DESCRIPTION

Title of Invention:

POLYVALENT CARBOXYLIC ACID COMPOSITION AND PROCESS FOR PRODUCING THE SAME, AND CURABLE RESIN COMPOSITION CONTAINING THE POLYVALENT CARBOXYLIC ACID COMPOSITION

Technical Field

[0001]

The present invention relates to a polyvalent carboxylic acid composition suitable for electric and electronic material uses and a process for producing the same. Furthermore, the present invention relates to a curable resin composition containing the polyvalent carboxylic acid composition as a curing component.

Background Art

[0002]

A polyvalent carboxylic acid possesses excellent performance as a crosslinking agent, a condensing agent and the like, such as formation of condensates and good reactivity together with high thermal stability, good electric properties, chemical resistance and the like. Thus, the acid has attracted much attention as a raw material for polymer production and has been increasingly widely employed.

Moreover, it is known that a polyvalent carboxylic acid can be also used as a curing agent.

[0003]

A curable resin composition containing an epoxy resin has been utilized in the fields of architecture, civil engineering, automobiles, aircrafts and the like as a resin excellent in heat resistance. Recently, particularly in the field of semiconductor-related materials, there are plenty of electronic devices in which words "light", "thin", "short", and "small" are keywords, such as mobile phones with camera, ultrathin liquid crystal or plasma TV sets, and light-weight laptops, and thereby extremely high properties are required also for packaging materials including an epoxy resin as a representative.

Furthermore, in recent years, attention is focused on utilization in opto-electronics-related fields. Particularly, with recent highly advanced information, in order to transmit and process enormous quantity of information smoothly, a technology utilizing optical signals has been developed instead of signal transmission by conventional electric wiring. Based on this situation, in the fields of optical components such as optical waveguides,

blue LEDs and optical semiconductors, it is desired to develop a resin composition which affords a cured material excellent in transparency.

[0004]

In general, as a curing agent for epoxy resins to be used in such fields, acid anhydride-based compounds are mentioned. Particularly, an acid anhydride formed of a saturated hydrocarbon is frequently used since it is excellent in light resistance (for example, see Patent Documents 1 and 2). As these acid anhydrides, alicyclic acid anhydrides such as methylhexahydrophthalic anhydride, hexahydrophthalic anhydride and tetrahydrophthalic anhydride are common. Of these, from the viewpoint of easy handling, methylhexahydrophthalic anhydride, methyltetrahydrophthalic anhydride and the like that are liquid at ordinary temperature have been mainly used.

However, in the case where the above alicyclic acid anhydrides are used as curing agents, these curing agents have high vapor pressure and a portion tends to vaporize in curing. Therefore, at thermal curing in an open system using these alicyclic acid anhydrides as curing agents for epoxy resins, the alicyclic acid anhydrides volatilize into the air and there is a concern that they cause environmental pollution and adverse influences on the human body through the emission of harmful substances into the air. Moreover, in addition thereto, not only there are problems that they cause contamination of production lines and insufficient curing of an epoxy resin composition attributable to the fact that a predetermined amount of the carboxylic anhydride (curing agent) is not present in a cured material but also the properties are largely changed depending on curing conditions, so that it is difficult to obtain a cured material having objective performance steadily.

[0005]

The influence on the cured material by the above volatilization remarkably appears at the time when an LED, especially an LED used for SMD (Surface Mount Device) is encapsulated with a cured material in which a conventional acid anhydride is used as a curing agent. Since the amount of a resin to be used is small in the encapsulation of an LED, a hollow may be generated when volatilization of the acid anhydride takes place and, at a severe case, there arises a problem that a wire may be exposed. Furthermore, since cracking and peeling occur in solder reflow or curing becomes insufficient, there is a problem that it is also difficult for the resulting cured material to endure long-term lighting.

Related Art

Patent Document

[0006]

Patent Document 1: JP-A-2003-277473

Patent Document 2: JP-A-2008-063333

## Summary of Invention

### Problems to Be Solved by the Invention

[0007]

For such problems, a method of using a polyvalent carboxylic acid as a curing agent may be considered. However, usual polyvalent carboxylic acids solidify, especially crystallize in many cases due to their hydrogen bonding and thus it is very difficult to use them as liquid compositions. In order to solve such a problem, the inventors of the present invention have investigated use of a silicone-based polyvalent carboxylic acid as a curing agent. However, in the case of using a silicone-based carboxylic acid as a curing agent, although the problem of volatilization can be solved, desired properties in view of close adhesiveness and resistance to corrosive gas permeation have not obtained. Thus, the use as a cured material for encapsulating materials and the like was difficult.

Furthermore, in curing of organosiloxane-type epoxy resins, obtained cured materials are prone to be brittle, and a problem in toughness has remained.

[0008]

An object of the present invention is to provide a polyvalent carboxylic acid composition which reduces the volatilization of a curing agent in curing and further affords cured materials excellent in heat resistance, light resistance, resistance to corrosive gas permeation, close adhesiveness, and toughness and a process for producing the same. Moreover, another object of the present invention is to provide a curable resin composition containing the polyvalent carboxylic acid composition.

### Means for Solving the Problems

[0009]

The present invention carried out extensive studies under the situation described above and accomplished the present invention.

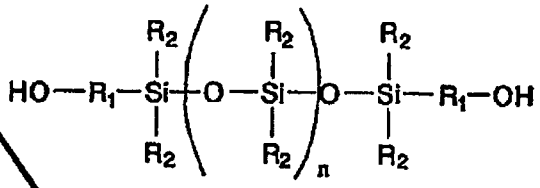
Thus, the present invention relates to:

[0010]

(1) a polyvalent carboxylic acid composition comprising:

a carboxylic acid compound (J) obtained by addition reaction of a silicone oil (a) represented by the following formula (1):

[Chem. 1]



(1)

wherein $R_1$ represents an alkylene group having 1 to 10 carbon atoms in total which may have an intervening ether linkage; $R_2$ represents a methyl group or a phenyl group; and n represents a repeating unit, weight-average molecular weight of the compound represented by the formula (1) being 500 to 5000,

with a compound (b) containing one or more carboxylic anhydride groups in the molecule and

a polyvalent carboxylic acid compound (K) obtained by addition reaction of a saturated aliphatic polyvalent alcohol (c) having two or more functional alcoholic hydroxyl groups with a compound (d) having one or more carboxylic anhydride groups in the molecule.

(2) The polyvalent carboxylic acid composition according to (1) above, wherein the compounds (b) and (d) are each an acid anhydride having a cyclic saturated hydrocarbon as a core skeleton.

(3) The polyvalent carboxylic acid composition according to (1) or (2) above, wherein the compounds (b) and (d) are each at least one acid anhydride selected from the group consisting of methylhexahydrophthalic anhydride, hexahydrophthalic anhydride, cyclohexane-1,2,4-tricarboxylic acid 1,2-anhydride and bicyclo[2,2,1]heptane-2,3-dicarboxylic anhydride.

(4) The polyvalent carboxylic acid composition according to (3) above, wherein the compounds (b) and (d) necessarily comprise methylhexahydrophthalic anhydride.

(5) The polyvalent carboxylic acid composition according to any one of (1) to (4) above, wherein the compound (c) is a polyvalent alcohol having 2 to 6 functional groups, total number of the carbon atoms in one molecule being 5 to 20.

(6) A process for producing the polyvalent carboxylic acid composition according to any one of (1) to (5) above, which comprises:

adding the compounds (b) and (d) having one or more carboxylic anhydride groups in the molecule to a mixture containing the silicone oil (a) and the saturated aliphatic polyvalent alcohol having two or more functional alcoholic hydroxyl groups and simultaneously carrying out the addition reaction of the silicone oil (a) with the compound (b) and the addition reaction of the compound (c) with the compound (d).

(7) A process for producing the polyvalent carboxylic acid composition according to any one of (1) to (5) above, which comprises sequentially reacting the following step (A) and step (B) in one pot:

Step (A): a step of addition reaction of the silicone oil (a) with the compound (b) containing one or more carboxylic anhydride groups in the molecule;

Step (B): a step of addition reaction of the saturated aliphatic polyvalent alcohol (c) having two or more functional alcoholic hydroxyl groups with the compound (d) having one or more carboxylic anhydride groups in the molecule.

(8) The process for producing the polyvalent carboxylic acid composition according to (6) or (7) above, wherein the addition reaction is carried out at 40 to 150°C with no solvent or in an organic solvent in an amount of 50% by weight or less based on the total amount of reaction substrates in the raw materials to be used.

(9) A curable resin composition containing the polyvalent carboxylic acid composition according to any one of (1) to (5) above and an epoxy resin.

(10) The curable resin composition according to (9) above, wherein the epoxy resin is an alicyclic epoxy resin and/or an epoxy group-containing silicone resin.

(11) The curable resin composition according to (9) above, wherein the epoxy resin is an epoxy group-containing silicone resin.

(12) A cured material obtained by curing the curable resin composition according to any one of (9) to (11) above.

Effects of the Invention

[0012]

The polyvalent carboxylic acid composition of the present invention is useful as a curing agent for epoxy resins. Particularly, the curable resin composition of the present invention not only exhibits extremely less volatility of the polyvalent carboxylic acid component as a curing agent in a temperature region that is usually adopted for curing epoxy resins but also is excellent in heat resistance, light resistance, close adhesiveness, resistance to corrosive gas permeation, toughness and the like. The polyvalent carboxylic acid composition of the present invention is useful as a raw material or modifier for paints, adhesives, molded articles, encapsulating resins for semiconductors, 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 toners. Particularly, the polyvalent carboxylic acid composition is extremely useful as a curing agent for epoxy resins for encapsulation of optical semiconductors including a highly luminous white LED or the like as a representative, because of curing ability toward epoxy reins and high transparency of cured materials obtained therefrom.

Best Embodiments for Carrying Out the Invention

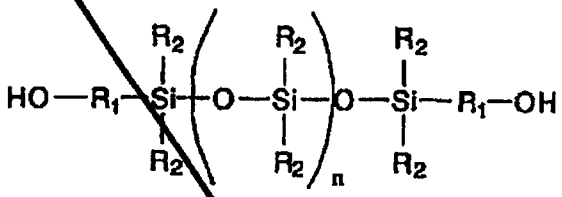
[0013]

The polyvalent carboxylic acid composition of the present invention comprises:

a carboxylic acid compound (J) obtained by addition reaction of a silicone oil (a) represented by the following formula (1):

[0014]

[Chem. 2]



(1)

[0015]

(in the formula (1), $R_1$ represents an alkylene group having 1 to 10 carbon atoms in total which may have an intervening ether linkage; $R_2$ represents a methyl group or a phenyl group; and n represents a repeating unit, weight-average molecular weight of the compound represented by the formula (1) being 500 to 5000)

with a compound (b) containing one or more carboxylic anhydride groups in the molecule and

a polyvalent carboxylic acid compound (K) obtained by addition reaction of a saturated aliphatic polyvalent alcohol (c) having two or more functional alcoholic hydroxyl groups with a compound (d) having one or more carboxylic anhydride groups in the molecule.

The polyvalent carboxylic acid compound (J) and the polyvalent carboxylic acid compound (K) at the production of the polyvalent carboxylic acid composition of the present invention may be each singly prepared and mixed, or individual raw materials may be sequentially reacted.

[0016]

The silicone oil (a) is represented by the above formula (1).

In the formula (1), specific examples of $R_1$ include alkylene groups having 1 to 10 carbon atoms in total which has no ether linkage, such as methylene, ethylene, propylene, butylene, pentylene, hexylene, heptylene and octylene; alkylene group having 1 to 10 carbon atoms in total which has an ether linkage, such as $-C_3H_6-O-C_2H_4-$, $-C_2H_4-O-C_2H_4-$ and $-C_3H_6-O-C_3H_6-$. Of these, from the viewpoint of easy commercial availability, a propylene group or $-C_3H_6-O-C_2H_4-$ is preferred.

In the case where the total carbon number of the chain of $R_1$ exceeds 10, for example, polyethylene oxide adducts and the like are present as commercially available products but are not preferable in view of heat resistance and light resistance.

As a preferable range of molecular weight of the silicone oil (a), the weight-average molecular weight is 500 to 5,000, more preferably 600 to 4,000, and particularly preferably 600 to 2,500. Moreover, the most preferable range is 600 to 1,500. When the molecular weight is less than 500, intermolecular force of the obtained product increases and viscosity is prone to increase. Moreover, when the molecular weight is more than 5,000, compatibility with the other components is poor and the system becomes turbid in many cases, so that the case is not preferred.

Such carbinol-modified silicone compounds can be synthesized, for example, using the procedure described in JP-A-2007-508424 and the like. As commercially available compounds, there may be mentioned Dow Corning 5562 (manufactured by Dow Corning Toray Co., Ltd.); X-22-160AS, KF6001, KF6002, KF6003 (all manufactured by Shin-Etsu Chemical Co., Ltd.); XF42-B0970 (manufactured by Momentive Performance Materials Inc.); Silaplane FM-4411, FM4421, FM-4425 (manufactured by Chisso Corporation); and the like.

[0017]

As the saturated aliphatic polyvalent alcohol (c) having two or more functional alcoholic hydroxyl groups, conventionally known alcohols may be mentioned but, from the viewpoint of a balance between heat and light resistance and toughness, particularly preferably, polyvalent alcohols having 2 to 6 functional groups and having 5 to 20 carbon atoms in total in one molecule are preferred. Further preferred are linear alkylene diols having a branched structure in the molecular structure, diols having a cyclic structure, triols, tetraols, hexaols and the like.

As the linear alkylene diols having a branched structure, there may be specifically mentioned neopentyl glycol, 2-ethyl-2-butylpropylene-1,3-diol, 2,4-diethylpentane-1,5-diol and the like.

As the diols having a cyclic structure, there may be mentioned tricyclodecanediol, pentacyclodecanediol, 1,4-cyclohexanediol, norbornanediol, dioxane glycol, spiro-glycol and the like.

There may be mentioned glycerin, trimethylolpropane and the like as the triols; pentaerythritol, ditrimethylolpropane and the like as the tetraols; and dipentaerythritol and the like as the hexaols.

From the viewpoint of excellent optical properties, heat coloring resistance and light coloring resistance, use of 2,4-diethylpentane-1,5-diol, tricyclodecanediol and pentaerythritol is preferred.

In the present invention, the alcohols are not limited to these specific examples and they may be used singly or as a mixture of two or more thereof.

[0018]

The compounds (b) and (d) having one or more carboxylic anhydride groups in the molecule (the compounds (b) and (d) may be the same or different) are preferably each a compound having one or two carboxylic anhydride groups in the molecule. Specifically, there may be mentioned 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, cyclohexane-1,2,4-tricarboxylic acid 1,2-anhydride, cyclobutanetetracarboxylic acid dianhydride, butanetetracarboxylic dianhydride and the like.

Of these, from the viewpoint of optical properties, particularly, compounds having a saturated hydrocarbon structure are preferred. Furthermore, from the viewpoint of a balance between heat resistance and toughness, those having a cyclic saturated hydrocarbon structure as a core skeleton are particularly preferred. Specifically, there may be mentioned methylhexahydrophthalic anhydride, hexahydrophthalic anhydride, cyclohexane-1,2,4-tricarboxylic acid 1,2-anhydride, bicyclo[2,2,1]heptane-2,3-dicarboxylic anhydride, cyclobutanetetracarboxylic acid dianhydride, butanetetracarboxylic dianhydride and the like but the compounds are not limited thereto and may be used singly or as a mixture of two or more thereof.

In the present invention, from the viewpoint of easy handling, particularly, those having one carboxylic anhydride group are particularly preferred. Of these, use of methylhexahydrophthalic anhydride, hexahydrophthalic anhydride, cyclohexane-1,2,4-tricarboxylic acid 1,2-anhydride and bicyclo[2,2,1]heptane-2,3-dicarboxylic anhydride is preferred. Particularly, based on optical properties, methylhexahydrophthalic anhydride or cyclohexane-1,2,4-tricarboxylic acid 1,2-anhydride is particularly preferred.

[0019]

A reaction of adding an alcohol to an acid anhydride, such as the addition reaction of the silicone oil (a) with the compound (b) having a carboxylic anhydride group or the addition reaction of the polyvalent alcohol (c) with the compound (d) having a carboxylic anhydride group, is generally an addition reaction using an acid or a base as a catalyst. In the present invention, from the viewpoint of convenience of post-treatment and removal of adverse influences of a remaining catalyst on products, a reaction with no catalyst is particularly preferred. Moreover, since removal is a problem, use of one or more agents selected from curing accelerators and additives used in the curable resin composition to be mentioned later is preferred because subsequent purification is not necessary.

In the case of using a catalyst, examples thereof include acidic compounds such as hydrochloric acid, sulfuric acid, methanesulfonic acid, trifluoromethanesulfonic acid, p-toluenesulfonic acid, nitric acid, trifluoroacetic acid and trichloroacetic acid; metal hydroxides such as sodium hydroxide, potassium hydroxide, calcium hydroxide and magnesium hydroxide; amine compounds such as triethylamine, tripropylamine and tributylamine; heterocyclic compounds such as pyridine, dimethylaminopyridine, 1,8-diazabicyclo[5.4.0]undec-7-ene, imidazole, triazole and tetrazole; quaternary ammonium salts such as tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, trimethylethylammonium hydroxide, trimethylpropylammonium hydroxide, trimethylbutylammonium hydroxide, trimethylcetylammonium hydroxide, trioctylmethylammonium hydroxide, tetramethylammonium chloride, 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.

The amount of the catalyst to be used is not particularly limited but is usually 0.001 to 5 parts by weight based on 100 parts by weight of the total weight of the raw materials.

[0020]

In the present reaction, the reaction with no solvent is preferred but an organic solvent may be used. The amount of the organic solvent to be used is 0.005 to 1, preferably 0.005 to 0.7 and more preferably 0.005 to 0.5 (i.e., 50% by weight or less as an outer ratio) relative to 1 of the total amount of the reaction substrates. When the weight ratio exceeds 1, the reaction proceeds extremely slowly, so that the case is not preferred. Examples of usable solvents include alkanes such as hexane, cyclohexane and heptane; aromatic hydrocarbons such as toluene and xylene; ketones such as methyl ethyl ketone, methyl isobutyl ketone, cyclopentanone and anone; ethers such as diethyl ether, tetrahydrofuran and dioxane; ester compounds such as ethyl acetate, butyl acetate and methyl formate; and the like.

[0021]

The reaction temperature is preferably from 40 to 200°C and particularly preferably from 40 to 150°C. Particularly in the case where the reaction is carried out with no solvent, the reaction at 100°C or less is preferred and the reaction at 40 to 100°C, particularly at 40 to 80°C is preferred, because of the volatilization of the acid anhydride.

Moreover, in the case of using a compound having high crystallinity at room temperature, for example, cyclohexane-1,2,4-tricarboxylic 1,2-anhydride or the like, it is

preferred to carry out the reaction at 100 to 150°C in order to dissolve the crystal thoroughly.

Furthermore, in the case of using a volatile acid anhydride and an acid anhydride having high crystallinity in combination, it is possible to prevent the volatilization of the acid anhydride by elevating the temperature stepwise.

[0022]

With regard to the reaction ratios of the compounds (a) to (b) and (c) to (d), theoretically, an equimolar reaction is preferred but the ratios can be changeable according to needs. That is, as mentioned later, in the curing agent composition of the present invention, in the case where the acid anhydride to be used in combination according to needs is the same as the acid anhydride to be used here, it is also possible to carry out the reaction in excess acid anhydride at production to form a mixture of the acid anhydride and the polyvalent carboxylic acid composition of the present invention at the time when the reaction of obtaining the polyvalent carboxylic acid (J) and the polyvalent carboxylic acid (K) is completed.

A specific reaction ratio is, when compared in terms of the functional group equivalent, 0.001 to 1.0, more preferably 0.01 to 1.0, and further preferably 0.1 to 1.0 of (a) (or (c)) in terms of molar ratio when (b) (or (d)) is regarded as 1. In the case of producing a mixture of the polyvalent carboxylic acid composition of the present invention and the other acid anhydride as mentioned above, the above ratio is preferably in the range of 0.01 to 0.7, preferably 0.01 to 0.4.

[0023]

The reaction time depends on the reaction temperature, the amount of the catalyst and the like but, from the viewpoint of industrial production, a reaction for a long time is not preferred since it consumes a large amount of energy. Also, exceedingly short reaction time means that the reaction is drastic, and thus is not preferred in view of safety. A preferable range is 1 to 48 hours, preferably 1 to 36 hours, and further preferably 1 to 24 hours.

[0024]

After completion of the reaction, in the case of using a catalyst, an objective polyvalent carboxylic acid (J) or (K) is obtained by removing the catalyst through neutralization, washing with water, adsorption and the like and removing the solvent through distillation.

In the case of the reaction with no catalyst, the polyvalent carboxylic acid (J) or, in the case of using no solvent and no catalyst, the polyvalent carboxylic acid (K) can be obtained by removing the solvent through distillation according to needs or by taking out the product without further treatment.

[0025]

The most suitable production method is a procedure in which the reaction is carried out at 40 to 150°C under conditions of no catalyst and no solvent and, after completion of the reaction, the product is taken out without further treatment.

[0026]

An objective polyvalent carboxylic acid composition can be obtained by mixing the polyvalent carboxylic acid (J) and polyvalent carboxylic acid (K) thus obtained. The ratio of (J)/(K) is 99.7/0.3 to 50/50 and more preferably 99.7/0.3 to 60/40 in terms of weight ratio. When the amount of the polyvalent carboxylic acid (J) is too large, there arise problems on resistance to corrosive gas permeation and reflow resistance. When the polyvalent carboxylic acid (K) is too much, solidification occurs and the handling becomes difficult.

Here, particularly, the ratio of (J)/(K) is preferably 99/1 to 80/20 and more preferably 99/1 to 85/15. This is because the performance of the resistance to corrosive gas permeation is especially improved by mixing (K) in a weight ratio of 1 or more and the performance that light resistance is excellent, peeling from the substrate and cracking hardly occur, and also illuminance deterioration in the case of using the composition as an encapsulating material of LED hardly occurs can be realized by mixing (J) in a weight ratio of 80 or more. Particularly, the above properties can be all achieved with good balance by mixing (J) in a weight ratio of 85 or more.

[0027]

Moreover, in the present invention, it is possible to produce the polyvalent carboxylic acid (J) and the polyvalent carboxylic acid (K) simultaneously. Specific procedures are as follows.

(i) The compounds (b) and (d) having one or more carboxylic anhydride groups in the molecule are charged into a mixture of the silicone oil (a) and the polyvalent alcohol (c) and they are reacted simultaneously.

(ii) The following step (A) and step (B) are sequentially reacted in one pot.

Step (A): a step of reacting the silicone oil (a) with the compound (b) containing one or more carboxylic anhydride groups in the molecule;

Step (B): a step of reacting the saturated aliphatic polyvalent alcohol (c) having two or more alcoholic hydroxyl groups with the compound (d) having one or more carboxylic anhydride groups in the molecule.

That is, the procedure of the above (ii) includes sequential charging of the compounds to be used in the step (B) (or step (A)) after the step (A) (or step (B)) is performed and performing the reaction and mixing in the system.

(iii) In the case where the compounds (b) and (d) having one or more carboxylic anhydride groups are the same, the silicone oil (a) (or the polyvalent alcohol (c)) and the compound

(b) (= (d)) having one or more carboxylic anhydride groups are charged and reacted and then the polyvalent alcohol (c) (or the silicone oil (a)) is charged and reacted.

[0028]

The thus obtained polyvalent carboxylic acid composition of the present invention becomes usually a colorless liquid to semi-solid substance.

The polyvalent carboxylic acid composition of the present invention is excellent in transparency, and it is useful as a curing agent for epoxy resins, a raw material or modifier for paints, adhesives, molded articles, encapsulating resins for semiconductors and optical semiconductors, resins for die-bonding materials of optical semiconductors, polyamide resins, polyimide resins and the like, a plasticizer or a lubricating oil raw material, an intermediate for medicaments and pesticides, a raw material for paint resins, and a resin for toner. Particularly, it is used as a curing agent for epoxy resins.

In the case where the polyvalent carboxylic acid composition of the present invention is used as a curing agent for epoxy resins, the polyvalent carboxylic acid composition of the present invention shows excellent curing ability and transparency of the cured material thereof is excellent, so that it is extremely useful as a curing agent for epoxy resins for use in encapsulation of optical semiconductors such as a highly luminous white LED.

[0029]

In the case where the polyvalent carboxylic acid composition of the present invention is used as a curing agent of curable resins such as epoxy resins, particularly as a liquid composition, it is preferred to use the composition in the form of a curing agent composition in which the polyvalent carboxylic acid composition of the present invention is mixed with the other acid anhydride.

As usable acid anhydride, a compound (e) having one or more carboxylic anhydride groups in the molecule is preferred and an acid anhydride having no aromatic ring in the structure is preferred. As the compound (e) having one or more carboxylic anhydride groups in the molecule, there may be specifically mentioned hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, butanetetracarboxylic anhydride, bicyclo[2,2,1]heptane-2,3-dicarboxylic anhydride, methylbicyclo[2,2,1]heptane-2,3-dicarboxylic anhydride, cyclohexane-1,2,4-tricarboxylic acid 1,2-anhydride and the like.

In the case of using a mixture with an acid anhydride as a curing agent composition, the ratio of the polyvalent carboxylic acid composition of the present invention is 0.1 to 50% by weight and preferably 0.1 to 30% by weight based on the total weight of the above other acid anhydride and the polyvalent carboxylic acid composition of the present invention. By using them in combination in such a range, effects are achieved on the flowability of the composition and heat-resistant mechanical strength of cured materials.

The following will describe the curable resin composition of the present invention containing the polyvalent carboxylic acid composition of the present invention.

The curable resin composition of the present invention contains an epoxy resin as an essential component.

[0030]

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

[0031]

Particularly, in the case where the curable resin composition of the present invention is used in optical uses, alicyclic epoxy resins and/or epoxy group-containing silicone resins are preferred and epoxy resins having a silsesquioxane structure are more preferred. Particularly, in the case of the alicyclic epoxy resins, compounds having an epoxycyclohexnae structure in the skeleton are preferred, and epoxy resins obtained by oxidation reaction of compounds having a cyclohexene structure are more preferred.

As these alicyclic epoxy resins, there may be mentioned those obtained by oxidation of compounds that can be produced by esterification reaction of cyclohexenecarboxylic acid with alcohols or esterification reaction of cyclohexenemethanol with carboxylic acids (procedures described in Tetrahedron Vol. 36 p.2409 (1980), Tetrahedron Letter p.4475 (1080) and the like), or Tishchenko reaction of cyclohexenealdehyde (procedures described in JP-A-2003-170059, JP-A-2004-262871 and

the like), or further ester-exchange reaction of cyclohexenecarboxylate esters (procedures described in JP-A-2006-052187 and the like).

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

[0032]

Further, as the alicyclic epoxy resins other than the above, acetal compounds obtained by acetalization reaction of cyclohexenealdehyde derivatives with alcohol compounds. As the reaction procedure, they can be produced by applying a common acetalization reaction. For example, there are disclosed a method of performing the reaction with azeotropic water removal using a solvent such as toluene or xylene as a reaction medium (US Patent No. 2945008), a method of performing the reaction with gradually adding an aldehyde after a polyvalent alcohol is dissolved in conc. hydrochloric acid (JP-A-48-96590), a method of using water as a reaction medium (US Patent No. 3092640), a method of using an organic solvent as a reaction medium (JP-A-7-215979), a method of using a solid acid catalyst (JP-A-2007-230992) and the like. From the viewpoint of structural stability, a cyclic acetal structure is preferred.

Specific examples of these epoxy resins include ERL-4221, UVR-6105, ERL-4299 (all trade names, all manufactured by Dow Chemical), Celloxide 2021P, Epolead GT401, EHPE3150, EHPE3150CE (all trade names, all manufactured by Daicel Chemical Industries, Co., Ltd.), dicyclopentadiene diepoxide and the like but they are not limited thereto (Reference Literature: Sosetsu Epokisi Rejin Kiso-hen I p76-85).

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

[0033]

In the curable resin composition of the present invention, the polyvalent carboxylic acid composition (or curing agent composition) of the present invention may be used in combination with the other curing agent. In the case of combination use, the ratio of the polyvalent carboxylic acid of the present invention in the whole curing agent is preferably 20% by weight or more and particularly preferably 30% by weight or more.

Examples of the other curing agent usable in combination include amine-based compounds, acid anhydride-based compounds, amide-based compounds, phenol-based compounds, carboxylic acid-based compounds and the like. Specific examples of usable curing agent include diaminodiphenylmethane, diethylenetriamine, triethylenetetramine,

diaminodiphenyl sulfone, isophoronediamine, dicyandiamide, polyamide resins synthesized from dimer of linolenic acid and ethylenediamine, 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, cyclohexane-1,3,4-tricarboxylic 3,4-anhydride, bisphenol A, bisphenol F, bisphenol S, fluorene bisphenol, terpene diphenol, 4,4'-biphenol, 2,2'-biphenol, 3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'-diol, hydroquinone, resorcin, naphthalenediol, tris-(4-hydroxyphenyl)methane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, polycondensates of phenols (phenol, alkyl-substituted phenols, naphthol, alkyl-substituted naphthaols, dihydroxybenzene, dihydroxynaphthalene, etc.) with formaldehyde, acetaldehyde, bezaldehyde, p-hydroxybenzaldehyde, o-hydroxybenzaldehyde, p-hydroxyacetophenone, o-hydroxyacetophenone, dicyclopentadiene, furfural, 4,4'-bis(chloromethyl)-1,1'-biphenyl, 4,4'-bis(methoxymethyl)-1,1'-biphenyl, 1,4'-bis(chloromethyl)benzene, 1,4'-bis(methoxymethyl)benzene or the like and modified compounds thereof, halogenated bisphenols such as tetrabromobisphenol A, imidazole, trifluoroborane-amine complexes, guanidine derivatives, condensates of terpenes with phenols and the like but they are not limited thereto. They may be used singly or two or more thereof may be used.

[0034]

In the curable resin composition of the present invention, the ratio of the whole curing agent to the epoxy resin is preferably 0.5 to 1.5 equivalents (the acid anhydride group is considered to be monofunctional) and particularly preferably 0.5 to 1.2 equivalents relative to 1 equivalent of the epoxy group of the epoxy resin. In the case where the ratio is less than 0.5 equivalent or is more than 1.5 equivalents relative to 1 equivalent of the epoxy group, there is a concern that curing is insufficient and good cured physical properties are not obtained in both cases.

[0035]

In the cured resin composition of the present invention, a curing accelerator may be used in combination 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 these imidazoles with polyvalent carboxylic acids such as phthalic acid, terephthalic acid, trimellitic acid, pyromellitic acid, naphthalenedicarboxylic acid, maleic acid and oxalic acid, amides such as dicyandiamide, diaza compounds such as 1,8-diazabicyclo[5.4.0]undecene-7 and salts thereof with tetraphenylborate, phenol novolak and the like, salts with the above polyvalent carboxylic acids or phosphinic acids, ammonium salts such as tetrabutylammonium bromide, cetyltrimethylammonium bromide and trioctylmethylammonium bromide, phosphines and phosphonium compounds such as triethylphosphine, tri(toluyl)phosphine, tetraphenylphosphonium bromide and tetraphenylphosphonium tetraphenylborate, phenols such as 2,4,6-trisaminomethylphenol, amine adducts, metal compounds such as tin octylate and the like, and microcapsulated curing accelerators obtained by microcapsulation of these curing accelerators, and the like.

[0036]

In the present invention, it is preferred to incorporate a zinc salt and/or a zinc complex. In the curable resin composition of the present invention, the zinc salt and/or the zinc complex contribute as a curing accelerator of the epoxy resin and the curing agent.

The zinc salt and/or zinc complex is a salt and/or complex containing a zinc ion as a central element and preferably has a counter ion and/or at lest one compound selected from carboxylic acids having an alkyl groups having 1 to 30 carbon atoms, phosphate esters and phosphoric acid as a ligand. As the alkyl groups having 1 to 30 carbon atoms, there may be mentioned a methyl group, an isopropyl group, a butyl group, a 2-ethylhexyl group, an octyl group, an isodecyl group, an isostearyl group, a decanyl group, a cetyl group and the like.

In the present invention, particularly, zinc carboxylate compounds and zinc phosphate esters are preferred. By using the zinc carboxylate compounds and zinc phosphate esters, the resistance to corrosive gas permeation can be enhanced.

[0037]

In the present invention, as particularly preferred zinc carboxylate compounds, those having in the compound an alkyl group having a linear branched structure or an alkyl group having a functional group such as olefin are preferred. Of these, those having 3 to 30 carbon atoms are preferred and particularly, those having 5 to 20 carbon atoms are preferred. They are preferred in view of compatibility. In the case where the number of carbon atoms is too large (the case where the number of carbon atoms exceeds 30) or where the compounds do not have any branched structure or structure of a functional group or the like, the compatibility with resins is bad, so that the case is not preferred.

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

[0038]

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

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

[0039]

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

[0040]

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

[0041]

The curing agent to be used is appropriately selected depending on the properties required for the resulting transparent resin composition, such as transparency, the curing rate, wording conditions. The curing accelerator is used in the range of usually 0.001 to 15 parts by weight, more preferably 0.01 to 5 parts by weight, and particularly preferably 0.01 to 3 parts by weight based on 100 parts by weight of the epoxy resin. In the present

reaction, curing is possible with no curing accelerator but the addition of the curing accelerator is preferred in view of the coloring problem at curing. Particularly, in order to prevent the coloring and also obtain a property of the resistance to corrosive gas permeation, use of the zinc salt and/or zinc complex is preferred.

[0042]

In the curable resin composition of the present invention, it is also possible to incorporate a phosphorus-containing compound as a flame retardancy-imparting component. The phosphorus-containing compound may be reaction type one or addition type one. Specific examples of the phosphorus-containing compound include phosphate esters such as trimethyl phosphate, triethyl phosphate, tricresyl phosphate, trixylylenyl phosphate, cresyl diphenyl phosphate, cresyl-2,6-dixylylenyl phosphate, 1,3-phenylenebis(dixylylenyl phosphate), 1,4-phenylenebis(dixylylenyl phosphate) and 4,4'-biphenyl(dixylylenylphosphate); phosphanes such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide and 10(2,5-dihydroxyphenyl)-10H-9-oxa-10-phosphaphenathrene-10-oxide, phosphorus-containing epoxy compounds obtained by reacting an epoxy resin with active hydrogen of the phosphanes, red phosphorus and the like. The phosphate esters, the phosphanes, or phosphorus-containing epoxy compounds are preferred and 1,3-phenylenebis(dixylylenyl phosphate), 1,4-phenylenebis(dixylylenyl phosphate), 4,4'-biphenyl(dixylylenyl phosphate) or a phosphorus-containing epoxy compound is particularly preferred. The content of the phosphorus-containing compound is preferably as follows: phosphorus-containing compound/total epoxy resins = 0.1 to 0.6 (weight ratio). When the content is less than 0.1, flame retardancy is insufficient and when the content exceeds 0.6, there is a concern that moisture absorbing properties and dielectric properties of the cured materials are adversely affected.

[0043]

Furthermore, in the curable resin composition of the present invention, an antioxidant may be added according to needs. As usable antioxidant, phenol-based, sulfur-based, and phosphorus-based antioxidants may be mentioned. The antioxidants can be used singly or two or more thereof can be used in combination. The amount of the antioxidant to be used is usually 0.008 to 1 part by weight and preferably 0.01 to 0.5 part by weight based on 100 parts by weight of the resin components in the curable resin composition of the present invention.

[0044]

As the antioxidant, there may be, for example, mentioned phenol-based antioxidants, sulfur-based antioxidants, phosphorus-based antioxidants and the like. Specific examples of the phenol-based antioxidants include monophenols such as 2,6-di-t-butyl-p-cresol, butylated hydroxylanisole, 2,6-di-t-butyl-p-ethylphenol, stearyl-β-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, isooctyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate,

2,4-bis-(n-octylthio)-6-(4-hydroxy-3,5-di-t-butylanilino)-1,3,5-triazine and 2,4-bis[(octylthio)methyl]-o-cresol; bisphenols such as 2,2'-methylenebis(4-methyl-6-t-butylphenol), 2,2'-methylenebis(4-ethyl-6-t-butylphenol), 4,4'-thiobis(3-methyl-6-t-butylphenol), 4,4'-butylidenebis(3-methyl-6-t-butylphenol), triethylene glycol-bis[3-(3-t-butyl-5-methyl-4-hydroxyphenyl)propionate], 1,6-hexanediol-bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], N,N'-hexamethylenebis(3,5-di-t-butyl-4-hydroxy-hydrocinnamide), 2,2-thio-diethylenebis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], 3,5-di-t-butyl-4-hydroxybenzylphosphonate-diethyl ester, 3,9-bis[1,1-dimethyl-2-{β-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyloxy}ethyl]2,4,8,10-tetraoxaspiro[5,5]undecane and bis(ethyl 3,5-di-t-butyl-4-hydroxybenzylsulfonate) calcium; polymeric phenols such as 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene, tetrakis-[methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate]methane, bis[3,3'-bis-(4'-hydroxy-3'-t-butylphenyl)butyric acid] glycol ester, tris-(3,5-di-t-butyl-4-hydroxybenzyl)-isocyanurate, 1,3,5-tris(3',5'-di-t-butyl-4'-hydroxybenzyl)-S-triazine-2,4,6-(1H,3H,5H)trione and tocopherol.

[0045]

Specific examples of the sulfur-based antioxidants include dilauryl-3,3'-thiodipropionate, dimyristyl-3,3'-thiodipropionate, distearyl-3,3'-thiodipropionate and the like.

[0046]

Specific examples of the phosphorus-based antioxidants include 1,1,3-tris(2-methyl-4-ditridecylphosphite-5-tert-butylphenyl)butane, distearyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl) pentaerythritol diphosphite, phenylbisphenol A pentaerythritol diphosphite, dicyclohexyl pentaerythritol diphosphite, tris(diethylphenyl) phosphite, tris(di-isopropylphenyl) phosphite, tris(di-n-butylphenyl) phosphite, tris(2,4-di-tert-butylphenyl) phosphite, tris(2,6-di-tert-butylphenyl) phosphite, tris(2,4-di-tert-butylphenyl) phosphite, 2,2'-methylenebis(4,6-di-tert-butylphenyl) (2,4-di-tert-butylphenyl) phosphite, 2,2'-methylenebis(4,6-di-tert-butylphenyl) (2-tert-butyl-4-methylphenyl) phosphite, 2,2'-methylenebis(4-methyl-6-tert-butylphenyl) (2-tert-butyl-4-methylphenyl) phosphite, 2,2'-ethylidenebis(4-methyl-6-tert-butylphenyl) (2-tert-butyl-4-methylphenyl) phosphite, tetrakis(2,4-di-tert-butylphenyl)-4,4'-biphenylene diphosphonite, tetrakis(2,4-di-tert-butylphenyl)-4,3'-biphenylene diphosphonite, tetrakis(2,4-di-tert-butylphenyl)-3,3'-biphenylene diphosphonite, tetrakis(2,6-di-tert-butylphenyl)-4,4'-biphenylene diphosphonite, tetrakis(2,6-di-tert-butylphenyl)-4,3'-biphenylene diphosphonite, tetrakis(2,6-di-tert-butylphenyl)-3,3'-biphenylene diphosphonite, bis(2,4-di-tert-butylphenyl)-4-phenyl-phenylphosphonite, bis(2,4-di-tert-butylphenyl)-3-phenyl-phenylphosphonite, bis(2,6-di-n-butylphenyl)-3-phenyl-phenylphosphonite, bis(2,6-di-tert-

butylphenyl)-4-phenyl-phenylphosphonite, bis(2,6-di-tert-butylphenyl)-3-phenyl-phenylphosphonite, tetrakis(2,4-di-tert-butyl-5-methylphenyl)-4,4'-biphenylene diphosphonite, tributyl phosphate, trimethyl phosphate, tricresyl phosphate, triphenyl phosphate, trichlorophenyl phosphate, triethyl phosphate, diphenyl cresyl phosphate, diphenyl monoorthoxenyl phosphate, tributoxyethyl phosphate, dibutyl phosphate, dioctyl phosphate and diisopropyl phosphate.

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

For example, as those manufactured by Adeka Corporation, there may be mentioned ADK STAB PEP-4C, ADK STAB PEP-8, ADK STAB PEP-24G, ADK STAB PEP-36, ADK STAB HP-10, ADK STAB 2112, ADK STAB 260, ADK STAB 522A, ADK STAB 1178, ADK STAB 1500, ADK STAB C, ADK STAB 135A, ADK STAB 3010 and ADK STAB TPP.

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

[0047]

These antioxidants can be each used singly or two or more thereof may be used in combination. Particularly in the present invention, the phosphorus-based antioxidants are preferred.

[0048]

Furthermore, in the curable resin composition of the present invention, a photo-stabilizer may be added according to needs.

As the photo-stabilizer, particularly, it is preferred to incorporate a hindered amine compound and, if necessary, it is preferred to incorporate a phosphorus-based compound. Examples of the above amine compound include hindered amine-based compounds such as tetrakis(1,2,2,6,6-pentamethyl-4-piperidyl)=1,2,3,4-butanetetracarboxylate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)=1,2,3,4-butanetetracarboxylate, a mixed esterified product of 1,2,3,4-butanetetracarboxylic acid with 1,2,2,6,6-pentamethyl-4-piperidinol and 3,9-bis(2-hydroxy-1,1-dimethylethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane, decanedioic acid bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate, bis(1-undecanoxy-2,2,6,6-tetramethylpiperidin-4-yl) carbonate, 2,2,6,6-tetramethyl-4-piperidyl methacrylate, bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate, 4-benzoyloxy-2,2,6,6-tetramethyl-4-piperidine, 1-[2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]ethyl]-4-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]-2,2,6,6-tetramethylpiperidine, 1,2,2,6,6-pentamethyl-4-piperidyl-methacrylate, bis(1,2,2,6,6-pentamethyl-4-piperidyl) [[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]methyl]butylmalonate, decanedioic acid bis(2,2,6,6-

tetramethyl-1(octyloxy)-4-piperidinyl) ester, a reaction product of 1,1-dimethylethyl hydroperoxide with octane, N,N',N",N"'-tetrakis-(4,6-bis-(butyl-(N-methyl-2,2,6,6-tetramethylpiperidin-4-yl)amino)-triazin-2-yl)-4,7-diazadecane-1,10-diamine, a polycondensate of dibutylamine·1,3,5-triazine·N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl-1,6-hexamethylenediamine with N-(2,2,6,6-tetramethyl-4-piperidyl)butylamine, poly[[6-(1,1,3,3-tetramethylbutyl)amino-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidyl)imino]hexamethylene[(2,2,6,6-tetramethyl-4-piperidyl)imino]], a polymerized product of dimethyl succinate with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinethanol, 2,2,4,4-tetramethyl-20-(β-lauryloxycarbonyl)ethyl-7-oxa-3,20-diazadispiro[5.1.11.2]heneicosan-21-one, β-alanine, N-(2,2,6,6-tetramethyl-4-piperidinyl)-dodecyl ester/tetradecyl ester, N-acetyl-3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidinyl)pyrrolidine-2,5-dione, 2,2,4,4-tetramethyl-7-oxa-3,20-diazadispiro[5,1,11,2]heneicosan-21-one, 2,2,4,4-tetramethyl-21-oxa-3,20-diazadicyclo[5,1,11,2]heneicosan-20-propanoic acid dodecyl ester/tetradecyl ester, propanedioic acid [(4-methoxyphenyl)-methylene]-bis(1,2,2,6,6-pentamethyl-4-piperidinyl) ester, higher fatty acid esters of 2,2,6,6-tetramethyl-4-piperidinol, 1,3-benzenedicarboxyamide and N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl).

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

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

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

In the case where the amount is less than 0.005% by weight, the effect is insufficient. In the excessive case where the amount exceeds 5% by weight, influence on the heat coloring resistance appears, so that the case is not preferred.

[0049]

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

[0050]

To the curable resin composition of the present invention, an inorganic filler can be added according to needs. As the inorganic filler, there may be mentioned powders of crystalline silica, fused silica, alumina, zircon, calcium silicate, calcium carbonate, silicon carbide, silicon nitride, boron nitride, zirconia, fosterite, steatite, spinel, titania and talc or beads obtained by forming them into spherical shape and the like but the filler is not limited thereto. They may be used singly or two or more thereof may be used. With regard to the content of the inorganic filler, an amount of 0 to 90 parts by weight is used in the curable resin composition of the present invention. Furthermore, to the curable resin composition of the present invention, various blending agents such as a silane-coupling agent, a releasing agent such as stearic acid, palmitic acid, zinc stearate or calcium stearate, a surfactant, a dye, a pigment, and a UV absorber and various thermosetting resins can be added.

[0051]

In the case where the curable resin composition of the present invention is used as an encapsulating agent for an optical semiconductor, a phosphor can be added according to needs. The phosphor has an action of forming a white light by absorbing a part of blue light emitted from a blue LED element and emitting yellow light resulting from wavelength conversion. The optical semiconductor is encapsulated after the phosphor is dispersed in the curable resin composition beforehand. The phosphor is not particularly limited and conventionally known phosphors can be used. Examples thereof include aluminate salts, thiogallate salts, orthosilicate salts and the like of rare earth elements. More specifically, there may be mentioned phosphors such as YAG phosphors, TAG phosphors, orthosilicate phosphors, thiogallate phosphors, and sulfide phosphors, and $YAlO_3$:Ce, $Y_3Al_5O_{12}$:Ce, $Y_4Al_2O_9$:Ce, $Y_2O_2S$:Eu, $Sr_5(PO_4)_3Cl$:Eu, $(SrEu)O \cdot Al_2O_3$ and the like are exemplified. As the particle diameter of such phosphors, those having a known particle diameter in this field are used but the average particle diameter is preferably 1 to 250 μm and particularly preferably 2 to 50 μm. In the case of using these phosphors, the amount of them to be used is 1 to 80 parts by weight and preferably 5 to 60 parts by weight based on 100 parts by weight of the resin components.

[0052]

In the case where the curable resin composition of the present invention is used as an optical material, particularly an encapsulating agent for an optical semiconductor, 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.

[0053]

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

[0054]

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

[0055]

Furthermore, the curable resin composition of the present invention can be also used as a modifier of a film-type composition. Specifically, it can be used in the case

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

[0056]

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

[0057]

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 curable resin composition is prepared by thoroughly mixing the curing agent containing the polyvalent carboxylic acid (curing agent composition) of the present invention with the epoxy resin and also other additives such as the curing accelerator, the coupling agent, the antioxidant, and the photo-stabilizer. As a mixing method, they are mixed at normal temperature or elevated temperature using a kneader, a three-roll roller, a universal mixer, a planetary mixer, a homomixer, a homodisper, a beads mill or the like.

[0058]

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 flame, a heat sink or a package using an adhesive (die-bonding material). There is a type where a wire such as a gold wire is connected for conducting an electric current. The periphery of such a semiconductor chip is encapsulated with an encapsulating material such as an epoxy resin. The encapsulating material is used for protecting the semiconductor chip from heat and moisture and playing a role of lens function. The curable resin composition of the present invention can be used as the encapsulating material or die-bonding material. In view of steps, it is convenient to use the curable resin composition of the present invention as both of the die-bonding material and the encapsulating material.

[0059]

As a method of adhering the semiconductor chip to the substrate using the curable resin composition of the present invention, there may be mentioned a method of placing

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

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

[0060]

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

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

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

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

[0061]

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

[0062]

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.

[0063]

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 QFP, BGA and CSP (including underfill for reinforcement) and the like.

[0064]

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

[0065]

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

Examples

[0066]

The following will describe the present invention more specifically with reference to Examples but "parts" means parts by weight in the following unless otherwise stated. Incidentally, the present invention is not limited to these Examples. Moreover, in Examples, the measurement of gel permeation chromatography (hereinafter referred to as "GPC") was performed under the following conditions.

Column: Shodex SYSTEM-21 column (KF-803L, KF-802.5 (×2 columns), KF-802)

Connection eluent: tetrahydrofuran, flow rate was 1 ml/min.

Column temperature: 40°C, detection was done by RI (Reflective index)

Calibration curve: standard polystyrenes manufactured by Shodex

[0067]

Synthetic Example 1

Into a flask fitted with a stirrer, a reflux condenser and a stirring apparatus were charged 500 parts of a dual-end carbinol-modified silicone X22-160AS (manufactured by Shin-Etsu Chemical Co., Ltd., in the formula (1), $R_1$=-$C_3H_6$-O-$C_2H_4$-, $R_2$=$CH_3$, weight-average molecular weight of about 1,000), 99 parts of HTMAn (1,2,4-cyclohexanetricarboxylic 1,2-anhydride, manufactured by Mitsubishi Gas Chemical Co., Inc.), 84 parts of MH-700 (a mixture of hexahydrophthalic anhydride and 4-methylhexahydrophthalic anhydride, manufactured by New Japan Chemical Co., Ltd.) and 50 parts of toluene into the reaction vessel while performing nitrogen purging. After a reaction at 90°C for 2 hours, temperature was elevated to 130°C and, after 3 hours, the peak of the acid anhydride disappeared upon GPC measurement. Thereafter, the reaction was continued for another 2 hours. After completion of the reaction, the solvent was removed under reduced pressure to thereby obtain 681 parts of a carboxylic acid compound (J-1) of a colorless to pale yellow liquid.

[0068]

Synthetic Example 2

Into a flask fitted with a stirrer, a reflux condenser and a stirring apparatus were charged 98 parts of tricyclodecanediol, 99 parts of HTMAn (1,2,4-cyclohexanetricarboxylic 1,2-anhydride, manufactured by Mitsubishi Gas Chemical Co., Inc.), 84 parts of MH-700 (a mixture of hexahydrophthalic anhydride and 4-methylhexahydrophthalic anhydride, manufactured by New Japan Chemical Co., Ltd.) and 10 parts of toluene into the reaction vessel while performing nitrogen purging. A reaction was carried out at 60°C for 1 hour and 100°C for 2 hours. After completion of the reaction, the solvent was removed under reduced pressure to thereby obtain 280 parts of a carboxylic acid compound (K-1) of a colorless solid resin.

[0069]

Example 1

Into a flask fitted with a stirrer, a reflux condenser and a stirring apparatus was charged 68.3 parts of the carboxylic acid compound (J-1) while performing nitrogen purging. Under stirring at 100°C, 28.1 parts of the carboxylic acid compound (K-1) was added and the whole was stirred for 1 hour without further treatment to achieve mutual dissolution, thereby obtaining a polyvalent carboxylic acid composition (MA-1) of the present invention as a colorless transparent liquid.

[0070]

Example 2, Comparative Example 1

Using the polyvalent carboxylic acid composition (MA-1) of the present invention obtained in Example 1 or MH-700 (a mixture of hexahydrophthalic anhydride and 4-methylhexahydrophthalic anhydride, manufactured by New Japan Chemical Co., Ltd., hereinafter referred to as H1) as a curing agent and using 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate (UVR-6105 manufactured by Dow Chemical Company, hereinafter referred to as epoxy resin (EP1)) as an epoxy resin and hexadecyltrimethylammonium hydroxide (a 25% methanolic solution manufactured by Tokyo Chemical Industry Co., Ltd., hereinafter referred to as C1) as a curing accelerator, they were blended in the blending ratio (weight ratio) shown in the following Table 1 and defoaming was performed for 20 minutes to obtain a curable resin composition of the present invention.

[0071]

Using the obtained curable resin composition, LED encapsulation test was performed in the manner as shown below. Results are shown in Table 1. In this connection, curing conditions are 150°C×3 hours after pre-cure of 120°C×1 hour.

[0072]

(LED Encapsulation Test)

After each of the curable resin compositions obtained in Examples and Comparative Examples was subjected to vacuum defoaming for 20 minutes, it was filled into a syringe and injected into a surface-mounted (SMD type, a surface-mounted LED package 5 mm square in outer diameter, inner diameter: 4.4 mm, height of outer wall: 1.25 mm) LED on which an emission element having an emission wavelength of 465 nm had been mounted, using a precise injection apparatus. Thereafter, an LED for test was obtained by cuing the composition under prescribed curing conditions.

Evaluation Item

Volatility: The presence of hollows on the cured material surface after encapsulation was visually evaluated. In the table, Good: no hollow is observed,

Moderate: some hollows are observed, Bad: many hollows are observed (a wire is exposed).

[0073]

[Table 1]

| | | Example 1 | Comparative Example 1 | Unit |
|---|---|---|---|---|
| Curing agent composition | MA-1 | 32.1 | | part(s) by weight |
| | B2 | | | part(s) by weight |
| Curing agent | H1 | | 16.8 | part(s) by weight |
| Epoxy resin | EP1 | 13.0 | 13.0 | part(s) by weight |
| Curing accelerator | C1 | 0.05 | 0.05 | part(s) by weight |
| LED test | (volatility) | Good | Bad | |

[0074]

When Example 2 and Comparative Example 1 are compared, the curable resin composition of the present invention exhibits a little volatilization volume and there does not arise a problem of exposure of a wire or the like even when an LED is encapsulated. Furthermore, it is understood that there is observed a tendency to be able to reduce cracking at reflow. From the above results, it is understood that the polyvalent carboxylic acid of the present invention and the curable resin composition containing the polyvalent carboxylic acid can afford a curable resin composition effective against volatilization.

[0075]

Synthetic Example 4

Into a reaction vessel were charged 59.1 parts of 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 130.6 parts of polydimethyldiphenylsiloxane having a silanol group of a molecular weight of 1,700 (a measured value on GPC) and 10.0 parts of a 0.5% by weight methanolic KOH solution, followed by temperature elevation to 75°C. After the temperature elevation, they were reacted at 75°C for 8 hours under reflux. After the reaction, 135 parts of methanol was added and then 26.9 parts of a 50% distilled water-methanol solution was added dropwise over a period of 60 minutes, followed by the reaction at 75°C for another 8 hours under reflux. After completion of the reaction, neutralization was performed with a 5% by weight aqueous primary hydrogen sodium phosphate solution and then recovery of methanol through distillation was performed at 80°C. Thereafter, 170 parts of methyl isobutyl ketone (MIBK) was added for washing and then washing with water was repeated three times. Then, the organic layer was subjected to solvent removal at 100°C under reduced pressure to thereby obtain 162 parts of an epoxy resin (EP2). The epoxy equivalent of the obtained compound was

707 g/eq, the weight-average molecular weight was 2,680, and the appearance was colorless and transparent.

[0076]

Example 3

Into a flask fitted with a stirrer, a reflux condenser and a stirring apparatus were added 500 parts of a dual-end carbinol-modified silicone X22-160AS (manufactured by Shin-Etsu Chemical Co., Ltd.) and 168 parts of MH (methylhexahydrophthalic anhydride, manufactured by New Japan Chemical Co., Ltd.) while performing nitrogen purging. After a reaction at 70°C for 2 hours, 80 parts of KYOWADIOL PD9 (2,4-diethylpentane-1,5-diol, manufactured by Kyowa Hakko Chemical Co., Ltd.) and 198 parts of HTMAn (1,2,4-cyclohexanetricarboxylic 1,2-anhydride, manufactured by Mitsubishi Gas Chemical Co., Inc.) were added thereto and a reaction was carried out at 70°C for 1 hour and 130°C for 5 hours to thereby obtain a polyvalent carboxylic acid composition (MA-2) of the present invention. The obtained polyvalent carboxylic acid composition was a colorless and transparent liquid (near to a semi-solid but flowable at room temperature). (Although it is impossible to perform accurate calculation, the composition contains about 70% by weight of the polyvalent carboxylic acid (J) derived from the dual-end carbinol-modified silicone and about 30% by weight of the polyvalent carboxylic acid (K) derived from 2,4-diethylpentane-1,5-diol)

[0077]

Example 4

Into a flask fitted with a stirrer, a reflux condenser and a stirring apparatus were added 500 parts of a dual-end carbinol-modified silicone X22-160AS (manufactured by Shin-Etsu Chemical Co., Ltd.), 168 parts of MH (methylhexahydrophthalic anhydride, manufactured by New Japan Chemical Co., Ltd.), 80 parts of KYOWADIOL PD9 (2,4-diethylpentane-1,5-diol, manufactured by Kyowa Hakko Chemical Co., Ltd.) and 198 parts of HTMAn (1,2,4-cyclohexanetricarboxylic 1,2-anhydride, manufactured by Mitsubishi Gas Chemical Co., Inc.) while performing nitrogen purging. After a reaction at 70°C for 2 hours and 130°C for 5 hours, the whole was cooled to 50°C and 33.6 parts of MH (methylhexahydrophthalic anhydride, manufactured by New Japan Chemical Co., Ltd.) was added thereto and they were completely mutually dissolved to thereby obtain a polyvalent carboxylic acid composition (MA-3) of the present invention. The obtained polyvalent carboxylic acid composition was a colorless and transparent liquid. (Although it is impossible to perform accurate calculation, the composition contains about 70% by weight of the polyvalent carboxylic acid (J) derived from the dual-end carbinol-modified silicone, about 27% by weight of the polyvalent carboxylic acid (K) derived from 2,4-diethylpentane-1,5-diol, and about 3% of the acid anhydride)

[0078]

Examples 5 and 6, Comparative Examples 2 and 3

Using each of the polyvalent carboxylic acid compositions (MA-2, MA-3) of the present invention obtained in Examples 3 and 4 or each of the carboxylic acid (J-1) produced in Synthetic Example 1 and the acid anhydride (H1) as a curing agent, using the epoxy resin (EP2) obtained in Synthetic Example 4 as an epoxy resin and using hexadecyltrimethylammonium hydroxide (a 25% methanolic solution manufactured by Tokyo Chemical Industry Co., Ltd., hereinafter referred to as C1) as a curing accelerator, they were blended in the blending ratio (weight ratio) shown in the following Table 2 and defoaming was performed for 20 minutes to obtain a curable resin composition of the present invention or a curable resin composition for comparison.

Using the obtained curable resin composition, various tests were performed in the manner as shown below. Results are shown in Table 2.

[0079]

(1) Hollow Test;

After each of the curable resin compositions obtained in Examples 5 and 6 and Comparative Examples 2 and 3 was subjected to vacuum defoaming for 20 minutes, it was filled into a syringe and injected into a surface-mounted LED on which an emission element having an emission wavelength of 465 nm had been mounted, using a precise injection apparatus so that an opening part became flat. After pre-cure of 120°C×3 hours, the resin composition was cured at 150°C×1 hour to encapsulate the surface-mounted LED. The presence of hollows on the resin surface in association with volatilization of the curing agent after thus encapsulated was visually evaluated. In the table, Good: no hollow is observed, Moderate: some hollows are observed, and Bad: many hollows are observed (a wire is exposed).

(2) Reflow Test;

After each of the curable resin compositions obtained in Examples 5 and 6 and Comparative Examples 2 and 3 was subjected to vacuum defoaming for 20 minutes, it was filled into a syringe and injected into a surface-mounted LED on which an emission element having an emission wavelength of 465 nm had been mounted, using a precise injection apparatus so that an opening part became flat. After pre-cure of 120°C×3 hours, the resin composition was cured at 150°C×1 hour to encapsulate the surface-mounted LED. After the obtained LED for test was moisturized at 30°C at 70%×72 hours, the occurrence of cracking on the LED for test under the following reflow conditions was visually observed using a high-temperature observing apparatus (SMT Scope SK-5000 manufactured by Sanyo Seiko K.K.). The test was performed with n=3 and evaluation was performed by (OK number)/(test number).

The conditions are as follows: temperature is elevated from 25°C to 150°C at a rate of 2°C/second, then kept at 150°C for 2 minutes, further elevated to 260°C at 2°C/second and, after the temperature is kept for 10 seconds, cooled to room temperature at 1.3°C/second.

(3) Test for Resistance to Gas Permeation (Corrosive Gas Permeation Test);

After each of the curable resin compositions obtained in Examples 5 and 6 and Comparative Examples 2 and 3 was subjected to vacuum defoaming for 20 minutes, it was filled into a syringe and injected into a surface-mounted LED package 5 mm square in outer diameter (inner diameter: 4.4 mm, height of outer wall: 1.25 mm) on which an emission element having an emission wavelength of 465 nm had been mounted, using a precise injection apparatus. The injected article was charged 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 a silver-plated lead frame part present inside the encapsulation was observed.

<Measurement Conditions>

Corrosive gas: A 20% by weight aqueous ammonium sulfide solution (which is to be colored black in the case where the sulfur component is reacted with silver)

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

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

[0080]

[Table 2]

| | | Example 5 | Example 6 | Comparative Example 2 | Comparative Example 3 | Unit |
|---|---|---|---|---|---|---|
| Curing agent | MA-2 | 15.8 | | | | part(s) by weight |
| | MA-3 | | 16.3 | | | part(s) by weight |
| | J-1 | | | 11.3 | | part(s) by weight |
| | H1 | | | | 8.4 | part(s) by weight |
| Epoxy resin | EP2 | 35.1 | 35.1 | 35.1 | 35.1 | part(s) by weight |
| Curing accelerator | C1 | 0.14 | 0.14 | 0.14 | 0.14 | part(s) by weight |
| Hollow test | | Good | Good | Good | Moderate | |
| Reflow test cracking | | 3/3 | 3/3 | 3/3 | 3/3 | |
| Resistance to gas permeation | | 2 hours or more | 2 hours or more | about 30 minutes | about 50 minutes | |

[0081]

As apparent from the results shown in Table 2, it is understood that the epoxy resin composition of the present invention affords a cured material having few hollows and not only excellent in reflow resistance but also excellent in resistance to corrosive gas permeation.

[0082]

Examples 7 to 13, Synthetic Examples 6 and 7

Into a flask fitted with a stirrer, a reflux condenser and a stirring apparatus were charged a dual-end carbinol-modified silicone (one compound selected from SI-1 and SI-2), a saturated aliphatic polyvalent alcohol (one compound selected from AL-1 and AL-2), and an acid anhydride (one compound selected from H1, H2 and H3) in blending amounts shown in the following Table 3 and a reaction was carried out at 70°C for 5 hours and 90°C for 3 hours to thereby obtain polyvalent carboxylic acid compositions (MA-4 to MA 10) and carboxylic acid resins (J-2 and J-3) as colorless and transparent liquids.

In this connection, SI-1: FM-4411 manufactured by Chisso Corporation, SI-2: X22-160As manufactured by Shin-Etsu Chemical Co., Ltd., AL-1: KYOWADIOL PD-9 manufactured by Kyowa Hakko Chemical Co., Ltd., AL-2: TCDAlchol-DM manufactured by OXEA, H1: RIKACID MH-700 manufactured by New Japan Chemical Co. Ltd., H1: RIKACID MH manufactured by New Japan Chemical Co. Ltd., H3: H-TMAn manufactured by Mitsubishi Gas Chemical Co., Inc.

[0083]

[Table 3]

| | Composition | | | | | | | Product | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | SI-1 | SI-2 | AL-1 | Al-2 | HI | H2 | H3 | Polyvalent carboxylic acid | Polyvalent carboxylic acid | (J)/(K) | Form |
| Example 7 | | 435 | 10 | | | 168 | | MA-4 | | 95/5 | colorless liquid |
| Example 8 | | 375 | 20 | | | 168 | | MA-5 | | 90/10 | colorless liquid |
| Example 9 | | 335 | 26 | | | 168 | | MA-6 | | 85/15 | colorless liquid |
| Example 10 | 390 | | | 22 | | 168 | | MA-7 | | 90/10 | colorless liquid |
| Example 11 | 300 | | | 39 | | 168 | | MA-8 | | 80/20 | colorless liquid |
| Example 12 | 300 | | | 39 | 164 | | | MA-9 | | 80/20 | colorless to pale yellow liquid |
| Example 13 | 450 | | | 18 | | 160 | 20 | MA-10 | | 86/14 | colorless liquid |
| Synthetic Example 6 | | 500 | | | | 168 | | | J-2 | 100/0 | colorless liquid |
| Synthetic Example 7 | 500 | | | | | 168 | | | J-3 | 100/0 | colorless liquid |

* In the table, (J)/(K) means weight of polyvalent carboxylic acid derived from dual-end carbinol-modified silicone/weight of polyvalent carboxylic acid derived from saturated aliphatic polyvalent alcohol

[0084]

Synthetic Example 8

Into a flask fitted with a stirrer, a reflux condenser and a stirring apparatus were charged 100 parts of the acid anhydride (H2) and the saturated aliphatic polyvalent alcohol (AL-1) while nitrogen purging, followed by stirring at 50°C for 3 hours and at 70°C for 30 minutes. Thereby, 120 parts of a colorless and transparent mixture of a carboxylic acid compound and the acid anhydride was obtained. The ratio of the obtained carboxylic acid and the acid anhydride was about 52:48 as a result of measurement by gel permeation chromatography.

[0085]

Examples 14 and 15

To 1 part (Example 14) or 2 parts (Example 15) of the colorless and transparent mixture of the carboxylic acid compound and the acid anhydride obtained in Synthetic Example 8 was added 100 parts of the polyvalent carboxylic acid compound (J-2) obtained

in Synthetic Example 6, and they were dissolved homogeneously. Thereby, colorless polyvalent carboxylic acid compositions MA-11 and MA-12 were obtained, respectively.

[0086]

Synthetic Example 9

Into a reaction vessel were charged 39.4 parts of β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 137 parts of a silanol-end methylphenylsilicone oil having a weight-average molecular weight of 1,900 (a measured value on GPC) (silanol equivalent: 950, calculated as a half of the weight-average molecular weight measured using GPC), and 10 parts of a 0.5% methanolic potassium hydroxide (KOH) solution, and the bath temperature was set at 75°C to elevate temperature. After temperature elevation, they were reacted for 10 hours under reflux. As a production step (ii), after 140 parts of methanol was additionally added, 17.3 parts of a 50% distilled water-methanol solution was added dropwise over a period of 60 minutes and the whole was reacted at 75°C for 8 hours under reflux. After completion of the reaction, neutralization was performed with a 5% aqueous dihydrogen sodium phosphate solution and then about 90% of methanol was recovered through distillation at 80°C. Then, 200 parts of methyl isobutyl ketone (MIBK) was added thereto and washing with water was repeated three times. By subjecting the organic layer to solvent removal at 100°C under reduced pressure, 152 parts of an epoxycyclohexyl group-containing organopolysiloxane (EP-3) was obtained. The epoxy equivalent of the obtained compound (EP-3) was 1040 g/eq, the weight-average molecular weight was 2,290, and the appearance was a colorless and transparent liquid resin.

[0087]

Synthetic Example 10

Into a reaction vessel were charged 375 parts of β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 475 parts of a silanol-end methylphenylsilicone oil having a weight-average molecular weight of 1,900 (a measured value on GPC) (silanol equivalent: 950, calculated as a half of the weight-average molecular weight measured using GPC), and 40 parts of a 0.5% methanolic potassium hydroxide (KOH) solution, and the bath temperature was set at 75°C to elevate temperature. After temperature elevation, they were reacted for 8 hours under reflux. After 655 parts of methanol was additionally added, 144 parts of a 50% distilled water-methanol solution was added dropwise over a period of 60 minutes and the whole was reacted at 75°C for 8 hours under reflux. After completion of the reaction, neutralization was performed with a 5% aqueous dihydrogen sodium phosphate solution and then about 90% of methanol was recovered through distillation at 80°C. Then, 750 parts of methyl isobutyl ketone (MIBK) was added thereto and washing with water was repeated three times. By subjecting the organic layer to solvent removal at 100°C under reduced pressure, 647 parts of an epoxycyclohexyl group-

containing organopolysiloxane (EP-4) was obtained. The epoxy equivalent of the obtained compound (EP-4) was 541 g/eq, the weight-average molecular weight was 2,100, and the appearance was a colorless and transparent liquid resin.

[0088]

Examples 16 to 19, Comparative Example 4

Using each of the polyvalent carboxylic acid compositions (MA-4, MA-5, MA-6 and MA-10) of the present invention or, as Comparative Example, the polyvalent carboxylic acid resin (J-3) as a curing agent, using the epoxy resin (EP-4) obtained in Synthetic Example 10 as an epoxy resin and using zinc octylate (18% Octope Zn manufactured by Hope Chemical Co., Ltd., hereinafter referred to as C2) as a curing accelerator, a photo-stabilizer (LA-81 manufactured by ADEKA, hereinafter referred to as additive AD-1) and an antioxidant (ADEKA 260 manufactured by ADEKA, referred to as additive AD-2)), they were blended in the blending ratio (weight ratio) shown in the following Table 4 and defoaming was performed for 20 minutes to obtain a curable resin composition of the present invention or a curable resin composition for comparison.

Using the obtained curable resin compositions, tests were performed in the manner as shown below. Results are shown in Table 4. In this connection, curing conditions are 150°C×5 hours after pre-cure of 120°C×2 hours unless otherwise stated.

(1) Tensile Test in accordance with JIS K 6911

Sample thickness: 0.9±0.05 mm, Sectional area: 4.5±0.2 $mm^2$

Speed: 5 mm/min, Distance between chucks: 15 mm

(2) Heat-durable Transmittance Test

The obtained curable resin composition was gently 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×1 hour after pre-cure of 120°C×3 hours, thereby obtaining a test piece for transmittance having a thickness of 1 mm.

Using the test piece, transmittance (measurement wavelength: 400 nm) before and after standing for 72 hr in an oven of 150°C was measured by a spectrophotometer and a change rate thereof was calculated.

Evaluation: the case where a decrease in the transmittance is less than 5% is Good, the case where a decrease in the transmittance is 5 % or more to less than 10% is Moderate, and the case where a decrease in the transmittance is 10% or more is Bad.

[0089]

[Table 4]

| | | | | Example 16 | Example 17 | Example 18 | Example 19 | Comparative Example 4 |
|---|---|---|---|---|---|---|---|---|
| Composition | Polyvalent carboxylic acid composition | | MA-4 | 9.2 | | | | |
| | | | MA-5 | | 8.3 | | | |
| | | | MA-6 | | | 7.8 | | |
| | | | MA-10 | | | | 7.0 | |
| | Polyvalent carboxylic acid resin | | J-3 | | | | | 9.9 |
| | Epoxy resin | | EP-4 | 10 | 10 | 10 | 10 | 10 |
| | Catalyst | | C-2 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 |
| | Additive | | AD-1 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 |
| | | | AD-2 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 |
| Cured physical properties | Tensile test | Elongation at maximum point | % | 38.4 | 49.6 | 65.1 | 39.4 | 20 |
| | Heat-durable transmittance test | | % | 96.1 | 95.9 | 95.5 | 95.1 | 95.6 |
| | | | Evaluation | Good | Good | Good | Good | Good |

[0090]

Examples 20 to 22, Comparative Example 5

Using each of the polyvalent carboxylic acid compositions (MA-7, MA-8 and MA-9) of the present invention or, as Comparative Example, the polyvalent carboxylic acid resin (J-3) as a curing agent, using the epoxy resins (EP-3 and EP-4) obtained in Synthetic Examples 9 and 10 as epoxy resins and using the curing accelerator (C2), and the additives (AD-1 and AD-2), they were blended in the blending ratio (weight ratio) shown in the following Table 5 and defoaming was performed for 20 minutes to obtain a curable resin composition of the present invention or a curable resin composition for comparison.

Using the obtained curable resin compositions, tests were performed in the manner as shown below. Results are shown in Table 5. In this connection, curing conditions are 150°C×5 hours after pre-cure of 120°C×2 hours.

(1) Peel Test in accordance with JIS K 6911

Support: a rough surface of a copper foil was used, Sample width: 10 mm, Peel speed: 3 mm/minute

(2) Tensile Test in accordance with JIS K 6911

Sample thickness: 0.9±0.05 mm, Sectional area: 4.5±0.2 $mm^2$

Speed: 5 mm/min, Distance between chucks: 15 mm

[0091]

[Table 5]

| | | | | Example 20 | Example 21 | Example 22 | Comparative Example 5 |
|---|---|---|---|---|---|---|---|
| Composition | Polyvalent carboxylic acid composition | | MA-7 | 6.3 | | | |
| | | | MA-8 | | 5.5 | | |
| | | | MA-9 | | | 5.4 | |
| | Polyvalent carboxylic acid resin | | J-3 | | | | 7.2 |
| | Epoxy resin | | EP-3 | 6.0 | 6.0 | 6.0 | 6.0 |
| | | | EP-4 | 4.0 | 4.0 | 4.0 | 4.0 |
| | Catalyst | | C-2 | 0.04 | 0.04 | 0.04 | 0.04 |
| | Additive | | AD-1 | 0.008 | 0.008 | 0.008 | 0.008 |
| | | | AD-2 | 0.008 | 0.008 | 0.008 | 0.008 |
| Cured physical properties | Peel test | Peel strength | N | 1.34 | 1.83 | 1.32 | ND |
| | Tensile test | Elongation at maximum point | % | 32.8 | 49.1 | 23.5 | ND |

*ND the cured material is brittle and is not a level capable of evaluation and is broken immediately after evaluation.

[0092]

From the above results, it is understood that the curable resin composition of the present invention is excellent in close adhesiveness, toughness and heat-resistant durability.

[0093]

Examples 23 and 24, Comparative Example 6

Using the polyvalent carboxylic acid composition (MA-11 or MA-12) of the present invention or, as Comparative Example, the polyvalent carboxylic acid resin (J-2) as a curing agent, using the epoxy resin (EP-4) obtained in Synthetic Example 10 as an epoxy resin and using the curing accelerator (C2) and the additives (AD-1 and AD-2), they were blended in the blending ratio (weight ratio) shown in the following Table 6 and defoaming was performed for 20 minutes to obtain a curable resin composition of the present invention or a curable resin composition for comparison.

Using the obtained curable resin compositions, tests were performed in the manner as shown below. Results are shown in Table 6. In this connection, curing conditions are 150°C×5 hours after pre-cure of 120°C×2 hours.

(1) Tensile Test in accordance with JIS K 6911

Sample thickness: 0.9±0.05 mm, Sectional area: 4.5±0.2 $mm^2$

Speed: 5 mm/min, Distance between chucks: 15 mm

(2) LED Lighting Test

After each of the curable resin compositions obtained in Examples and Comparative Example was subjected to vacuum defoaming for 20 minutes, it was filled into a syringe and injected into a surface-mounted LED (ϕ 5 mm) on which an emission

element having an emission wavelength of 465 nm had been mounted, using a precise injection apparatus. Thereafter, an LED for lighting test was obtained by curing under prescribed curing conditions. For the lighting test, a lighting test at 210 mA that was 7 times the specified current was performed for accelerated test. Detailed conditions were shown below. As a measurement item, illuminance before and after lighting for 20 hours was measured using an integrating sphere and a retention rate of illuminance of the LED for test was calculated.

Detailed conditions for lighting

Emission wavelength: 465 nm

Driving method: constant current method, 210 mA (specified current of the emission element was 30 mA)

Driving environment: 25°C, 65%RH

(3) Test for Resistance to Gas Permeation (Corrosive Gas Permeation Test);

An LED package prepared with each of the obtained curable resin compositions 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.

<Measurement Conditions>

Corrosive gas: A 20% by weight aqueous ammonium sulfide solution (which is to be colored black in the case where the sulfur component is reacted with silver)

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

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

[0094]

[Table 6]

| | | | | Example 23 | Example 24 | Comparative Example 6 |
|---|---|---|---|---|---|---|
| Composition | Polyvalent carboxylic acid composition | | MA-11 | 7.8 | | |
| | | | MA-12 | | 7.6 | |
| | Polyvalent carboxylic acid resin | | J-2 | | | 9.9 |
| | Epoxy resin | | EP-4 | 10.0 | 10.0 | 10.0 |
| | Catalyst | | C-2 | 0.1 | 0.1 | 0.1 |
| | Additive | | AD-1 | 0.02 | 0.02 | 0.02 |
| | | | AD-2 | 0.02 | 0.02 | 0.02 |
| Cured physical properties | Tensile test | Elongation at maximum point | % | 36.9 | 38.7 | 22.1 |
| | Lighting test | Illuminance retention rate | % | 101 | 103 | 103 |
| | Corrosive gas permeation test | Retention time | hour | >2 hours | >2 hours | 1 hour |

[0095]

Example 25

Into a flask fitted with a stirrer, a reflux condenser and a stirring apparatus were charged 365 parts of the dual-end carbinol-modified silicone compound (SI-2), 9 parts of pentaerythritol (hereinafter referred to as saturated aliphatic polyvalent alcohol AL-3), and 168 parts of the acid anhydride (H2) and a reaction was carried out at 90°C for 2 hours and 110°C for 3 hours to thereby obtain 542 parts of a polyvalent carboxylic acid composition (MA-13) as a colorless and transparent liquid. (weight of the polyvalent carboxylic acid derived from SI-2 (J)/weight of the polyvalent carboxylic acid derived from AL-3 (K)=90/10)

[0096]

Example 26, Comparative Example 7

Using the polyvalent carboxylic acid compositions (MA-13) of the present invention or, as Comparative Example, the polyvalent carboxylic acid resin (J-3) as a curing agent, using the epoxy resins (EP-3 and EP-4) obtained in Synthetic Examples 9 and 10 as epoxy resins and using the curing accelerator (C2) and the additives (AD-1 and AD-2), they were blended in the blending ratio (weight ratio) shown in the following Table 7 and defoaming was performed for 20 minutes to obtain a curable resin composition of the present invention or a curable resin composition for comparison.

Using the obtained curable resin compositions, tests were performed in the manner as shown below. Results are shown in Table 7. In this connection, curing conditions are 150°C×5 hours after pre-cure of 120°C×2 hours.

(1) Peel Test in accordance with JIS K 6911

Support: a rough surface of a copper foil was used, Sample width: 10 mm, Peel speed: 3 mm/minute

(2) Tensile Test in accordance with JIS K 6911

Sample thickness: 0.9±0.05 mm, Sectional area: 4.5±0.2 $mm^2$

Speed: 5 mm/min, Distance between chucks: 15 mm

(3) LED Lighting Test

After each of the curable resin compositions obtained in Example and Comparative Example was subjected to vacuum defoaming for 20 minutes, it was filled into a syringe and injected into a surface-mounted LED ($\phi$ 5 mm) on which an emission element having an emission wavelength of 465 nm had been mounted, using a precise injection apparatus.. Thereafter, an LED for lighting test was obtained by curing under prescribed curing conditions. For the lighting test, a lighting test at 210 mA that was 7 times the specified current was performed for accelerated test. Detailed conditions were shown below. As a measurement item, iluminance before and after lighting for 20 hours was measured using an integrating sphere and a retention rate of illuminance of the LED for test was calculated.

Detailed conditions for lighting

Emission wavelength: 465 nm

Driving method: constant current method, 210 mA (specified current of the emission element was 30 mA)

Driving environment: 25°C, 65%RH

(4) Test for Resistance to Gas Permeation (Corrosive Gas Permeation Test);

An LED package prepared with each of the obtained curable resin compositions 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.

<Measurement Conditions>

Corrosive gas: A 20% by weight aqueous ammonium sulfide solution (which is to be colored black in the case where the sulfur component is reacted with silver)

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

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

[0097]

[Table 7]

| | | | | Example 26 | Comparative Example 7 |
|---|---|---|---|---|---|
| Composition | Polyvalent carboxylic acid composition | | MA-13 | 9.8 | |
| | Polyvalent carboxylic acid resin | | J-2 | | 8.7 |
| | Epoxy resin | | EP-3 | 6.0 | 6.0 |
| | | | EP-4 | 4.0 | 4.0 |
| | Catalyst | | C-2 | 0.1 | 0.1 |
| | Additive | | AD-1 | 0.008 | 0.008 |
| | | | AD-2 | 0.008 | 0.008 |
| Cured physical properties | Peel test | Peel strength | N | 2.0 | ND |
| | Tensile test | Elongation at maximum point | % | 33.1 | ND |
| | Lighting test | Illuminance retention rate | % | 105 | 104 |
| | Resistance to corrosive gas permeation test | Retention time | hour | >2 hours | 1 hour |

*ND the cured material is brittle and is not a level capable of evaluation and is broken immediately after evaluation.

[0098]

As apparent from the above results, it is understood that the epoxy resin composition of the present invention affords a cured material not only excellent in heat resistance and light resistance but also excellent in close adhesiveness and toughness and further excellent in resistance to corrosive gas permeation.

[0099]

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

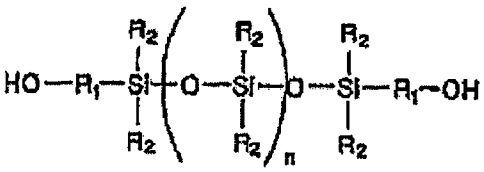
The present application is based on Japanese Patent Application No. 2009-232113 filed on October 6, 2009, and the contents are incorporated herein by reference. Also, all the references cited herein are incorporated as a whole.

Claims

[Claim 1] A polyvalent carboxylic acid composition comprising:

a carboxylic acid compound (J) obtained by addition reaction of a silicone oil (a) represented by the following formula (1):

[Chem.1]



(1)

wherein $R_1$ represents an alkylene group having 1 to 10 carbon atoms in total which may have an intervening ether linkage; $R_2$ represents a methyl group or a phenyl group; and n represents a repeating unit, weight-average molecular weight of the compound represented by the formula (1) being 500 to 5000,

with a compound (b) containing one or more carboxylic anhydride groups in the molecule and

a polyvalent carboxylic acid compound (K) obtained by addition reaction of a saturated aliphatic polyvalent alcohol (c) having two or more functional alcoholic hydroxyl groups with a compound (d) having one or more carboxylic anhydride groups in the molecule wherein the polyvalent carboxylic acid composition is produced by a process comprising adding the compounds (b) and (d) having one or more carboxylic anhydride groups in the molecule to a mixture containing the silicone oil (a) and the saturated aliphatic polyvalent alcohol having two or more functional alcoholic hydroxyl groups and simultaneously carrying out the addition reaction of the silicone oil (a) with the compound (b) and the addition reaction of the compound (c) with the compound (d).

[Claim 2] The polyvalent carboxylic acid composition according to claim 1, wherein the compounds (b) and (d) are each an acid anhydride having a cyclic saturated hydrocarbon as a core skeleton.

[Claim 3] The polyvalent carboxylic acid composition according to claim 1 or 2, wherein the

compounds (b) and (d) are each at least one acid anhydride selected from the group consisting of methylhexahydrophthalic anhydride, hexahydrophthalic anhydride, cyclohexane-l,2,4-tricarboxylic acid 1,2-anhydride and bicyclo[2,2,1]heptane-2,3-dicarboxylic anhydride.

[Claim 4] The polyvalent carboxylic acid composition according to claim 3, wherein the compounds (b) and (d) necessarily comprise methylhexahydrophthalic anhydride.

[Claim 5] The polyvalent carboxylic acid composition according to anyone of claims 1 to 4, wherein the compound (c) is a polyvalent alcohol having 2 to 6 functional groups, total number of the carbon atoms in one molecule being 5 to 20.

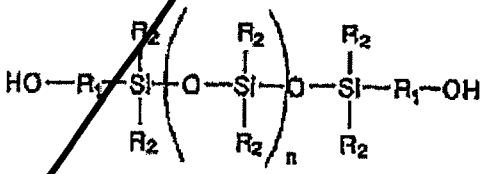
[Claim 6] A process for producing the polyvalent carboxylic acid composition according to anyone of claims 1 to 5, which comprises:

adding the compounds (b) and (d) having one or more carboxylic anhydride groups in the molecule to a mixture containing the silicone oil (a) and the saturated aliphatic polyvalent alcohol having two or more functional alcoholic hydroxyl groups and simultaneously carrying out the addition reaction of the silicone oil (a) with the compound (b) and the addition reaction of the compound (c) with the compound (d).

[Claim 7] A polyvalent carboxylic acid composition comprising:

a carboxylic acid compound (J) obtained by addition reaction of a silicone oil (a) represented by the following formula (1):

[Chem.1]



(1)

wherein $R_1$ represents an alkylene group having 1 to 10 carbon atoms in total which may have an intervening ether linkage; $R_2$ represents a methyl group or a phenyl group; and n represents a repeating unit, weight-average molecular weight of the compound represented by the formula (1) being 500 to 5000,

with a compound (b) containing one or more carboxylic anhydride groups in the molecule and

a polyvalent carboxylic acid compound (K) obtained by addition reaction of a saturated aliphatic polyvalent alcohol (c) having two or more functional alcoholic hydroxyl groups with a compound (d) having one or more carboxylic anhydride groups in the molecule wherein the process for producing the polyvalent carboxylic acid composition comprises sequentially reacting the following step (A) and step (B) in one pot:

Step (A): a step of addition reaction of the silicone oil (a) with the compound (b) containing one or more carboxylic anhydride groups in the molecule;

Step (B): a step of addition reaction of the saturated aliphatic polyvalent alcohol (c) having two or more functional alcoholic hydroxyl groups with the compound (d) having one or more carboxylic anhydride groups in the molecule.

[Claim 8] The polyvalent carboxylic acid composition according to claim 7, wherein the compounds (b) and (d) are each an acid anhydride having a cyclic saturated hydrocarbon as a core skeleton.

[Claim 9] The polyvalent carboxylic acid composition according to claim 7 or claim 8, wherein the compounds (b) and (d) are each at least one acid anhydride selected from the group consisting of methylhexahydrophthalic anhydride, hexahydrophthalic anhydride, cyclohexane-1,2,4-tricarboxylic acid 1,2-anhydride and bicyclo[2,2,1]heptane-2,3-dicarboxylic anhydride.

[Claim 10] The polyvalent carboxylic acid composition according to claim 9, wherein the compounds (b) and (d) necessarily comprise methylhexahydrophthalic anhydride.

[Claim 11] The polyvalent carboxylic acid composition according to anyone of claims 7 to 10, wherein the compound (c) is a polyvalent alcohol having 2 to 6 functional groups, total number of the carbon atoms in one molecule being 5 to 20.

[Claim 12] A process for producing the polyvalent carboxylic acid composition according to anyone of claims 7 to 11, which comprises sequentially reacting the following step (A) and step (B) in one pot:

Step (A): a step of addition reaction of the silicone oil (a) with the compound (b) containing one or more carboxylic anhydride groups in the molecule;

Step (B): a step of addition reaction of the saturated aliphatic polyvalent alcohol (c) having two or more functional alcoholic hydroxyl groups with the compound (d) having one or more carboxylic anhydride groups in the molecule.

[Claim 13] The process for producing the polyvalent carboxylic acid composition according to claim 12, wherein the addition reaction is carried out at 40 to 150°C with no solvent or in an organic solvent in an amount of 50% by weight or less based on the total amount of reaction substrates in the raw materials to be used.

[Claim 14] A curable resin composition containing the polyvalent carboxylic acid composition according to anyone of claims 7 to 11 and an epoxy resin.

[Claim 15] The curable resin composition according to claim 14, wherein the epoxy resin is an alicyclic epoxy resin and/or an epoxy group-containing silicone resin.

[Claim 16] The curable resin composition according to claim 14, wherein the epoxy resin is an epoxy group-containing silicone resin.

[Claim 17] A cured material obtained by curing the curable resin composition according to anyone of claims 14 to 16.

[Claim 18] The process for producing the polyvalent carboxylic acid composition according to claim 6, wherein the addition reaction is carried out at 40 to 150°C with no solvent or in an organic solvent in an amount of 50% by weight or less based on the total amount of reaction substrates in the raw materials to be used.

[Claim 19] A curable resin composition containing the polyvalent carboxylic acid composition according to anyone of claims 1 to 5 and an epoxy resin.

[Claim 20] The curable resin composition according to claim 18, wherein the epoxy resin is an alicyclic epoxy resin and/or an epoxy group-containing silicone resin.

[Claim 21] The curable resin composition according to claim 18, wherein the epoxy resin is an epoxy group-containing silicone resin.

[Claim 22] A cured material obtained by curing the curable resin composition according to anyone of claims 18 to 20.