatography) manufactured by Shimadzu Corporation. A guard column SHODEX GPC LF-G LF-804 (three columns) were used as columns and a flow rate of 1.0 ml/min, a column temperature of 40°C, a use solvent of THF (tetrahydrofuran), and a detector of RI (differential refractometer detector) were used. For calibration curves, standard
20 polystyrenes manufactured by Shodex were used.

Thermal weight decrease: Using TG/DTA 6200 manufactured by Shimadzu Corporation, a weight decrease ratio was measured after a sample was heated from 30°C to 120°C at a temperature elevation rate of 20°C/min and was kept at 120°C for 60 minutes. The measurement was performed at an air-flow of 200 ml/min.

25 Transmittance: Measurement of light transmittance at 400 nm was performed using U-3300 manufactured by Hitachi, Ltd.

[0075]

MH700G used in Examples is a mixture of methylhexahydrophthalic anhydride and hexahydrophthalic anhydride manufactured by New Japan Chemical Co. Ltd. With
30 regard to the mixing ratio, methylhexahydrophthalic anhydride accounts for 70% by weight (68 mol%).

Similarly, HNA-100 is a mixture of methylnorbornane-2,3-dicarboxylic anhydride and norbornane-2,3-dicarboxylic anhydride manufactured by New Japan Chemical Co. Ltd. With regard to the mixing ratio, methylnorbornane-2,3-dicarboxylic anhydride
35 accounts for 80% by weight (79 mol%).

[0076]

Synthetic Example 1 (Synthesis of condensate of silicon compound having epoxy group and the other silicon compound)

Into a reaction vessel were charged 59.1 parts of 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 130.6 parts of polydimethyldiphenylsiloxane having a silanol group whose molecular weight was 1,700 (measured value on GPC), and 10.0 parts of a 0.5% KOH methanol solution, and temperature was elevated to 75°C.

After temperature elevation, they were reacted under refluxing at 75°C for 8 hours. After the reaction, 135 parts of methanol was added thereto and then 25.9 parts of a 50% distilled water-methanol solution was added dropwise over a period of 60 minutes, followed by further reaction under refluxing at 75°C for another 8 hours. After completion of the reaction, the mixture was neutralized with a 5% aqueous sodium dihydrogen phosphate solution and then recovery of methanol by distillation was performed at 80°C. Thereafter, for washing, 170 parts of MIBK was added and then washing with water was repeated three times. Then, the organic phase was subjected to solvent removal under reduced pressure at 100°C, thereby obtaining 162 parts of a siloxane compound (B-1) having an epoxy groups. The epoxy equivalent of the resulting compound was 707 g/eq., the weight-average molecular weight was 2,680, and the appearance was transparent and colorless.

[0077]

Example 1

Into a reaction vessel were charged 50 parts of dual-end carbinol-modified silicone X22-160AS (manufactured by Shin-Etsu Chemical Co., Ltd.), 15.4 parts of RIKACID MH (methylhexahydrophthalic anhydride manufactured by New Japan Chemical Co. Ltd.), and 10 parts of toluene, and temperature was elevated to 130°C. When GPC was measured after 3 hours, the peak of RIKACID MH had disappeared. Thereafter, the reaction was carried out for another 2 hours. After completion of the reaction, the solvent was removed under reduced pressure, thereby obtaining 65.0 parts of a carboxylic acid compound (A-1). The weight-average molecular weight of the resulting compound was 1,700.

[0078]

Example 2

Into a reaction vessel were charged 50 parts of dual-end carbinol-modified silicone X22-160AS (manufactured by Shin-Etsu Chemical Co., Ltd.), 16.8 parts of RIKACID MH700G (a mixture of methylhexahydrophthalic anhydride and hexahydrophthalic anhydride manufactured by New Japan Chemical Co. Ltd.), and 10 parts of toluene, and temperature was elevated to 130°C. When GPC was measured after 3 hours, the peak of RIKACID MH700G had disappeared. Thereafter, the reaction was carried out for another 2 hours. After completion of the reaction, the solvent was removed under reduced pressure, thereby obtaining 66.8 parts of a carboxylic acid compound (A-2). The weight-average molecular weight of the resulting compound was 1,700.

[0079]

Example 3

Into a reaction vessel were charged 50 parts of dual-end carbinol-modified silicone X22-160AS (manufactured by Shin-Etsu Chemical Co., Ltd.), 9.9 parts of HTMAN (1,2,4-cyclohexanetricarboxylic-1,2-anhydride, manufactured by Mitsubishi Gas Chemical Co., Inc.), 8.4 parts of RIKACID MH700G (a mixture of methylhexahydrophthalic anhydride and hexahydrophthalic anhydride manufactured by New Japan Chemical Co. Ltd.), and 10 parts of toluene, and temperature was elevated to 130°C. When GPC was measured after 3 hours, the peaks of HTMAN and RIKACID MH700G had disappeared. Thereafter, the reaction was carried out for another 2 hours. After completion of the reaction, the solvent was removed under reduced pressure, thereby obtaining 68.2 parts of a carboxylic acid compound (A-3). The weight-average molecular weight of the resulting compound was 1,900.

[0080]

Example 4

Into a reaction vessel were charged 50 parts of dual-end carbinol-modified silicone X22-160AS (manufactured by Shin-Etsu Chemical Co., Ltd.), 9.2 parts of RIKACID MH (methylhexahydrophthalic anhydride manufactured by New Japan Chemical Co. Ltd.), 4.0 parts of RIKACID BT-100 (1,2,3,4-butanetetracarboxylic dianhydride manufactured by New Japan Chemical Co. Ltd.), and 10 parts of toluene, and temperature was elevated to 130°C. When GPC was measured after 3 hours, the peaks of RIKACID MH and RIKACID BT-100 had disappeared. Thereafter, the reaction was carried out for another 2 hours. After completion of the reaction, the solvent was removed under reduced pressure, thereby obtaining 63.0 parts of a carboxylic acid compound (A-4). The weight-average molecular weight of the resulting compound was 4,640.

[0081]

Example 5

Into a reaction vessel were charged 50 parts of dual-end carbinol-modified silicone X22-160AS (manufactured by Shin-Etsu Chemical Co., Ltd.), 17.0 parts of RIKACID HNA-100 (a mixture of norbornane-2,3-dicarboxylic anhydride and methylnorbornane-2,3-dicarboxylic anhydride manufactured by New Japan Chemical Co. Ltd.), and 10 parts of toluene, and temperature was elevated to 130°C. When GPC was measured after 3 hours, the peak of RIKACID HNA-100 had disappeared. Thereafter, the reaction was carried out for another 2 hours. After completion of the reaction, the solvent was removed under reduced pressure, thereby obtaining 66.8 parts of a carboxylic acid compound (A-5). The weight-average molecular weight of the resulting compound was 1,730.

[0082]

Example 6

An epoxy resin composition was obtained by charging 100 parts of the carboxylic acid compound (A-1) obtained in Example 1 and 108 parts of the siloxane compound (B-1) having an epoxy group obtained in Synthetic Example 1 as an epoxy resin, mixing them, and performing defoaming for 20 minutes.

[0083]

Example 7

An epoxy resin composition was obtained in the same manner as in Example 6 except that the carboxylic acid compound was changed from A-1 to A-2 in Example 6.

[0084]

Example 8

An epoxy resin composition was obtained in the same manner as in Example 6 except that the carboxylic acid compound was changed from A-1 to A-3 in Example 6.

[0085]

Example 9

An epoxy resin composition was obtained in the same manner as in Example 6 except that the carboxylic acid compound was changed from A-1 to A-4 in Example 6.

[0086]

Example 10

An epoxy resin composition was obtained in the same manner as in Example 6 except that the carboxylic acid compound was changed from A-1 to A-5 in Example 6.

[0087]

Example 11

An epoxy resin composition was obtained in the same manner as in Example 6 except that the epoxy resin in Example 6 was changed to ERL-4221 (3,4-epoxycyclohexylmethyl-(3,4-epoxy)cyclohexylcarboxylate, manufactured by Dow Chemical Company).

[0088]

Comparative Example 1

An epoxy resin composition was obtained by mixing 841 parts of the siloxane compound (B-1) having an epoxy group obtained in Synthetic Example 1 as an epoxy resin, 100 parts of RIKACID MH700G (a mixture of methylhexahydrophthalic anhydride and hexahydrophthalic anhydride manufactured by New Japan Chemical Co. Ltd.) that is a liquid carboxylic anhydride as an epoxy resin curing agent, and 0.8 parts of PX-4MP (a phosphonium salt-based curing accelerator, manufactured by Nippon Chemical Industrial Co., Ltd.) as a curing accelerator, and performing defoaming for 20 minutes.

[0089]

Comparative Example 2

An epoxy resin composition was obtained in the same manner as in Comparative Example 1 except that the epoxy resin in Comparative Example 1 was changed to ERL-4221 (3,4-epoxycyclohexylmethyl-(3,4-epoxy)cyclohexylcarboxylate, manufactured by Dow Chemical Company).

[0090]

Example in which an epoxy resin composition was used as an encapsulating material for an optical semiconductor

Each of the curable resin compositions obtained in Examples 6 to 11 and Comparative Examples 1 to 2 was filled into a syringe and injected into a surface-mounted LED on which an emission element having an emission wavelength of 405 nm had been mounted using a precise injection apparatus and the resin composition was cured at 150°C for 1 hour after pre-curing at 120°C for 3 hours, thereby encapsulating the surface-mounted LED.

[0091]

Physical Property Test

Properties of the carboxylic acid compounds A-1 to A-5 obtained in Examples 1 to 5 and RIKACID MH700G that is a liquid carboxylic anhydride as a comparative example were summarized in Table 1.

[0092]

[Table 1]

Table 1 Physical Property Test

	Example 1	Example 2	Example 3	Example 4	Example 5	Comparative Example 1, 2
Compound	A-1	A-2	A-3	A-4	A-5	MH700G
Weight-average molecular weight	1700	1700	1900	4640	1730	-
Acid value (mgKOH/g)	80	81	116	81	80	-
Viscosity (25°C, Pa·s)	0.75	0.11	13	5.01	0.85	0.06
Transmittance (% , 400 nm)	98	98	98	98	98	99
Thermal weight decrease (%)	-1.1	-1.5	-0.5	-1.2	-1.3	-42.8

[0093]

MH700G: a mixture of methylhexahydrophthalic anhydride and hexahydrophthalic anhydride manufactured by New Japan Chemical Co. Ltd.

[0094]

Evaluation Tests

Mixing ratios of the epoxy resin compositions obtained in Examples 6 to 11 and Comparative Examples 1 to 2 and transmittance of their cured products, dents of the cured products in association with cured product vaporization, and results of surface tackiness are shown in Table 2. The tests in Table 2 were performed as follows.

[0095]

(1) Cured Product Transmittance;

After each of the epoxy resin compositions obtained in Examples 6 to 11 and Comparative Examples 1 to 2 was subjected to vacuum defoaming for 20 minutes, it was poured onto a glass substrate on which a dam had been formed with a heat-resistant tape so as to be 30 mm × 20 mm × 1 mm height. The poured article was cured at 150°C for 1 hour after pre-curing at 120°C for 3 hours, thereby obtaining a test piece for transmittance having a thickness of 1 mm.

(2) Dent Test;

After each of the epoxy resin compositions obtained in Examples 6 to 11 and Comparative Examples 1 to 2 was subjected to vacuum defoaming for 20 minutes, it was filled into a syringe and injected into a surface-mounted LED on which an emission element having an emission wavelength of 405 nm had been mounted using a precise injection apparatus so that an opening part became flat and the resin composition was cured at 150°C for 1 hour after pre-curing at 120°C for 3 hours, thereby encapsulating the surface-mounted LED. The presence of dents on the resin surface in association with vaporization of the curing agent after thus encapsulated was visually evaluated. In the table, Good means that no dents are observed, Moderate means that dents are slightly observed, and Bad means that many dents are observed.

(3) Surface tackiness;

A test piece the same as in the above test for cured product transmittance was prepared and surface tackiness (surface stickiness) of the test piece was confirmed by finger touch. In the table, Good means that no stickiness is observed and Bad means that stickiness is observed.

[0096]

[Table 2]

Table 2 Evaluation Test

	Exam- ple 6	Exam- ple 7	Exam- ple 8	Exam- ple 9	Exam- ple 10	Exam- ple 11	Compar- ative Example 1	Compar- ative Example 2
A-1	100					100		
A-2		100						
A-3			100					
A-4				100				
A-5					100			
MH700G							100	100
Epoxy resin (B-1)	108	106	147	112	108		421	
ERL-4221						19		77
PX-4MP							0.4	0.1
(1) Cured product transmittance (%)	91	91	91	91	91	91	92	91
(2) Dent	Good	Good	Good	Good	Good	Good	Bad	Bad
(3) Surface tackiness	Good	Good	Good	Good	Good	Good	Bad	Good

5 [0097]

As apparent from the results shown in Table 1, a large thermal weight decrease was observed under a condition of 120°C in the case of RIKACID MH700G of Comparative Example but weight decrease was hardly observed in the case of the carboxylic acid compounds A-1 to A-5 of Examples 1 to 5 although they are liquid.

10 Moreover, as apparent from the results shown in Table 2, many dents of the cured products were observed in Comparative Examples 1 to 2 but dents were hardly observed in Examples 6 to 11, further the transmittance of the cured products were excellent, and no surface stickiness was observed.

[0098]

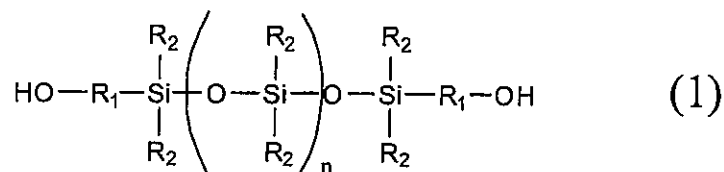
15 While the present invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

20 The present application is based on Japanese Patent Application No. 2008-324305 filed on December 19, 2008, and the contents are incorporated herein by reference. Also, all the references cited herein are incorporated as a whole.

Claims

[Claim 1] A carboxylic acid compound (A) obtainable by an addition reaction of a silicone compound (a) represented by the following formula (1):

5 [Chem. 1]

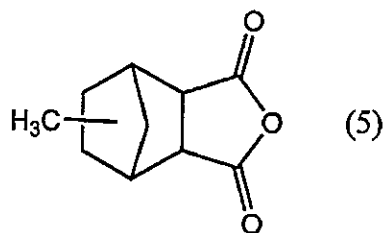
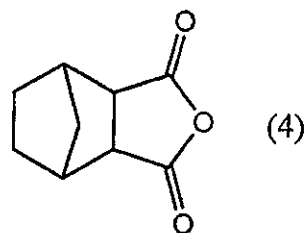
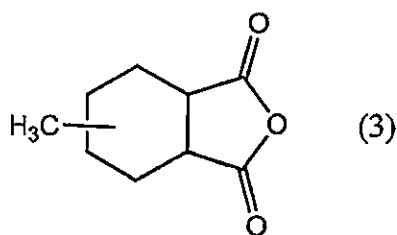


wherein R_1 represents an alkylene group having 1 to 10 carbon atoms in total which may contain an ether group, R_2 represents a methyl group or a phenyl group, and n represents from 1 to 100 as an average value, respectively,

10 with a compound having one or more carboxylic anhydride group in the molecule,

wherein the compound having one or more carboxylic anhydride group in the molecule is at least one selected from compounds (c) represented by the following formulae (3) to (5):

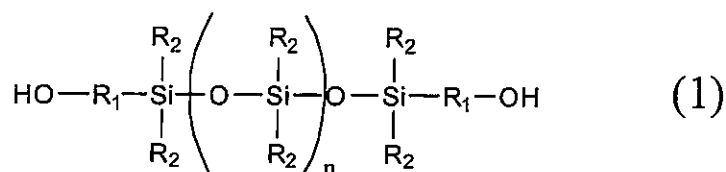
[Chem. 2]



15

[Claim 2] A carboxylic acid compound (A) obtainable by an addition reaction of a silicone compound (a) represented by the following formula (1):

[Chem. 3]

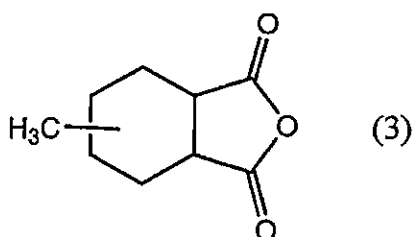


wherein R_1 represents an alkylene group having 1 to 10 carbon atoms in total which may contain an ether group, R_2 represents a methyl group or a phenyl group, and n represents from 1 to 100 as an average value, respectively,

with a compound having one or more carboxylic anhydride group in the molecule,

wherein the compound having one or more carboxylic anhydride group in the molecule is the compound represented by the formula (3):

[Chem. 4]



[Claim 3] An epoxy resin curing agent containing the carboxylic acid compound (A) according to claim 1 or 2 and a curing accelerator.

[Claim 4] An epoxy resin composition containing the carboxylic acid compound (A) according to claim 1 or 2 or the epoxy resin curing agent according to claim 3 and an epoxy resin.

[Claim 5] The epoxy resin composition according to claim 4, wherein epoxy equivalent of the epoxy resin is from 400 to 1,500 g/eq. and weight-average molecular weight is from 1,500 to 10,000.

[Claim 6] The epoxy resin composition according to claim 5, wherein use of the epoxy resin composition is an encapsulating material for optical semiconductors.

[Claim 7] The epoxy resin composition according to claim 5, wherein use of the epoxy resin composition is a die-bonding material for optical semiconductors.

[Claim 8] A cured product of the epoxy resin composition according to any one of claims 4 to 7.