

DESCRIPTION

TITLE OF THE INVENTION

EPOXY RESIN, EPOXY RESIN COMPOSITION AND CURED PRODUCT

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TECHNICAL FIELD

[0001]

The present invention relates to an epoxy resin, an epoxy resin composition and a cured product thereof, each being suitable for electrical and electronic material applications for which heat resistance is required.

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BACKGROUND ART

[0002]

Epoxy 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 because cured products thereof are excellent in terms of electrical characteristics, heat resistance, adhesive properties, humidity resistance (water resistance), and the like.

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[0003]

But, in recent years, in the electrical or electronic field, with the development thereof, much more enhancements in various characteristics including not only an 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 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 high fluidity are demanded. Incidentally, in particular, with the expansion of plastic packages to onboard applications, a requirement for an enhancement of the heat

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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.

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CITATION LIST

NON-PATENT DOCUMENT

[0004]

Non-Patent Document 1: "STRJ Report, 2008: Report of FY 2008 by
10 Semiconductor Technology Roadmap Committee of Japan", Chapter 8, p1-1, [online],
March 2009, JEITA, Japan Electronics and Information Technology Industries
Association, Semiconductor Technology Roadmap Committee of Japan [retrieved on
May 30, 2012], <<http://strj-jeita.elisasp.net/strj/nenjihoukoku-2008.cfm>>

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

SUMMARY OF THE INVENTION

20 PROBLEM TO BE SOLVED BY THE INVENTION

[0005]

Heat resistance is exemplified as one of characteristics which are required
especially for high functionality. Although the heat resistance has hitherto been
regarded as important, in general, if the heat resistance is increased problems such as
25 deterioration of water absorption characteristics, deterioration of flame retardancy, etc.
are caused at the same time, and it is difficult to make them compatible with each other.

Then, it has been desired to develop an epoxy resin capable of making both
heat resistance and reciprocal characteristics compatible with each other.

30 MEANS FOR SOLVING THE PROBLEM

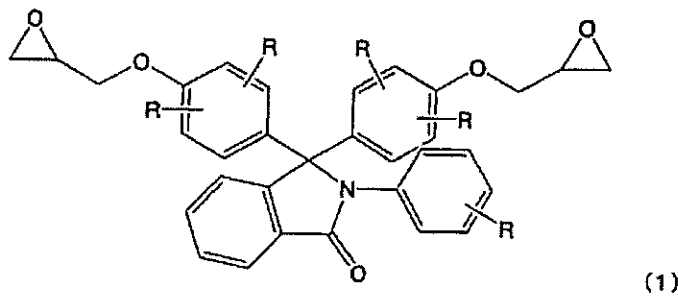
[0006]

In view of the above-described actual circumstances, the present inventor made extensive and intensive investigations, and as a result, he has accomplished the present invention.

That is, the present invention relates to the following.

- 5 (1) An epoxy resin containing, as a main component, a compound represented by the following formula (1) in a content of from 70 to 95% (in terms of an area% according to the gel permeation chromatography).

[0007]



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[0008]

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.

- 15 (2) The epoxy resin described in (1) above, wherein an epoxy equivalent is from 1.02 times to 1.11 times relative to a theoretical epoxy equivalent.
- (3) The epoxy resin described in (1) above, wherein a total chlorine content is not more than 5,000 ppm.
- (4) An epoxy resin composition comprising, as essential components, the epoxy resin described in any one of (1) to (3) above and a curing agent.
- 20 (5) An epoxy resin composition comprising, as essential components, the epoxy resin described in any one of (1) to (3) above and a curing catalyst.
- (6) A cured product obtained by curing the epoxy resin composition described in (4) or (5) above.

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EFFECT OF THE INVENTION

[0009]

The epoxy resin 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 because a cured product thereof has excellent characteristics in heat resistance, water absorption characteristics, and flame retardancy.

MODES FOR CARRYING OUT THE INVENTION

[0010]

The epoxy resin of the present invention is concerned with an epoxy resin having a phenolphthalein skeleton derivative structure. A basic skeleton of the epoxy resin of the present invention is disclosed in British Patent No. 1,158,606 (Patent Document 1). Patent Document 1 discloses an epoxy resin having a phenolphthalein skeleton derivative structure 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 1 discloses curing physical properties with DDS (diaminodiphenylsulfone).

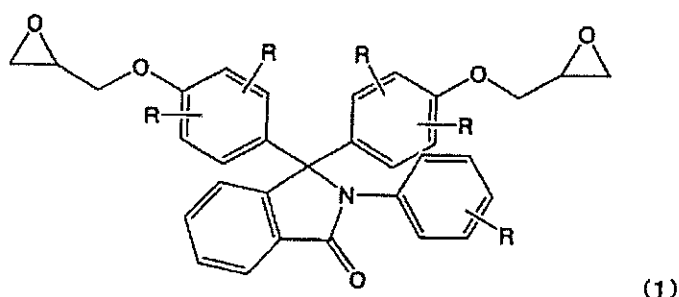
It is suggested from those data that the subject resin is very high in the chlorine amount and unsuitable for electronic material applications; and also that it is very high in coloration so that it is hardly useful for applications for which a tint is needed. In addition, the epoxy equivalent is so 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.

[0011]

5 The epoxy resin of the present invention is an epoxy resin containing a compound represented by the following formula (1):

[0012]



[0013]

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) in a content of 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 a compound having a purity in which the content of the compound

15 represented by the foregoing formula (1) exceeds 95%, a very great amount of energy is required, and hence, such is not preferable from the industrial standpoint. In addition, in the case where the purity is excessively high, there may be a possibility that crystallinity becomes high, or a possibility that a lowering of toughness is found. When the content is less than 70%, a lot of compounds in which the epoxy ring is not

20 completely cyclized and which do not have a functional group are contained, and hence, such is not preferable. 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, there is a concern about liberation of a chlorine ion under a high-temperature and high-

25 humidity condition and corrosion of wirings to be caused due to this matter, and hence, such is not preferable.

[0014]

In addition, in the case where the epoxy resin having a phenolphthalein 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 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.

[0015]

R is most preferably a hydrogen atom. 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.

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.

[0016]

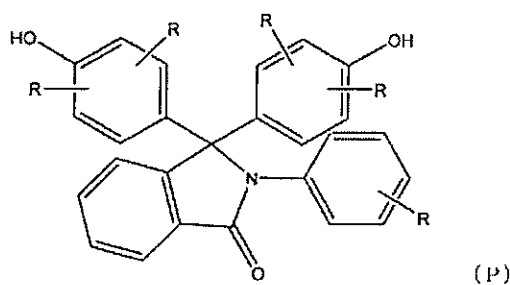
As for preferred resin characteristics of the epoxy group containing the compound represented by the foregoing formula (1), an epoxy equivalent is from 1.02 times to 1.13 times relative to a theoretical epoxy equivalent. The epoxy equivalent is more preferably from 1.03 to 1.10 times. In the case where the epoxy equivalent is less than 1.02 times, there is a concern that synthesis or purification of an epoxy resin costs a lot of money, whereas in the case where it exceeds 1.11 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 epoxy resin obtained by the reaction 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 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 a phenolic hydroxyl group of a phenol compound represented by the following formula (P) is glycidylated neither too much nor too little.

[0017]



[0018]

(In the formula, R has the same meanings as those described above.)

[0019]

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.

[0020]

The 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 are caused such problems that fluidity is poor; and that in a glass cloth or the like, the meshes thereof are smaller, so that impregnation properties are inferior.

5 [0021]

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

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
15 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.

20 [0022]

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

The epoxy resin containing the compound represented by the foregoing formula (1) according to the present invention is obtained through a reaction of a phenol
25 compound (DPPI) represented by the foregoing formula (P) (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.

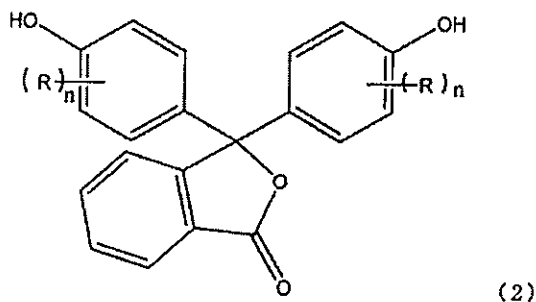
[0023]

30 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, xlenol, methylbutylphenol, and the like.

In addition, examples of the phenolphthalein derivative obtained from the above-described synthesis include those having a structure represented by the following
5 formula (2).

[0024]



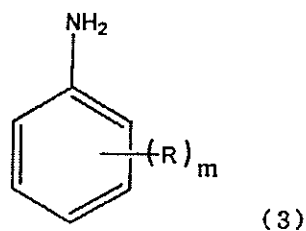
[0025]

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

[0026]

Examples of the aminobenzene derivative include those having a structure represented by the following formula (3).

[0027]



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[0028]

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

[0029]

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 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.

[0030]

In the reaction for obtaining the epoxy resin of the present invention, 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).

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 possibility that workability of the epoxy resin is deteriorated. When the use amount of the epihalohydrin exceeds 15 moles, a solvent amount becomes large.

[0031]

Examples of an alkali metal hydroxide which may be used in the above-described reaction 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 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.

[0032]

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.

[0033]

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 therefore, 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.

[0034]

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, a by-product is formed, and hence, such is not preferable.

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 reactor, 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 reactor can be substituted for from 0.5 to 10 hours.

[0035]

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.

[0036]

The epoxy resin composition of the present invention is composed of the epoxy resin of the present invention and a curing catalyst as essential components. In addition, it is preferable that the epoxy resin composition of the present invention contains other epoxy resin or a curing agent as an arbitrary component.

[0037]

The epoxy resin composition of the present invention may contain an epoxy resin other than the epoxy resin of the present invention. In all the epoxy resins, a proportion of the epoxy resin of the present invention is preferably 20% by weight or more, more preferably 30% by weight or more, and especially preferably 40% by weight or more.

[0038]

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.

[0039]

In particular, in the case where the epoxy 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-
5 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-
10 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
15 not be construed that the carboxylic acid is limited thereto.

[0040]

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
20 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 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
25 an aldehyde step by step (see JP-A-S48-96590), a method of using water as a reaction medium (see 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.

30 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.

[0041]

Specific examples of the curing catalyst which can be used in the present invention include amine compounds such as triethylamine, tripropylamine, tributylamine, etc.; various heterocyclic compounds such as pyridine, dimethylaminopyridine, 1,8-diazabicyclo[5.4.0]undeca-7-ene, imidazole, triazole, tetrazole, 2-methylimidazole, 2-phenylimidazole, 2-undecylimidazole, 2-heptadecylimidazole, 2-phenyl-4-methylimidazole, 1-benzyl-2-phenylimidazole, 1-benzyl-2-methylimidazole, 1-cyanoethyl-2-methylimidazole, 1-cyanoethyl-2-phenylimidazole, 1-cyanoethyl-2-undecylimidazole, 2,4-diamino-6(2'-methylimidazole(1'))ethyl-s-triazine, 2,4-diamino-6(2'-undecylimidazole(1'))ethyl-s-triazine, 2,4-diamino-6(2'-ethyl-4-methylimidazole(1'))ethyl-s-triazine, a 2,4-diamino-6(2'-methylimidazole(1'))ethyl-s-triazine-isocyanuric acid adduct, a 2:3 adduct of 2-methylimidazole-isocyanuric acid, a 2-phenylimidazole-isocyanuric acid adduct, 2-phenyl-3,5-dihydroxymethylimidazole, 2-phenyl-4-hydroxymethyl-5-methylimidazole, 1-cyanoethyl-2-phenyl-3,5-dicyanoethoxymethylimidazole, etc., and salts formed from such a heterocyclic compound and a polybasic acid such as phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, pyromellitic acid, naphthalenedicarboxylic acid, maleic acid, oxalic acid, etc.; amides such as dicyandiamide, etc.; diaza compounds such as 1,8-diaza-bicyclo(5.4.0)undecene-7, etc.; salts such as tetraphenyl borate and phenol novolak thereof, etc., and salts formed from such a compound and the above-described polybasic carboxylic acid or a phosphinic acid; ammonium salts such as tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, trimethylethylammonium hydroxide, trimethylpropylammonium hydroxide, trimethylbutylammonium hydroxide, trimethylcetylammmonium hydroxide, trioctylmethylammonium hydroxide, tetramethylammonium chloride, tetramethylammonium bromide, tetramethylammonium iodide, tetramethylammonium acetate, trioctylmethylammonium acetate, etc.; phosphines and phosphonium

compounds such as triphenylphosphine, tri(tolyl)phosphine, tetraphenylphosphonium bromide, tetraphenylphosphonium tetraphenylborate, etc.; phenols such as 2,4,6-trisaminomethylphenol, etc.; amine adducts; metal compounds such as carboxylic acid metal salts (e.g., zinc salts, tin salts, and zirconium salts of 2-ethylhexanoic acid, stearic acid, behenic acid, myristic acid, etc.), phosphoric acid ester metal salts (e.g., zinc salts of octylphosphoric acid, stearylphosphoric acid, etc.), alkoxy metal salts (e.g., tributylaluminum, tetrapropylzirconium, etc.), acetylacetone salts (e.g., acetylacetone zirconium chelate, acetylacetone titanium chelate, etc.); and the like. In the present invention, a phosphonium salt, an ammonium salt, and a metal compound are especially preferable from the standpoints of coloration at the time of curing and changes thereof. In addition, in the case of using a quaternary salt, there is a concern that a salt with a halogen retains the halogen in a cured product thereof.

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.

[0042]

It is preferable that the epoxy resin composition of the present invention contains a curing agent. Examples thereof include amine-based compounds, acid anhydride-based compounds, amide-based compounds, phenol resins, carboxylic acid-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, methylnadic anhydride, nadic anhydride, hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, butanetetracarboxylic anhydride, bicyclo[2,2,1]heptane-2,3-dicarboxylic anhydride, methylbicyclo[2,2,1]heptane-2,3-dicarboxylic anhydride, cyclohexane-1,3,4-tricarboxylic 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; phenol resins 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.

In the present invention, in particular, the above-described phenol resins are preferable for the purpose of being used for electronic material applications.

[0043]

A use amount of the curing agent in the curable resin composition 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.

[0044]

Incidentally, it is preferable to use a cyanate ester compound as other component. By using the cyanate ester compound, it is possible to produce a heat-resistant cured product with a higher crosslinking density by, in addition to a curing reaction due to the single use, the reaction with the epoxy resin. Examples of the cyanate ester compound include 2,2-bis(4-cyanatophenyl)propane, bis(3,5-dimethyl-4-cyanatophenyl)methane, 2,2-bis(4-cyanatophenyl)ethane, and derivatives thereof, aromatic cyanate ester compounds, and the like. In addition, it is also possible to synthesize the cyanate ester compound through, for example, a reaction of the phenol resin of every kind as described above for the curing agent with cyanic acid or a salt thereof. In the present invention, in particular, a cyanate ester compound having a

structure not having a methylene structure at the benzyl position in a molecule thereof as in 2,2-bis(4-cyanatophenyl)propane or its derivative (e.g., a partial polymerization product, etc.) is preferable, and such a compound may be used solely, or may be used in combination of two or more kinds thereof.

5 [0045]

The epoxy resin composition 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
10 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-
15 phosphaphenanthrene-10-oxide, etc.; phosphorus-containing epoxy compounds 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 compounds are preferable, with 1,3-phenylenebis(dixylenyl phosphate), 1,4-phenylenebis(dixylenyl phosphate), 4,4'-
20 biphenyl(dixylenyl phosphate), or phosphorus-containing epoxy compounds being especially preferable. A content of the phosphorus-containing compound is preferably from 0.1 to 0.6 in terms of a weight ratio of the phosphorus-containing compound to all the epoxy resins. When the content of the phosphorus-containing compound is not more than 0.1, the flame retardancy is insufficient, whereas when it is 0.6 or more, there
25 is a concern that adverse influences are given to hygroscopicity or dielectric characteristics of the cured product.

[0046]

Furthermore, the epoxy resin composition of the present invention can also be compounded with a binder resin as the need arises. Examples of the binder resin
30 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 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 as the need arises 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 a total sum of the epoxy resin and the curing agent.

[0047]

To the epoxy resin composition of the present invention, an inorganic filler can be added as the need arises. Examples of the inorganic filler include powders 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; but, it should not be construed that the inorganic filler is limited thereto. Such a filler may be used solely, or may be used in combination of two or more kinds thereof. Such an inorganic filler is used in an amount such that its content accounts for from 0 to 95% by weight in the epoxy resin composition of the present invention. Furthermore, to the epoxy resin composition of the present invention, various compounding agents such as an antioxidant, a light stabilizer, a silane coupling agent, a mold releasing agent, e.g., stearic acid, palmitic acid, zinc stearate, calcium stearate, etc., a pigment, etc. or various thermosetting resins can be added. In particular, with respect to the coupling agent, the addition of a coupling agent having an epoxy group or a coupling agent having a thiol is preferable.

[0048]

The epoxy resin composition of the present invention is obtained by uniformly mixing the respective components. The epoxy resin composition 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 component and the curing agent component and optionally, the curing promoter, the phosphorus-containing compound, the binder resin, the inorganic filler, the compounding agent, or the like are thoroughly mixed until the mixture becomes uniform by using an extruder, a kneader, a roll, a planetary mixer, or the like as the need arises, thereby obtaining an epoxy resin composition, and in the case where the obtained epoxy resin composition is liquid, the resulting composition is impregnated in a base material or subjected to pouring casting into a die by means of potting or casting, followed by curing by heating. In addition, in

the case where the obtained epoxy resin composition is solid, after fusion, the resulting composition is cast or molded by using a transfer molding machine or the like and further cured by heating. Curing temperature and time are from 80 to 200°C and from 2 to 10 hours, respectively. As for a curing method, although the curing can be performed at once at a high temperature, it is preferable that the temperature is raised stepwise to allow the curing reaction to proceed. Specifically, initial curing is performed at from 80 to 150°C, and postcuring is performed at from 100°C to 200°C. As for a stage of the curing, the temperature is raised by dividing it into preferably from 2 to 8 stages, and more preferably from 2 to 4 stages.

[0049]

In addition, the cured product of the epoxy resin composition of the present invention can be produced by dissolving the epoxy resin composition of the present invention in a solvent such as toluene, xylene, acetone, methyl ethyl ketone, methyl isobutyl ketone, dimethylformamide, diethylacetamide, 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, and 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 weight, and preferably from 15 to 70% by weight in a mixture of the epoxy resin composition of the present invention and the solvent.

[0050]

In addition, the epoxy resin composition of the present invention can also be used as a film-type composition for encapsulation. In the case of obtaining such a film-type resin composition, the curable resin composition of the present invention is coated as the above-described varnish on a release film, the solvent is removed under heating, and transformation into a B-stage is then performed to obtain a sheet-shaped adhesive. This sheet-shaped adhesive can be used as an interlayer insulating layer in multilayer substrates and the like and en bloc film encapsulation of optical semiconductors.

[0051]

Examples of specific applications of such a composition include adhesives, paints, coating agents, molding materials (including sheets, films, FRP, and the like), insulating materials (e.g., encapsulation materials including printed substrates, electric

wire coverings, and the like, and besides, cyanate resin compositions for encapsulation materials or substrates), additives to other resins such as acrylate-based resins, etc. as a curing agent for resist, and the like. In the present invention, the use of insulating materials (e.g., encapsulation materials including printed substrates, electric wire coverings, and the like, and besides, cyanate resin compositions for encapsulation materials or substrates) for electronic materials is especially preferable.

[0052]

Examples of the adhesive include, in addition to adhesives for civil 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.

[0053]

As for the encapsulation materials and substrates, there may be mentioned 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 also suitable for applications to substrates for which functionality is required, such as network substrates or module substrates.

EXAMPLES

[0054]

Next, the present invention is more specifically described by reference to the following Examples, but in the following, the term “part” means a part by weight unless otherwise indicated. Incidentally, it should not be construed that the present invention is limited to these Examples.

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)

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

Sodium ion: Measured by means of ion chromatography

5 Iron: ICP emission spectroscopy

Refractive index: In conformity with ISO 5661

Gardner color scale: In conformity with ISO 4630-1

GPC:

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

10 Consolidated eluent: Tetrahydrofuran

Flow rate: 0.5 mL/min

Column temperature: 40°C

Detection: RI (refractive index detector)

[0055]

15 Example 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 (P), wherein all the substituent Rs are a
 20 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-
 25 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
 30 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 (EP1). 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).

[0056]

Example 2

A reaction was performed in the same manner as that in Example 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 (P), 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) 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).

[0057]

Example 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 (P), 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 (EP3). 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).

[0058]

Example 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 (DPP11) (a compound represented by the foregoing formula (P), 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 (EP4). 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).

[0059]

Example 5

A reaction was performed in the same manner as that in Example 1, except that a flask equipped with a stirrer, a reflux condenser, and a stirring device was once evacuated in vacuum and substituted with nitrogen, and thereafter, a phenol compound (DPPI3) (a compound represented by the foregoing formula (P), wherein all the substituent Rs are a hydrogen atom, SABIC PPPBP (purity: 99% or more, residual phenolphthalein: 210 ppm, iron: <5 ppm), to which 1% of phenolphthalein had been added) was used while purging with nitrogen (2 L/hr). The obtained epoxy resin (EP5) had an epoxy equivalent of 262 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 3,200 ppm, a hydrolyzable chlorine content of 2,700 ppm, a chlorine ion content of 5 ppm, a sodium ion content of 0.5 ppm, and a hue of 3 (Gardner in a 40% MEK solution). In addition, the structure of the foregoing formula (1) accounted for 90 area% (GPC).

[0060]

Comparative Example 1

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 (P), 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 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 (EP6). 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 4 (Gardner in a 40% MEK solution). In addition, the structure of the foregoing formula (1) accounted for 65 area% (GPC).

[0061]

Example 6 and Comparative Example 2

Each of the above-obtained epoxy resin (EP1) and an epoxy resin for comparison (EP7; a trisphenolmethane type epoxy resin “EPPN-502H”, available from Nippon Kayaku Co., Ltd.), and a phenol aralkyl resin (MILEX XLC-3L, available from Mitsui Chemicals, Inc.; hereinafter referred to as “PN1”) as a curing agent were used and compounded in a proportion (parts by weight) shown in Table 1, and the contents were uniformly mixed and kneaded by using a mixing roll, thereby obtaining an epoxy resin composition for encapsulation. This epoxy resin composition was pulverized by a mixer and further tableted by a tablet machine. This tableted epoxy resin composition was subjected to transfer molding (at 175°C for 60 seconds) and then demolding, and the resultant was cured under conditions at 160°C for 2 hours and subsequently at 180°C for 6 hours, thereby obtaining a specimen for evaluation.

Incidentally, physical properties of the cured product were measured in the following way.

TMA (a thermomechanical measuring apparatus TM-7000, available from Shinku-Riko Inc., temperature rise rate: 2°C/min)

[0062]

Table 1

		Equivalent of functional group	Example 6	Comparative Example 2
Epoxy resin	EP1	266	26.6	
	EP7	166		16.6
Curing agent	PN1	106	10.6	10.6
Curing promoter	C1		0.3	0.2
TMA Tg (°C)			173	160

[0063]

From the foregoing results, it could be confirmed that the epoxy resin of the present invention has higher heat resistance (Tg) than the trisphenolmethane type epoxy resin that is general as a highly heat-resistant resin.

[0064]

Examples 7 and 8 and Comparative Example 3

Each of the above-obtained epoxy resins (EP1 and EP3) and the epoxy resin for comparison (EP5), and phenol novolak (H-1, available from Meiwa Kasei Industries, Ltd.; hereinafter referred to as "PN2") as a curing agent were used and compounded in a proportion (parts by weight) shown in Table 2, and the contents were uniformly mixed and kneaded by using a mixing roll, thereby obtaining an epoxy resin composition for encapsulation. This epoxy resin composition was pulverized by a mixer and further tableted by a tablet machine. This tableted epoxy resin composition was subjected to transfer molding (at 175°C for 60 seconds) and then demolding, and the resultant was cured under conditions at 160°C for 2 hours and subsequently at 180°C for 6 hours, thereby obtaining a specimen for evaluation.

Incidentally, physical properties of the cured product were measured in the following way.

TMA (a thermomechanical measuring apparatus TM-7000, available from Shinku-Riko Inc., temperature rise rate: 2°C/min)

[0065]

Table 2

		Example 7	Example 8	Comparative Example 3
Epoxy resin	EP1	26.6		
	EP3		27.7	
	EP5			29.7
Curing agent	PN2	10.6	10.6	10.6
Curing promoter	C2	0.14	0.14	0.14
TMA Tg (°C)		184	181	173

[0066]

From the foregoing results, it could be confirmed that as compared with the epoxy resin of the Comparative Example, the epoxy resin of the present invention is able to give a cured product having high heat resistance.

[0067]

Examples 9 to 12 and Comparative Examples 4 and 5

Each of the above-obtained epoxy resins (EP1 to EP4) and the epoxy resin (EP6) for comparison and an epoxy resin for comparison (EP8; an o-cresol novolak type epoxy resin "EOCN-1020-65", available from Nippon Kayaku Co., Ltd.), a phenol aralkyl resin (MILEX XLC-3L, available from Mitsui Chemicals, Inc.; hereinafter referred to as "PN1") as a curing agent, fused silica (a trade name: MSR-2212, available from Tatsumori Ltd.) as an inorganic filler, triphenylphosphine (a trade name: TPP, available from Hokko Chemical Industry Co., Ltd.) as a curing promoter, carnauba wax No. 1 (available from Cerarica Noda Co., Ltd.) as a mold releasing agent, and a silane coupling agent (a trade name: KBM-403, available from Shin-Etsu Chemical Co., Ltd.) as an additive were compounded in a proportion (parts by weight) shown in Table 3, and the contents were uniformly mixed and kneaded by using a mixing roll, thereby obtaining an epoxy resin composition for encapsulation. This epoxy resin composition was pulverized by a mixer and further tableted by a tablet machine. This tableted epoxy resin composition was subjected to transfer molding (at 175°C for 60 seconds) and then demolding, and the resultant was cured under conditions at 160°C for 2 hours and subsequently at 180°C for 6 hours, thereby obtaining a specimen for evaluation.

[0068]

DMA measurement conditions

Dynamic viscoelasticity analyzer: DMA-2980, available from TA Instruments

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

Temperature rise rate: 2°C/min

5 Specimen size: A specimen obtained by cutting out into a size of 5 mm × 50 mm was used (thickness: about 800 μm).

Analysis condition

Tg: A peak point of $\tan \delta$ ($\tan \delta$ MAX) in the DMA measurement was defined as Tg.

Flame retardancy

- 10 • Determination of flame retardancy: The flame retardancy 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.
- After flame time: A total sum of after flame times after subjecting a sample of one set of five pieces to flame contact ten times.

[0069]

Table 3

				Example				Comparative Example	
			Equivalent of functional group	9	10	11	12	4	5
Compounding composition									
	Epoxy resin	EP1	266	26.6					
		EP2	266		26.6				
		EP3	277			27.7			
		EP4	270				27		
	Epoxy resin for comparison	EP6	201					20.1	
		EP8	238						23.8
	Curing agent	PN1	106	10.6	10.6	10.6	10.8	8.0	9.5
	Curing promoter	Triphenylphosphine		0.40	0.40	0.42	0.41	0.30	0.36
	Inorganic filler	Fused silica	Content: 86%	231	231	238	234	175	207
	Additive	Coupling agent		1.15	1.15	1.19	1.17	0.87	1.03
	Mold releasing agent	Carnauba wax		1.04	1.04	1.07	1.05	0.79	0.93
Characteristics of cured product	DMA	tan δ MAX	210	209	201	204	196	150	
	Flame retardancy	After flame time	39	38	44	39	>200	48	
		Determination	V-0	V-0	V-0	V-0	-	V-0	

[0070]

Example 13

In a one-liter four-necked flask equipped with a stirrer, a reflux condenser, and a stirring device, 295 parts of a phenol compound (DPPI1) (a compound represented by the foregoing formula (P), wherein all the substituent Rs are a hydrogen atom, SABIC BPPPP, purity: 99% or more, residual phenolphthalein: 200 ppm, iron: <5 ppm), 694 parts of epichlorohydrin, and 173 parts of dimethyl sulfoxide were added, and a water bath was subjected to temperature rise to 50°C. When the internal temperature exceeded 45°C, 66 parts of flaky sodium hydroxide was added dividedly over 90 minutes, and thereafter, a post-reaction was further performed at 45°C for 2 hours and subsequently 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, 760 parts of methyl isobutyl ketone was added for dissolution, sodium chloride and the like formed by water washing were removed, and thereafter, an organic layer was subjected to temperature rise to 70°C. 30 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 355 parts of an epoxy resin (EP10). The obtained epoxy resin had an epoxy equivalent of 268 g/eq., a softening point of 99°C, an ICI melt viscosity of 1.03 Pa·s (at 150°C), a total chlorine content of 305 ppm, a hydrolyzable chlorine content of 270 ppm, a chlorine ion content of 0.1 ppm, a sodium ion content of 0.1 ppm, and a hue of 0.6 (Gardner in a 40% THF solution). In addition, the structure of the foregoing formula (1) accounted for 85.2 area% (GPC).

[0071]

Example 14

In a one-liter four-necked flask equipped with a stirrer, a reflux condenser, and a stirring device, 295 parts of a phenol compound (DPPI1) (a compound represented by the foregoing formula (P), wherein all the substituent Rs are a hydrogen atom, SABIC BPPPP, purity: 99% or more, residual phenolphthalein: 200 ppm, iron: <5 ppm), 971 parts of epichlorohydrin, and 165 parts of dimethyl sulfoxide were added, and a water

bath was subjected to temperature rise to 45°C. When the internal temperature exceeded 40°C, 66 parts of flaky sodium hydroxide was added dividedly over 90 minutes, and thereafter, a post-reaction was further performed at 45°C for 2 hours and subsequently 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, 760 parts of methyl isobutyl ketone was added for dissolution, sodium chloride and the like formed by water washing were removed, and thereafter, an organic layer was subjected to temperature rise to 70°C. 30 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 353 parts of an epoxy resin (EP11). The obtained epoxy resin had an epoxy equivalent of 267 g/eq., a softening point of 99°C, an ICI melt viscosity of 0.91 Pa·s (at 150°C), a total chlorine content of 540 ppm, a hydrolyzable chlorine content of 430 ppm, a chlorine ion content of 0.1 ppm, a sodium ion content of 0.1 ppm, and a hue of 0.8 (Gardner in a 40% THF solution). In addition, the structure of the foregoing formula (1) accounted for 87.1 area% (GPC).

[0072]

Example 15

The above-obtained epoxy resin (EP10), an alicyclic epoxy resin (a trade name: SEJ-01R, available from Nippon Kayaku Co., Ltd.) as an epoxy resin to be used in combination, and a cation-based catalyst (a trade name: SI-150, available from Sanshin Chemical Industry Co., Ltd.) as a curing promoter were compounded in a proportion (weight parts) of 50/50/2, thereby obtaining an epoxy resin composition. This epoxy resin composition was cast in a die and cured under a condition at 150°C for 3 hours, thereby obtaining a specimen for evaluation. The obtained specimen was used and measured for DMA. As a result, the T_g was found to be 184°C. (The measurement conditions are the same as those described above.)

[0073]

Example 16

The evaluation was performed in the same manner as that in Example 15, except for changing the epoxy resin (EP10) to the epoxy resin (EP11). As a result of measuring DMA, the Tg was found to be 189°C. (The measurement conditions are the same as those described above.)

5 [0074]

From the foregoing results, it has been clarified that the epoxy resin of the present invention is able to make both high heat resistance and flame retardancy.

[0075]

10 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.

Incidentally, the present application is based on a Japanese patent application filed on June 7, 2012 (Japanese Patent Application No. 2012-129407), the entirety of which is incorporated by reference. In addition, all references cited herein are
15 incorporated as a whole.

INDUSTRIAL APPLICABILITY

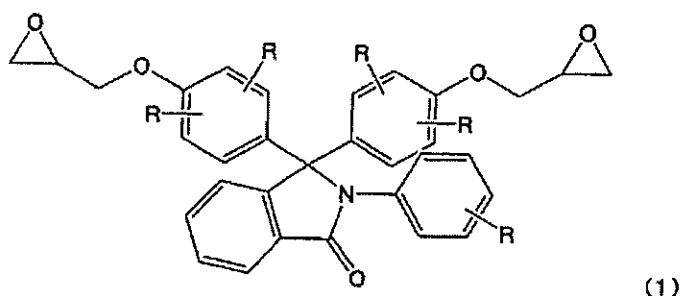
[0076]

20 When the epoxy resin of the present invention is formed into an epoxy resin composition together with a curing agent and the like, it can be used for adhesives, paints, coating agents, molding materials (including sheets, films, FRP, and the like), insulating materials (e.g., encapsulation materials including printed substrates, electric wire coverings, and the like, and besides, cyanate resin compositions for encapsulation
25 materials or substrates, additives to other resins such as acrylate-based resins, etc. as a curing agent for resist, and the like.

CLAIMS

[Claim 1]

An epoxy resin containing, as a main component, a compound represented by the following formula (1) in a content of from 70 to 95% (in terms of an area% according to the gel permeation chromatography):



(1)

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 according to claim 1, wherein an epoxy equivalent is from 1.02 times to 1.11 times relative to a theoretical epoxy equivalent.

[Claim 3]

The epoxy resin according to claim 1, wherein a total chlorine content is not more than 5,000 ppm.

[Claim 4]

An epoxy resin composition comprising, as essential components, the epoxy resin according to any one of claims 1 to 3 and a curing agent.

[Claim 5]

An epoxy resin composition comprising, as essential components, the epoxy resin according to any one of claims 1 to 3 and a curing catalyst.

[Claim 6]

A cured product obtained by curing the epoxy resin composition according to claim 4 or 5.