

DESCRIPTION

PHENOL RESIN MIXTURE, EPOXY RESIN MIXTURE, EPOXY RESIN COMPOSITION AND CURED PRODUCT

Technical Field

[0001]

The present invention relates to a novel phenol resin mixture, an epoxy resin mixture, an epoxy resin composition and a cured product.

Background Art

[0002]

Epoxy resin compositions are utilized in a very wide range of fields such as electric · electronic part materials, reinforcement fiber composite materials, resist materials, optical materials, liquid crystal sealing materials, overcoat materials, prepregs, mold materials, adhesives, adhesive materials, coatings and the like, by taking advantage of their characteristics such as workability, and excellent electrical properties, heat resistance, chemical resistance, mechanical strength, adhesiveness, moisture fastness (water fastness), dimensional stability and optical properties of their cured products.

For example, electric · electronic part materials include (1) semiconductor sealing materials, specifically (a) underfill for potting, dipping, transfer mold sealing, flip chip and the like for condenser, transistor, diode, light-emitting diode, IC, LSI and the like, and (b) underfill for sealing and reinforcement in mounting IC packages such as QFP, BGA and CSP, and the like, (2) adhesives for semiconductors such as interlayer adhesives for substrate materials such as printed wiring board, build-up laminated sheet and multilayer board, dye-bonding agents, and underfills, and (3) adhesives for mounting, such as underfill for BGA reinforcement, anisotropically conductive film and anisotropically conductive paste, and the like. In addition, the reinforcement fiber composite materials include structure materials typified by CFRP

used for structure materials of automobile bodies, ships and aircrafts, materials for leisure sport tools such as shaft of tennis racket and golf club, separators for fuel cells, and the like. The resist materials include solder resists, color resists, black matrixes and the like. The optical materials include materials for lens, and the like.

Recently, in application of electric·electronic part materials, along with high performance of electric·electronic devices, wide range and upgraded properties are required due to advance in high densification·high integration of electric·electronic parts, due to advance in expansion of application field to high-temperature environment in neighborhood of automobile engines, outdoor environment, environment in neighborhood of human bodies, and the like, and due to advance in conversion to environment-responding techniques.

For example, in the fields of semiconductor sealing material and substrate, flame retardancy and solder cracking resistance in addition to heat resistance, water-absorbability, electric insulating, low coefficient of thermal expansion and the like are required for epoxy resin.

[0003]

For flame retardancy of epoxy resin, flame retarding of resin itself, such as halogen-type epoxy resin and phosphorus atom-containing epoxy resin, and flame retardant techniques using a flame retarder such as antimony trioxide in combination has been under consideration. However, it is pointed out that using halogen or antimony contributes to generation of toxic substances such as dioxine if products using them are not properly disposed. This is why the requirement for flame retardant techniques as "halogen-free ·antimony-free ·phosphorus-free" has been increasing. For this requirement, such a resin skeleton as exhibiting flame retardancy without using halogen or a flame retarder has been proposed. For example, phenol-biphenyl aralkyl-based epoxy resin is known as a resin exhibiting flame retardancy without using halogen or a flame retarder (Patent Literature 1 and Patent Literature 2).

[0004]

In addition, solder cracking resistance is affected by change of the mounting process. Specifically, in the method of mounting semiconductor, the surface mounting method became common so semiconductor packages are more often exposed directly to a high temperature of the solder reflow, and in addition, it is often the case that a lead-free solder is used when mounting semiconductor, as awareness of environmental problem has been recently improved. The melting temperature of the lead-free solder is higher by about 20°C (which is about 260°C) compared with conventional solder, whereby the possibility of generation of package cracking during solder reflow is much higher than before. Further, the requirements of high densification·high integration·downsizing are increased more and more for printed wiring substrates loading electronic parts such as LSI, and therefore it is necessary to make the plate thinner by reducing the wiring width or the through hole diameter. However, when the plate is thinner, there is a possibility of generation of cracking in thermal shock, whereby higher solder cracking resistance is required for wiring substrates. This is why, in the lead-free solder with a higher temperature than that of conventional solder, performance of hardly causing cracking of the cured products is required for epoxy resin compositions used for electric·electronic materials as peripheral materials for semiconductor, such as semiconductor sealing materials, printed wiring substrates and the like. This cracking is caused by generation of stress on the cured products when receiving thermal shock of the lead-free solder. As an evaluation index, the storage elastic modulus by dynamic viscoelasticity test can be used. It is known that the storage elastic modulus generally at a high temperature is preferably lower when the storage elastic modulus at, for example, 160°C is 100 MPa or more (Patent Literature 3). On the other hand, it is known that the storage elastic modulus at a high temperature is preferred high above a certain level even in the case of the glass-transition temperature or more, and as a resin having high reliability of causing no cracking during solder reflow at 220°C to 260°C and in heat cycle test at -50 to 150°C, an epoxy resin composition having a storage elastic modulus of 0.5 GPa to 0.9 GPa at 220°C is disclosed (Patent Literature 4).

Therefore, it is considered that a proper storage elastic modulus at a high temperature is very important to suppress generation of cracking by thermal shock.

[0005]

As a commercial product of phenol-biphenyl aralkyl-based epoxy resin excellent in flame retardancy, for example, NC-3000 series and the like manufactured by Nippon Kayaku Co., Ltd. is known. This epoxy resin can be produced by reacting phenol with 4,4'-dimethylol biphenyl, by isolating the resulting bisphenol compound, and subsequently by epoxidizing the isolated bisphenol compound with epichlorohydrin or the like (for example, Patent Literature 5). In addition, the method of using 4,4'-bis(chloromethyl)-biphenyl instead of the above-described 4,4'-dimethylol biphenyl is also known (Patent Literature 6).

In recent development for phenol-biphenyl aralkyl-based epoxy resin, a phenol resin by condensation of, for example, a biphenyl derivative oligomerized in advance, such as 4,4'-bis(chloromethyl)-biphenyl with a phenol is proposed (Patent Literature 7).

Further, the method of synthesizing 4,4'-bis(chloromethyl)-biphenyl as the above-described raw material by bischloromethylation of biphenyl is generally known, and for example, 4,4'-bis(chloromethyl)-biphenyl can be obtained by reaction of biphenyl, paraformaldehyde and zinc chloride in cyclohexane solvent with introduction of hydrogen chloride gas while vigorously stirring (Patent Literature 8, pp.10, columns 19 to 20).

Related Technical Literature

Patent Literature

[0006]

[Patent Literature 1] Japanese Patent Laid-Open No. 11-140277 A

[Patent Literature 2] Japanese Patent Laid-Open No. 11-140166 A

[Patent Literature 3] Japanese Patent No. 4027332

[Patent Literature 4] Japanese Patent Laid-Open No. 2001-288244 A

[Patent Literature 5] Japanese Patent No. 2952094

[Patent Literature 6] Japanese Patent Laid-Open No. 2002-338656 A

[Patent Literature 7] Japanese Patent Laid-Open No. 2007-254685 A

[Patent Literature 8] Japanese Patent Publication No. 54-929

Summary of the Invention

Problems to Be Solved by the Invention

[0007]

It is an object of the present invention to provide an epoxy resin cured product having a flame retardancy equaling or surpassing that of a cured product using phenol-biphenyl aralkyl-based epoxy resin excellent in flame retardancy and having an more optimum storage elastic modulus, an epoxy resin mixture to obtain it or/and an epoxy resin composition, and a phenol resin mixture for the epoxy resin.

Means of Solving the Problems

[0008]

The present inventors have intensively studied to solve the above problems and surprisingly found that a phenol resin mixture obtained by reacting, with phenol without isolation purification, a reaction product (mixture) obtained by halomethylation of biphenyl, which contains bishalomethyl biphenyl as a main component and a certain amount of tri- and tetra-halomethyl biphenyls as a side reaction product and further contains a small amount of monohalomethyl biphenyl and bisbiphenylmethane compound as the rest is very suitable as a raw material of an epoxy resin mixture satisfying the above-described required performance, and thus the present invention has been completed.

[0009]

That is, the present invention relates to:

- (1) A phenol resin mixture obtained by methylene cross-linking reaction of, with phenol, a reaction product which is obtained by halomethylation reaction of biphenyl

and contains 60% or more and less than 80% of bis(halomethyl) biphenyl and 15 to 30% of the total of tri(halomethyl)biphenyl and tetra(halomethyl)biphenyl, as the ratio relative to the whole reaction product as determined by GC-MS (GC area ratio), and contains side products other than those above as the rest;

(2) The phenol resin mixture according to the above (1), wherein the softening point is 65 to 85°C, the number average molecular weight is 350 to 1200 and the weight average molecular weight is 400 to 2000 as determined by GPC (gel permeation chromatography), and the OH equivalent is 160 to 250 g/eq;

(3) An epoxy resin mixture obtained by epoxidation of the phenol resin mixture according to the above (1) or (2);

(4) The epoxy resin mixture according to the above (3), wherein the softening point is 50 to 75°C, the ICI viscosity is 0.02 to 0.50 Pa·s, the number average molecular weight is 400 to 1200 and the weight average molecular weight is 800 to 2000 as determined by GPC (gel permeation chromatography), and the epoxy equivalent is 200 to 360 g/eq;

(5) An epoxy resin composition containing the epoxy resin mixture according to the above (3) and a curing agent;

(6) The epoxy resin composition according to the above (5), wherein the content of the curing agent is 0.7 equivalent to 1.2 equivalents relative to 1 equivalent of the epoxy group in the epoxy resin mixture;

(7) The epoxy resin composition according to the above (6), which further contains 50 to 90% by weight of a filler relative to the total amount of the epoxy resin composition;

[0010]

(8) A cured product obtained by curing an epoxy resin composition containing an epoxy resin mixture obtained by epoxidation of the phenol resin mixture according to the above (1) and containing 0.7 equivalent to 1.2 equivalents of a curing agent relative to 1 equivalent of the epoxy group in said epoxy resin mixture;

(9) A cured product obtained by curing an epoxy resin composition containing an

epoxy resin mixture obtained by epoxidation of the phenol resin mixture according to the above (1), containing 0.7 equivalent to 1.2 equivalents of a curing agent relative to 1 equivalent of the epoxy group in said epoxy resin mixture, and containing 50 to 90% by weight of an inorganic filler relative to the total amount of the epoxy resin composition;

(10) A method for producing a phenol resin mixture, characterized in that halomethylation of biphenyl is carried out by reacting biphenyl, 2 to 8 equivalents of a formaldehyde relative to 1 mol of biphenyl, and a hydrogen halide in the presence of zinc halide and an excessive amount of hydrogen halide to obtain a reaction product containing 60% or more and less than 80% of bis(halomethyl) biphenyl and 15 to 30% of the total of tri(halomethyl)biphenyl and tetra(halomethyl)biphenyl, as the ratio relative to the whole reaction product as determined by GC-MS (GC area ratio), and containing side products other than those above as the rest, and said reaction product is reacted with phenol without purification;

(11) A method for producing an epoxy resin mixture, characterized in that a phenol resin mixture obtained by the method for production according to the above (10) is reacted with 0.8 to 12 equivalents of epihalohydrin relative to 1 equivalent of the hydroxy group in said phenol resin mixture;

(12) An epoxy resin composition containing the phenol resin mixture according to the above (1) or (2) as a curing agent.

Effect of the Invention

[0011]

The phenol resin mixture obtained by the present invention is useful as a raw material for epoxy resin mixtures or epoxy resin compositions, giving a cured product having an excellent flame retardancy and an appropriate storage elastic modulus, and also it is easy to produce. In addition, the epoxy resin mixture or the epoxy resin composition of the present invention can be, as described above, a cured product having flame retardancy and an appropriate storage elastic modulus when it is cured.

Therefore, the epoxy resin mixture of the present invention or the epoxy resin composition of the present invention can be utilized for a wide range of application including semiconductor sealing material and printed wiring board substrate.

Mode for Carrying Out the Invention

[0012]

Hereinafter, the present invention will be more specifically explained.

First, the halomethylation reaction of biphenyl to obtain the phenol resin mixture of the present invention will be explained.

The halomethylation reaction of biphenyl is a reaction to obtain halomethylated biphenyl by using biphenyl, a formaldehyde or an acetal as an equivalent body thereof (hereinafter, these are together referred to as a carbon source), a hydrogen halide, a catalyst and a solvent. There are some cases that the halomethylated biphenyl is further reacted to produce diarylmethane depending on the reaction conditions. In general, the chloromethylation reaction described in, for example, The Fifth Series of Experimental Chemistry, 13 (2) p. 439 (2005), and SYNTHESIS, 1003 (1991) can be seen by reference.

[0013]

For example, according to the above Patent Literature 8 (Japanese Patent Publication No. 54-929), 4,4'-bis(chloromethyl)-1,1'-biphenyl can be produced by chloromethylation reaction using biphenyl, paraformaldehyde, hydrogen chloride gas, zinc chloride and cyclohexane. In addition, other production methods can include, for example, the methods described in Japanese Patent Laid-Open No. 9-208506, Japanese Patent Laid-Open No. 10-139699 and Japanese Patent No. 3784865.

The halomethylation reaction of the present invention can be carried out by any of the above methods or another method as long as a reaction product containing the above composition, specifically 60 to 80% by weight of bis(halomethyl) biphenyl, 15 to 30% of the total of tri(halomethyl)biphenyl and tetra(halomethyl)biphenyl, and side products other than those above as the rest can be obtained.

Hereinafter, the halomethylation reaction of the present invention will be explained with reference to the reaction example of Patent Literature 8 as the most typical example.

[0014]

Preferable carbon sources for the methyl group in halomethylation include formaldehydes such as formalin, paraformaldehyde, methylal and trioxane, and paraformaldehyde is preferable.

The addition equivalent of the carbon source (for example, formaldehyde in the reaction example of Patent Literature 8) varies depending on the halomethylation ratio (the number of the halomethyl group per 1 molecule) relative to biphenyl, but preferably 1 equivalent to 15 equivalents, more preferably 1.5 equivalents to 10 equivalents and further preferably 2 equivalents to 8 equivalents, relative to 1 mol of biphenyl.

If it is 1 equivalent or less, there are some cases where the reaction sites with biphenyl having a phenolic hydroxy group are insufficient, and if it is more than 15 equivalents, there are some cases where the molecular weight is too large due to too many reaction sites cross-linking sites or where the stirring state is deteriorated due to the increased concentration of solid content.

[0015]

The halogen source for halogenation is a hydrogen halide or any can be used as long as it generates hydrogen halide by reaction. As said halogen source, a hydrogen halide is most commonly used. Preferable hydrogen halides include hydrogen chloride, hydrogen bromide and hydrogen iodide, and hydrogen chloride is preferable. These hydrogen halides can be utilized in gas form. When the hydrogen halide is used in gas form, reaction can be carried out by directly blowing into the raw material mixtures other than the hydrogen halide

The hydrogen halide can be also dissolved in water, acetic acid or in addition, an organic solvent for use as a hydrogen halide solution, but the method using hydrogen chloride in gas form is most preferable.

In the halomethylation reaction, it is preferred to suppress generation of methylene cross-linked diarylmethane observed as a by-product, in order to obtain a reaction product having the above composition. It is known that when the concentration of hydrogen halide in a reaction system is low, diarylmethane is predominantly produced. In order to suppress generation of said by-product, it is preferred to increase the concentration of hydrogen halide. Therefore, it is desirable to introduce an excessive amount of hydrogen chloride gas into the reaction liquid. The method of introducing an excessive amount of hydrogen chloride gas includes a method where hydrogen chloride gas is introduced under pressurized conditions or under low temperature, and otherwise.

[0016]

In said reaction, preferable catalysts include Friedel-Crafts type reaction catalysts such as sulfuric acid, thionyl chloride, orthophosphoric acid, zinc chloride, aluminum chloride, ferric chloride and tin chloride and quaternary ammonium salts such as tetrabutylammonium bromide, trimethylbenzyl chloride and cetylpyridinium chloride. Among them, zinc chloride, aluminum chloride, ferric chloride, tin chloride, tetrabutylammonium bromide, trimethylbenzyl chloride and cetylpyridinium chloride are more preferable, and zinc chloride is particularly preferable due to low cost and handling easiness.

These catalysts may be used alone or can be also used as a mixture of 2 or more kinds thereof.

The use amount of catalyst is not particularly limited but preferably in the range of 0.01 mol to 3 mol and more preferably 0.1 mol to 1 mol, relative to biphenyl.

[0017]

The solvent used in said reaction is not particularly limited as long as it is an unreactive solvent. Preferable solvents include organic solvents such as aliphatic hydrocarbon solvent (for example, chain alkanes such as hexane and heptane, cyclic alkanes such as cyclopentane and cyclohexane, kerosene and the like), aliphatic carboxylic acid solvent (for example, formic acid, acetic acid, propionic acid and the

like), aromatic carbon hydride solvent with a low electron density of the aromatic ring (for example, chlorobenzene, nitrobenzene, ortho dichlorobenzene, trichlorobenzene and the like) and aliphatic halogenated hydrocarbon solvent (for example, chloroform, dichloromethane, dichloroethane, tetrachloroethane and the like).

These solvents may be used alone or may be also a mixed solvent of 2 or more kinds thereof. Preferable solvents can include C5-C6 cyclic alkane, and the most preferable is cyclohexane because it is inexpensive, has a low boiling point and thus is easily removed.

In addition, when zinc chloride is used as a catalyst, an aliphatic alcohol such as 1-pentanol or 1-hexanol or water may be added in an about equimolar amount of the catalyst. It is known that addition of these possibly increases the solubility of catalyst and improves the reaction activity (Bull. Chem. Soc. Jpn. 66, 3520 (1993)). In the present invention, the addition is not particularly necessary.

The use amount of the solvent is not particularly limited but is preferably 1/2 part by weight to about 10 times the part by weight of the solid content and more preferably 8 parts by weight or less.

[0018]

The reaction temperature is not particularly limited as long as it is usually in the temperature range acceptable in a solvent used. It is usually 0°C to 100°C and preferably about 15 to 60°C. When the reaction proceeds around room temperature, it is preferably room temperature.

In general, it is known that methylene cross-linked diarylmethane observed as a by-product in chloromethylation reaction is predominantly produced when the reaction temperature is high, whereby it is preferred that the reaction temperature is low in order to suppress such a by-product.

The reaction time is not particularly limited. The reaction can be carried out for usually about 6 hours to 36 hours.

The addition method is not particularly limited. As a preferable method, it is preferred that the raw materials other than the hydrogen halide are first added and

hydrogen halide gas is blown into the system during the reaction so as to maintain the state that the hydrohalic acid in the system excessively exists. Hydrogen chloride is preferable as the hydrogen halide.

[0019]

In the present invention, with regard to the composition of the reaction product obtained above, preferable is a mixture (hereinafter also referred to as mixture of a biphenyl compound having a halomethyl group, in some cases) where the content of bishalomethyl biphenyl (preferably, bischloromethyl biphenyl) is 60% or more and less than 80% and the total content of tri(halomethyl)biphenyl (preferably, tri(chloromethyl)biphenyl) and tetra(halomethyl)biphenyl (preferably, tetra(chloromethyl)biphenyl) is 15% to 30%, as a ratio (GC area ratio: hereinafter as is the same unless otherwise noted) relative to the whole reaction product (total amount) determined by GC-MS (Gas Chromatograph / Mass Spectrometry), and other side products are the rest. In addition, the total of the three of bishalomethyl biphenyl, tri(halomethyl)biphenyl and tetra(halomethyl)biphenyl is preferably 75% to 97% and more preferably 80% to 95%.

Bishalomethyl biphenyl as the main component comprises 4,4'-bishalomethyl biphenyl and positional isomers thereof, and in the bishalomethyl biphenyl, 4,4'-bishalomethyl biphenyl accounts for about 50 to 98% and preferably about 60 to 95%, and the rest is considered to be isomers thereof.

[0020]

The main compounds contained in the reaction product are as shown in the later-described Table A where they are shown in a formula typified by a compound in which the halomethyl group is a chloromethyl group. Any of the "chloromethyl" group in Table A and "chloromethyl" in the below-described explanation can be compatible with "halomethyl" in the present invention.

4,4'-bischloromethyl-biphenyl represented by the formula 1-3 is the main component in the bischloromethyl biphenyl and considered to account for about 50 to 98% and preferably about 60 to 98% of the bischloromethyl biphenyl. In the

bischloromethyl biphenyl, the rest other than 4,4'-bischloromethyl-biphenyl is considered to be positional isomers such as 2,4'-bischloromethyl-biphenyl represented by the formula 1-4.

[0021]

Tri(chloromethyl)biphenyl and tetra(chloromethyl)biphenyl is considered to comprise compounds represented by, for example, the formula 1-5 to the formula 1-8, and their isomers (substitution position isomers).

Other side products can include, for example, monochloromethyl biphenyl (for example, compounds represented by the formula 1-1 and the formula 1-2, and the like), bisbiphenylmethane (the formula 1-9), monochloromethyl-bisbiphenylmethane (compounds represented by the formula 1-10, and the like), bischloromethyl-bisbiphenylmethane (compounds represented by the formula 1-11, and the like) and the like.

[0022]

The content of bischloromethyl biphenyl relative to the total amount of the reaction product is 60% or more and less than 80% and more preferably 65 to 75%.

The total content of tri(chloromethyl)biphenyl and tetra(chloromethyl)biphenyl relative to the total amount of the reaction product is about 15 to 30% and preferably about 15 to 25%. Each ratio of tri(chloromethyl)biphenyl and tetra(chloromethyl)biphenyl varies depending on the reaction conditions so it is not necessarily appropriate to suggest, but the content of trichloromethyl biphenyl relative to the total amount of the reaction product is about 5% to 25% and preferably 10% to 20%.

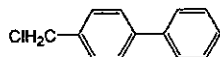
The content of tetra(chloromethyl)biphenyl relative to the total amount of the reaction product is preferably 1% to 15% and more preferably 2% to 10%.

Among other side products described above, monochloromethyl biphenyl is usually contained the most and is about 1% to 10% as the ratio relative to the whole reaction product as determined by GC-MS (GC area ratio) (hereinafter, as is the same unless otherwise noted).

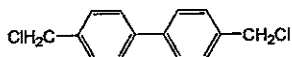
[0023]

Table A

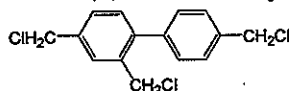
Formula 1-1: 2-chloromethyl-biphenyl



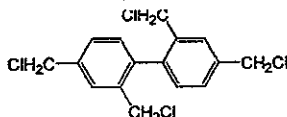
Formula 1-3: 4,4'-bis(chloromethyl)-biphenyl



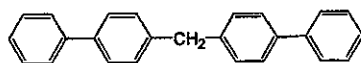
Formula 1-5: 2,4,4'-trichloromethyl-biphenyl



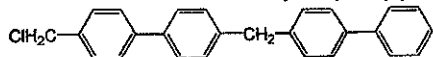
Formula 1-7: 2,4,2',4'-tetrachloromethyl-biphenyl



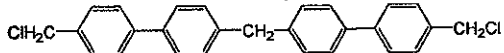
Formula 1-9: bisphenylylmethane



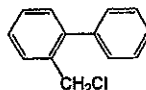
Formula 1-10: 4-monochloromethyl-bisphenylylmethane



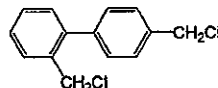
Formula 1-11: 4,4'-bis(chloromethyl)-bisphenylylmethane



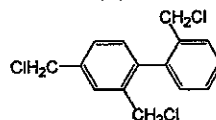
Formula 1-2: 2-chloromethyl-biphenyl



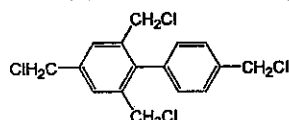
Formula 1-4: 2,4'-bis(chloromethyl)-biphenyl



Formula 1-6: 2,4,2'-trichloromethyl-biphenyl



Formula 1-8: 2,4,6,4'-tetrachloromethyl-biphenyl



[0024]

Next, the reaction (also referred to as methylene cross-linking reaction) of the above-obtained reaction product with phenol and the phenol resin mixture of the present invention obtained by said reaction will be explained.

The methylene cross-linking reaction is a condensation reaction, where the reaction product (mixture of biphenyl compound having the above halomethyl group)

obtained as described above and phenol are condensed. Said methylene cross-linking reaction is preferably carried out under acidic conditions, for example, at about pH 1 to 4.

For example, The Fifth Series of Experimental Chemistry 26 (2) p. 142 (2005) can be generally referenced for said reaction.

[0025]

As described above, the halomethylation reaction product of biphenyl is a mixture, and the present invention is characterized in that said mixture is used as it is in methylene cross-linking reaction with phenol. Therefore, the reaction liquid obtained in halomethylation reaction can be usually used as it is.

In addition, according to necessity, said reaction liquid can be used as a raw material for the reaction with phenol after treatments such as condensation, dilution, degassing, washing with water, neutralization and filtration. Also in that case, it is preferred to be substantially within the range of the composition in the above reaction product.

Usually, it is preferred that the reaction liquid from the halomethylation reaction of biphenyl is used as it is in the subsequent methylene cross-linking reaction with phenol.

[0026]

In said methylene cross-linking reaction, an acid catalyst can be added according to necessity and it is usually preferred to carry out in the presence of an acid catalyst. As the acid catalyst, various acid catalysts can be used including, for example, organic or inorganic acids such as sulfuric acid, p-toluene sulfonic acid, oxalate, methanesulfonic acid and trifluoromethanesulfonic acid and Friedel-Crafts type Lewis acid catalysts such as zinc chloride, aluminum chloride, ferric chloride and tin chloride.

The use amount of these acid catalysts varies depending on the kind of catalyst and can be within the range of 0.001 to 10 times the molar ratio relative to phenol for addition. Preferably, the amount is about 0.05 to 3 mol.

In a preferable aspect in the present invention, the reaction liquid from the halomethylation reaction is used as it is and subsequently the above-described condensation reaction is carried out, whereby the acid catalyst used in the halomethylation reaction can be used as it is and it is not necessary to add an acid catalyst again.

The halomethylation reaction product of biphenyl and phenol can be reacted in an optional ratio. Usually, phenol is used in an amount of preferably 1.5 mol to 40 mol and more preferably 2 mol to 10 mol relative to 1 mol of the halomethyl group in the halomethylation reaction product of biphenyl. This is because 1.5 mol or less leads to the concern of increase in molecular weight and more than 40 mol leads to decrease in pot efficiency.

The addition amount of phenol is roughly 0.3 to 2 times and preferably 0.5 to 1.5 times (by weight ratio) of the total amount of biphenyl, the carbon source and the acid catalyst added for halomethylation of biphenyl.

In this regard, it is preferred, in tracing this reaction, to analyze the remaining amount of the halomethyl group and confirm disappearance of the halomethyl group. In addition, the amount of all saponifiable chlorine can be applied in accordance with, for example, the description of JIS K7246. Otherwise, tracing can be also carried out by applying pretreatment where a coloring matter or the like as a marker is reacted with the halomethyl group in a reactive mixture for analysis.

[0027]

The methylene cross-linking reaction (condensation reaction) can be also carried out without a solvent or in the presence of a solvent. Usually, the reaction liquid from the above halomethylation reaction is preferably used as it is, and the organic solvents listed in the section of the above halomethylation reaction can be used as they are. Therefore, preferable solvents can likewise include C5-C6 cyclic alkane and most preferably cyclohexane.

The use amount of the solvent is usually 5 to 300% by weight and preferably 10 to 200% by weight relative to the total weight of the halomethylation reaction product

of biphenyl and phenol. The reaction temperature of the methylene cross-linking reaction is usually 0 to 120°C and preferably about 15 to 100°C. The reaction time is usually 1 to 10 hours.

[0028]

For the methylene cross-linking reaction, it is the most convenient that after the halomethylation reaction is carried out, phenol is added directly to the reaction liquid from the halomethylation reaction and reacted. According to necessity, the reaction liquid from the halomethylation reaction can be also added to phenol (and if needed, a mixture of an acid catalyst and a solvent). In addition, according to necessity, operations such as dilution, degassing, washing with water and neutralization can be carried out before and after them in the range that the composition of the reaction product is not widely changed.

[0029]

After completion of condensation reaction, the intended phenol resin mixture can be taken out by removing the acid catalyst by neutralization, washing with water, and the like and then by removing the solvent used for heating under reduced pressure. It is desired to remove unreacted phenol together with the solvent used for heating under reduced pressure.

In the present invention, it is usually preferred to transfer, to the next epoxidation reaction, a phenol resin mixture obtained by removing the acid catalyst by neutralization, washing with water, and the like and then by removing the solvent and the unreacted phenol without treatment of recrystallization after completion of methylene cross-linking reaction.

The reaction liquid after completion of methylene cross-linking reaction can be subsequently used in the next epoxidation process without removing the solvent and the unreacted phenol, but in this case, an operation of treating alkali metal hydroxides, such as sodium hydroxide and potassium hydroxide, with a base is necessary for neutralization of the hydrogen halide and the acid catalyst used in the reaction. In addition, this cannot be said to be particularly preferred because the unreacted

phenol is reacted with epichlorohydrin and the like by epoxidation.

The phenol resin mixture of the present invention obtained as described above is a phenol resin mixture where phenol and biphenyl are linked by a methylene cross-linking group (including some phenol resins where biphenyls are linked by methylene cross-linking and further phenol is linked with biphenyl by methylene cross-linking) and it is useful as a raw material for the epoxy resin mixture of the present invention and can be utilized as an epoxy resin mixture after the next epoxidation reaction.

[0030]

The phenol resin mixture of the present invention obtained as described above has a softening point of 65 to 85°C, and a number average molecular weight of about 350 to 1200, preferably about 400 to 1000, further preferably about 450 to 950 and most preferably about 500 to 900 and a weight average molecular weight of about 400 to 2000, preferably about 500 to 1700, further preferably about 550 to 1600 and most preferably about 600 to 1000, as determined by GPC (gel permeation chromatography). It has an OH equivalent of about 160 to 250 g/eq, preferably about 170 to 240 g/eq and most preferably about 180 to 230 g/eq.

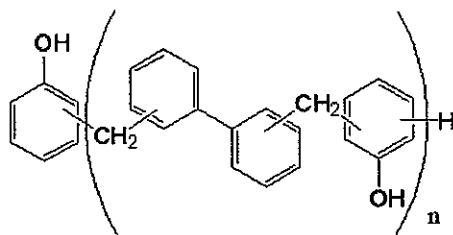
The chemical structures of representative compounds of the phenol resin mixture of the present invention are considered to be F2-1 to F2-6 and the like exemplified below, judging from the analysis results of the reaction product of halomethylation reaction, and the like. In the formulas, n is about 1 to 10.

The phenol resin mixture of the present invention is a mixture of a straight-chain molecule or a branched molecule, as is clear from, for example, the below-described exemplification.

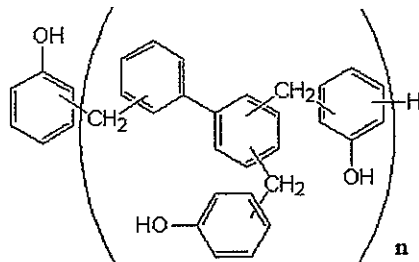
[0031]

(F2-1 to F2-3)

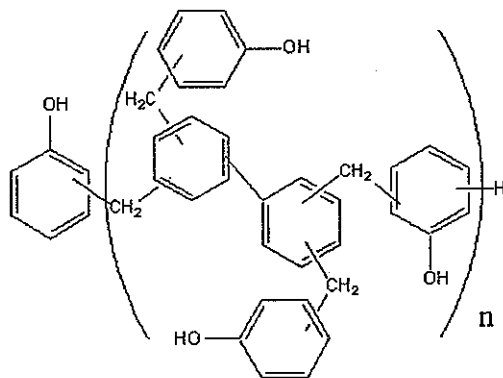
F2-1



F2-2



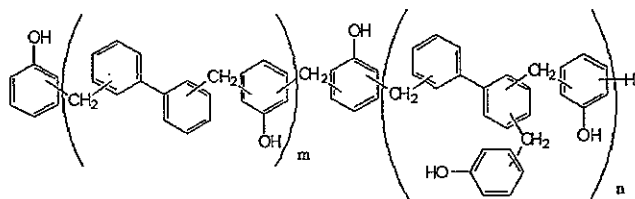
F2-3



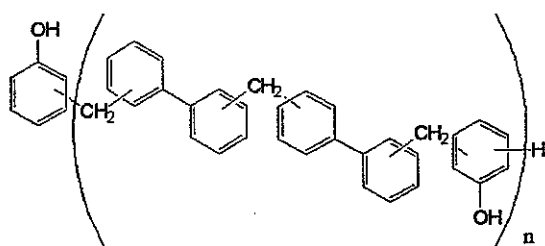
[0032]

(F2-4 to F2-6)

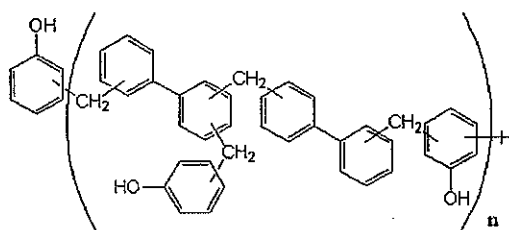
F2-4



F2-5



F2-6



[0033]

Next, the epoxidation reaction to obtain the epoxy resin mixture of the present invention will be explained.

The epoxy resin mixture of the present invention is an epoxidized product of the phenol resin mixture of the present invention obtained above and can be obtained by epoxidation of said phenol resin mixture by reaction with epihalohydrin in a conventional manner. More specifically, the following method is included.

Preferable methods for epoxidation can include a method where the phenol resin mixture of the present invention is reacted with epihalohydrin in the presence or absence of a solvent and in the presence of an alkali metal hydroxide for glycidyl etherification. In said method, the reaction temperature is usually about 10 to 100°C and preferably about 30 to 90°C. The epoxidation reaction using said epihalohydrin

includes an epoxidation reaction described in Japanese Patent No. 3934829, a one-step method described in Japanese Patent Laid-Open No. 2007-308642 A, and a fusion method.

In the reaction to obtain the epoxy resin of the present invention, an alkali metal hydroxide can be used as an aqueous solution thereof. In that case, a method may be also used where an aqueous solution of said alkali metal hydroxide is continuously added to the reaction system while water and epihalohydrin are also continuously distilled under reduced pressure or under ordinary pressure, and it is further separated to remove water and to continuously return epihalohydrin to the reaction system. In addition, in the present invention, the catalyst used in the former process is not removed and remains unless any operation is particularly done, whereby the reaction can smoothly proceed with an operation of neutralization by adding an alkali metal hydroxide more excessively than usual.

Further, the method can be a method where a quaternary ammonium salt such as tetramethylammonium chloride, tetramethylammonium bromide or trimethylbenzylammonium chloride is added as an catalyst to a mixture of the phenol resin mixture of the present invention and epihalohydrin, the mixture is reacted at 50°C to 150°C for 0.5 to 8 hours to obtain halohydrin-etherified phenol resin, thereto a solid or an aqueous solution of an alkali metal hydroxide is further added, and the mixture is reacted at 20°C to 120°C for 1 hour to 10 hours for dehydrohalogenation (ring closure).

[0034]

Preferable epihalohydrin includes epichlorohydrin, epibromohydrin, epiiodohydrin, beta-methylepichlorohydrin, alpha-methylepichlorohydrin and gamma-methylepichlorohydrin, and industrially, epichlorohydrin is preferable.

The use amount of epihalohydrin used in the above-described epoxidation reaction is usually 0.8 equivalent to 12 equivalents and preferably 0.9 equivalent to 11 equivalents relative to 1 equivalent of the hydroxy group in the phenol resin of the present invention. In this case, it is preferable to carry out the reaction with addition

of a polar solvent, preferably an alcohol (for example, C1-C4 alcohol such as methanol or ethanol), or an aprotic polar solvent (for example, dimethyl sulfone, dimethylsulfoxide and the like) in order that the reaction smoothly proceeds. The use amount of said polar solvent may be appropriately selected between usually 2% by weight to 150% by weight relative to the amount of epihalohydrin, according to the kind of solvent and the like. For example, when using an alcohol, its use amount is usually 2% by weight to 20% by weight and preferably 4% by weight to 15% by weight relative to the amount of epihalohydrin. In addition, when using an aprotic polar solvent, it is usually 5% by weight to 150% by weight and preferably 10% by weight to 140% by weight relative to the amount of epihalohydrin.

[0035]

The alkali metal hydroxide includes lithium hydroxide, sodium hydroxide, potassium hydroxide, rubidium hydroxide and cesium hydroxide, and sodium hydroxide and potassium hydroxide are preferable.

[0036]

By removing epihalohydrin, the solvent and the like by heating under reduced pressure after washing the reaction product of epoxidation reaction with water or without washing it, an epoxy resin mixture of the present invention can be obtained.

In addition, in order to give an epoxy resin mixture with less hydrolyzable halogen, it is preferred that the collected epoxy resin mixture is dissolved in a solvent, for example, toluene, methylisobutylketone and the like, thereto an aqueous solution of an alkali metal hydroxide such as sodium hydroxide, potassium hydroxide or the like is added to react with hydrolyzable halogen contained in the reaction product, and then the hydrolyzable halogen is removed. By this after-treatment, the epoxy ring can be also assured. The use amount of alkali metal hydroxide in this after-treatment is usually 0.01 equivalent to 0.3 equivalent and preferably 0.05 equivalent to 0.2 equivalent relative to 1 equivalent of the epoxy group in the reaction product. The temperature of this after-treatment is usually 50°C to 120°C and the reaction time is usually 0.5 hours to 2 hours.

After this after-treatment, by removing the produced salt by filtration, washing with water, or the like and further by distilling away the solvent by heating under reduced pressure, the epoxy resin mixture of the present invention is obtained.

[0037]

The epoxy resin mixture of the present invention obtained as described above has a softening point of 50 to 75°C, preferably 52 to 65°C and more preferably 54 to 60°C, an ICI viscosity of 0.02 to 0.50 Pa·s, preferably 0.04 to 0.40 Pa·s and more preferably 0.06 to 0.20 Pa·s, and a number average molecular weight of about 400 to 1200, preferably about 500 to 1000, further preferably about 600 to 900 and most preferably about 600 to 850 and a weight average molecular weight of about 800 to 2000, preferably about 900 to 1800, further preferably about 1000 to 1600 and most preferably about 1000 to 1500, as determined by GPC (gel permeation chromatography). The epoxy equivalent is about 200 to 360 g/eq, preferably about 230 to 340 g/eq and most preferably about 250 to 310 g/eq.

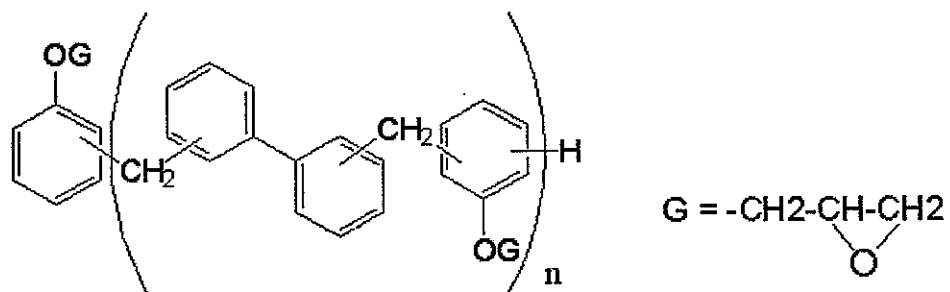
Representative chemical structures of the epoxy resin mixture of the present invention are exemplified in F3-1 to F3-6 described below. The epoxy resin mixture of the present invention is a reactant of the phenol resin mixture of the present invention and epihalohydrin, whereby it is a mixture of a straight-chain molecule or a branched molecule as is clear from the below-described exemplification.

In this regard, n in the formulas is the same as in the above F2-1 to F2-6.

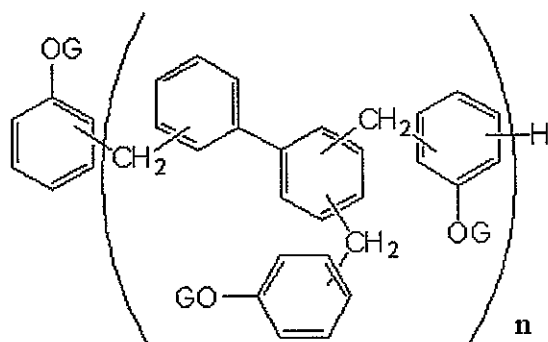
[0038]

(F3-1 to F3-3)

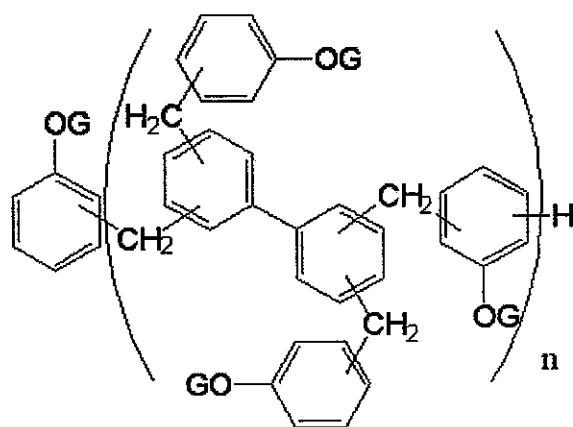
F3-1



F3-2



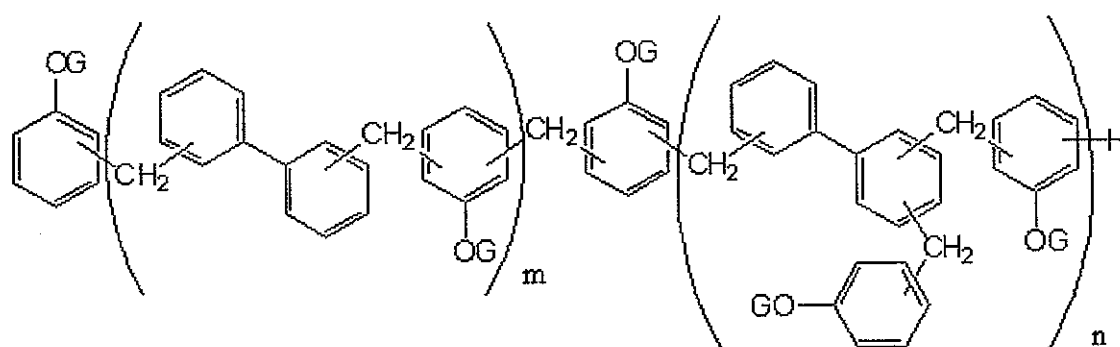
F3-3



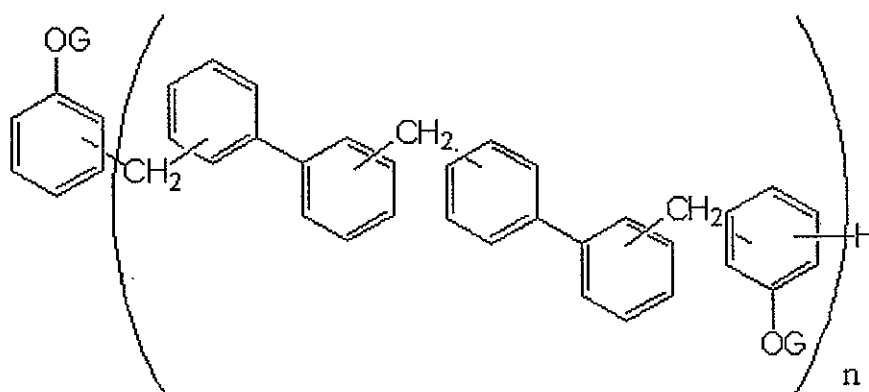
[0039]

(F3-4 to F3-6)

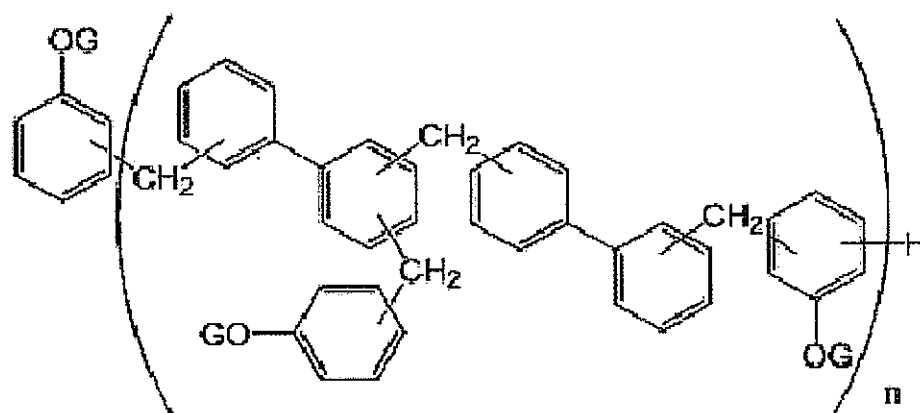
F3-4



F3-5



F3-6



[0040]

Next, the epoxy resin composition of the present invention will be explained.

As for the epoxy resin composition of the present invention, an optional other additional component is not particularly limited as long as the epoxy resin mixture of the present invention and a curing agent are contained.

For example, in the epoxy resin composition of the present invention, another epoxy resin can be used in combination as one of optional additional components other than the epoxy resin mixture of the present invention. When using it in combination, the ratio of the epoxy resin mixture of the present invention in the whole epoxy resin is 30% by weight or more, preferably 100% by weight or less, more preferably 40% by weight or more and 100% by weight or less, and further preferably 50% by weight or more and 100% by weight or less. In terms that the properties of the epoxy resin mixture of the present invention, particularly excellent flame retardancy and appropriate storage elastic modulus in the cured product are fully achieved, the epoxy resin mixture of the present invention is preferably 60% by weight or more, more preferably 70% by weight or more, further preferably 80% by weight or more and most preferably 90% by weight or more. The upper limit is up to 100% by weight.

[0041]

Other epoxy resins which can be used in combination with the epoxy resin mixture of the present invention include novolak-type epoxy resin, bisphenol A-type epoxy resin, triphenylmethane-type epoxy resin and the like.

Specifically, it includes solid or liquid epoxy resins of glycidyl etherified products of aromatic compounds having 2 to 4 hydroxy groups {for example, bisphenol A, bisphenol F, bisphenol S, fluorenylidene diphenol, 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-hydroxy)ethane}; or glycidyl etherified products of polycondensates of phenols (such as phenol, alkyl-substituted phenol, naphthol, alkyl-substituted naphthol, dihydroxybenzene, dihydroxy naphthalene) and aldehydes or ketones, or their reactivity derivatives {for example, formaldehyde, acetaldehyde, benzaldehyde, p-hydroxybenzaldehyde,

o-hydroxybenzaldehyde, p-hydroxyacetophenone or 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, and the like}, and glycidyl etherified products of modified products of said polycondensate; glycidyl etherified products introduced from halogenated bisphenols such as tetrabromo bisphenol A or alcohols; alicyclic epoxy resins; glycidyl amine-type epoxy resins; glycidyl ester-type epoxy resins, or the like. These may be used alone or in combination of 2 or more kinds thereof. In addition, other epoxy resins other than these can be used in combination.

[0042]

In the epoxy resin composition of the present invention, the phenol resin mixture of the present invention can be used as a curing agent, alone or in combination with another curing agent. When used in combination, the ratio of the phenol resin mixture of the present invention in the whole curing agent is preferably 30% by weight or more and particularly preferably 40% by weight or more. The upper limit is 100% by weight.

The curing agent used in the epoxy resin composition of the present invention includes, for example, amine compounds, acid anhydride compounds, amide compounds, phenol compounds and the like. Specific examples thereof include amine compounds such as diaminodiphenylmethane, diethylenetriamine, triethylenetetramine, diaminodiphenylsulfone, isophoronediamine and trifluoroborane-amine complex; amide compounds such as dicyandiamide and polyamide resin synthesized from dimer linolenic acid and ethylenediamine; acid anhydride compounds such as phthalic anhydride, trimellitic anhydride, pyromellitic dianhydride, maleic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic acid anhydride, nadic methyl anhydride, hexahydrophthalic anhydride, methylhexahydrophthalic anhydride; phenols having 2 to 4 hydroxy groups {bisphenol A, bisphenol F, bisphenol S, fluorenylidene diphenol, terpene diphenol, 4,4'-biphenol, 2,2'-biphenol, 3,3'-5,5'-tetramethyl-[1,1'-biphenyl]-4,4'-diol,

hydroquinone, resorcin, naphthalenediol, tris-(4-hydroxyphenyl)methane, 1,1,2,2-tetrakis (4-hydroxyphenyl)ethane}, polycondensates of phenols (benzene or naphthalene having 1 to 2 hydroxy groups such as phenol, alkyl-substituted phenol, naphthol, alkyl-substituted naphthol, dihydroxybenzene and dihydroxy naphthalene, which may have an alkyl-substitution, and the alkyl group is preferably C1-C4 alkyl) and aldehyde or ketone {formaldehyde, acetoaldehyde, benzaldehyde, p-hydroxybenzaldehyde, o-hydroxybenzaldehyde, p-hydroxyacetophenone, o-hydroxyacetophenone}, or polycondensates of the above-described phenols and reactivity derivatives of aldehyde or ketone {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 and the like}, and modified products of these polycondensates, phenol compounds such as tetrabromo bisphenol A; imidazoles; guanidine derivatives; and the like, but not limited thereto.

These may be used alone, or 2 or more kinds thereof may be used.

Among these curing agents, phenol compounds or amine compounds are preferable, and phenol compounds, also phenolic aralkyl resin or the phenol resin mixture of the present invention are preferable. Most preferable is phenolic aralkyl resin.

[0043]

In the epoxy resin composition of the present invention, the use amount of the curing agent is preferably 0.7 equivalent to 1.2 equivalents as the equivalent of active groups reacting with epoxy in the curing agent (the hydroxy group equivalent in the phenol compound and the amino group equivalent in the amine compound), relative to 1 equivalent of the epoxy group in the epoxy resin. If the active group equivalent in the curing agent is less than 0.7 equivalent or if it is more than 1.2 equivalents relative to 1 equivalent of the epoxy group, there is a possibility that curing is incomplete, whereby good properties of cured products is not obtained in any case.

[0044]

In the epoxy resin composition of the present invention, there is no harm in

using a curing accelerator. Specific examples of curing accelerators which can be used include imidazoles such as 2-methylimidazole, 2-ethylimidazole and 2-ethyl-4-methylimidazole; tertiary amines such as 2-(dimethylaminomethyl)phenol and 1,8-diaza-bicyclo(5,4,0)undecene-7; phosphines such as triphenylphosphine; metal compounds such as tin octylate; and the like. The curing accelerator may be not used, but when used, 0.1 part by weight to 5.0 parts by weight thereof relative to 100 parts by weight of the epoxy resin can be appropriately used according to necessity.

[0045]

In the epoxy resin composition of the present invention, an inorganic filler (also referred to as filler) can be added according to necessity. The inorganic filler includes powder forms of crystals silica, molten silica, alumina, zircon, calcium silicate, calcium carbonate, silicon carbide, silicon nitride, boron nitride, zirconia, forsterite, steatite, spinel, titania, talc and the like, or beads where these are spheronized, but not limited thereto. These may be used alone, and 2 or more kinds thereof may be used. The content of these inorganic fillers is 0 to 95% by weight, preferably 20% by weight to 95% by weight, more preferably 50% by weight to 95% by weight, further preferably about 70% by weight to 95% by weight and most preferably 70% by weight to 90% by weight relative to the total amount of the epoxy resin composition.

[0046]

Further in the epoxy resin composition of the present invention, an additive may be added according to necessity, including lubricants such as silane coupling agent, stearic acid, palmitic acid, zinc stearate and calcium stearate; colorants such as carbon black, phthalocyanine blue and phthalocyanine green; resins such as polybutadiene and modified one, modified one of acrylonitrile copolymer, polyphenylene ether, polystyrene, polyethylene, polyimide, fluorine resin, maleimide-type compound, cyanate resin (or its prepolymer), silicone gel and silicone oil; and the like.

[0047]

The preferable epoxy resin composition of the present invention is specifically shown as described below.

(1) An epoxy resin composition containing the epoxy resin mixture of the present invention and a curing agent, wherein the curing agent is contained in an amount of 0.7 to 1.2 equivalents as the equivalent of the active group reacting with the epoxy group in the curing agent relative to 1 equivalent of the epoxy group in said epoxy resin, the epoxy resin mixture of the present invention is contained in an amount of 4% by weight to 80% by weight relative to the total amount of the epoxy resin composition, and the rest is an optional additional component.

(2) The epoxy resin composition of the above (1), wherein the optional additional component is an inorganic filler and contained in an amount of 50% by weight to 95% by weight and preferably 70% by weight to 90% by weight relative to the whole volume of the epoxy resin composition.

(3) The epoxy resin composition according to the above (2), wherein the epoxy resin mixture of the present invention is 5% by weight to 30% by weight relative to the total amount of the epoxy resin mixture of the present invention and the inorganic filler, and the rest is an inorganic filler.

(4) The epoxy resin compositions of the above (1) to (3), wherein the optional additional component is either or both of a lubricant and a coupling agent and contained in an amount of 0.05% by weight to 1% by weight relative to the whole volume of the epoxy resin composition.

(5) The epoxy resin composition according to any one of the above (1) to (4), wherein the epoxy resin mixture of the present invention has a softening point of 52 to 65°C, an ICI viscosity of 0.04 to 0.40 Pa·s, a number average molecular weight of 400 to 1200 and a weight average molecular weight of 800 to 2000 as determined by GPC (gel permeation chromatography), and an epoxy equivalent of 200 to 360 g/eq.

[0048]

(6) The epoxy resin compositions according to the above (1) to (5), wherein the

epoxy resin mixture of the present invention is an epoxy resin mixture obtained by epoxidation of a phenol resin mixture obtained by methylene cross-linking reaction of a reaction product, which is obtained by halomethylation reaction of biphenyl and contains 60% or more and less than 80% of bis(halomethyl) biphenyl and 15 to 30% of the total of tri(halomethyl)biphenyl and tetra(halomethyl)biphenyl as the ratio relative to the whole reaction product as determined by GC-MS (GC area ratio) and other side products as the rest, with phenol.

(7) The epoxy resin composition according to the above (6), wherein the phenol resin mixture has a softening point of 65 to 85°C, a number average molecular weight of 350 to 1200 and a weight average molecular weight of 400 to 2000 as determined by GPC (gel permeation chromatography), and an OH equivalent of 160 to 250 g/eq.

(8) The epoxy resin compositions according to the above (1) to (7), wherein the curing agent is a phenol compound.

[0049]

The epoxy resin composition of the present invention is obtained by uniformly mixing an epoxy resin mixture of the present invention, a curing agent and an optional additional component. The epoxy resin composition of the present invention can be easily cured into a cured product thereof by a manner similar to a conventionally known manner.

More specifically, first, for example, an epoxy resin mixture of the present invention and a curing agent, and if needed, an optional additional component (for example, a component selected from the group consisting of a curing accelerator, an inorganic filler, a coupling agent and a lubricant, and the like) are mixed enough to be uniformized using, for example, an extruder, a kneader, a roll and the like to give a epoxy resin composition of the present invention. Subsequently, the obtained epoxy resin composition can be melted and then molded employing a cast molding or transfer molding machine, an injection molding machine, a casting machine and the like, and further preferably heated at 80 to 200°C for 2 to 16 hours for post-cure to give a cured product of the epoxy resin composition of the present invention.

[0050]

In addition, it is also possible that the epoxy resin composition of the present invention is melted by heating or said epoxy resin composition is mixed with a solvent so that the viscosity is reduced, and it is impregnated in a substrate such as glass fiber, Carbon fiber, polyester fiber, polyamide fiber, alumina fiber, paper or the like and semidried by heating to obtain a prepreg, which is hot press molded to obtain a cured product thereof. The above-described solvent can include solvents such as aromatic-type solvents such as toluene and xylene; ketone-type solvents such as acetone, methyl ethyl ketone and methyl isobutyl ketone; amide-type solvents such as N,N-dimethylformamide, N,N-dimethylacetoamide and N,N-dimethylimidazolidinone; sulfone-type solvents such as dimethyl sulfoxide and tetramethylene sulphone; lactam-type solvents such as N-methylpyrrolidone; lactone-type solvents such as gamma-butyrolactone; ether-type solvents such as diethylene glycol dimethyl ether, diethylene glycol diethyl ether, propylene glycol monomethyl ether, propylene glycol monomethyl ether monoacetate and propylene glycol monobutyl ether; and the like.

[0051]

The solvent used above may be a single solvent or also a mixed solvent of 2 or more kinds. In addition, when mixing a solvent as described above, it is used in an amount of usually 10% by weight to 70% by weight and preferably 15% by weight to 70% by weight relative to the total amount of the mixture of the epoxy resin composition of the present invention and said solvent.

The above-described prepreg can be cut into a desired form and, if needed, laminated with copper foil or the like, and then cured by heating under increased pressure in a method such as the press molding method, the autoclave molding method and the sheet-winding molding method to give a cured product of the prepreg or a laminated sheet having said cured product. In addition, it is also possible that a circuit is formed on a laminated sheet where copper foil is laminated on the surface, and the above-described prepreg and copper foil are laminated thereon, otherwise

copper foil or the like having the above-described prepreg is laminated thereon to form a circuit, and according to necessity, the operation is repeated to obtain a multilayered circuit substrate.

[0052]

Semiconductor devices which can be produced by sealing a semiconductor element (semiconductor tip) with the epoxy resin composition of the present invention include, for example, DIP (dual inline package), QFP (quad flat package), BGA (ball grid array), CSP (chip size package), SOP (small outline package), TSOP (thin small outline package), TQFP (thin quad flat package) and the like. In addition, in the field of optical semiconductor, products are included where an optical semiconductor element (semiconductor tip) is sealed, such as light-emitting diode (LED), phototransistor, CCD (charge coupled device), EPROM such as UV-EPROM, and the like.

[0053]

The epoxy resin composition of the present invention can be also used as a photo-heat curable resin composition by mixing with a compound having an ethylenically unsaturated group. This composition further contains a compound having an ethylenically unsaturated group, preferably an aqueous alkali-soluble resin (A), and further a cross-linking agent (B) and a photopolymerization initiator (C), as an optional additional component in the epoxy resin composition of the present invention.

In such a photo-curable resin composition, the content of the epoxy resin mixture of the present invention is usually 1% by weight to 50% by weight and preferably 2% by weight to 30% by weight as an internal ratio.

Each component and the like in the photo-curable resin composition containing the epoxy resin mixture of the present invention will be more specifically explained below.

[0054]

Aqueous alkali-soluble resin (A); for example, reaction products of, with

polybasic acid anhydride, an epoxy carboxylate compound obtained by reaction of an epoxy compound having 2 or more epoxy groups in the molecule with a monocarboxylic acid compound having an ethylenically unsaturated group in the molecule, or the like, specifically including KAYARAD CCR-1159H, KAYARAD PCR-1169H, KAYARAD TCR-1310H, KAYARAD ZFR-1401H and KAYARAD ZAR-1395H (which are all manufactured by Nippon Kayaku Co., Ltd.), and the like.

[0055]

Cross-linking agent (B); compounds having an ethylenically unsaturated group, for example, acrylate, methacrylate compounds and the like, specifically including KAYARAD HX-220, KAYARAD HX-620, KAYARAD DPHA and KAYARAD DPCA-60 (which are all manufactured by Nippon Kayaku Co., Ltd.), and the like.

[0056]

Photopolymerization initiator (C); for example, benzoin, acetophenones, anthraquinones, thioxanthenes, ketals, benzophenones, phosphine oxides and the like, specifically including KAYACURE DETX-S (manufactured by Nippon Kayaku Co., Ltd.), IRGACURE 907 (Ciba Specialty Chemicals), and the like.

[0057]

Further according to necessity, various additives, for example, fillers such as talc, barium sulfate, aluminum hydroxide, aluminum oxide, silica and clay; thixotropy-imparting agents such as Aerosil; colorants such as phthalocyanine blue, phthalocyanine green and titanium oxide; silicone or fluorine-type leveling agents and antifoaming agents; polymerization inhibitors such as hydroquinone and hydroquinone monomethyl ether; and the like can be added for the purpose of improving various performances of the composition.

[0058]

The photo-curable resin composition can contain a solvent according to necessity. Usable solvents include, for example, ketones such as acetone, methyl ethyl ketone and cyclohexanone; aromatic carbon hydrides such as benzene, toluene, xylene and tetramethyl benzene; glycol ethers such as ethylene glycol dimethyl ether,

ethylene glycol diethyl ether, dipropylene glycol dimethyl ether, dipropylene glycol diethyl ether, triethylene glycol dimethyl ether and triethylene glycol diethyl ether; esters such as ethyl acetate, butyl acetate, methyl cellosolve acetate, ethyl cellosolve acetate, butyl cellosolve acetate, carbitol acetate, propylene glycol monomethyl ether acetate, glutaric acid dialkyl, succinic acid dialkyl and adipic acid dialkyl; cyclic esters such as gamma-butyrolactone; petroleum solvents such as petroleum ether, petroleum naphtha, hydrogenated petroleum naphtha and solvent naphtha; and the like, and these may be used alone or in combination of 2 or more kinds thereof.

[0059]

The photo-curable resin composition containing the epoxy resin mixture of the present invention is useful as an interlayer insulating material of electronic parts, as a solder resists for optical waveguide connecting optical components and for printed substrates, and as a resist material of cover lays and the like, and in addition it can be used as a color filter, a printing ink, a sealant, a paint, a coating agent and an adhesive.

[0060]

The photo-curable resin composition containing the epoxy resin mixture of the present invention can be cured by irradiation of energy ray such as ultraviolet ray and the like. Curing by irradiation of energy ray such as ultraviolet ray and the like can be carried out in a conventional manner. For example, when ultraviolet ray is irradiated, an ultraviolet ray-generating apparatus may be used, such as low pressure mercury lamp, high pressure mercury lamp, ultrahigh pressure mercury lamp, xenon lamp and ultraviolet ray-emitting laser (such as excimer laser).

[0061]

The photo-curable resin composition containing the epoxy resin mixture of the present invention is utilized for, for example, electric · electronic · optical base materials such as printed substrate, optoelectronic substrate and optical substrate, as a resist film, an interlayer insulating material for the build-up construction method and an optical waveguide. Specific products using these include, for example,

computers, household electric appliances, mobile devices and the like. Specifically, when a printed wiring board configuring a printed substrate is manufactured using a liquid resin composition for example, firstly a printed wiring board is coated with a photo-curable resin composition containing the epoxy resin of the present invention, in a film thickness of 5 to 160 μm by a method such as the screen printing method, the spray method, the roll coating method, the electrostatic coating method or the curtain coating method, and the coating film is dried at usually 50 to 110°C and preferably 60 to 100°C to form a coating film. After that, high energy rays such as ultraviolet ray and the like are directly or indirectly irradiated on the coating film at a strength of usually about 10 to 2000 mJ/cm^2 through a photomask where an exposure pattern such as negative film is formed, and the unexposed part is developed using the developer mentioned later by, for example, spraying, oscillating immersion, blushing, scrubbing or the like. After that, ultraviolet rays are further irradiated according to necessity, and subsequently heat treatment is carried out at a temperature of usually 100 to 200°C and preferably 140 to 180°C to obtain a printed wiring board having a permanent protective film which is excellent in gold plating properties and satisfies various properties such as heat resistance, solvent resistance, acid resistance, adhesion properties and flexibility.

[0062]

As the above-described developer, aqueous inorganic alkaline solutions such as potassium hydroxide, sodium hydroxide, sodium carbonate, potassium carbonate, sodium hydrogen carbonate, potassium hydrogen carbonate, sodium phosphate and potassium phosphate, and aqueous organic alkaline solutions such as tetramethyl ammonium hydroxide, tetraethyl ammonium hydroxide, tetrabutyl ammonium hydroxide, monoethanolamine, diethanolamine and triethanolamine can be used.

Examples

[0063]

Hereinafter, the present invention will be more specifically explained with

reference to Examples.

In this regard, the resin physical properties described below were measured by following method.

- Measurement of softening point: Measured by a method accordance with JIS K-7234.

- Measurement by GC-MS (gas chromatography-mass spectrometry):

Model: 5975 Inert MSD (manufactured by Agilent);

Column: HP-5 MS 15 m-0.25 mm-0.25 μ m;

Carrier gas: Helium 1.0 mL/min (constant flow mode);

Oven: 50°C (2 min)-10°C/min-300°C (23 min);

Injection: 1 μ l, Split (30:1), 300°C;

Ion source: EI.

- Measurement by SEM-EDS (scanning electron microscopy-energy disperse spectroscopy):

Model: JED-2140 (manufactured by JEOL);

Accelerating voltage: 20 kV;

Working distance: 10 mm.

- Measurement of number average molecular weight and weight average molecular weight by GPC (gel permeation chromatography):

Column: Shodex KF-801, KF-802, KF-802.5 and KF-803 manufactured by Showa Denko K.K.;

Column temperature: 40°C;

Injection volume: 0.02 mL;

Delivered volume of fluid: 1.0 mL/min;

Detector: RI;

Solvent: tetrahydrofuran.

- Measurement of viscosity: Measured at 150°C using an ICI viscometer (manufactured by K.K. Codix).

- Measurement of OH equivalent: Average mass number of compound per OH group,

measured by the acetylation method in accordance with JIS K-0070.

- Measurement of epoxy equivalent: Average mass number of compound per epoxy group, measured in accordance with JIS K-7236.

- DMA (dynamic mechanical analysis) analysis: Storage elastic modulus measured at T_g and 250°C using a frequency of 10 Hz by DMA 2980 (dynamic mechanical analysis machine) manufactured by TA Instruments.

[0064]

Example 1

(1) Chloromethylation reaction of biphenyl

To a glass-made 300 mL flask equipped with a stirrer, a thermometer and a cooler, 200 mL of cyclohexane, 77.05 g of biphenyl, 33.55 g of paraformaldehyde and 46.38 g of zinc chloride were added. While vigorously stirring them, hydrogen chloride gas was strongly blown therein and reacted until giving a homogeneous solution. Meanwhile, the liquid temperature was maintained at 50°C. Further, the liquid temperature was lowered by 30°C, hydrogen chloride gas was blown for 24 hours and the reaction was continued to obtain a reaction liquid.

A small amount of the obtained reaction liquid was taken out and measured as a dichloromethane solution by GC-MS. As a result, 2.5% of mono(chloromethyl)biphenyl, 72.0% of bis(chloromethyl) biphenyl, 14.9% of tri(chloromethyl)biphenyl and 5.8% of tetra(chloromethyl)biphenyl were detected. In addition, as other side products other than the above-described mono(chloromethyl)biphenyl, 0.3% of penta(chloromethyl)biphenyl, 0.5% of bisbiphenylylmethane and 1.1% of monochloromethyl-bisbiphenylylmethane and 0.6% of bis(chloromethyl)-bisbiphenylylmethane were detected. Further, as other side products including components whose compound cannot be identified, 2.3% (all by GC area %) was detected.

Furthermore, from insoluble matter generated when the reaction liquid was made into a dichloromethane solution for GC-MS measurement, zinc element (Zn) was detected by elemental analysis using SEM-EDS (Scanning Electron Microscopy /

Energy Dispersive Spectroscopy).

[0065]

(2) Reaction of chloromethylation reaction product with phenol

Subsequently, to the reaction liquid obtained in the above-described (1), 157.77 g of phenol was added, and the mixture was stirred at room temperature for 2 hours. After degassing of the reaction container was carried out, the temperature was raised to 180°C under reduced pressure over 10 hours, and cyclohexane as a solvent and unreacted phenol were distilled away.

As a result, 181.5 g of a phenol resin mixture of the present invention was obtained. Said resin mixture had a softening point of 74.9°C, a number average molecular weight of 513 and a weight average molecular weight of 639 as determined by GPC (gel permeation chromatography), and an OH equivalent of 215 g/eq.

The composition of said phenol resin mixture is estimated that the component from bischloromethyl biphenyl (the above F2-1) is 72%, the component from trichloromethyl biphenyl (the above F2-2) is 15%, the component from tetrachloromethyl biphenyl (the above F2-3) is 6% and other components (the above F2-4, F2-5, F2-6 and the like) is 7%, judging from the composition of the chloromethylation reaction product of biphenyl obtained in the above-described (1).

[0066]

Example 2

Synthesis of epoxy resin mixture

To a glass-made 300 mL flask equipped with a stirrer, a thermometer and a cooler, 26.3 g of the phenol resin mixture of the present invention obtained in Example 1, 52.0 g of epichlorohydrin, 8.6 g of dimethylsulfoxide and 12.3 g of a 30 wt.% aqueous sodium hydroxide solution were placed, and they were mixed by stirring at 45°C for 1 hour. Subsequently, 3.95 g of flake sodium hydroxide were added thereto in divided addition, and the mixture was stirred at 45°C for 2 hours and at 70°C for 1 hour. To the resulting reaction liquid, methylisobutylketone was added for dilution, and then water was added to carry out water-washing by liquid-liquid

separation. To the obtained organic layer, 0.93 g of a 30 wt.% aqueous sodium hydroxide solution were added, and the mixture was stirred at 70°C for 1 hour. Likewise described above, water-washing by liquid-liquid separation was carried out again. The resulting reaction liquid was condensed to obtain 20.5 g of an epoxy resin mixture of the present invention.

The obtained resin mixture had a softening point of 57.6°C, an ICI viscosity of 0.11 Pa·s, an epoxy equivalent of 292 g/eq, and a number average molecular weight of 668 and a weight average molecular weight of 1187 as determined by GPC (gel permeation chromatography).

The composition of said epoxy resin mixture is estimated that the component from bischloromethyl biphenyl (F3-1) is 72%, the component from trichloromethyl biphenyl (F3-2) is 15%, the component from tetrachloromethyl biphenyl (F3-3) is 6% and other components (F3-4, F3-5, F3-6 and the like) is 7%, judging from the composition of the chloromethylation reaction product of biphenyl obtained in the above-described (1).

[0067]

Example 3 and Comparative Example 1

Preparation of flame retardant resin composition and evaluation of cured product thereof

Using the epoxy resin mixture of the present invention obtained in Example 2 or phenol-biphenyl aralkyl-based epoxy resin NC-3000 (having a softening point of 57.4°C, an ICI viscosity of 0.08 Pa·s, an epoxy equivalent of 277 g/eq, and a number average molecular weight of 793 and a weight average molecular weight of 1229 as determined by GPC) manufactured by Nippon Kayaku Co., Ltd. as Comparative Example, a flame retardant resin composition having the composition shown in Table 1 described below was prepared and molded at 175°C by a transfer molding machine to obtain a cured product.

[0068]

Table 1

	Example 3	Comparative Example 1
Epoxy resin	(Epoxy resin mixture of Example 2)	(NC-3000)
	6.17 g	6.17 g
Curing agent (XLC-3L)	3.6 g	3.8 g
Curing catalyst (TPP)	0.105 g	0.105 g
Filler (MSR-2212)	50.2 g	51.2 g
Lubricant (Carnauba 1)	0.18 g	0.19 g
Coupling agent (KBM-303)	0.20 g	0.20 g

[0069]

Note:

XLC-3L: Phenolic aralkyl resin, manufactured by Mitsui Chemical, Inc.;

TPP: Triphenylphosphine;

MSR-2212: KYKLOS MSR-2212, manufactured by Tatsumori Ltd.;

Carnauba 1: Carnauba wax 1, manufactured by Cerarica Noda;

KBM-303: Silane coupling agent, manufactured by Shin-Etsu Chemical Co., Ltd.

[0070]

With regard to the thus obtained cured product, evaluation results of flame retardancy and storage elastic modulus at 250°C based on the method shown below are shown in Table 2.

· Measurement of flame retardancy: In accordance with UL-94, the total burning time (the time to self-extinguish) of test piece (cured product) having a thickness of 0.8 mm was measured in flame retardancy test.

· Measurement of storage elastic modulus at 250°C: Using DMA 2980 (dynamic mechanical analysis machine) manufactured by TA Instruments, the storage elastic modulus at T_g and 250°C was measured with a frequency of 10 Hz.

[0071]

Table 2

	Example 3	Comparative Example 1
Total burning time (sec)	32 (V-0)	35 (V-0)

Storage elastic modulus (MPa, 250°C)	933	2218
Tg (glass transition temperature: °C)	136	146

[0072]

It is found that the epoxy resin composition containing the epoxy resin mixture of the present invention has flame retardancy equal or better than NC-3000 generally used as an excellent flame retardancy resin and thus is excellent in flame retardancy, and in addition, its storage elastic modulus at a high temperature of 250°C higher than the glass transition temperature is within the range of 500 to 1000 MPa considered to be preferable for solder cracking resistance, compared with the value 2000 MPa or more of NC-3000, whereby it has also excellent properties in terms of that.

The epoxy resin mixture of the present invention has excellent properties as described above, and in addition, allows consecutive production from biphenyl and easy production.

[0073]

Example 4

(1) Chloromethylation reaction of biphenyl

To a glass-made 1000 mL flask equipped with a stirrer, a thermometer and a cooler, 200 mL of cyclohexane, 154 g of biphenyl, 66 g of paraformaldehyde and 93 g of zinc chloride were added. While stirring them, hydrogen chloride gas was strongly blown therein and reacted until giving a homogeneous solution. Meanwhile, the liquid temperature was maintained at 30°C. After that, hydrogen chloride gas was further blown at 50°C for 10 hours and the reaction was continued to obtain a reaction liquid.

A part of the reaction liquid was taken out and measured as an N,N'-dimethylformamide solution by LC, resulting in that 8.1% of monochloromethyl biphenyl, 68.2% of bischloromethyl biphenyl and 18.2% of tri(chloromethyl)biphenyl and tetra(chloromethyl)biphenyl together were detected (LC area %).

(2) Reaction of chloromethylation reaction product with phenol

Subsequently, to the reaction liquid obtained in the above-described (1), 301 g of phenol was added, and the mixture was stirred at 70°C for 2 hours. While raising the temperature to 180°C under reduced pressure, cyclohexane as a solvent and unreacted phenol were distilled away.

As a result, 329 g of a phenol resin mixture of the present invention were obtained.

Said resin mixture had a softening point of 79.6°C, a number average molecular weight of 855 and a weight average molecular weight of 1332 as determined by GPC (gel permeation chromatography), and an OH equivalent of 196 g/eq.

The composition of said phenol resin mixture is estimated that 8% of monochloromethyl biphenyl, 68% of the component from bischloromethyl biphenyl (F2-1), 18% of the component from tri(chloromethyl)biphenyl (F2-2) and the component from tetra(chloromethyl)biphenyl (F2-3 and the like) together are contained, judging from the composition of the chloromethylation reaction product obtained in the above-described (1).

[0074]

Example 5

Synthesis of epoxy resin mixture

To a glass-made 1000 mL flask equipped with a stirrer, a thermometer and a cooler, 196 g of the phenol resin mixture of the present invention obtained in Example 4, 555 g of epichlorohydrin and 29.6 g of methanol were placed, and the mixture was stirred. While stirring said mixture at 70°C, 42 g of flake sodium hydroxide were added in some portions. After that, the mixture was further stirred at 70°C for 1 hour. To the resulting reaction liquid, 150 g of water were added and mixed, and then the mixture was left to stand still, followed by removing the aqueous layer which was a lower layer of the two separated layers. After washing with water, unreacted epichlorohydrin was distilled away from the reaction liquid. Methylisobutylketone was added thereto for dilution, subsequently 13.3 g of a 30 wt.% aqueous sodium hydroxide solution was added, and the mixture was stirred at 70°C for 1 hour. Water

was added thereto to carry out water-washing by liquid-liquid separation. The reaction liquid after said water-washing was condensed to obtain 215 g of an epoxy resin mixture of the present invention.

Said epoxy mixture had a softening point of 56.5°C, an ICI viscosity of 0.11 Pa·s, an epoxy equivalent of 264 g/eq, and a number average molecular weight of 803 and a weight average molecular weight of 1419 as determined by GPC (gel permeation chromatography).

The composition of said epoxy resin mixture is estimated that 8% of the component from monochloromethyl biphenyl, 68% of the component from bischloromethyl biphenyl (structural formula: F3-1 and the like), and 18% of the component from tri(chloromethyl)biphenyl (structural formula: F3-2 and the like) and the component from tetra(chloromethyl)biphenyl (structural formula: F3-3 and the like) together are contained, judging from the composition of the chloromethylation reaction product obtained in the above-described Example 4 (1).

[0075]

Example 6

In the same manner as in Example 3, an epoxy resin mixture of the present invention obtained in Example 5 was prepared into a flame retardant resin composition having the composition shown in Table 3 described below, and molded by a transfer molding machine to obtain a cured product.

[0076]

Table 3

Example 6	
Epoxy resin	(Epoxy resin mixture in Example 5)
	12g
Curing agent (XLC-3L)	7.7g
Curing catalyst (TPP)	0.204g
Filler (MSR-2212)	100.8g
Lubricant (Carnauba 1)	0.36g

Coupling agent (KBM-303) 0.40g

[0077]

With regard to the obtained cured product, the flame retardancy and the storage elastic modulus were measured in the same manner as shown in Example 3. The results are shown in Table 4.

[0078]

Table 4

	Example 6
Total burning time (sec)	35 (V-0)
Storage elastic modulus (MPa, 250°C)	608
Tg (°C)	145

[0079]

Example 7

In 1000 ml of methylisobutylketone, 500g of the phenol resin mixture of the present invention obtained in the same manner as in Example 4 were dissolved, insoluble matter was filtered, and then water was added thereto to carry out water-washing by liquid-liquid separation. As a result, a phenol resin mixture (referred to as EX 7 Phnol Mix) having a hydroxy group (OH) equivalent of 204 g/eq was obtained.

Using the obtained phenol resin mixture as a curing agent and using the above phenol-biphenyl aralkyl-based epoxy resin NC-3000 manufactured by Nippon Kayaku Co., Ltd. as an epoxy resin, an epoxy resin composition of the present invention having the composition shown Table 5 described below was prepared, and molded by a transfer molding machine to obtained a cured product.

[0080]

Table 5

	Example 7
Epoxy resin (NC-3000)	18g
Curing agent (EX 7 Phnol Mix)	13.3g

Curing catalyst (TPP)	0.45g
Filler (MSR-2212)	160.8g
Lubricant (carnauba 1)	0.58g
Coupling agent (KBM-303)	0.64g

[0081]

With regard to the obtained cured product, the flame retardancy and the storage elastic modulus were measured in the same manner as shown in Example 3. The results are shown in Table 6 described below.

[0082]

Table 6

	Example 7
Total burning time (sec)	27
Storage elastic modulus (250°C) (MPa)	449
Tg (°C)	147

[0083]

Example 8 and Comparative Example 2

Using the phenol resin mixture of the present invention (EX 7 Phnol Mix) obtained in Example 7 as a curing agent and using the above phenol-biphenyl aralkyl-based epoxy resin NC-3000 manufactured by Nippon Kayaku Co., Ltd. as an epoxy resin, an epoxy resin composition of the present invention (EX 8 EPOXY COM) having the composition shown in Table 7 below was prepared.

On the other hand, as Comparative Example 2, using phenol-biphenyl aralkyl-based phenol resin GPH-65 (having an OH equivalent of 199 g/eq and a softening point of 65.1°C) manufactured by Nippon Kayaku Co., Ltd. instead of the phenol resin mixture of the present invention (EX 7 Phnol Mix), as a curing agent, an epoxy resin composition for comparison (Comparative Example 2) (CPA 2 EPOXY COM) shown in Table 7 described below was prepared.

The epoxy resin compositions prepared above were rolled and kneaded to give epoxy resin compositions for evaluation.

[0084]

Table 7

	EX 8 EPOXY COM	CPA 2 EPOXY COM
Epoxy resin (NC-3000)	15g	15g
Curing agent EX 7 Phnol Mix	11g	-
GPH-65	-	10.8g
Curing catalyst (TPP)	0.315g	0.405g
Filler (MSR-2212)	156g	155g
Lubricant (Carnauba 1)	0.55g	0.55g
Coupling agent (KBM-303)	0.62g	0.62g

[0085]

For evaluation of curing properties of each epoxy resin composition obtained as described above, the maximum value of torque was measured by a curelasterometer manufactured by JSR Corporation.

In addition, for evaluation of flowability, the spiral flow was measured under the conditions of 175°C and a molding pressure of 70 kg/cm² (in accordance with ASTM F3133). The results are shown in Table 8.

[0086]

Table 8

	EX 8 EPOXY COM	CPA 2 EPOXY COM
Curelast torque (N·m)	10.5	9.3
Spiral flow (inch, n = 5)	33.5	30.7
Gel time (sec)	29.4	29.6

[0087]

The larger curelast torque as an index of curing properties means stronger curing, whereby it is shown that the epoxy resin composition of Example 8 has more excellent curing properties than the epoxy resin composition of Comparative Example 2.

In addition, in epoxy resin compositions with the same gel time, a longer spiral

flow as an index of flowability means higher flowability, whereby it is shown that the epoxy resin composition of Example 8 has more excellent flowability compared with the epoxy resin composition of Comparative Example 2.

Industrial Applicability

[0088]

The cured product of the epoxy resin composition containing the epoxy resin mixture of the present invention is excellent not only in flame retardancy but also in solder cracking resistance because the storage elastic modulus thereof at 250°C is lower within a certain range than conventional flame retardant epoxy resin cured products, and the epoxy resin mixture of the present invention and the epoxy resin composition containing it are suitable as electric·electronic materials in and around semiconductor, such as semiconductor sealing material and printed wiring substrate.

In addition, the phenol resin mixture of the present invention is an intermediate material for the epoxy resin mixture of the present invention having excellent properties described above, and it can be produced without isolation and purification of halomethyl biphenyl as an intermediate, whereby it allows easy production and has high industrial usability.

Claims

1. A phenol resin mixture obtained by methylene cross-linking reaction of a reaction product which is obtained by halomethylation reaction of biphenyl and contains 60% or more and less than 80% of bis(halomethyl) biphenyl and 15 to 30% of the total of tri(halomethyl)biphenyl and tetra(halomethyl)biphenyl, as the ratio relative to the whole reaction product as determined by GC-MS (GC area ratio), and contains side products other than those above as the rest, with phenol.
2. The phenol resin mixture according to Claim 1, wherein the softening point is 65 to 85°C, the number average molecular weight is 350 to 1200 and the weight average molecular weight is 400 to 2000 as determined by GPC (gel permeation chromatography), and the OH equivalent is 160 to 250 g/eq.
3. An epoxy resin mixture obtained by epoxidation of the phenol resin mixture according to Claim 1 or 2.
4. The epoxy resin mixture according to Claim 3, wherein the softening point is 50 to 75°C, the ICI viscosity is 0.02 to 0.50 Pa·s, the number average molecular weight is 400 to 1200 and the weight average molecular weight is 800 to 2000 as determined by GPC (gel permeation chromatography), and the epoxy equivalent is 200 to 360 g/eq.
5. An epoxy resin composition containing the epoxy resin mixture according to Claim 3 and a curing agent.
6. The epoxy resin composition according to Claim 5, wherein the content of the curing agent is 0.7 equivalent to 1.2 equivalents relative to 1 equivalent of the epoxy group in the epoxy resin mixture.
7. The epoxy resin composition according to Claim 6, which further contains 50 to 90% by weight of a filler relative to the total amount of the epoxy resin composition.
8. A cured product obtained by curing an epoxy resin composition containing an epoxy resin mixture obtained by epoxidation of the phenol resin mixture according to Claim 1 and a curing agent in 0.7 equivalent to 1.2 equivalents relative to 1 equivalent of the epoxy group in said epoxy resin mixture.

9. A cured product obtained by curing an epoxy resin composition containing an epoxy resin mixture obtained by epoxidation of the phenol resin mixture according to Claim 1, a curing agent in 0.7 equivalent to 1.2 equivalents relative to 1 equivalent of the epoxy group in said epoxy resin mixture, and an inorganic filler in 50 to 90% by weight relative to the total amount of the epoxy resin composition.
10. A method for producing a phenol resin mixture, characterized in that halomethylation of biphenyl is carried out by reacting biphenyl, 2 to 8 equivalents of a formaldehyde relative to 1 mol of biphenyl, and a hydrogen halide in the presence of zinc halide and an excessive amount of hydrogen halide to obtain a reaction product containing 60% or more and less than 80% of bis(halomethyl) biphenyl and 15 to 30% of the total of tri(halomethyl)biphenyl and tetra(halomethyl)biphenyl, as the ratio relative to the whole reaction product as determined by GC-MS (GC area ratio), and containing side products other than those above as the rest, and said reaction product is reacted with phenol without purification.
11. A method for producing an epoxy resin mixture, characterized in that a phenol resin mixture obtained by the method for production according to Claim 10 is reacted with 0.8 to 12 equivalents of epihalohydrin relative to 1 equivalent of the hydroxy group in said phenol resin mixture.
12. An epoxy resin composition containing the phenol resin mixture according to Claim 1 or 2 as a curing agent.