

DESCRIPTION

TITLE OF THE INVENTION

5 EPOXY RESIN COMPOSITION AND CURED PRODUCT THEREOF AND
CURABLE RESIN COMPOSITION

TECHNICAL FIELD

[0001]

10 The present invention relates to an epoxy resin composition which is suitable
for electrical and electronic material applications, especially optical material
applications and also to a cured product thereof. Furthermore, another present invention
relates to a curable resin composition which is suitable for electrical and electronic
material applications for which heat resistance and flame retardancy are required.

15 BACKGROUND ART

[0002]

In applications of LED products, transparent substrate materials, and the like,
an epoxy resin composition has hitherto been adopted from the standpoint of a balance
between performance and economy. In particular, an epoxy resin composition using a
20 bisphenol A type epoxy resin which is excellent in a balance among heat resistance,
transparency, and mechanical characteristics has been widely used (Patent Documents 1
to 3).

[0003]

As described previously, though bisphenol A type epoxy resins have a
25 multiplicity of uses as an optical resin, these are generally liquid and involve problems
such as generation of a tack when formed into a sheet or a prepreg, etc. In addition,
though there are variations which are solidified by increasing a molecular weight
thereof, since they are merely stretched in a straight line, cured products thereof are too
soft, so that heat resistance is hardly revealed.

30 [0004]

Meanwhile, there is advanced development of a technology for fabricating a
substitute of glass by means of impregnation in a glass cloth as one of transparent
materials, followed by curing. Although it is known that various epoxy resin

compositions can be used for glass substitution, in conventional epoxy resins, in the case where a difference in refractive index from a glass cloth is large, or in the case where a birefringent index is high, visibility is lowered by irregular reflection or the like, so that it was difficult to use the conventional epoxy resins for LCD or polarized
5 light. In addition, in particular, in transparent base materials such as glass-substituting epoxy resins for LCD utilizing polarization, etc., they are keenly required to be low in the birefringent index.

Then, development of an epoxy resin for optical material which is satisfied with the above-described requiring characteristics has been keenly desired.

10 [0005]

In addition, separately from the foregoing, curable resin compositions are widely used in the fields of, for example, electrical and electronic components, structural materials, adhesives, paints, or the like in view of workability and also in view of the fact that cured products thereof are excellent in terms of electrical
15 characteristics, heat resistance, adhesive properties, humidity resistance (water resistance), and the like.

[0006]

But, in recent years, in the electrical or electronic field, with the development thereof, much more enhancements in various characteristics including not only an
20 improvement of purity but humidity resistance, adhesion, dielectric characteristics, a lowering of viscosity for the purpose of highly filling a filler (inorganic or organic filler), an improvement of reactivity for the purpose of shortening a molding cycle, and the like in resin compositions are demanded. In addition, as for structural materials, materials which are lightweight and excellent in mechanical physical properties are
25 demanded in aerospace materials, applications of leisure and sport equipment, and the like. In particular, in the semiconductor encapsulation field or a substrate (a substrate itself or its circumferential material), the material becomes complicated with the changes of its semiconductor, inclusive of sliming, stacking, systematization, and three-dimensionality, and required characteristics such as very high-level heat resistance and
30 high fluidity are demanded. Incidentally, in particular, with the expansion of plastic packages to onboard applications, a requirement for an enhancement of the heat resistance becomes much more severe, and in resins having a high TG and a low coefficient of linear thermal expansion, as a matter of course, correspondence to the

solder reflow is necessary, and at the same time, a lowering or maintenance of the water absorption is demanded. Furthermore, in view of an environmental issue, in recent years, halogen-based epoxy resins and antimony trioxide are frequently used as a flame retarder, especially as a flame retarder for electrical and electronic components.

- 5 However, it is pointed out that products using such a material contribute to generation of a toxic substance such as dioxin, etc. due to an inappropriate treatment after disposal thereof.

CITATION LIST

10 PATENT DOCUMENT

[0007]

Patent Document 1: JP-A-H07-157536

Patent Document 2: JP-A-2005-082798

Patent Document 3: JP-A-2007-284680

15 NON-PATENT DOCUMENT

[0008]

Non-Patent Document 1: "STRJ Report, 2008: Report of FY 2008 by Semiconductor Roadmap Committee of Japan", Chapter 8, pp.1-17, [online], March 2009, JEITA, Japan Electronics and Information Technology Industries Association, Semiconductor Technology Roadmap Committee of Japan [retrieved on May 30, 2012],
20 <<http://strj-jeita.elisasp.net/strj/nenjhoukoku-2008.cfm>>

Non-Patent Document 2: TAKAKURA, Nobuyuki and others, "Matsushita Electric Works Technical Report, Automobile Related Device Technology: High Temperature ICs for Automotive Applications", No. 74, Japan, pp.35-40, May 31, 2001

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SUMMARY OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0009]

- In response to the foregoing problems regarding the optical material applications, VG3105, available from Printec Corporation, which is an epoxy resin of a tris-phenol compound having a benzylmethylene bond-free structure similar to the bisphenol A type epoxy resin, and the like are used. However, in these resins, initial
- 30

coloration is found, and much more transparency is required for uses as an optical material.

As a method for solving such a problem, application of an epoxy resin having a silsesquioxane structure or an alicyclic epoxy resin is also investigated. However, in the epoxy resin having a silsesquioxane structure, though its heat resistance is high, its brittleness is conspicuous, and its coefficient of linear expansion tends to become high. Furthermore, its refractive index becomes low. In addition, in the alicyclic epoxy resin, though its heat resistance is enhanced in implications in terms of a glass transition point, its brittleness or low refractive index is of a problem. An aromatic glycidyl ether compound having good optical characteristics and also high toughness is desired.

[0010]

In addition, as one of methods for solving the above-described problems in applications in the electrical and electronic field, epoxy resins having a phosphorus atom in a skeleton thereof are proposed. In particular, since general compounds of a phosphoric acid ester type are low in stability, cyclic phosphoric acid ester compounds having good stability are used. In addition, even if a phosphoric acid ester compound is not used, those having excellent flame retardancy as compared with conventional epoxy resins have been developed by selecting a resin skeleton. However, at present, especially in the field of semiconductor encapsulation materials, development of a system in which the flame retardancy can be achieved without using a phosphorus-based flame retarder is investigated, and in general, flame retardancy called "non-halogen", "non-antimony", or "non-phosphorus" is being demanded.

[0011]

Then, a first aspect of the present invention is aimed to provide an epoxy resin composition capable of being applied to optical members for which high-level optical characteristics are required in view of excellent transparency and heat resistance, high refractive index, low birefringent index, and low retardation.

In addition, a second aspect of the present invention is aimed to provide a curable resin composition that is advantageous in applications in the electrical and electronic field, and which is capable of making high heat resistance and flame retardancy compatible with each other.

MEANS FOR SOLVING THE PROBLEM

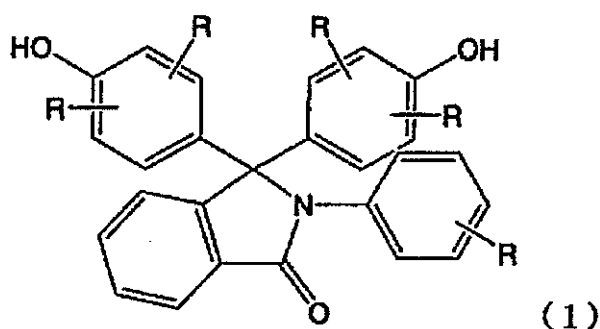
[0012]

In view of the above-described actual circumstances, the present inventors made extensive and intensive investigations, and as a result, they have accomplished the present invention.

5 That is, the present invention relates to (1) to (11) described below.

(1) An epoxy resin composition containing an epoxy resin obtained through a reaction of a phenol resin represented by the following formula (1) with an epihalohydrin and a carboxylic acid and/or a cationic polymerization catalyst, the epoxy resin having a hue by the Gardner colorimetry (in a 40% MEK solution) of not more than 2:

[0013]



[0014]

15 (In the formula, each of plurally existent Rs independently represents a hydrogen atom, an alkyl group having from 1 to 6 carbon atoms, or an alkoxy group having from 1 to 6 carbon atoms.)

(2) The epoxy resin composition described in (1) above, wherein an amount of a residual phenolphthalein derivative in the phenol resin to be allowed to react with the epihalohydrin is not more than 2%.

(3) The epoxy resin composition described in (1) above, wherein an amount of remaining iron in the phenol resin to be allowed to react with the epihalohydrin is not more than 50 ppm.

(4) The epoxy resin composition described in (3) above, containing a transition metal salt.

(5) The epoxy resin composition described in (3) above, containing a quaternary phosphonium salt.

(6) The epoxy resin composition described in (3) above, containing a cationic polymerization initiator.

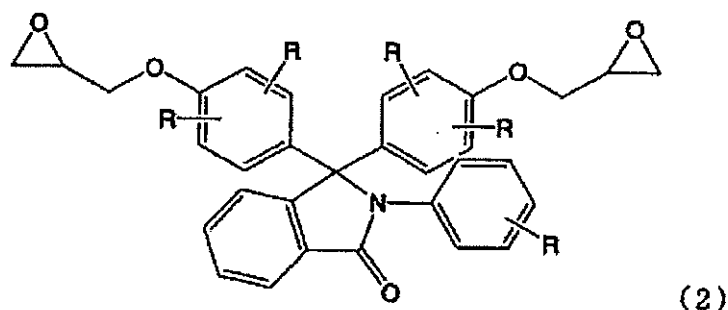
5 (7) An epoxy resin cured product obtained by curing the epoxy resin composition described in any one of (4) to (6) above.

(8) The epoxy resin composition described in any one of (1) to (6) above, which is used for a substitute of glass.

[0015]

10 (9) A curable resin composition containing an epoxy resin represented by the following formula (2) and a phenol resin and/or a polymerization catalyst:

[0016]



[0017]

(In the formula, each of plurally existent Rs independently represents a hydrogen atom, an alkyl group having from 1 to 6 carbon atoms, or an alkoxy group having from 1 to 6 carbon atoms.)

(10) The curable resin composition described in (9) above, wherein the phenol resin is a phenol aralkyl resin (resin having an aromatic alkylene structure).

(11) The curable resin composition described in (9) above, wherein the polymerization catalyst is a cationic polymerization catalyst.

EFFECT OF THE INVENTION

[0018]

The epoxy resin composition that is concerned with the first aspect of the present invention can be applied to optical members for which high-level optical characteristics are required in view of excellent transparency and heat resistance, high refractive index, and low birefringent index.

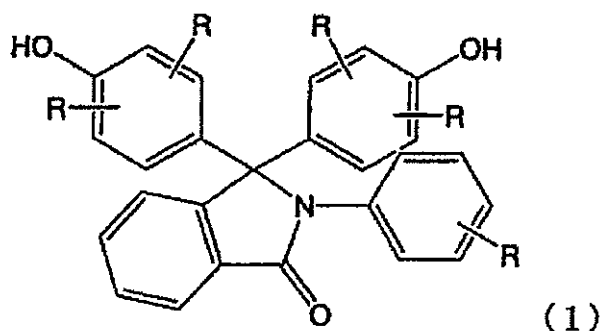
In addition, the curable resin composition that is concerned with the second aspect of the present invention is a composition containing an epoxy resin which reveals flame retardancy even without using a flame retarder or a phosphorus-based compound while ensuring sufficient curing properties and which contributes to a decrease of a flame retarder or a phosphorus-based compound in the composition, and the curable resin composition of the present invention is useful for insulating materials for electrical and electronic components, various composite materials inclusive of laminated boards (e.g., printed wiring boards, build-up substrates, etc.) and CFRP, adhesives, paints, and the like. In particular, the curable resin composition of the present invention is extremely useful for semiconductor encapsulation materials or substrate materials for protecting semiconductor elements.

MODES FOR CARRYING OUT THE INVENTION

[0019]

The first aspect of the present invention (hereinafter also referred to as "first invention") is concerned with an epoxy resin composition containing an epoxy resin obtained through a reaction of a phenol resin represented by the following formula (1) with an epihalohydrin and a carboxylic acid and/or a cationic polymerization catalyst, the above-described epoxy resin having a hue by the Gardner colorimetry (in a 40% MEK solution) of not more than 2.

[0020]



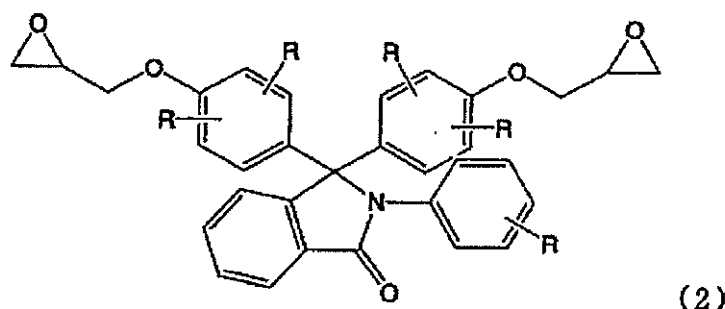
[0021]

(In the formula, each of plurally existent Rs independently represents a hydrogen atom, an alkyl group having from 1 to 6 carbon atoms, or an alkoxy group having from 1 to 6 carbon atoms.)

5 [0022]

In addition, the second aspect of the present invention (hereinafter also referred to as "second invention") is concerned with a curable resin composition containing an epoxy resin represented by the following formula (2) and a phenol resin and/or a polymerization catalyst.

10 [0023]



[0024]

(In the formula, each of plurally existent Rs independently represents a hydrogen atom, an alkyl group having from 1 to 6 carbon atoms, or an alkoxy group having from 1 to 6 carbon atoms.)

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[0025]

The epoxy resin which the resin composition of each of the first and second inventions contains is an epoxy resin having a phenolphthalein skeleton. A basic skeleton of the subject epoxy resin is disclosed in British Patent No. 1,158,606 (Patent Document 4). Patent Document 4 discloses results in which an epoxy equivalent per kg is 3.4 (294 g/eq. when converted into a current epoxy equivalent), a hue is Gardner 8 (40% in methyl glycol), a softening point is 66°C (kolfer heater), and a chlorine content is 2.2%. In addition, Patent Document 4 discloses curing physical properties with DDS (diaminodiphenylsulfone).

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If things go on like this, it is difficult to spread the subject epoxy resin into optical materials, and a resin with higher transparency is demanded.

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In addition, it is suggested from those data of Patent Document 4 that the subject resin is very high in the chlorine amount and unsuitable for electronic material applications; and also that it is very high in coloration so that it is hardly useful for applications for which a tint is needed. In addition, the epoxy equivalent is so high as 294 g/eq. as compared with a theoretical value (252.7 g/eq.), and it is suggested from the chlorine amount that a lot of an epihalohydrin structure in which the epoxy remains without being cyclized is contained. Thus, so far as the structure in which nevertheless it is bifunctional, such an epoxy ring is not accomplished is concerned, there is often found the case where crosslinking does not proceed well, and on the occasion of performing curing with a phenol resin, anionic polymerization with a basic catalyst such as an imidazole, etc., or cationic polymerization with an onium salt or the like, a problem is caused in its mechanical characteristics or characteristics such as water absorption properties. In particular, in the electronic material applications, in not only curing thereof but curing of amine-based compounds, corrosion or the like of wirings to be caused due to liberation of chlorine at the time of curing is anticipated, leading to a cause of lowering the electrical reliability.

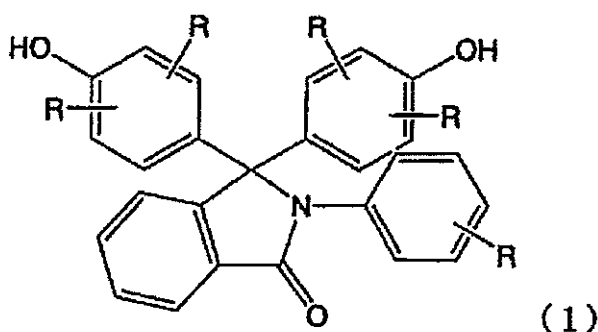
In recent years, a copper wire have been being frequently used especially for junction between a semiconductor chip and a substrate, and such an electrical corrosion issue is becoming much more important and is a problem to be solved.

In addition, Patent Document 4 does not describe the flame retardancy.

[0026]

The epoxy resin which is used for the epoxy resin composition that is the first invention is an epoxy resin obtained through a reaction of a phenol resin represented by the following formula (1):

[0027]

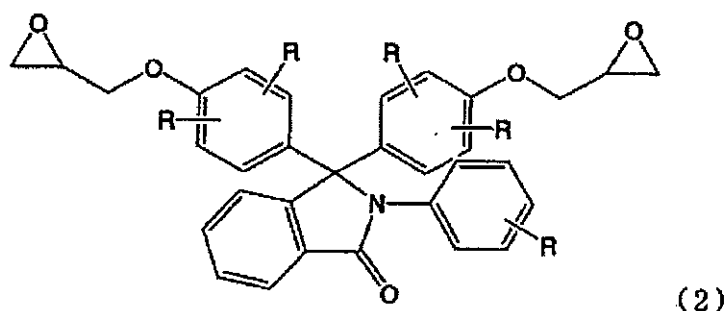


[0028]

(in the formula, each of plurally existent Rs independently represents a hydrogen atom, an alkyl group having from 1 to 6 carbon atoms, or an alkoxy group having from 1 to 6 carbon atoms) with an epihalohydrin, and specifically, it is an epoxy resin represented

5 by the following formula (2):

[0029]



[0030]

10 (in the formula, each of plurally existent Rs independently represents a hydrogen atom, an alkyl group having from 1 to 6 carbon atoms, or an alkoxy group having from 1 to 6 carbon atoms).

[0031]

Here, the epoxy resin which is used for the epoxy resin composition that is the first invention is an epoxy resin containing the above-described epoxy compound in a content of preferably from 70 to 95% (in terms of an area% according to the gel permeation chromatography), and more preferably from 70 to 93%. Here, in synthesizing an epoxy resin having a purity in which the content of the above-described epoxy compound exceeds 95%, there is a concern that a very great amount of energy is required, and in the case where the purity is excessively high, there may be a possibility that crystallinity becomes high, or there is a concern that a lowering of toughness is found. When the content is less than 70%, there is a concern that a lot of compounds in which the epoxy ring is not completely cyclized and which do not have a functional group are contained. In addition, there is frequently found the case where in the majority of such compounds in which the epoxy ring is not completely cyclized, chlorine is contained, and so far as the electronic material applications are concerned,

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there is a concern about liberation of a chlorine ion under a high-temperature and high-humidity condition and corrosion of wirings to be caused due to this matter.

[0032]

In addition, in the case where the epoxy resin having a phenolphthalein
5 structure remains in the subject epoxy resin, in view of the fact that a lowering of the electrical reliability and large coloration are caused, remaining of the epoxy resin having a phenolphthalein structure is not preferable, and a proportion of the remaining epoxy resin having a phenolphthalein structure is preferably not more than 2%, and especially preferably not more than 1%. This epoxy resin having a phenolphthalein
10 structure is largely influenced by impurities derived from a raw material. When the proportion of the remaining epoxy resin having a phenolphthalein structure exceeds 2%, in particular, the coloration becomes strong, and hence, such is not preferable.

[0033]

In the foregoing formulae (1) and (2), R is most preferably a hydrogen atom.
15 Examples of the above-described alkyl group having from 1 to 6 carbon atoms as represented by R include alkyl groups having a linear, branched or cyclic structure, such as a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, etc. Here, R is preferably a methyl group or an ethyl group, and especially preferably a methyl group.

20 Examples of the alkoxy group having from 1 to 6 carbon atoms as represented by R include alkoxy groups having a linear, branched or cyclic structure, such as a methoxy group, an ethoxy group, a propoxy group, a butoxy group, etc. Here, R is preferably a methoxy group, an ethoxy group, or a propoxy group, and especially preferably a methoxy group.

25 [0034]

As for preferred resin characteristics of the epoxy resin represented by the foregoing formula (2), an epoxy equivalent is from 1.02 times to 1.13 times relative to a theoretical epoxy equivalent (252.7 g/eq.). The epoxy equivalent is more preferably from 1.03 to 1.10 times. In the case where the epoxy equivalent is less than 1.02 times,
30 synthesis or purification of an epoxy resin costs a lot of money, and hence, such is not preferable from the industrial standpoint; whereas in the case where it exceeds 1.13 times, similar to the foregoing, there is a concern that a problem to be caused due to the chlorine amount is generated.

In addition, the total chlorine remaining in the obtained epoxy resin is preferably not more than 5,000 ppm, more preferably not more than 3,000 ppm, and especially preferably not more than 2,000 ppm. The adverse influence to be caused due to the chlorine amount is the same as that described above. Incidentally, an amount of each of a chlorine ion and a sodium ion is preferably not more than 5 ppm, and more preferably not more than 3 ppm. The chlorine ion is previously described, and needless to say, a cation such as a sodium ion, etc. is a very important factor especially in power device applications, and when a high voltage is impressed, it becomes one of causes of defective modes.

The "theoretical epoxy equivalent" as referred to herein means an epoxy equivalent calculated when the phenolic hydroxyl group of the phenol compound represented by the foregoing formula (1) is glycidylated neither too much nor too little.

In addition, in the case where all of Rs are a hydrogen atom, a specific epoxy equivalent value is preferably from 257.8 g/eq. to 285.6 g/eq., and especially preferably from 260.3 g/eq. to 278.0 g/eq. When the epoxy equivalent falls within the foregoing range, an epoxy resin which is excellent in heat resistance and electrical reliability in terms of a cured product thereof can be obtained.

[0035]

The epoxy resin which is used for the resin composition of the present invention (also referred to simply as "epoxy resin of the present invention") has a resinous form having a softening point. Here, the softening point is preferably from 70 to 130°C, and more preferably from 80 to 120°C. In the case where all the substituent Rs are a hydrogen atom, in particular, the softening point is from 70 to 120°C, and more preferably from 80 to 110°C. When the softening point is excessively low, blocking at the time of storage becomes problematic, and a lot of problems such as necessity of handling at a low temperature, etc. are caused. Conversely, in the case where the softening point is excessively high, on the occasion of kneading with other resin, there is a concern that problems such as deterioration of handling, etc. are caused. In addition, a melt viscosity is preferably not more than 1 Pa·s (ICI melt viscosity at 150°C according to the cone and plate method). In the case of using a mixture with an inorganic material (e.g., a filler, etc.), there is a concern that fluidity is poor, and there is also a concern that in a glass cloth or the like, the meshes thereof are smaller, so that impregnation properties are inferior.

[0036]

The epoxy resin which is used in the first invention is excellent in transparency (hue). The hue by the Gardner colorimetry (through visual inspection in a 40% methyl ethyl ketone solution) is not more than 2, and preferably not more than 1.5. In particular, in view of not only spreading into optical materials but influences against the color of a substrate in usual PCB substrates or the like, an epoxy resin with less coloration is desired.

Although it is not necessary that the epoxy resin which is used in the second invention is excellent in transparency (hue) as described above, it is preferable that the epoxy resin is excellent in transparency (hue) similar to the foregoing.

In addition, the epoxy resin of the present invention has a high refractive index. The refractive index is preferably 1.61 or more, more preferably 1.62 or more, and especially preferably from 1.62 to 1.65. In particular, in the field where the adjustment of refractive index is required, so long as the refractive index is high, an amount of the aromatic ring of the composition to be used can be decreased, thereby making it possible to contribute to an enhancement of light fastness characteristics. In addition, in applications to lenses or the like, when the refractive index is higher, lenses with a smaller strain can be prepared, and hence, such is preferable.

[0037]

A production method of the epoxy resin of the present invention is hereunder described.

The compound represented by the foregoing formula (2) is obtained through a reaction of a phenol compound (DPPI) (see, for example JP-A-2005-290378) which is synthesized from a phenolphthalein derivative and an aminobenzene derivative, with an epihalohydrin. A specific production method of the epoxy resin of the present invention is described below.

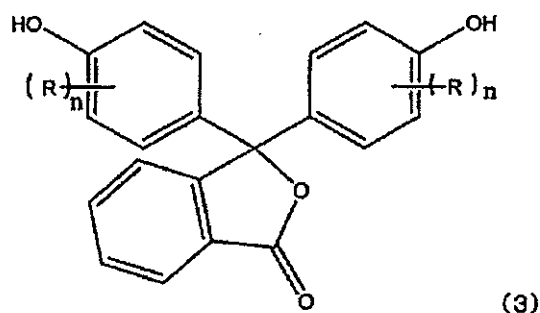
[0038]

It is known that it is possible to synthesize the phenolphthalein derivative from phthalic acid and a corresponding phenol of every kind. When the used phenol is phenol, phenolphthalein is obtained, and when the used phenol is cresol, cresolphthalein is obtained.

Here, examples of the above-described phenol of every kind include phenol, cresol, ethylphenol, propylphenol, xylanol, methylbutylphenol, and the like.

In addition, examples of the phenolphthalein derivative obtained from the above-described reaction include those having the following structure.

[0039]



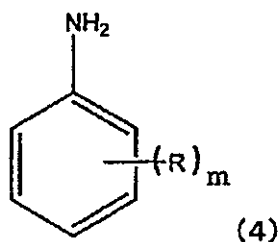
5 [0040]

(In the formula, R has the same meanings as those described above; and n represents an integer of from 1 to 2.)

[0041]

10 Examples of the aminobenzene derivative include those having the following structure.

[0042]



[0043]

15 (In the formula, R has the same meanings as those described above; and m represents an integer of from 1 to 2.)

[0044]

20 An amount of the residual phenolphthalein derivative in the phenol compound (DPPI) is preferably not more than 2%, more preferably not more than 1%, still more preferably not more than 0.5%, and especially preferably not more than 0.1% (as measured by means of high-performance liquid chromatography). In the case where this phenolphthalein derivative remains, the coloration tends to become large at the time of reaction. The same is also applicable to the aminobenzene derivative. In addition, an

amount of remaining iron (by the ICP emission spectroscopy) is one of factors to be caused due to the coloration. The amount of remaining iron is preferably not more than 100 ppm, more preferably not more than 50 ppm, and especially preferably not more than 10 ppm. In addition, it is desirable that the phenol compound (DPPI) as the main
5 body has a purity of 98% or more.

It is possible to adjust the amount of the residual phenolphthalein derivative by means of purification (e.g., washing, recrystallization, reprecipitation, etc.) of DPPI.

[0045]

In the reaction for obtaining the epoxy resin of the present invention,
10 epichlorohydrin that is easily available from the industrial standpoint is preferable as the epihalohydrin. A use amount of the epihalohydrin is generally from 3.0 to 15 moles, preferably from 3.0 to 10 moles, more preferably from 3.5 to 8.5 moles, and especially preferably from 5.5 to 8.5 moles per mole of the hydroxyl group of the phenol compound (DPPI).

15 When the use amount of the epihalohydrin is less than 3.0 moles, there is a concern that the epoxy equivalent becomes large, and in addition, there is a concern that workability of the epoxy resin is deteriorated. When the use amount of the epihalohydrin exceeds 15 moles, a solvent amount becomes large.

[0046]

20 In the above-described reaction of a phenol resin with an epihalohydrin, an alkali metal hydroxide can be used. Examples of the alkali metal hydroxide which may be used include sodium hydroxide, potassium hydroxide, and the like. Although a solid may be utilized as the alkali metal hydroxide, or its aqueous solution may be used, in the present invention, it is preferable to use a solid molded in a flaky form especially
25 from the standpoints of solubility and handling.

A use amount of the alkali metal hydroxide is generally from 0.90 to 1.5 moles, preferably from 0.95 to 1.25 moles, and more preferably from 0.99 to 1.15 moles per mole of the hydroxyl group of the raw material phenol mixture.

[0047]

30 In order to promote the reaction, a quaternary ammonium salt such as tetramethylammonium chloride, tetramethylammonium bromide, trimethylbenzylammonium chloride, etc. may be added as a catalyst. A use amount of

the quaternary ammonium salt is generally from 0.1 to 15 g, and preferably from 0.2 to 10 g per mole of the hydroxyl group of the raw material phenol mixture.

[0048]

In the subject reaction, in addition to the above-described epihalohydrin, it is preferable to use a non-polar protic solvent (e.g., dimethyl sulfoxide, dioxane, dimethyl imidazolidinones, etc.) or an alcohol having from 1 to 5 carbon atoms in combination. Examples of the alcohol having from 1 to 5 carbon atoms include alcohols such as methanol, ethanol, isopropyl alcohol, and the like. A use amount of the non-polar protic solvent or alcohol having from 1 to 5 carbon atoms is generally from 2 to 50% by weight, and preferably from 4 to 25% by weight relative to the use amount of the epihalohydrin. In addition, epoxidation may be performed while controlling the moisture in the system by a technique such as azeotropic dehydration, etc.

In the case where a lot of moisture is contained in the system, there is a concern that the electrical reliability is deteriorated in the resulting epoxy resin, and hence, such is not preferable. It is preferable to perform the synthesis by controlling the moisture to not more than 5%. In addition, on the occasion of obtaining the epoxy resin by using a non-polar protic solvent, an epoxy resin with excellent electrical reliability is obtained, and therefore, the non-polar protic solvent can be suitably used.

[0049]

A reaction temperature is generally from 30 to 90°C, and preferably from 35 to 80°C. In particular, in the present invention, in order to perform the epoxidation with a higher purity, the reaction temperature is preferably 60°C or higher, and a reaction under a condition close to a reflux condition is especially preferable. A reaction time is generally from 0.5 to 10 hours, preferably from 1 to 8 hours, and especially preferably from 1 to 3 hours. When the reaction time is too short, the reaction does not proceed completely, whereas when the reaction time is too long, there is a concern that a by-product is formed.

The epihalohydrin or solvent or the like is removed by heating under reduced pressure after (or without) washing a reaction product of such an epoxidation reaction with water. In addition, for the purpose of producing an epoxy resin having a smaller amount of a hydrolyzable halogen, the cyclization can also be made sure by dissolving the recovered epoxy resin in a ketone having from 4 to 7 carbon atoms (examples thereof include methyl isobutyl ketone, methyl ethyl ketone, cyclopentanone,

cyclohexanone, and the like) as a solvent and adding an aqueous solution of an alkali metal hydroxide such as sodium hydroxide, potassium hydroxide, etc. to perform the reaction. In that case, a use amount of the alkali metal hydroxide is generally from 0.01 to 0.3 moles, and preferably from 0.05 to 0.2 moles per mole of the hydroxyl group of the raw material phenol mixture used for the epoxidation. A reaction temperature is generally from 50 to 120°C, and a reaction time is generally from 0.5 to 2 hours.

In addition, in the reaction with the epihalohydrin, it is preferable that the system is substituted with an inert gas such as nitrogen, etc. from the initial stage of the reaction, and an oxygen concentration in the cavity is preferably not more than 10%. Remaining of oxygen influences the coloration. Examples of the technique include a method in which before charging the phenol compound (DPPI), an inert gas such as nitrogen, etc. is blown (in a gas or in a liquid), or after reducing the pressure to make the system vacuum, the system is substituted with an inert gas. In the case of not performing substitution with an inert gas, there is a concern that coloration of the resulting resin is caused. In the case of blowing an inert gas, though its amount varies with a capacity of the furnace, it is preferable to blow the inert gas in an amount at which the amount of from 1 to 3 times the capacity of the furnace can be substituted for from 0.5 to 10 hours.

[0050]

After completion of the reaction, by removing the formed salt by means of filtration, water washing, or the like and further distilling off the solvent by heating under reduced pressure, the epoxy resin of the present invention is obtained.

[0051]

The curable resin compositions of the first invention and the second invention each containing the epoxy resin of the present invention are hereunder described.

The epoxy resin composition of the first invention (hereinafter also referred to as "curable resin composition") contains the epoxy resin of the present invention as an essential component.

In the curable resin composition of the first invention, two kinds of methods of heat curing with a curing agent composed of a carboxylic acid as an essential component (curable resin composition A) and cationic curing in the presence of a cationic polymerization catalyst such as an acid, etc. as a curing catalyst (curable resin composition B) can be adapted.

[0052]

In the curable resin composition A and the curable resin composition B, the epoxy resin of the present invention can be used solely or in combination with other epoxy resin. In the case of a combined use, a proportion of the epoxy resin of the present invention occupying in all the epoxy resins is preferably 30% by mass or more, and especially preferably 40% by mass or more. However, in the case where the epoxy resin of the present invention is used as a modifier of the curable resin composition, it may be added in a proportion of from 1 to 30% by mass.

[0053]

Examples of other epoxy resin which may be used in combination with the epoxy resin of the present invention include novolak type epoxy resins, bisphenol type epoxy resins, biphenyl type epoxy resins, triphenylmethane type epoxy resins, phenolaralkyl type epoxy resins, and the like. Specifically, examples thereof include solid or liquid epoxy resins such as polycondensates of 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, or a phenol (e.g., phenol, an alkyl-substituted phenol, naphthol, an alkyl-substituted naphthol, dihydroxybenzene, dihydroxynaphthalene, etc.) with formaldehyde, acetaldehyde, benzaldehyde, 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 products thereof; glycidyl etherified products derived from a halogenated bisphenol such as tetrabromobisphenol A, etc. and an alcohol; alicyclic epoxy resins; glycidyl amine-based epoxy resins; glycidyl ester-based epoxy resins; silsesquioxane-based epoxy resins (e.g., epoxy resins having a glycidyl group and/or an epoxycyclohexane structure in a siloxane structure of a chain, cyclic or ladder structure or a mixed structure of at least two or more kinds thereof); etc. However, it should not be construed that the epoxy resin is limited thereto.

[0054]

In particular, in the case where the curable resin composition of the present invention is used for optical applications, it is preferable that the epoxy resin of the present invention is used in combination with an alicyclic epoxy resin or an epoxy resin of a silsesquioxane structure. In particular, in the case of an alicyclic epoxy resin, a compound having an epoxycyclohexane structure in a skeleton thereof is preferable, and an epoxy resin obtained through an oxidation reaction of a compound having a cyclohexene structure is especially preferable.

Examples of the compound having a cyclohexene structure include compounds which can be produced through an esterification reaction between cyclohexene carboxylic acid and an alcohol or an esterification reaction between cyclohexene methanol and a carboxylic acid (see techniques described in *Tetrahedron*, Vol. 36, p.2409 (1980), *Tetrahedron Letters*, p.4475 (1980), and the like), or the Tishchenko reaction of cyclohexene aldehyde (see techniques described in JP-A-2003-170059, JP-2004-262871, and the like), or an ester interchange reaction of a cyclohexene carboxylic acid ester (see techniques described in JP-A-2006-052187 and the like).

Although the alcohol is not particularly limited so long as it is a compound having an alcoholic hydroxyl group, examples thereof include diols such as ethylene glycol, propylene glycol, 1,3-propanediol, 1,2-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, cyclohexanedimethanol, etc.; triols such as glycerin, trimethylolethane, trimethylolpropane, trimethylolbutane, 2-hydroxymethyl-1,4-butanediol, etc.; tetraols such as pentaerythritol, etc.; and the like. In addition, examples of the carboxylic acid include oxalic acid, maleic acid, fumaric acid, phthalic acid, isophthalic acid, adipic acid, cyclohexanedicarboxylic acid, and the like; but it should not be construed that the carboxylic acid is limited thereto.

[0055]

Furthermore, examples of compounds having a cyclohexene structure other than those described above include acetal compounds obtained through an acetal reaction between a cyclohexene aldehyde derivative and an alcohol. As for a reaction technique, the compound can be produced by applying a general acetalization reaction; and for example, there are disclosed a method of performing the reaction by using, as a reaction medium, a solvent such as toluene, xylene, etc. while performing azeotropic dehydration (see Specification of U.S. Patent No. 2,945,008), a method of dissolving a polyhydric alcohol in concentrated hydrochloric acid and then performing the reaction

while adding an aldehyde step by step (see JP-A-S48-96590), a method of using water as a reaction medium (see Specification of U.S. Patent No. 3,092,640), a method of using an organic solvent as a reaction medium (see JP-A-H7-215979), a method of using a solid acid catalyst (see JP-A-2007-230992), and the like. In view of stability of the structure, a cyclic acetal structure is preferable.

Specific examples of such an epoxy resin include ERL-4221, UVR-6105, and ERL-4299 (all of which are a trade name available from The Dow Chemical Company); CELLOXIDE 2021P, EPOLEAD GT401, EHPE 3150, and EHPE 3150CE (all of which are a trade name available from Daicel Corporation); dicyclopentadiene epoxide; and the like, but it should not be construed that the epoxy resin is limited thereto (reference: *Sosetsu Epokishi Jushi Kisoheh I* (General Remarks: Epoxy Resins, Fundamental Volume I), p.76-85).

These may be used solely, or may be used in combination of two or more kinds thereof.

[0056]

The respective curable resin compositions are hereunder mentioned.

Curable resin composition A (heat curing with a curing agent)

The curing agent which the curable resin composition A of the present invention contains is composed of a resin having a carboxylic acid structure (hereinafter referred to as "carboxylic acid") as an essential component. In particular, as the carboxylic acid, bifunctional to tetrafunctional carboxylic acids are preferable, and polycarboxylic acids obtained through an addition reaction of a bifunctional to tetrafunctional polyhydric alcohol with an acid anhydride are more preferable. In addition, a structure having an acid anhydride and a carboxylic acid, such as cyclohexane-1,3,4-tricarboxylic acid-3,4-anhydride, etc., is also preferable. In general, though an acid anhydride is used in optical material applications, in the curable composition A of the present invention, a carboxylic acid is made as an essential component from the standpoint of suppressing volatility.

Although the bifunctional to tetrafunctional polyhydric alcohol is not particularly limited so long as it is a compound having an alcoholic hydroxyl group, examples thereof include diols such as ethylene glycol, propylene glycol, 1,3-propanediol, 1,2-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, cyclohexanedimethanol, 2,4-diethylpentanediol, 2-ethyl-2-butyl-1,3-propanediol,

neopentyl glycol, tricyclodecane dimethanol, norbornene diol, etc.; triols such as glycerin, trimethylolethane, trimethylolpropane, trimethylolbutane, 2-hydroxymethyl-1,4-butanediol, etc.; tetraols such as pentaerythritol, ditrimethylolpropane, etc.; and the like.

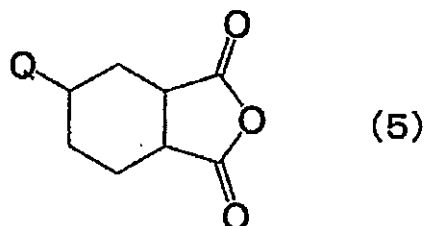
5 Above all, branched or cyclic polyhydric alcohols such as cyclohexanedimethanol, 2,4-diethylpentanediol, 2-ethyl-2-butyl-1,3-propanediol, neopentyl glycol, tricyclodecane dimethanol, and norbornene diol, etc. are especially preferable.

[0057]

10 As the acid anhydride, in particular, methyltetrahydrophthalic anhydride, methylnadid 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 acid-3,4-anhydride, and the
15 like are preferable.

Hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, or cyclohexane-1,3,4-tricarboxylic acid-3,4-anhydride, each of which is represented by the following formula (5):

[0058]



20

[0059]

(in the formula, Q represents at least one member of a hydrogen atom, a methyl group, and a carboxyl group) is especially preferable.

[0060]

25 Examples of the curing agent which can be used in combination with such a carboxylic acid include amine-based compounds, acid anhydride-based compounds, amide-based compounds, phenol-based compounds, and the like. Specific examples of the curing agent which may be used include nitrogen-containing compounds (e.g.,

amine or amide compounds) such as diaminodiphenylmethane, diethylenetriamine, triethylenetetramine, diaminodiphenylsulfone, isophoronediamine, dicyandiamide, a polyamide resin synthesized from a dimer of linolenic acid and ethylenediamine, etc.; acid anhydrides such as phthalic anhydride, trimellitic anhydride, pyromellitic anhydride, maleic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, methyl nadic 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 acid-3,4-anhydride, etc.;

carboxylic acid resins obtained through an addition reaction between various alcohol- or carbitol-modified silicones and the above-described acid anhydrides; polycondensates of 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, or a phenol (e.g., phenol, an alkyl-substituted phenol, naphthol, an alkyl-substituted naphthol, dihydroxybenzene, dihydroxynaphthalene, etc.) with formaldehyde, acetaldehyde, benzaldehyde, 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 products thereof; polyphenols such as halogenated bisphenols, e.g., tetrabromobisphenol A, etc., a condensate between terpene and a phenol, etc.; compounds of imidazole, a trifluoroborane-amine complex, or a guanidine derivative; and the like. It should not be construed that the curing agent is limited thereto. These may be used solely, or may be used in combination of two or more kinds thereof.

[0061]

A use amount of the curing agent in the curable resin composition A of the present invention is preferably from 0.7 to 1.2 equivalents to one equivalent of the epoxy group of the epoxy resin. In the case where the use amount of the curing agent is less than 0.7 equivalents to one equivalent of the epoxy group, or in the case where it exceeds 1.2 equivalents, there is a concern that in all the cases, the curing becomes incomplete, so that favorable curing physical properties are not obtained.

[0062]

In the curable resin composition A of the present invention, a curing promoter (curing catalyst) may be used in combination together with the curing agent. Specific examples of the curing promoter which may be used include imidazoles such as 2-methylimidazole, 2-ethylimidazole, 2-ethyl-4-methylimidazole, etc.; tertiary amines such as 2-(dimethylaminomethyl)phenol, 1,8-diaza-bicyclo(5,4,0)undecene-7, etc.; phosphines such as triphenylphosphine, etc.; quaternary ammonium salts such as tetrabutylammonium salts, triisopropylmethylammonium salts, trimethyldecylammonium salts, cetyltrimethylammonium salts, hexadecyltrimethylammonium hydroxide, etc.; quaternary phosphonium salts such as triphenylbenzylphosphonium salts, triphenylethylphosphonium salts, tetrabutylphosphonium salts, etc. (though a counter ion of the quaternary salt, such as a halogen, an organic acid ion, a hydroxide ion, etc., is not particularly specified, an organic acid ion or a hydroxide ion is especially preferable); tin octylate; transition metal compounds (transition metal salts) such as zinc compounds, for example, zinc carboxylates (e.g., zinc 2-ethylhexanonate, zinc stearate, zinc behenate, or zinc myristate) or zinc phosphates (e.g., zinc octyl phosphate, zinc stearyl phosphate, etc.), etc.; and the like. The curing promoter is used in an amount of from 0.01 to 5.0 parts by weight based on 100 parts by weight of the epoxy resin as the need arises.

In the present invention, in particular, for the purpose of keeping the optical characteristics, it is preferable to use a quaternary phosphonium salt or a transition metal compound (transition metal salt).

[0063]

The curable resin composition A of the present invention can also contain a phosphorus-containing compound as a flame retardancy-imparting component. The phosphorus-containing compound may be either a reaction type or an addition type. Specific examples of the phosphorus-containing compound include phosphoric acid esters such as trimethyl phosphate, triethyl phosphate, tricresyl phosphate, trixylenyl phosphate, cresyldiphenyl phosphate, cresyl-2,6-dixylenyl phosphate, 1,3-phenylenebis(dixylenyl phosphate), 1,4-phenylenebis(dixylenyl phosphate), 4,4'-biphenyl(dixylenyl phosphate), etc.; phosphanes such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, 10-(2,5-dihydroxyphenyl)-10H-9-oxa-10-phosphaphenanthrene-10-oxide, etc.; phosphorus-containing epoxy resins obtained

through a reaction of an epoxy resin with active hydrogen of the above-described phosphane; red phosphorus; and the like; but, phosphoric acid esters, phosphanes, or phosphorus-containing epoxy resins are preferable, with 1,3-phenylenebis(dixylenyl phosphate), 1,4-phenylenebis(dixylenyl phosphate), 4,4'-biphenyl(dixylenyl phosphate),
 5 or phosphorus-containing epoxy resins being especially preferable. A content of the phosphorus-containing compound is preferably not more than 0.6 times relative to a total amount of the epoxy resin component in the curable resin composition A of the present invention. In the case where the content of the phosphorus-containing compound exceeds 0.6 times, there is a concern that adverse influences are given to
 10 hygroscopicity or dielectric characteristics of the cured product.

[0064]

Furthermore, an antioxidant may be added to the curable resin composition A of the present invention as the need arises. Examples of the antioxidant which can be used include phenol-based, sulfur-based, or phosphorus-based antioxidants. The
 15 antioxidant can be used solely or in combination of two or more kinds thereof. A use amount of the antioxidant is generally from 0.008 to 1 part by weight, and preferably from 0.01 to 0.5 parts by weight based on 100 parts by weight of the resin component in the curable resin composition A of the present invention.

[0065]

20 Specific examples of the phenol-based antioxidant include monophenols such as 2,6-di-t-butyl-p-cresol, butylated hydroxyanisole, 2,6-di-t-butyl-p-ethylphenol, stearyl- β -(3,5-di-t-butyl-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, 2,4-bis[(octylthio)methyl]-o-cresol, etc.; bisphenols such as 2,2'-
 25 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-
 30 (3,5-di-t-butyl-4-hydroxyphenyl) propionate], 3,5-di-t-butyl-4-hydroxybenzyl phosphonate-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, bis(3,5-di-t-butyl-4-hydroxybenzyl sulfonic acid ethyl) calcium, etc.; and polymer-type 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)propionato]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, tocophenol, etc.

[0066]

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

[0067]

Specific examples of the phosphorus-based antioxidant include phosphites such as triphenyl phosphite, diphenyl isodecyl phosphite, phenyl diisodecyl phosphite, tris(nonylphenyl) phosphite, diisodecyl pentaerythritol phosphite, tris(2,4-di-*t*-butylphenyl) phosphite, cyclic neopentanetetraylbis(octadecyl) phosphite, cyclic neopentanetetraylbis(2,4-di-*t*-butylphenyl) phosphite, cyclic neopentanetetraylbis(2,4-di-*t*-butyl-4-methylphenyl) phosphite, bis[2-*t*-butyl-6-methyl-4-{2-(octadecyloxycarbonyl)ethyl}phenyl] hydrogenphosphite, etc.; oxaphosphaphenanthrene oxides such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, 10-(3,5-di-*t*-butyl-4-hydroxybenzyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, 10-decyloxy-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, etc.; and the like.

[0068]

Although each of these antioxidants can be used solely, two or more kinds thereof may also be used in combination. In particular, in the present invention, a phosphorus-based antioxidant is preferable.

[0069]

Furthermore, a light stabilizer may be added to the curable resin composition A of the present invention as the need arises.

As the light stabilizer, hindered amine-based light stabilizers, especially HALS and the like are especially suitable. Although HALS is not particularly limited, representative examples thereof include a polycondensate of dibutylamine·1,3,5-triazine-*N,N'*-bis(2,2,6,6-tetramethyl-4-piperidyl)-1,6-hexamethylenediamine and *N*-(2,2,6,6-tetramethyl-4-piperidyl)butylamine, a dimethyl succinate-1-(2-hydroxyethyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine polycondensate, 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}], bis(1,2,2,6,6-pentamethyl-4-piperidyl)[[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]methyl]butyl malonate, bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate, bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl) sebacate, 2-(3,5-di-
 5 t-butyl-4-hydroxybenzyl)-2-n-butyl malonic acid bis(1,2,2,6,6-pentamethyl-4-piperidyl), and the like. HALS may be used solely, or may be used in combination of two or more kinds thereof.

[0070]

10 Furthermore, a binder resin can be added to the curable resin composition A of the present invention as the need arises. Examples of the binder resin include butyral-based resins, acetal-based resins; acrylic resins, epoxy-nylon-based resins, NBR-phenol-based resins, epoxy-NBR-based resins, polyamide-based resins, polyimide-based resins, silicone-based resins, and the like, but it should not be construed that the binder resin is
 15 limited thereto. A compounding amount of the binder resin is preferably an amount falling within the range where the flame retardancy or heat resistance of the cured product is not impaired. The binder resin is used in a compounding amount of generally from 0.05 to 50 parts by weight, and preferably from 0.05 to 20 parts by weight based on 100 parts by weight of the resin component in the curable resin composition A of the
 20 present invention (a total amount of the epoxy resin and the binder resin) as the need arises.

[0071]

An inorganic filler can be added to the curable resin composition A of the present invention as the need arises. Examples of the inorganic filler include powders
 25 of crystalline silica, fused silica, alumina, zirconium, calcium silicate, calcium carbonate, silicon carbide, silicon nitride, boron nitride, zirconia, fosterite, steatite, spinel, titania, talc, or the like, or spheroidized beads thereof, and the like; however, it should not be construed that the inorganic filler is limited thereto. Such an inorganic filler may be used solely, or may be used in combination of two or more kinds thereof.
 30 Such an inorganic filler is used in an amount such that its content accounts for not more than 95% by mass in the curable resin composition A of the present invention. Furthermore, various compounding agents such as a silane coupling agent, stearic acid, palmitic acid, calcium stearate, a zinc compound, for example, a zinc carboxylate (e.g.,

zinc 2-ethylhexanoate, zinc stearate, zinc behenate, or zinc myristate) or a zinc phosphate (e.g., zinc octyl phosphate, zinc stearyl phosphate, etc.), a surfactant, a dye, a pigment, an ultraviolet absorber, etc. or various thermosetting resins can be added to the curable resin composition A of the present invention.

5 [0072]

In the case of using the curable resin composition A of the present invention for an optical semiconductor encapsulating agent, a fluorescent material can be added as the need arises. The fluorescent material is, for example, a material having an action of forming white light by absorbing a part of blue light emitted from a blue LED element, thereby emitting wavelength-converted yellow light. The fluorescent material is dispersed into the curable resin composition in advance and then, an optical semiconductor is encapsulated. The fluorescent material is not particularly limited, and conventionally known fluorescent materials can be used. Examples thereof include aluminates of rare earth elements, thiogallates, orthosilicates, and the like. More specifically, examples thereof include fluorescent materials such as YAG fluorescent materials, TAG fluorescent materials, orthosilicate fluorescent materials, thiogallate fluorescent materials, sulfide fluorescent materials, etc.; and $\text{YAlO}_3\text{:Ce}$, $\text{Y}_3\text{Al}_5\text{O}_{12}\text{:Ce}$, $\text{Y}_4\text{Al}_2\text{O}_9\text{:Ce}$, $\text{Y}_2\text{O}_2\text{S:Eu}$, $\text{Sr}_5(\text{PO}_4)_3\text{Cl:Eu}$, $(\text{SrEu})\text{O}\cdot\text{Al}_2\text{O}_3$, and the like are exemplified. As for a particle diameter of such a fluorescent material, those having a particle diameter known in this field are used; and an average particle diameter is preferably from 1 to 250 μm , and especially preferably from 2 to 50 μm . In the case of using such a fluorescent material, its addition amount is preferably from 1 to 80 parts by weight, and especially preferably from 5 to 60 parts by weight based on 100 parts by weight of the resin component.

25 [0073]

The curable resin composition A of the present invention is obtained by uniformly mixing the above-described respective components. The curable resin composition A of the present invention can be easily formed into a cured product thereof by the same method as a conventionally known method. For example, the epoxy resin of the present invention and the curing agent and optionally, the curing promoter, the phosphorus-containing compound, the binder resin, the inorganic filler, and the compounding agent are thoroughly mixed until the mixture becomes uniform by using an extruder, a kneader, a roll, or the like as the need arises, thereby obtaining a

curable resin composition, and the resulting curable resin composition is subjected to potting, melted (without being melted in the case where the curable resin composition is liquid), then cast or molded by using a transfer molding machine or the like, and further heated at from 80 to 200°C for from 2 to 10 hours, whereby the cured product of the present invention can be obtained.

[0074]

In addition, if desired, the cured product of the curable resin composition A of the present invention can be produced by dissolving the curable resin composition A of the present invention in a solvent such as toluene, xylene, acetone, methyl ethyl ketone, methyl isobutyl ketone, N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone, etc., to form a curable resin composition varnish, impregnating the varnish in a base material such as a glass fiber, a carbon fiber, a polyester fiber, a polyamide fiber, an alumina fiber, paper, etc. and then drying by heating to obtain a prepreg, followed by subjecting the prepreg to heat press molding. On that occasion, the solvent is used in an amount accounting for generally from 10 to 70% by mass, and preferably from 15 to 70% by mass in a mixture of the curable resin composition A of the present invention and the solvent. In addition, when the curable resin composition A of the present invention is a liquid composition, an epoxy resin cured product containing a carbon fiber can also be obtained as it is by, for example, the RTM mode.

[0075]

In addition, in the case where the curable resin composition A of the present invention is used in a film or sheet shape, it has such characteristics that it is excellent in flexibility characteristics and the like at a B-stage. Such a resin composition in a film or sheet shape is obtained by forming the curable resin composition A of the present invention into the above-described curable resin composition varnish, which is then coated on a release film, and after removing the solvent under heating, performing a B-stage process. This resin composition in a film or sheet shape can be used as an adhesive (interlayer insulating layer) in multilayer substrates and the like.

[0076]

Curable resin composition B (cationic curing with an acidic curing catalyst)

The curable resin composition B of the present invention to be cured by using an acidic curing catalyst (cationic polymerization catalyst) contains a photopolymerization initiator or a thermal polymerization initiator as the acidic curing

catalyst. Furthermore, the curable resin composition B of the present invention may contain various known compounds or materials, and the like, such as a diluent, a polymerizable monomer, a polymerizable oligomer, a polymerization initiation assistant, a photosensitizer, etc. In addition, if desired, the curable resin composition B
 5 of the present invention may contain various known additives such as an inorganic filler, a coloring pigment, an ultraviolet absorber, an antioxidant, a stabilizer, etc.

[0077]

As the acidic curing catalyst, a cationic polymerization initiator is preferable, and a photocationic or thermal cationic polymerization initiator is especially preferable.

10 By compounding a cationic polymerization initiator which is activated with an active energy ray and/or a cationic polymerization initiator which is activated by heat, the resultant can be used as the curable resin composition B.

[0078]

Examples of the cationic polymerization initiator which initiates the cationic
 15 polymerization of the curable resin composition B of the present invention upon irradiation with an active energy ray include diazonium salts, iodonium salts, sulfonium salts, selenium salts, pyridinium salts, ferrocenium salts, phosphonium salts, thiopyrylium salts, and the like. Of these, iodonium salts and sulfonium salts are preferable, and diaryliodonium salts and dialkylphenacylsulfonium salts are more
 20 preferable, and in particular, diaryliodonium salts can be suitably used.

[0079]

In the case of using a photocationic polymerization initiator such as an iodonium salt, a sulfonium salt, etc. for the cationic curable resin composition B of the present invention, examples of an anion thereof include BF_4^- , AsF_6^- , SbF_6^- , PF_6^- ,
 25 $\text{B}(\text{C}_6\text{F}_5)_4^-$, and the like. Of these, SbF_6^- , PF_6^- , or $\text{B}(\text{C}_6\text{F}_5)_4^-$ is preferable, and SbF_6^- or $\text{B}(\text{C}_6\text{F}_5)_4^-$ is especially preferable.

[0080]

Specific examples of the photocationic polymerization initiator include bis(dodecylphenyl)iodonium hexafluoroantimonate (a main component of UV-9380C,
 30 available from GE Toshiba Silicone Co., Ltd.), tolylcumyliodonium tetrakis(pentafluorophenyl) borate (PHOTOINITIATOR 2074, available from Rhodia), bis(alkyl(C10-C14)phenyliodonium) hexafluoroantimonate (a photocationic

polymerization initiator WPI-016, available from Wako Pure Chemical Industries, Ltd.), and the like.

[0081]

As the active energy ray at the time when the curable resin composition B of the present invention is cured, though X-rays, electron beams, ultraviolet rays, visible light, and the like can be used, ultraviolet rays or visible light is preferable, and ultraviolet rays are especially preferable. In the case of using ultraviolet rays, though a wavelength range thereof is not particularly limited, it is preferably from 150 to 400 nm, and more preferably from 200 to 380 nm. In the case of using ultraviolet rays, the cationic polymerization can be efficiently initiated.

[0082]

In addition, in the curable resin composition B of the present invention, for the purpose of more increasing the activity of the photocationic polymerization initiator, a sensitizer can also be used in combination as the need arises. As the sensitizer which can be used in the present invention, it is possible to use compounds disclosed in, for example, *Adv. in Polymer Sci.*, 62, 1 (1984) by Crivello. Specifically, examples thereof include pyrene, perylene, acridine orange, thioxanthone, 2-chlorothioxanthone, benzoflavin, and the like. In addition, compounds which are widely used as a photo-radical polymerization initiator can also be used. Specifically, examples thereof include benzophenone; thioxanthenes such as 2,4-diethylthioxanthone, 2-isopropylthioxanthone, 2,4-dichlorothioxanthone, etc.; benzoin ethers such as benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, etc.; benzyl dimethyl ketals such as 2,2-dimethoxy-1,2-diphenylethan-1-one, etc.; α -hydroxyalkylphenones such as 2-hydroxy-2-methyl-1-phenylpropan-1-one, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, 1-hydroxycyclohexyl phenyl ketone, etc.; α -dicarbonyl compounds such as camphor quinone, etc.; and the like. In the present invention, thioxanthenes or α -hydroxyalkylphenones can be especially suitably used.

[0083]

A compounding amount of the photocationic polymerization initiator in the curable resin composition B of the present invention can be properly adjusted according to the kind or irradiation dose of the active energy ray. For example, in the case of ultraviolet rays, the compounding amount of the photocationic polymerization initiator is preferably from 0.1 to 10 parts by mass, more preferably from 0.5 to 5 parts, and still

more preferably from 1 to 3 parts based on 100 parts by mass of a total amount of the cationic curable resin composition B. In the case where the compounding amount of the cationic polymerization initiator is less than 0.1 parts, there is a concern that the curing properties are inferior. Conversely, in the case where the compounding amount of the cationic polymerization initiator is more than 10 parts by mass, there may be the case where the components which are truly needed in the cured product are decreased, resulting in a lowering of physical properties of the cured product, or there is a concern that the coloration of the cured product becomes vigorous.

[0084]

In the case of adding the sensitizer to the curable resin composition B of the present invention, its compounding amount can be properly adjusted according to the kind or irradiation dose of the active energy ray. For example, in the case of ultraviolet rays, the compounding amount of the sensitizer is preferably not more than 5 parts by mass, and more preferably from 0.2 to 2 parts based on 100 parts by mass of a total amount of the curable resin composition B. In the case where the compounding amount of the photosensitizer is more than 5 parts by mass, there may be the case where the components which are truly needed in the cured product are decreased, resulting in a lowering of physical properties of the cured product, or there may be the case where the coloration of the cured product becomes vigorous.

[0085]

In the case where the active energy ray is ultraviolet rays or visible light, the cationic curable resin composition is exposed to air. At that time, it is preferable that the humidity of the atmosphere is low, and the humidity is preferably not more than 80% RH, and more preferably not more than 70% RH. Here, in the case of installing ultraviolet rays or visible light in the production line, a method of sending dry air before a light irradiation device or a method of installing a heating device to decrease the humidity can also be adopted.

[0086]

A compound which is activated by heat to initiate the cationic polymerization, namely a thermal cationic polymerization initiator can also be used for the curable resin composition B of the present invention. As such a compound, various onium salts such as quaternary ammonium salts, phosphonium salts, sulfonium salts, etc., combinations of an alkoxy silane with an aluminum complex, and the like can be exemplified.

Examples of available products include ADEKA OPTON CP-66 and ADEKA OPTON CP-77 (all of which are a trade name, available from Adeka Corporation); SAN-AID SI-60L, SAN-AID SI-80L, and SAN-AID SI-100L (all of which are a trade name, available from Sanshin Chemical Industry Co., Ltd.); CI Series (available from Nippon Soda Co., Ltd.); and the like.

[0087]

A compounding proportion of the thermal cationic polymerization initiator in the curable resin composition B of the present invention is in the range of preferably from 0.01 to 10 parts by mass, more preferably from 0.1 to 5 parts, and still more preferably from 0.5 to 3 parts based on 100 parts by mass of the cationic curable resin composition. In the case where this compounding proportion is less than 0.01 parts by mass, there is a concern that even when the activation is performed by the action of heat, a ring-opening reaction of the ring-opening polymerizable group cannot be thoroughly advanced. In addition, even when the thermal cationic polymerization initiator is compounded in a proportion exceeding 10 parts by mass, the action of advancing the polymerization does not increase any more, and there is a concern that physical properties of the cured product are lowered, and hence, such is not preferable.

[0088]

Furthermore, an inorganic filler, a variety of compounding agents such as a silane coupling material, a mold releasing agent, a pigment, etc., or a variety of compounding agents of various thermosetting resins can be added in the curable resin composition B of the present invention as the need arises. Specific examples thereof are as follows.

[0089]

The curable resin composition B of the present invention is obtained by uniformly mixing the respective components. In addition, after uniformly dissolving the curable resin composition B of the present invention in an organic solvent such as polyethylene glycol monoethyl ether, cyclohexanone, γ -butyrolactone, etc., the solvent is removed by heating, thereby making it possible to use the resultant. On that occasion, the solvent is used in a proportion of generally from 10 to 70% by mass, and preferably from 15 to 70% by mass in the mixture of the curable resin composition B of the present invention and the solvent.

Although the curable resin composition B of the present invention can be cured by heating and/or irradiation with ultraviolet rays (for example, reference: *Sosetsu Epokishi Jushi Dai 1-kan Kisoheh I* (General Remarks: Epoxy Resins, Vol. 1, Fundamental I), p.82-84), on that occasion, the amount of heat and/or the irradiation dose of ultraviolet rays varies depending upon the formulation of the curable resin composition B, and therefore, a curing condition is determined in conformity with the respective formulation. Basically, the curing condition has to only be a condition under which the cured product is able to reveal the intensity that is considered to be necessary for the purpose of use. In general, since it is difficult to completely cure such a curable resin composition only upon irradiation with light, in applications for which heat resistance is required, it is necessary to completely accomplish the reaction by heating after the irradiation with light. In addition, since it is necessary to allow the irradiation light on the occasion of photocuring to transmit to details, in the epoxy resin and the curable resin composition B of the present invention, a compound and a composition each having high transparency are desired.

[0090]

In the case of performing heating after the irradiation with light, the heating can be performed in a usual curing temperature region of the curable resin composition B. For example, a range at from ordinary temperature to 150°C for from 30 minutes to 7 days is suitable. Although the heating varies with compounding of the curable resin composition B, in particular, the higher the temperature region, the more effective for curing promotion after the irradiation with light is, and the effect is exhibited by a heat treatment within a shorter period of time. In addition, the lower the temperature, the longer the time is required for the heat treatment. By performing such thermal after-curing, there is brought an aging treatment, too.

[0091]

In addition, the cured product obtained by curing such a curable resin composition B can take various shapes according to an application, and hence, it is not particularly limited in terms of the shape, but for example, it can be formed into a shape such as a film shape, a sheet shape, a bulk shape, etc. Although a molding method varies with a site or member to be adapted, examples thereof include a cast method, a casting method, a screen printing method, a spin coating method, a spraying method, a transfer method, a dispenser mode, and the like. However, it should not be construed

that the molding method is limited thereto, and a method which is adequate for the purpose of obtaining a desired shape may be adopted. For a molding die, a polished glass, a hard stainless steel polished plate, a polycarbonate board, a polyethylene terephthalate board, a polymethyl methacrylate board, and the like can be used. In addition, in order to enhance mold releasing properties between the molding die and the curable resin composition B, a polyethylene terephthalate film, a polycarbonate film, a polyvinyl chloride film, a polyethylene film, a polytetrafluoroethylene film, a polypropylene film, a polyimide film, and the like can be used.

[0092]

For example, on the occasion of using for a cationic curable resist, first of all, the curable resin composition B dissolved in an organic solvent such as polyethylene glycol monoethyl ether, cyclohexanone, γ -butyrolactone, etc. is coated in a film thickness of from 5 to 160 μm on a substrate such as a copper-cladded laminated board, a ceramic substrate, a glass substrate, etc. by a technique such as screen printing, a spin coating method, etc., and the coated film is preliminarily dried at from 60 to 110°C. The obtained curable resin composition B on the substrate is irradiated with ultraviolet rays (for example, those from a low-pressure mercury vapor lamp, a high-pressure mercury vapor lamp, an ultrahigh-pressure mercury vapor lamp, or a xenon lamp, electron beams, etc.) through a negative film having a desired pattern drawn thereon and subsequently exposed at from 70 to 120°C, followed by performing a baking treatment. Thereafter, an unexposed portion is dissolved and removed (developed) with a solvent such as polyethylene glycol monoethyl ether, etc., and if desired, thorough curing is performed by irradiation with ultraviolet rays and/or heating (for example, at from 100 to 200°C for from 0.5 to 3 hours), thereby obtaining a cured product. In this way, it is also possible to obtain a printed wiring board. Incidentally, though the above-described method is concerned with the case of a negative type resist, it is also possible to use the curable resin composition B of the present invention as a positive type resist.

[0093]

The cured product obtained by curing the curable resin composition A or the curable resin composition B of the present invention can be used for various applications inclusive of optical component materials. The optical material refers to a general material to be used for applications in which light such as visible light, infrared rays, ultraviolet rays, X-rays, lasers, etc. passes through the material. More specifically,

besides encapsulation materials for LED such as a lamp type, an SMD type, etc., in the display-related field, examples thereof include substrate materials, light guide plates, prism sheets, polarizing plates, phase difference plates, viewing angle correction films, adhesives, liquid crystal films inclusive of polarizer protective films, and the like of liquid crystal display; encapsulation materials, antireflection films, optical correction films, housing materials, protective films of front glass, substitution materials for front glass, adhesives, and the like of color PDP (plasma display panel) which is expected as a next-generation flat panel display; molding materials, LED encapsulation materials, protective films of front glass, substitution materials for front glass, adhesives, and the like of LED to be used for LED display device; substrate materials, light guide plates, prism sheets, polarizing plates, phase difference plates, viewing angle correction films, adhesives, polarizer protective films, and the like in plasma addressed liquid crystal (PALC) display; protective films of front glass, substitution materials for front glass, adhesives, and the like in organic EL (electroluminescence) display; and various film substrates, protective films of front glass, substitution materials for front glass, adhesives, and the like in field emission display (FED). In the optical recording field, examples thereof include disk substrate materials for VD (video disk), CD/CD-ROM, CD-R/RW, DVD-R/DVD-RAM, MO/MD, PD (phase change disk), and optical card, pickup lenses, protective films, encapsulation materials, adhesives, and the like.

[0094]

In the optical equipment field, examples thereof include lens materials, finder prisms, target prisms, finder covers, light-receiving sensor parts, and the like of still camera; taking lenses, finders, and the like of video camera; projection lenses, protective films, encapsulation materials, adhesives, and the like of projection television system; and lens materials, encapsulation materials, adhesives, films, and the like of optical sensing equipment. In the optical component field, fiber materials in the optical switch periphery, lenses, waveguides, encapsulation materials of element, adhesives, and the like in optical communication system; optical fiber materials, ferrules, encapsulation materials, adhesives, and the like in the optical connector periphery; lenses, waveguides, encapsulation materials of LED, encapsulation materials of CCD, adhesives, and the like in passive optical component or optical circuit component; and substrate materials, fiber materials, encapsulation material of element, adhesives, and the like in the opto-electronic integrated circuit (OEIC) periphery. In the optical fiber

field, examples thereof include lightings or light guides for decoration display, and the like; sensors for industrial application, displays or signs, and the like; and optical fibers for communication infrastructure and digital equipment connection in the home, and the like. In the peripheral material of semiconductor integrated circuit, examples thereof

5 include resist materials to be used for microlithography for LSI or VLSI material, and the like. In the automobile or transportation field, examples thereof include automobile lamp reflectors, bearing retainers, gear portions, corrosion-resistant coatings, switch portions, headlamps, components in engine, electrical equipment components, various interior and exterior articles, drive engines, brake oil tanks, rust-preventive steel sheets

10 for automobile, interior panels, interior materials, wire harnesses for protection or binding, fuel hoses, automobile lamps, substitution materials for glass, and the like; laminated glasses for railway vehicle, and the like; and toughening agents of structural material, engine peripheral members, wire harnesses for protection or binding, rust-preventing coatings, and the like of air plane. In the construction field, examples

15 thereof include interior or processing materials, electrical covers, sheets, glass interlayers, substitution materials for glass, peripheral materials of solar cell, and the like. In the agricultural use, examples thereof include house coating films and the like. Examples of next-generation optical or electronic functional organic materials include organic EL element peripheral materials, organic photo-reflective elements, optical

20 amplifiers that are a light-light conversion device, optical arithmetic elements, substrate materials in the periphery of organic solar cell, fiber materials, encapsulation materials of element, adhesives, and the like.

[0095]

As for the encapsulation materials, there can be mentioned potting, dipping, or

25 transfer-mold encapsulation to be used for capacitors, transistors, diodes, light emitting diodes, IC, LSI, and the like, potting encapsulation to be used for COB, COF, TAB, and the like for IC and LSI, underfills for flip chips and the like, encapsulation at the time of mounting an IC package such as BGA, CSP, etc. (including underfills for reinforcement), and the like.

30 [0096]

As other applications of the optical material, there are exemplified general applications for which the curable resin composition A or the curable resin composition B is used. Examples thereof include adhesives, paints, coating agents, molding

materials (including sheets, films, FRP, and the like), insulating materials (including printed substrates, electric wire coverings, and the like), encapsulating agents, additives to other resins, etc., and the like. Examples of the case of using the curable resin composition A or the curable resin composition B of the present invention as an additive to other resin include the case of using as an encapsulation material or a curing agent for a cyanate resin composition to be used for a substrate; and the case of using as a resist curing agent for acrylate-based resin or the like. Examples of the adhesive include adhesives for civil engineering, architecture, automobiles, general office works, medical uses, or electronic materials. Of these, examples of the adhesive for electronic materials include interlayer adhesives of multilayer substrates such as build-up substrates, etc., die-bonding agents, semiconductor adhesives such as underfills, etc., underfills for BGA reinforcement, anisotropic conductive films (ACF), adhesives for mounting such as anisotropic conductive pastes (ACP), etc., and the like.

[0097]

The curable resin composition of the second invention is hereunder described. In the curable resin composition of the second invention, a phenol resin or a polymerization catalyst is used as an essential component.

[0098]

Examples of the phenol resin which is contained in the second invention include polycondensates of 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, or a phenol (e.g., phenol, an alkyl-substituted phenol, naphthol, an alkyl-substituted naphthol, dihydroxybenzene, dihydroxynaphthalene, etc.) with formaldehyde, acetaldehyde, benzaldehyde, 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 products thereof; halogenated bisphenols such as tetrabromobisphenol A, etc.; and polyphenols such as a condensate of terpene with a phenol, etc. However, it should not be construed that the phenol resin is limited thereto, and it may be used solely, or may be used in combination of two or more kinds thereof.

The phenol resin is preferably a phenol aralkyl resin (a resin having an aromatic alkylene structure); and especially preferably a resin having a structure of at least one member selected from phenol, naphthol, and cresol, which is characterized in that an alkylene moiety thereof as a linker is at least one member selected from a
5 benzene structure, a biphenyl structure, and a naphthalene structure (specifically, examples thereof include xyloc, naphthol xyloc, a phenol biphenylene novolak resin, a cresol-biphenylene novolak resin, a phenol-naphthalene novolak resin, and the like).

[0099]

In the curable resin composition of the second invention, a use amount of the
10 curing agent including the phenol resin is preferably from 0.7 to 1.2 equivalents to one equivalent of the epoxy group of all the epoxy resins. In the case where the use amount of the curing agent is less than 0.7 equivalents to one equivalent of the epoxy resin, or in the case where the use amount of the curing agent exceeds 1.2 equivalents, there is a concern that in all the cases, the curing becomes incomplete, so that favorable curing
15 physical properties are not obtained.

[0100]

Although the polymerization catalyst which the curable resin composition of the second invention contains can be used without limitations so long as it is a catalyst capable of initiating the polymerization by heat or light, specifically, a curing promoter
20 or an acidic curing catalyst can be used.

[0101]

Specific examples of the curing promoter which may be used include the same materials as those which may be used in the curable resin composition A of the first invention as described above. In the case of using the curing promoter, its use amount
25 is also the same as that in the curable resin composition A of the first invention as described above.

[0102]

The acidic curing catalyst is preferably a cationic polymerization initiator, and especially preferably a photocationic or thermal cationic polymerization initiator. By
30 compounding a cationic polymerization initiator which is activated with an active energy ray and/or a cationic polymerization initiator which is activated by heat, the resultant can be used as a curable resin composition 2B as described later.

[0103]

Examples of the cationic polymerization initiator which initiates the cationic polymerization of a curable resin composition 2B of the present invention as described later upon irradiation with an active energy ray include the same materials as those which may be used in the curable resin composition B of the first invention as described
5 above.

[0104]

A compound which is activated by heat to initiate the cationic polymerization, namely a thermal cationic polymerization initiator can also be used for the curable resin composition 2B of the present invention. Examples of such a compound include the
10 same materials as those which may be used in the curable resin composition B of the first invention as described above.

[0105]

In the curable resin composition of the second invention, two kinds of methods of heat curing with a curing agent using a polymerization catalyst as an essential
15 component (curable resin composition 2A) and cationic curing in the presence of an acid as a curing catalyst (curable resin composition 2B) can be adapted.

[0106]

Similar to the curable resin composition of the first invention as described above, in the curable resin composition 2A and the curable resin composition 2B, the
20 epoxy resin of the present invention can be used solely or in combination with other epoxy resin. In the case of a combined use, a use amount of other epoxy resin which may be used in combination and specific examples thereof are the same as those in the curable resin composition of the first invention as described above.

[0107]

25 The respective curable resin compositions are hereunder mentioned.

Heat curing with a curing agent (curable resin composition A)

The curing agent which the curable resin composition 2A of the present invention contains is the same as the carboxylic acid which may be used in the curable resin composition A of the first invention as described above or other curing agent
30 which can be used in combination with the carboxylic acid.

In the present invention, in particular, compounds having an acid anhydride structure and/or a carboxylic acid structure represented by the above-described acid anhydrides or carboxylic acid resins are preferable.

[0108]

A use amount of the curing agent in the curable resin composition 2A of the present invention is also the same as that in the curable resin composition A of the first invention as described above.

5 [0109]

In the curable resin composition 2A of the present invention, a curing promoter may also be used in combination together with the curing agent. Specific examples of the curing promoter which may be used include the same materials as those described above. In the case of using the curing promoter, its use amount is the same as that in the
10 curable resin composition A of the first invention as described above.

[0110]

Similar to the curable resin composition A of the first invention as described above, the curable resin composition 2A of the present invention can also contain a phosphorus-containing compound as a flame retardancy-imparting component. Specific
15 examples and use amount of the phosphorus-containing compound are also the same as those in the curable resin composition A of the first invention as described above.

[0111]

Furthermore, similar to the curable resin composition A of the first invention as described above, the curable resin composition 2A of the present invention may also be
20 added with an antioxidant as the need arises. Specific examples and use amount of the antioxidant which can be used are also the same as those in the curable resin composition A of the first invention as described above.

[0112]

Furthermore, similar to the curable resin composition A of the first invention as
25 described above, the curable resin composition 2A of the present invention may also be added with a light stabilizer as the need arises.

Specific examples of the light stabilizer are the same as those in the curable resin composition A of the first invention as described above.

[0113]

30 Furthermore, similar to the curable resin composition A of the first invention as described above, the curable resin composition 2A of the present invention may also be compounded with a binder resin as the need arises. Specific examples and use amount

of the binder resin are also the same as those in the curable resin composition A of the first invention as described above.

[0114]

Similar to the curable resin composition A of the first invention as described
5 above, the curable resin composition 2A of the present invention can be added with an inorganic filler as the need arises. Specific examples and use amount of the inorganic filler are also the same as those in the curable resin composition A of the first invention as described above.

[0115]

10 Similar to the case of the curable resin composition A of the first invention as described above, in the case of using the curable resin composition 2A of the present invention for an optical semiconductor encapsulating agent, a fluorescent material can be added as the need arises. Specific examples and use amount of the fluorescent material are also the same as those in the curable resin composition A of the first
15 invention as described above.

[0116]

Similar to the curable resin composition of the first invention as described above, the curable resin composition 2A of the present invention is obtained by unfirmly mixing the respective components and can be easily formed into a cured
20 product thereof by the same method as a conventionally known method.

[0117]

In addition, the curable resin composition A of the present invention can be formed into a cured product in the same technique as that in the curable resin composition A of the first invention as described above.

25 [0118]

Curable resin composition 2B (cationic curing with an acidic curing catalyst)

Similar to the curable resin composition B of the first invention as described above, the curable resin composition 2B of the present invention to be cured by using an acidic curing catalyst contains a photopolymerization initiator or a thermal
30 polymerization initiator as the acidic curing catalyst. Furthermore, the curable resin composition 2B of the present invention may contain various known compounds or materials, and the like, such as a diluent, a polymerizable monomer, a polymerizable oligomer, a polymerization initiation assistant, a photosensitizer, etc. In addition, if

desired, the curable resin composition 2B of the present invention may contain various known additives such as an inorganic filler, a coloring pigment, an ultraviolet absorber, an antioxidant, a stabilizer, etc.

[0119]

5 Similar to the case of the curable resin composition B of the first invention as described above, as the acidic curing catalyst, a cationic polymerization initiator is preferable, and a photocationic or thermal cationic polymerization initiator is especially preferable. By compounding a cationic polymerization initiator which is activated with an active energy ray and/or a cationic polymerization initiator which is activated by
10 heat, the resultant can be used as the curable resin composition 2B.

[0120]

 As the cationic polymerization initiator which initiates the cationic polymerization of the curable resin composition 2B of the present invention upon irradiation with an active energy ray, the same materials as those which may be used in
15 the curable resin composition B of the first invention as described above are exemplified.

[0121]

 The active energy ray at the time of curing the curable resin composition 2B of the present invention is the same as that in the case of the curable resin composition B
20 of the first invention as described above.

[0122]

 In addition, similar to the case of the curable resin composition B of the first invention as described above, in the curable resin composition 2B of the present invention, a sensitizer can also be further used in combination for the purpose of
25 increasing the activity of the photocationic polymerization initiator as the need arises. As the sensitizer which can be used in the present invention, the same materials as those which may be used in the curable resin composition B of the first invention as described above can be suitably used, and a compounding amount thereof is also the same as that in the curable resin composition B of the first invention as described above.

30 [0123]

 In the case of adding the sensitizer to the curable resin composition 2B of the present invention, its compounding amount, an irradiation condition of the active energy

ray, and the like are also the same as those in the curable resin composition B of the first invention as described above.

[0124]

5 A compound which is activated by heat to initiate the cationic polymerization, namely a thermal cationic polymerization initiator can also be used for the curable resin composition 2B of the present invention. Specific examples of such a compound, a compounding proportion thereof, and the like are the same as those in the curable resin composition B of the first invention as described above.

[0125]

10 Furthermore, similar to the curable resin composition B of the first invention as described above, the curable resin composition 2B of the present invention can be added with an inorganic filler, a variety of compounding agents such as a silane coupling material, a mold releasing agent, a pigment, etc., or various thermosetting resins as described above as the need arises.

15 [0126]

Similar to the curable resin composition A of the first invention as described above, the curable resin composition 2B of the present invention can be obtained by uniformly mixing the respective components, used, and then cured.

[0127]

20 The cured product obtained by curing each of the curable resin composition 2A and the curable resin composition 2B of the present invention can be used for various applications.

[0128]

25 Examples of the application include general applications for which the curable resin composition 2A or the curable resin composition 2B is used, and for example, adhesives, paints, coating agents, molding materials (including sheets, films, FRP, and the like), insulating materials (including printed substrates, electric wire coverings, and the like), encapsulating agents, and besides, additives to other resins, etc., and the like are exemplified. Examples of the adhesive include, in addition to adhesives for civil
30 engineering, architecture, automobiles, general office works, and medical uses, adhesives for electronic materials. Of these, examples of the adhesive for electronic materials include interlayer adhesives of multilayer substrates such as build-up substrates, etc., die-bonding agents, semiconductor adhesives such as underfills, etc.,

underfills for BGA reinforcement, anisotropic conductive films (ACF), adhesives for mounting such as anisotropic conductive pastes (ACP), etc., and the like.

[0129]

As for the encapsulation materials and substrates, there may be mentioned
 5 potting, dipping, transfer-mold encapsulation used for capacitors, transistors, diodes, light emitting diodes, IC, LSI, and the like, potting encapsulation used for COB, COF, TAB, and the like for IC and LSI, underfills for flip chips and the like, encapsulation at mounting of IC packages such as QFP, BGA, CSP, etc. (including underfills for reinforcement), package substrates, and the like. In addition, the encapsulating agent is
 10 also suitable for applications to substrates for which functionality is required, such as network substrates or module substrates.

EXAMPLES

[0130]

15 Next, the present invention is more specifically described by reference to the following Synthesis Examples and Examples. Incidentally, it should not be construed that the present invention is limited to these Synthesis Examples and Examples. Incidentally, the respective physical properties in the Examples were measured in the following methods.

20 Various analysis methods used in the Examples are hereunder described.

Epoxy equivalent: In conformity with JIS K7236 (ISO 3001)

ICI melt viscosity: In conformity with JIS K7117-2 (ISO 3219)

Softening point: In conformity with JIS K7234

Total chlorine: In conformity with JIS K7243-3 (ISO 21672-3)

25 Chlorine ion: In conformity with JIS K7243-1 (ISO 21672-1)

Sodium ion: Measured by means of ion chromatography

Iron: ICP emission spectroscopy

Refractive index: In conformity with ISO 5661

Gardner color scale: In conformity with ISO 4630-1

30 GPC:

Column (Shodex KF-603, KF-602 $\times$ 2, KF-601 $\times$ 2)

Consolidated eluent: Tetrahydrofuran

Flow rate: 0.5 mL/min

Column temperature: 40°C

Detection: RI (refractive index detector)

[0131]

Synthesis Example 1

5 A flask equipped with a stirrer, a reflux condenser, and a stirring device was once evacuated in vacuum and substituted with nitrogen (oxygen concentration: 4.9%); and thereafter, 255 parts of a phenol compound (DPPI1) (a compound represented by the foregoing formula (1), wherein all the substituent Rs are a hydrogen atom, SABIC PPPBP, purity: 99% or more, residual phenolphthalein: 200 ppm, iron: <5 ppm), 842
10 parts of epichlorohydrin, and 168 parts of methanol were added while purging with nitrogen (2 L/hr), and a water bath was subjected to temperature rise to 75°C. When the internal temperature exceeded 65°C, 21 parts of flaky sodium hydroxide was added dividedly over 90 minutes, and thereafter, a post-reaction was further performed at 70°C for one hour. After completion of the reaction, water washing was performed, and the
15 excessive solvent such as epichlorohydrin, etc. was distilled off from an oil layer at 140°C under reduced pressure by using a rotary evaporator. To the residue, 200 parts of methyl isobutyl ketone was added for dissolution, and the resulting solution was subjected to temperature rise to 70°C. 26 parts of a 30% by weight sodium hydroxide aqueous solution was added under stirring, and the contents were allowed to react with
20 each other for one hour. Thereafter, water washing was performed until the washings became neutral, and as for the obtained solution, the methyl isobutyl ketone and the like were distilled off at 180°C under reduced pressure by using a rotary evaporator, thereby obtaining 301 parts of an epoxy resin (EP1). The obtained epoxy resin had an epoxy equivalent of 266 g/eq., a softening point of 88°C, an ICI melt viscosity of 0.44 Pa·s (at
25 150°C), a chlorine ion content of 2 ppm, a sodium ion content of 0.5 ppm, and a hue of not more than 0.2 (Gardner in a 40% THF solution). In addition, the structure of the foregoing formula (1) accounted for 93 area% (GPC). Incidentally, a refractive index was found to be 1.63. (This refractive index is very large because the refractive index of a usual epoxy or cresol novolak type epoxy resin is 1.59.)

30 [0132]

Synthesis Example 2

In a one-liter flask equipped with a stirrer, a reflux condenser, and a stirring device, 255 parts of a phenol compound (DPPI1) (a compound represented by the

foregoing formula (1), wherein all the substituent Rs are a hydrogen atom, SABIC PPPBP, purity: 99% or more, residual phenolphthalein: 200 ppm, iron: <5 ppm), 601 parts of epichlorohydrin, and 180 parts of methanol were added while purging with nitrogen (2 L/hr), and a water bath was subjected to temperature rise to 75°C. After
 5 elapsing 1.5 hours (blown in a nitrogen amount of about 3 times the flask) since the initiation of nitrogen purge, and furthermore, after confirming the fact that the internal temperature exceeded 65°C, 21 parts of flaky sodium hydroxide was added dividedly over 90 minutes. Thereafter, a post-reaction was further performed at 70°C for one hour. After completion of the reaction, water washing was performed, and the
 10 excessive solvent such as epichlorohydrin, etc. was distilled off from an oil layer at 140°C under reduced pressure by using a rotary evaporator. To the residue, 200 parts of methyl isobutyl ketone was added for dissolution, and the resulting solution was subjected to temperature rise to 70°C. 5 parts of a 30% by weight sodium hydroxide aqueous solution was added under stirring, and the contents were allowed to react with
 15 each other for one hour. Thereafter, water washing was performed until the washings became neutral, and as for the obtained solution, the methyl isobutyl ketone and the like were distilled off at 180°C under reduced pressure by using a rotary evaporator, thereby obtaining 300 parts of an epoxy resin (EP2). The obtained epoxy resin had an epoxy equivalent of 270 g/eq., a softening point of 90°C, an ICI melt viscosity of 0.46 Pa·s (at
 20 150°C), a chlorine ion content of 2 ppm, a sodium ion content of 0.5 ppm, and a hue of not more than 0.2 (Gardner in a 40% THF solution). In addition, the structure of the foregoing formula (1) accounted for 93 area% (GPC). Incidentally, a refractive index was found to be 1.63.

[0133]

25 Synthesis Example 3

In a flask equipped with a stirrer, a reflux condenser, and a stirring device, 256 parts of a phenol compound (DPPI1) (a compound represented by the foregoing formula (1), wherein all the substituent Rs are a hydrogen atom, SABIC PPPBP, purity: 99% or more, residual phenolphthalein: 200 ppm, iron: <5 ppm), 661 parts of epichlorohydrin,
 30 and 3 parts of benzyltrimethylammonium chloride were added, and a water bath was subjected to temperature rise to 70°C. 100 parts of a 49% sodium hydroxide aqueous solution was added dropwise thereto over 90 minutes, and thereafter, a post-reaction was further performed at 70°C for 4 hours. After completion of the reaction, water

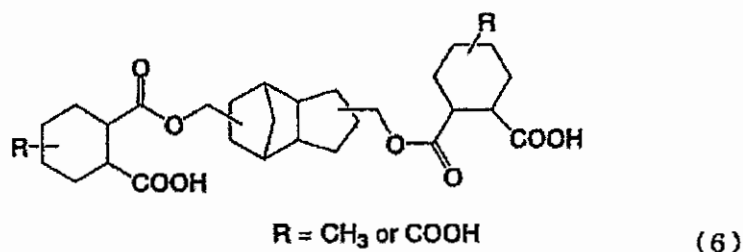
washing was performed, and the excessive solvent such as epichlorohydrin, etc. was distilled off from an oil layer at 140°C under reduced pressure by using a rotary evaporator, thereby obtaining 290 parts of an epoxy resin (EP3). The obtained epoxy resin had an epoxy equivalent of 297 g/eq., a softening point of 95°C, an ICI melt viscosity of 0.70 Pa·s (at 150°C), a total chlorine content of 10,450 ppm, a hydrolyzable chlorine content of 9,700 ppm, a chlorine ion content of 0.5 ppm, a sodium ion content of 0.5 ppm, and a hue of 3 (Gardner in a 40% THF solution). In addition, the structure of the foregoing formula (1) accounted for 65 area% (GPC).

[0134]

10 Synthesis Example 4

In a flask equipped with a stirrer, a reflux condenser, and a stirring device, 15 parts of tricyclodecane dimethanol, 70 parts of methylcyclohexane dicarboxylic anhydride (RIKACID MH, available from New Japan chemical Co., Ltd.), and 15 parts of cyclohexane-1,2,4-tricarboxylic acid-1,2-anhydride (H-TMA_n, available from Mitsubishi Gas Chemical Company, Inc.) were added while purging with nitrogen, the contents were allowed to react with each other at 40°C for 3 hours, and thereafter, the resultant was heated and stirred at 70°C for one hour, thereby obtaining 100 parts of a curing agent composition (H-1) containing the carboxylic acid and the acid anhydride (disappearance (not more than 1 area%) of the tricyclodecane dimethanol was confirmed by means of GPC). The obtained curing agent composition (H-1) was a colorless liquid resin, the purity by GPC was 37 area% for the carboxylic acid (the following formula (6)), 11 area% for the acid anhydride (cyclohexane-1,2,4-tricarboxylic acid-1,2-anhydride), and 52 area% for the acid anhydride (methylcyclohexane dicarboxylic anhydride), respectively. In addition, a functional group equivalent was found to be 171 g/eq.

[0135]



[0136]

Example 1 and Comparative Example 1

Each of the epoxy resin (EP1) obtained in Synthesis Example 1 as the Example and a bisphenol A type epoxy resin (JER 828, available from Mitsubishi Chemical Corporation) as the Comparative Example was compounded with an alicyclic epoxy resin (CELLOXIDE 3150, available from Daicel Corporation) and a cationic curing catalyst (SI-150L, available from Sanshin Chemical Industry Co., Ltd.) in a proportion of 53/47/2, thereby fabricating a methyl ethyl ketone 55% solution. A glass cloth of E-glass having a thickness of 40 μm (available from Unitika Ltd.) was impregnated with the obtained solution, and the solvent was then evaporated off at 150°C for 4 minutes, thereby fabricating a prepreg. Thereafter, the prepreg was preheated at 150°C for one minute, then pressed under a pressure of 30 kg/cm^2 at 150°C for 15 minutes, and finally cured at 150°C over 3 hours. A film thus obtained was cut out into a size of 10 $\times$ 40 mm and measured for retardation that is an index of birefringence. Incidentally, a thickness of the film was found to be 56 μm .

[0137]

The retardation was measured under the following condition.

Measuring equipment: ELLIPSO M-220 (available from JASCO Corporation)

Angle of incidence: 90 degrees
Band width: 1.0 nm
Measuring range: 0.1 to 0.4 kgf
Measuring wavelength: 550 nm

[0138]

As a result, the sample using the epoxy resin EP1 exhibited a retardation of from 0.4 to 0.8 μm , whereas the sample using the bisphenol A type epoxy resin as a comparison exhibited a retardation in the range of from 0.7 to 1.6 μm .

Incidentally, the retardation means a phase difference, and it is preferable that the retardation is small as far as possible. It could be confirmed from the foregoing results that the epoxy resin composition of the present invention has a low retardation, namely low birefringence.

[0139]

Examples 2, 3 and 4 and Comparative Example 2

Each of the epoxy resins (EP1) and (EP2) obtained in Synthesis Examples 1 and 2 as the Examples and the epoxy resin (EP3) obtained in Synthesis Example 3 as the Comparative Examples was used, and compounding was performed in a compounding ratio described in the following Table 1. With respect to each of the
5 obtained curable resin compositions, the solvent was evaporated off on a TEFLON (a registered trademark) plate under a condition at 80°C for 20 minutes in Examples 2 and 3 and Comparative Example 2 and under a condition at 150°C for 3 minutes in Example 4, respectively; the formed film was cut out and overlaid on and press packed in a die for test specimen having a size of 7 mm in width and 5 cm in length; and the resultant
10 was pressed under a pressure of 30 kg/cm² at 150°C for 15 minutes and finally cured at 160°C over 3 hours. In all the samples, molding was performed in a thickness of from 0.7 to 0.8 mm. Each of the obtained plates was evaluated for transparency. Incidentally, the transparency was evaluated by means of comparison in terms of a measured value of YI by using a color meter for simultaneous transmittance color and
15 turbidity measurements, COH400, available from Nippon Denshoku Industries Co., Ltd. The results are shown in Table 1.

[0140]

Table 1

		Example			Comparative Example
		2	3	4	2
Compounding formulation					
Epoxy resin	EP1	26.6		26.6	
	EP2		27		
	EP3				29.7
	EHPE-3150			7.98	
Curing agent	H-1	15.39	15.39		15.39
Curing promoter	PX-4MP	0.08			0.09
	Zinc ethylhexanoate		0.08		
Cationic polymerization catalyst	SI-150L			0.69	
Solvent	Methyl ethyl ketone	8.4	8.48	6.92	9.02
Characteristic of cured product	Tint (YI)	0.4	0.7	1.2	38.1

[0141]

Synthesis Example 2-1

A one-liter four-necked flask equipped with a stirrer, a reflux condenser, and a stirring device was once evacuated in vacuum and substituted with nitrogen (oxygen concentration: 4.9%); and thereafter, 256 parts of a phenol compound (DPPI1) (a compound represented by the foregoing formula (1), wherein all the substituent Rs are a hydrogen atom, SABIC PPPBP, purity: 99% or more, residual phenolphthalein: 200 ppm, iron: <5 ppm), 842 parts of epichlorohydrin, and 180 parts of methanol were added while purging with nitrogen (2 L/hr), and a water bath was subjected to temperature rise to 75°C. When the internal temperature exceeded 65°C, 21 parts of flaky sodium hydroxide was added dividedly over 90 minutes, and thereafter, a post-reaction was further performed at 70°C for one hour. After completion of the reaction, water washing was performed, and the excessive solvent such as epichlorohydrin, etc. was distilled off from an oil layer at 140°C under reduced pressure by using a rotary evaporator. To the residue, 600 parts of methyl isobutyl ketone was added for dissolution, and the resulting solution was subjected to temperature rise to 70°C. 26 parts of a 30% by weight sodium hydroxide aqueous solution was added under stirring, and the contents were allowed to react with each other for one hour. Thereafter, water washing was performed until the washings became neutral, and as for the obtained solution, the methyl isobutyl ketone and the like were distilled off at 180°C under reduced pressure by using a rotary evaporator, thereby obtaining 305 parts of an epoxy resin (EP2-1). The obtained epoxy resin had an epoxy equivalent of 266 g/eq., a softening point of 89°C, an ICI melt viscosity of 0.42 Pa·s (at 150°C), a total chlorine content of 1,600 ppm, a hydrolyzable chlorine content of 1,540 ppm, a chlorine ion content of 2 ppm, a sodium ion content of 0.5 ppm, and a hue of not more than 0.2 (Gardner in a 40% MEK (methyl ethyl ketone) solution). In addition, the structure of the foregoing formula (1) accounted for 93 area% (GPC).

[0142]

Synthesis Example 2-2

A reaction was performed in the same manner as that in Synthesis Example 2-1, except that a one-liter four-necked flask equipped with a stirrer, a reflux condenser, and a stirring device was once evacuated in vacuum and substituted with nitrogen (oxygen concentration: 5.3%), and thereafter, a phenol compound (DPPI2) (a compound

represented by the foregoing formula (1), wherein all the substituent Rs are a hydrogen atom, SABIC PPPBP (purity: 99% or more, residual phenolphthalein: 200 ppm, iron: <5 ppm), to which 500 ppm of phenolphthalein had been added) was used while purging with nitrogen (2 L/hr). The obtained epoxy resin (EP2-2) had an epoxy equivalent of 266 g/eq., a softening point of 90°C, an ICI melt viscosity of 0.44 Pa·s (at 150°C), a total chlorine content of 2,000 ppm, a hydrolyzable chlorine content of 1,950 ppm, a chlorine ion content of 1 ppm, a sodium ion content of 0.3 ppm, and a hue of not more than 0.2 (Gardner in a 40% MEK solution). In addition, the structure of the foregoing formula (1) accounted for 93 area% (GPC).

[0143]

Synthesis Example 2-3

A one-liter four-necked flask equipped with a stirrer, a reflux condenser, and a stirring device was substituted with nitrogen (oxygen concentration: 6.5%) at 4 L/h for 30 minutes; and thereafter, 256 parts of a phenol compound (DPPI1) (a compound represented by the foregoing formula (1), wherein all the substituent Rs are a hydrogen atom, SABIC PPPBP, purity: 99% or more, residual phenolphthalein: 200 ppm, iron: <5 ppm), 661 parts of epichlorohydrin, and 165 parts of methanol were added while purging with nitrogen (2 L/hr), and a water bath was subjected to temperature rise to 75°C. When the internal temperature exceeded 65°C, 57 parts of flaky sodium hydroxide was added dividedly over 90 minutes, and thereafter, a post-reaction was further performed at 70°C for one hour. After completion of the reaction, water washing was performed, and the excessive solvent such as epichlorohydrin, etc. was distilled off from an oil layer at 140°C under reduced pressure by using a rotary evaporator. To the residue, 600 parts of methyl isobutyl ketone was added for dissolution, and the resulting solution was subjected to temperature rise to 70°C. 5 parts of a 30% by weight sodium hydroxide aqueous solution was added under stirring, and the contents were allowed to react with each other for one hour. Thereafter, water washing was performed until the washings became neutral, and as for the obtained solution, the methyl isobutyl ketone and the like were distilled off at 180°C under reduced pressure by using a rotary evaporator, thereby obtaining 297 parts of an epoxy resin (EP2-3). The obtained epoxy resin had an epoxy equivalent of 277 g/eq., a softening point of 96°C, an ICI melt viscosity of 0.62 Pa·s (at 150°C), a total chlorine content of 2,230 ppm, a hydrolyzable chlorine content of 2,100 ppm, a chlorine ion

content of 0.5 ppm, a sodium ion content of 0.5 ppm, and a hue of not more than 0.2 (Gardner in a 40% MEK solution). In addition, the structure of the foregoing formula (1) accounted for 82 area% (GPC).

[0144]

5 Synthesis Example 2-4

A one-liter four-necked flask equipped with a stirrer, a reflux condenser, and a stirring device was once evacuated in vacuum and substituted with nitrogen (oxygen concentration: 5.2%); and thereafter, 256 parts of a phenol compound (DPPI1) (a compound represented by the foregoing formula (1), wherein all the substituent Rs are a hydrogen atom, SABIC PPPBP, purity: 99% or more, residual phenolphthalein: 200 ppm, iron: <5 ppm), 661 parts of epichlorohydrin, and 200 parts of dimethyl sulfoxide were added while purging with nitrogen (2 L/hr), and a water bath was subjected to temperature rise to 45°C. When the internal temperature exceeded 40°C, 57 parts of flaky sodium hydroxide was added dividedly over 90 minutes, and thereafter, a post-reaction was further performed at 70°C for one hour. After completion of the reaction, water washing was performed, and the excessive solvent such as epichlorohydrin, etc. was distilled off from an oil layer at 140°C under reduced pressure by using a rotary evaporator. To the residue, 600 parts of methyl isobutyl ketone was added for dissolution, and the resulting solution was subjected to temperature rise to 70°C. 16 parts of a 30% by weight sodium hydroxide aqueous solution was added under stirring, and the contents were allowed to react with each other for one hour. Thereafter, water washing was performed until the washings became neutral, and as for the obtained solution, the methyl isobutyl ketone and the like were distilled off at 180°C under reduced pressure by using a rotary evaporator, thereby obtaining 300 parts of an epoxy resin (EP2-4). The obtained epoxy resin had an epoxy equivalent of 270 g/eq., a softening point of 92°C, an ICI melt viscosity of 0.48 Pa·s (at 150°C), a total chlorine content of 1,050 ppm, a hydrolyzable chlorine content of 960 ppm, a chlorine ion content of 0.3 ppm, a sodium ion content of 0.1 ppm, and a hue of 0.6 (Gardner in a 40% MEK solution). In addition, the structure of the foregoing formula (1) accounted for 90 area% (GPC).

[0145]

Examples 2-1, 2-2 and 2-3 and Comparative Example 2-1

Each of the above-obtained epoxy resins was used and compounded in a compounding proportion as shown in the following Table 2, and the contents were successively cured at 120°C for 2 hours, at 160°C for 2 hours, and at 180°C for 4 hours, thereby performing a test for flame retardancy. Incidentally, a technique of the test for flame retardancy is shown below.

Flame retardancy

. Determination of flame retardancy: The determination was performed in conformity with UL94. However, the test was performed in a sample having a size of 12.5 mm in width, 150 mm in length, and 0.8 mm in thickness.

[0146]

Table 2

		Equivalent of functional group	Example				Comparative Example
			2-1	2-2	2-3	2-4	2-1
Compounding formulation							
Epoxy resin	EP2-1	266	26.6				26.6
	EP2-2	266		26.6			
	EP2-3	277			27.7		
	EP	270				27	
Curing agent	HA1	106	10.6		10.6	10.8	
	HA2	154					13.9
Curing promoter	C1		0.4		0.42		
	C2					0.41	0.53
Cationic polymerization catalyst	C3			0.80			
Inorganic filler	Fused silica	Content: 86%	231	231	238	234	252
Additive	Coupling agent		1.15	1.15	1.19	1.17	1.26
Mold releasing agent	Carnauba wax		1.04	1.04	1.07	1.05	1.13
Curing physical property	Flame retardancy	In conformity with UL94	V-0	V-0	V-0	V-0	Total loss by fire

HA1	Phenol resin: Phenol aralkyl resin (MILEX XLC-, available from Mitsui Chemicals, Inc.)
HA2	Acid anhydride: Hexahydrophthalic anhydride (RIKACID HH, available from New Japan chemical Co., Ltd.)
C1	Phosphorus-based catalyst: TPP, available from Hokko Chemical Industry Co., Ltd.
C2	Imidazole catalyst: 2E4MZ, available from Shikoku Chemicals Corporation
C3	Onium salt catalyst: SI-150L, available from Sanshin Chemical Industry Co., Ltd.
Inorganic filler	Fused silica: MSR-2212, available from Tatsumori Ltd.
Coupling agent	Silane coupling agent: KBM-403, available from Shin-Etsu Chemical Co., Ltd.
	Carnauba wax: Carnauba wax No. 1, available from Cerarica Noda Co., Ltd.
Curing condition	120°C for 2 hours, 160°C for 2 hours, and 180°C for 4 hours

[0147]

From the foregoing results, it has been clarified that the curable resin composition of the present invention is able to make high heat resistance and flame retardancy compatible with each other.

5 [0148]

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.

10 Incidentally, the present application is based on Japanese patent applications filed on June 7, 2012 (Japanese Patent Applications Nos. 2012-129406 and 2012-129408), the entireties of which are incorporated by reference. In addition, all references cited herein are incorporated as a whole.

15 INDUSTRIAL APPLICABILITY

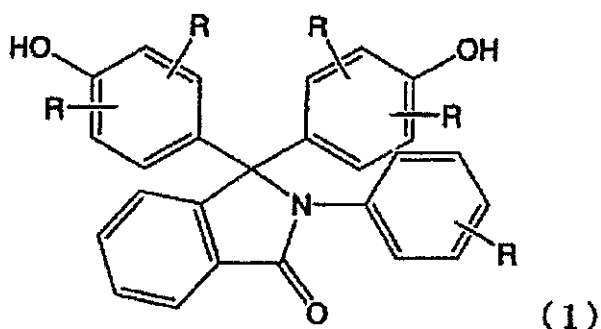
[0149]

The epoxy resin composition of the first invention can be used for a variety of applications inclusive of optical component materials. In addition, the curable resin composition of the second invention can be used for adhesives, paints, coating agents,
20 molding materials (including sheets, films, FRP, and the like), insulating materials (including printed substrates, electric wire coverings, and the like), encapsulating agents, and besides, additives to other resins, etc., and the like.

CLAIMS

[Claim 1]

An epoxy resin composition containing an epoxy resin obtained through a
 5 reaction of a phenol resin represented by the following formula (1) with an
 epihalohydrin and a carboxylic acid and/or a cationic polymerization catalyst, the epoxy
 resin having a hue by the Gardner colorimetry (in a 40% MEK solution) of not more
 than 2:



10 wherein each of plurally existent Rs independently represents a hydrogen atom, an alkyl
 group having from 1 to 6 carbon atoms, or an alkoxy group having from 1 to 6 carbon
 atoms.

[Claim 2]

The epoxy resin composition according to claim 1, wherein an amount of a
 15 residual phenolphthalein derivative in the phenol resin to be allowed to react with the
 epihalohydrin is not more than 2%.

[Claim 3]

The epoxy resin composition according to claim 1, wherein an amount of
 remaining iron in the phenol resin to be allowed to react with the epihalohydrin is not
 20 more than 50 ppm.

[Claim 4]

The epoxy resin composition according to claim 3, containing a transition
 metal salt.

[Claim 5]

25 The epoxy resin composition according to claim 3, containing a quaternary
 phosphonium salt.

[Claim 6]

The epoxy resin composition according to claim 3, containing a cationic polymerization initiator.

[Claim 7]

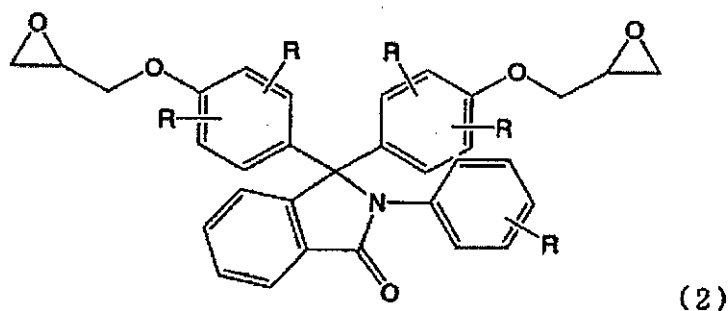
- 5 An epoxy resin cured product obtained by curing the epoxy resin composition according to any one of claims 4 to 6.

[Claim 8]

The epoxy resin composition according to any one of claims 1 to 6, which is used for a substitute of glass.

10 [Claim 9]

A curable resin composition containing an epoxy resin represented by the following formula (2) and a phenol resin and/or a polymerization catalyst:



- 15 wherein each of plurally existent Rs independently represents a hydrogen atom, an alkyl group having from 1 to 6 carbon atoms, or an alkoxy group having from 1 to 6 carbon atoms.

[Claim 10]

The curable resin composition according to claim 9, wherein the phenol resin is a phenol aralkyl resin (resin having an aromatic alkylene structure).

20 [Claim 11]

The curable resin composition according to claim 9, wherein the polymerization catalyst is a cationic polymerization catalyst.