

TITLE OF THE INVENTION

PHOSPHORUS-CONTAINING EPOXY RESIN, COMPOSITION
CONTAINING THE PHOSPHORUS-CONTAINING EPOXY RESIN
AS AN ESSENTIAL COMPONENT, AND CURED PRODUCT

DESCRIPTION

FIELD OF THE INVENTION

The present invention relates to a halogen free flame retardant epoxy resin containing phosphorus atom in molecular frame thereof and an epoxy resin composition containing said epoxy resin as an essential component, further relates to an epoxy resin cured product obtained by curing said epoxy resin composition. And the present invention provides an epoxy resin suited to a prepreg used for an electronic circuit board, film materials used for a copper-clad laminate or electronic parts, a sealing material, a molding material, a potting material, an adhesive, an electric insulation material, a composite material which needs flame retardation or a powder coating.

DESCRIPTION OF THE PRIOR ART

Usually, flame retardant processing of epoxy resin is performed by halogenation as represented by a brominated epoxy resin which is produced from tetrabromo-bisphenol A as a starting material. However, when a halogenated epoxy resin is used, a problem of generation of strong harmful halide caused by thermal decomposition when cured product of the composition is burned. To dissolve said problem, in recent years, halogen free flame retardant techniques using phosphorus compound are studied, and phosphorus-containing epoxy resins or phosphorus-containing phenolic resins disclosed in Patent Document 1 to Patent Document 7 are proposed.

Although the phosphorus-containing epoxy resins disclosed in Patent Document 1 and Patent Document 2 display high adhering feature, heat resistance represented by glass transition point is not sufficient. And, regarding the phosphorus-containing epoxy resin disclosed in Patent Document 3, glass transition point is improved, however, adhering feature is not sufficient. Further, the phosphorus-containing epoxy resin disclosed in Patent Document 4 is attempting to improve both adhering feature and

heat resistance by use of quinone compound. Furthermore, in Patent Document 5, further improvement of both adhering feature and heat resistance is attempted by together use of specific bifunctional epoxy resin, and regarding the phosphorus-containing epoxy resin disclosed in Patent Document 6, improvement of both adhering feature and heat resistance is discussed. However, regarding glass transition point, further excellent requirement for improvement is arising, that is, improvement of glass transition point maintaining high adhering feature becomes to be required.

In a case of the phosphorus-containing epoxy resin obtained by flame retardant means using phosphorous compound, it is difficult to improve to have both high heat resistance and excellent adhering feature, that is, when poly functionalization is carried out to improve heat resistance, adhering future is deteriorated, and when bifunctionalization of phosphorus compound is carried out to improve adhering feature, heat resistance is deteriorated. To dissolve this problem, in Patent Document 5, further improvement of heat resistance and adhering feature by use of specific bifunctional epoxy resin in limits of from 20% to 45% is proposed.

PRIOR TECHNICAL DOCUMENTS

PATENT DOCUMENTS

- Patent Document 1: JP H04-11662 publication
- Patent Document 2: JP 2000-309623 publication
- Patent Document 3: JP H11-166035 publication
- Patent Document 4: JP H11-279258 publication
- Patent Document 5: JP No.4588834
- Patent Document 6: JP 2001-123049 publication
- Patent Document 7: JP 2003-040969 publication

BRIEF SUMMARY OF THE INVENTION

SUBJECT OF THE INVENTION

Recently, in a case of electronic circuit board or in other cases, for the purpose to endure rising of solder reflowing temperature or to maintain long term reliability, further improvement of heat resistance, especially, glass transition point is required. The subject of the present invention is to provide an epoxy resin maintaining high adhering feature, while heat resistance is further improved.

BRIEF ILLUSTRATION OF THE INVENTION

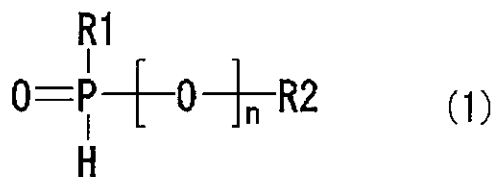
To dissolve above mentioned subject, the inventors of the present invention have found that among epoxy resins, a phosphorus-containing epoxy resin obtained by use of novolac epoxy resins having specific molecular weight distribution, phosphorus compound and quinone compound can improve heat resistance while maintaining high adhering feature, and accomplished the present invention.

That is, the essential points of the present invention are,

(1) A phosphorus-containing epoxy resin (A) which is obtained by reacting a phosphorus compound represented by general formula (1), a quinone compound and an epoxy resin (a) as essential components, and which is characterized in that the epoxy resin (a) is a novolac epoxy resin that has a molecular weight distribution having a dinuclear component content of 15 area % or less, trinuclear content of 15-60 area %, and a number average molecular weight of 350-700 as determined by gel permeation chromatography.

(Measuring condition of gel permeation chromatography)

TSKgel G4000HXL, TAKgel G3000HXL and TSKgel 2000HXL (all are the products of Toso Co., Ltd.) are placed in series, column temperature is set up to 40°C. Tetrahydrofuran (THF) is used as an eluate, flowing rate is set up to 1ml/min, and RI (differential refractometer) is used as a detector. 0.1g of specimen is dissolved in 10ml of THF, thus a sample solution is prepared. From obtained chromatogram, containing ratio of dinuclear component and trinuclear component are calculated and a number average molecular weight is measured from calibration curve prepared by using standard polystyrene.



(in the formula, R1 and R2 represents hydrocarbon group and can be same or can be different, further, R1 and R2 can be cyclic structure with phosphorus atom. n is 0 or 1)

(2) A phosphorus-containing epoxy resin composition comprising the phosphorus-containing epoxy resin (A) described in above mentioned (1) and a curing agent, as essential components, wherein active group of the

curing agent is 0.3-1.5 equivalent weight per 1 equivalent weight of epoxy group of the phosphorus-containing epoxy resin (A),

(3) An epoxy resin cured product obtained by curing of the phosphorus-containing epoxy resin composition of (2),

(4) A prepreg prepared by impregnating the phosphorus-containing epoxy resin composition of (2) into a substrate,

(5) A laminated board prepared by curing the phosphorus-containing epoxy resin composition of (2),

(6) An electronic printed circuit board prepared by curing the phosphorus-containing epoxy resin composition of (2).

EFFECT OF THE INVENTION

The present invention is a phosphorus-containing epoxy resin obtained by reacting novolac epoxy resins having specific molecular weight distribution, phosphorus compound and quinone compound as essential components. And, by use of novolac epoxy resins having specific molecular weight distribution, the phosphorus-containing epoxy resin showing excellent physical properties as cured product i.e. high glass transition point maintaining high adhering feature can be obtained. Further, since viscosity of the epoxy resin is low, working efficiency and impregnation into substrate are excellent, further flame retardation is also good.

BRIEF ILLUSTRATION OF DRAWINGS

Fig.1 is a chart of gel permeation chromatography (GPC) of YDPN-638 which is conventional phenol novolac epoxy resins. Abscissa indicates elution time and left ordinate indicates signal intensity. Right ordinate indicates number average molecular weight M by logarithm. Measured values of number average molecular weight of used standard reference material are plotted by black points and used as calibration curve. Peak indicated by A is dinuclear and peak indicated by B is trinuclear.

Fig.2 is GPC chart of novolac epoxy resins of Synthesis Example 2. Peak indicated by A is dinuclear and peak indicated by B is trinuclear.

PREFERRED EMBODIMENT OF THE INVENTION

Detail of the invention is illustrated below.

Epoxy resin (a) used in the present invention is a reacted product of

phenols with aldehydes, and is polyfunctional novolac epoxy resins obtained by reaction of novolac resin having specific molecular weight distribution with epihalohydrin. As phenols to be used, phenol, cresol, ethyl phenol, butyl phenol, styrenated phenol, cumyl phenol, naphthol, catechol, resorcinol, naphthalene diol or bisphenol A can be mentioned, and as aldehydes, formalin, formaldehyde, hydroxybenzaldehyde or salicyl aldehyde can be mentioned. Further, in the present invention, aralkyl phenol resins which use xylilene dimethanol, xylilene dichloride, bischloromethyl naphthalene or bischloromethylbiphenyl instead of aldehydes, are involved in novolac resins. Novolac epoxy resins can be obtained by epoxydation of above mentioned novolac resin with epihalohydrin.

As definite examples of conventional novolac epoxy resin, Epotohto YDPN-638 (product of Nippon Steel Chemical Co., Ltd.; phenol novolac epoxy resins), Epicoat 152, Epicoat 154 (product of Mitsubishi Chemical Co., Ltd.; phenol novolac epoxy resins), Epiclone N-740, Epiclone N-770, Epiclone N-775 (product of DIC Co., Ltd.; phenol novolac epoxy resins), Epotohto YDCN-700 series (product of Nippon Steel Chemical Co., Ltd.; cresol novolac epoxy resins), Epiclone N-660, Epiclone N-665, Epiclone N-670, Epiclone N-673, Epiclone N-695 (product of DIC Co., Ltd.; cresol novolac epoxy resins), EOCN-1020, EOCN-102S, EOCN-104S (product of Nippon Kayaku Co., Ltd.; cresol novolac epoxy resins), Epotohto ZX-1071T, ZX-1270, ZX-1342 (product of Nippon Steel Chemical Co., Ltd.; alkyl novolac epoxy resins), Epotohto ZX-1247, GK-5855 (product of Nippon Steel Chemical Co., Ltd.; styrenated phenol novolac epoxy resin), Epotohto ZX-1142L (product of Nippon Steel Chemical Co., Ltd.; naphthol novolac epoxy resins), ESN-155, ESN-185V, ESN-175 (product of Nippon Steel Chemical Co., Ltd.; β naphthol aralkyl epoxy resin), ESN-355 and ESN-375 in ESN-300 series (product of Nippon Steel Chemical Co., Ltd.; dinaphthol aralkyl epoxy resin), ESN-475V and ESN-485 in ESN-400 series (product of Nippon Steel Chemical Co., Ltd.; α naphthol aralkyl epoxy resin) or bisphenol novolac epoxy resins can be mentioned, however, these epoxy resins do not have specific molecular weight distribution prescribed in the present invention.

To obtain the epoxy resin (a) which has specific molecular weight distribution of the present invention, it is necessary to regulate molar ratio

of phenols and aldehydes, and to remove lower molecular weight components from obtained novolac resin. Further, the epoxy resin (a) can be obtained by epoxydation of epoxy resin prepared by methods disclosed in Patent Document 8 or Patent Document 9.

Patent Document 8: JP 2002-194041 publication

Patent Document 9: JP 2007-126683 publication

Molar ratio of phenols and aldehydes is indicated by molar ratio of phenols to 1 mol of aldehydes, and the epoxy resin (a) is produced by 1 molar ratio or. And when said molar ratio is high, large amount of dinuclear and trinuclear are foamed, and when the molar ratio is low, large amount of higher molecular weight product is formed and formation of dinuclear and trinuclear becomes small.

As a method to obtain the epoxy resin (a) which has specific molecular weight distribution of the present invention, a method to remove dinuclear from obtained novolac resins by use of solubility difference of various solvents or a method to remove dinuclear by dissolving in alkali aqueous solution can be mentioned. Further, other public known separation methods can be used.

A novolac epoxy resins can be obtained by treating novolac resin whose molecular weight is controlled by public known epoxidation method. Or, an epoxy resin having specific molecular weight distribution can be obtained by removing dinuclear component from novolac epoxy resins being on the market. Further, other public known separation methods can be used too.

Dinuclear containing ratio of the epoxy resin (a) which has specific molecular weight distribution of the present invention is desirably 15 area % or less, and more desirably from 5 area % to 12 area %. By containing small amount of dinuclear, physical property such as adhering feature can be improved. Trinuclear containing ratio of the epoxy resin (a) is desirably from 15 area % to 60 area % and more desirably to be from 20 area % to 50 area %. When trinuclear containing ratio is less than 15 area %, heat resistance deteriorates, and when is more than 60 area %, adhering feature deteriorates. Further, regarding containing ratio of tetranuclear, pentanuclear or more, there is no intention to restrict, however, desirably total containing ratio of trinuclear and tetranuclear is to be from 30 area % to 70 area %. When total containing ratio of trinuclear

and tetranuclear is within the range of from 30 area % to 70 area %, flame retardation can be further improved. Containing ratio of pentanuclear or more is desirably to be 45 area % or less and more desirably 40 area % or less. When the containing ratio of pentanuclear or more is 45 area % or less, a cured product having more strong adhering feature can be obtained. Number average molecular weight of the epoxy resin (a) is desirably to be from 350 to 700, more desirably to be from 380 to 600. When number average molecular weight exceeds 700, viscosity of obtained phosphorus-containing epoxy resin (A) becomes high, accordingly have apprehension to affect working efficiency and impregnation feature into substrate. The reason why the flame retardation of the phosphorus-containing epoxy resin (A) obtained by these condition is improved, can be explained as follows. That is, since elastic modulus of the obtained cured product becomes low, char which is generated at burning becomes more firm, and bring higher adiabatic effect. But this theory is not verified yet.

As the phosphorus compound represented by general formula (1) of the present invention, concretely, dimethylphosphine, diethylphosphine, diphenylphosphine, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (HCA; product of Sanko Co., Ltd.), dimethylphosphineoxide, diethylphosphineoxide, dibutylphosphineoxide, diphenylphosphineoxide, 1,4-cyclooctylenephosphineoxide, 1,5-cyclooctylenephosphineoxide (CPHO; product of Nippon Chemical Industrial Co., Ltd.) or others can be mentioned. These phosphorus compounds can be used by alone or by mixing together with, further not intending to be restricted to above mentioned compounds.

As an example of quinone compound in this invention, benzoquinone, naphthoquinone, toluquinone, anthraquinone and isomers thereof or compound having substitution group of hydrocarbon group can be mentioned. These compounds can be used by alone or by mixing together with, and not intending to be restricted to above mentioned compounds. Desirable molar ratio of phosphorus compound represented by general formula (1) and quinone compound is "phosphorus compound : quinone compound = 1:1 or less", more desirable ratio is 1:0.99-0.2, furthermore desirable ratio is 1:0.98-0.40. When quinone compound become excess, since it remains in the phosphorus-containing epoxy resin (A), problem of

deterioration of physical feature maybe caused, and when the molar ratio is smaller than 0.2, there is apprehension to affect heat resistance and flame retardation. And, after reaction of phosphorus compound and quinone compound, only reacted component obtained by purification can be used.

The phosphorus-containing epoxy resin (A) of the present invention can be obtained by reacting phosphorus compound represented by general formula (1), quinone compound and epoxy resin (a) as essential components, and other public known and conventional epoxy resins or denaturants can be used within the range not to affect the effects of the present invention.

Reaction of phosphorus compound represented by general formula (1), quinone compound and epoxy resin (a) having specific molecular weight distribution can be carried out according to public known methods. As a concrete method, a method to further react with epoxy resin (a) after phosphorus compound is reacted with quinone compound or a method to obtain a reacted product of phosphorus compound and quinone compound in advance then react with epoxy resin (a) can be mentioned, and in the present invention, order of reaction arrangement is not restricted.

Regarding reaction temperature, the temperature of 100-250°C which is conventionally used in indirect synthesis of epoxy resin can be adopted, desirable temperature 120-200°C.

Actually, for the purpose to shorten reaction time and to bring reaction temperature down, a catalyst can be used. Regarding a catalyst, there is no restriction, and any catalyst used in indirect synthesis of epoxy resin can be adopted. For example, various catalysts, e.g., tertiary amines such as benzyldimethylamine, quaternary ammonium salts such as tetramethyl-ammoniumchloride, triphenylphosphine, phosphines such as tris(2,6-dimethoxyphenyl) phosphine, phosphonium salts such as ethyltriphenylphosphoniumbromide, imidazoles such as 2methylimidazole or 2ethyl-4methylimidazole can be used. These catalysts can be used by alone or by mixing together with, and not intending to be restricted to above mentioned compounds. Further, these catalysts can be used by divided to plural times.

Amount of volume of catalyst is not restricted, however, desirably is 5 mass % or less to total weight of epoxy resin (a) and other public known conventional epoxy resins which can be used together with, more desirably 1 mass % or less, further desirably 0.5 mass % or less. When the amount of

catalyst is too much, sometimes self polymerization reaction of epoxy group progresses and viscosity of resin becomes high, therefore, too much amount of catalyst is not desirable.

At the actual reaction of phosphorus compound represented by general formula (1), quinone compound and epoxy resin (a) having specific molecular weight distribution, various epoxy resin denaturants can be used within the range not to affect the effects of the present invention. As a denaturant, various phenols such as bisphenol A, bisphenol F, bisphenol AD, tetrabutylbisphenol A, hydroquinone, methylhydroquinone, dimethyl hydroquinone, dibutylhydroquinone, resorcin, methylresorcin, biphenol, tetramethylbiphenol, dihydroxynaphtalene, dihydroxydiphenylether, hydroxystilbenes, phenol novolac resin, cresol novolac resin, bisphenol A novolac resin, dicyclopentadienephenol resin, phenolalkyl resin, naphthol novolac resin, terphenephenol resin, heavy oil denatured phenol resin or brominated phenol novolac resin, poly valent phenol resins obtainable by condensation reaction of various phenols and various aldehydes such as hydroxybenzaldehyde, crotonaldehyde or glyoxal or amine compounds such as aniline, phenylenediamine, toluidine, xylylene, diethyltoluenediamine, diaminodiphenylmethane, diaminodiphenylethane, diaminodiphenylpropane, diaminodiphenylketone, diaminodiphenylsulfide, diaminodiethylsulfone bis (aminophenyl)fluorine, diaminodiethyldimethyldiphenylmethane, diamino-diphenylether, diaminobenzanilide, diaminobiphenyl, dimethyldiamino-biphenyl, biphenyltetraamine, bisaminophenylanthracene, bisaminophenoxybenzene, bisaminophenoxyphenylether, bisaminophenoxybiphenyl, bisaminophenoxyphenylsulfone, bisaminophenoxyphenylpropane or diaminonaphthalene can be mentioned, however, not restricted to these compounds and these compounds can be used together with.

At the reaction of phosphorus compound represented by general formula (1), quinone compound and epoxy resin (a) having specific molecular weight distribution, other various epoxy resins can be used together with at need within the range not to affect the effects of the present invention. As epoxy resins possible to be used together with, following epoxy resins can be mentioned concretely. That is, an epoxy resin prepared by reaction of phenol compound e.g. polyvalent phenol resin such as Epotohto YDC-1312, ZX-1027 (product of Nippon Steel Chemical Co., Ltd.; hydroquinone epoxy resin), YX-4000 (product of Mitsubishi Chemical

Co., Ltd.), ZX-1251 (product of Nippon Steel Chemical Co., Ltd.; biphenol epoxy resin), Epotohto YD-127, Epotohto YD-128, Epotohto YD-8125, Epotohto YD-825GS, Epotohto YD-011, Epotohto YD-900, Epotohto YD-901 (product of Nippon Steel Chemical Co., Ltd.; BPA epoxy resin), Epotohto YDF-170, Epotohto YDF-8170, Epotohto YDF-870GS, Epotohto YDF-2001 (product of Nippon Steel Chemical Co., Ltd.; BPF epoxy resin), Epotohto YDPN-638 (product of Nippon Steel Chemical Co., Ltd. phenol novolac epoxy resin), Epotohto YDCN-701 (product of Nippon Steel Chemical Co., Ltd.; cresol novolac epoxy resin), ZX-1201 (product of Nippon Steel Chemical Co., Ltd.; bisphenol fluorine novolac epoxy resin), NC-3000 (product of Nippon Kayaku Co., Ltd.; biphenol aralkyl phenol epoxy resin), EPPN-501H, EPPN-502H (product of Nippon Kayaku Co., Ltd.; polyfunctional epoxy resin), ZX-1355 (product of Nippon Steel Chemical Co., Ltd.; naphthalene diol epoxy resin), ESN-155, ESN-185V, ESN-175 (product of Nippon Steel Chemical Co., Ltd.; β -naphthol aralkyl epoxy resin), ESN-355, ESN-375 (product of Nippon Steel Chemical Co., Ltd.; dinaphthol aralkyl epoxy resin), ESN-475V, ESN-485 (product of Nippon Steel Chemical Co., Ltd.; α -naphthol aralkyl epoxy resin) with epihalohydrin, an epoxy resin prepared by reaction of amine compound such as Epotohto YH-434, Epotohto YH-434GS (product of Nippon Steel Chemical Co., Ltd.; diamino diphenylmethantetraglycidylether) with epihalohydrin or an epoxy resin prepared by reaction of carboxylic acid such as YD-171 (product of Nippon Steel Chemical Co., Ltd.; dimeric acid epoxy resin) with epihalohydrin can be mentioned, however, not intending to restrict to these epoxy resins, and these epoxy resins can be used alone or can be used together with.

At the reaction of phosphorus compound represented by general formula (1), quinone compound and epoxy resin (a) having specific molecular weight distribution, an inactive solvent can be used at needs. Concretely, various hydrocarbons such as hexane, heptane, octane, decane, dimethylbutane, pentene, cyclohexane, methylcyclohexane, benzene, toluene, xylene or ethylbenzene, ethers such as ethylether, isopropylether, butylether, diisoamylether, methylphenylether, ethylphenylether, amylphenylether, ethylbenzylether, dioxane, methylfuran or tetrahydrofuran, methyl cellosolve, methyl cellosolve acetate, ethyl cellosolve, cellosolve acetate, ethylene glycol isopropylether, diethylene

glycol dimethylether, methylethylcarbitol, propylene glycol monomethylether, dimethylformamide or dimethylsulfoxide can be used, however, not intending to restrict to these solvents, and these solvents can be used by alone or can be used together with.

By blending a curing agent, the phosphorus-containing epoxy resin (A) of the present invention becomes curable phosphorus-containing epoxy resin composition. As a curing agent, conventional curing agents for epoxy resin such as various phenol resins, acid anhydride, amines, hydrazides or acidic polyesters can be mentioned, and these curing agents can be used by alone or can be used together with. Among these curing agents, as a curing used to be contained in curable phosphorus-containing epoxy resin composition, dicyandiamide or phenolic curing agents are especially desirable. In the curable phosphorus-containing epoxy resin composition of the present invention, amount of curing agent is desirably 0.4-2.0 equivalent weight of functional group of curing agent to 1 equivalent weight of epoxy group which is functional group of epoxy resin, more desirably 0.5-1.5 equivalent weight and particularly desirable range is 0.5-1.0 equivalent weight. When equivalent weight of curing agent to 1 equivalent weight of epoxy group is less than 0.4 equivalent weight or exceed 2.0 equivalent weight, curing becomes incomplete and good physical feature of cured product cannot be accomplished.

As concrete examples of phenol curing agents usable for the curable epoxy resin composition of the present invention, bisphenols such as bisphenol A, bisphenol F, bisphenol C, bisphenol K, bisphenol Z, bisphenol S, tetramethylbisphenol A, tetramethylbisphenol F, tetramethylbisphenol S, tetramethylbisphenol Z, dihydroxydiphenylsulfide, 4,4'-thiobis(3-methyl 6-tert-butylphenol), dihydroxybenzenes such as catechol, resorcin, methyl resorcin, hydroquinone, monomethylhydroquinone, dimethylhydroquinone, trimethylhydroquinone, mono-tert-butylhydroquinone or di-tert-butyl hydroquinone, hydroxynaphthalenes such as dihydroxynaphthalene, dihydroxymethylnaphthalene, dihydroxyethylnaphthalene or trihydroxy naphthalene, condensation products of phenols such as phenol novolac resin, DC-5 (product of Nippon Steel Chemical Co., Ltd.; cresol novolac resin) or naphtol novolac resins and/or naphtols and aldehydes, condensation products of phenols such as SN-160, SN-395, SN-485 (product of Nippon Steel Chemical Co., Ltd.) and/or naphtols and xylyleneglycol,

condensation products of phenols and/or naphthols and isopropenylacetophenone, reacted products of phenols and/or naphthols and dicyclopentadiene or condensation products of phenols and/or naphthols and biphenyl condensing agents can be mentioned.

As above mentioned phenols, phenol, cresol, xylenol, butylphenol, amylphenol, nonylphenol, butylmethylphenol, trimethylphenol or phenyl phenol can be mentioned, and as naphthols 1-naphthol or 2-naphthol can be mentioned.

As aldehydes, formaldehyde, acetaldehyde, propylaldehyde, butyl aldehyde, barrelaldehyde, capronaldehyde, benzaldehyde, chloraldehyde, bromaldehyde, glyoxal, malonoaldehyde, succinaldehyde, glutaraldehyde, adipinaldehyde, pimelinaldehyde, sebacinaldehyde, acrolein, croton aldehyde, salicylaldehyde, phthalaldehyde or hydroxybenzaldehyde can be mentioned. As biphenyl condensing agents, bis(methylol)biphenyl, bis(methoxymethyl)biphenyl, bis(ethoxymethyl)biphenyl or bis(chloromethyl)biphenyl can be mentioned.

As other public known conventional curing agent which can be used in curable epoxy resin composition of the present invention, acid anhydrides such as methyltetrahydro phthalic anhydride, hexahydro phthalic anhydride, pyromellitic anhydride, phthalic anhydride, trimellitic anhydride or methylnadic acid, diethylenetriamine, triethylenetetramine, methaxylenediamine, isoholonediamine, diaminodiphenylmethane, diaminodiphenylsulphone, diaminodiphenylethere, dicyandiamide or amine compounds such as polyamide amine which is condensation product of acids such as dimeric acid and polyamines.

Further, as a curing agent which cures curable epoxy resin composition of the present invention by causing polymerization of epoxy group, phosphine compounds such as triphenyl phosphine, phosphonium salt such as tetraphenylphosphoniumbromide, imidazole salts which is a salt of imidazoles such as 2-methylimidazole, 2-phenylimidazole, 2-ethyl-4-methylimidazole, 2-undecylimidazole or 1-cyanoethyl-2-methyl imidazole with trimellitic acid, isocyanuric acid or boric acid, amines such as benzyldimethylamine or 2,4,6-tris(dimethylaminomethyl)phenol, quaternary ammonium salts such as trimethylammoniumchloride, salts of diazabicyclo compounds and phenols or phenol novolac resins, complex compounds composed of boron-trifluoride, amines or ether compounds,

aromatic phosphonium or iodonium salt can be mentioned. These curing agents can be used by alone or can be used together with.

Blending ratio of other public known conventional epoxy resin curing agent which can be used in epoxy resin composition is 0.5-1.5 equivalent weight of functional group of curing agent to 1 equivalent weight of epoxy group and desirably 0.8-1.2 equivalent weight. And blending ratio of curing agent which cures the resin by causing polymerization of epoxy group is 0.1-10 mass parts to 100 mass parts of epoxy resin and desirably is 0.2-5 mass parts.

To the flame retardant epoxy resin composition containing the phosphorus-containing epoxy resin (A) of the present invention, organic solvent can be used as a viscosity regulator. As organic solvents which can be used in the present invention, amides such as N,N-dimethyl formamide, ethers such as ethyleneglycol monomethylether, ketones such as acetone or methylethylketone, alcohols such as methanol or ethanol or aromatic hydrocarbon such as benzene or toluene can be mentioned, however not intending to restrict to these organic solvents. Among these solvents, one or mixture of plural solvents can be blended within the limit of 20-90 mass % as epoxy resin concentration.

In the composition of the present invention, a curing accelerator can be used at need. As a curing accelerator which can be used, imidazoles such as 2-methylimidazole, 2-ethylimidazole or 2-ethyl-4-methylimidazole, tertiary amines such as 2-(dimethylaminomethyl)phenol, 1,8-diaza-bicyclo (5,4,0)undecen-7, phosphines such as triphenylphosphine, tricyclohexylphosphine or triphenylphosphinetriphenylborane, metal compound such as tin octylate can be mentioned. 0.02-5.0 mass % of curing accelerator to 100 mass % of epoxy resin in epoxy resin composition can be used at need. By use of curing accelerator it becomes possible to bring curing temperature down and to shorten curing time.

In the composition of the present invention, a filler can be used at need. Concretely, inorganic fillers such as aluminum hydroxide, magnesium hydroxide, talk, calcined talk, clay, caoline, boehmite, titanium oxide, pulverized glass or silica balloon can be mentioned, further, pigments can be blended. As the reason to use conventional inorganic filler, effect of improvement of shock resistance can be mentioned. Further, in the case when metal hydroxide such as aluminum hydroxide, magnesium

hydroxide is used, it acts as a flame retardant promoter and flame retardant feature can be maintained even if phosphorus-containing ratio is small. Especially, if blending amount of the inorganic filler is 10 mass % or less, improvement of shock resistance is not sufficient. However, when blending amount exceeds 150 mass %, adhering feature which is important feature to usage as a laminated board deteriorates. Further, fibrous filler such as glass fiber, pulp fiber, synthetic fiber or ceramic fiber or organic filler such as fine particles of rubber or thermo elastic elastomer can be contained in above mentioned resin composition.

By accomplishing curing of epoxy resin composition of the present invention, epoxy resin cured product can be obtained. At curing process, for example, shape of resin sheet, copper foil with resin or prepreg is given and by laminating then curing by heat press, the phosphorus-containing epoxy resin cured product as a laminated board can be obtained.

Phosphorus-containing epoxy resin cured product using the phosphorus-containing epoxy resin (A) of the present invention is prepared, then the phosphorus-containing epoxy resin cured product of laminated board shape is prepared by heat curing, and evaluated. According to the evaluation result, when the phosphorus-containing epoxy resin (A) is compared with a phosphorus-containing epoxy resin obtained from public known conventional phosphorus compound and epoxy resins, it gives not only good working efficiency due to low viscosity, but also gives excellent heat resistance and excellent adhering feature, further, flame retardant feature can be improved.

EXAMPLES

Details of the present invention will be illustrated actually, however, not intending to restrict the present invention. Unless otherwise provided, "part" indicates mass part and "%" indicates mass %. Measurements are respectively carried out according to following methods.

Measuring methods are shown below.

Epoxy equivalent weight: Conformed to JIS K7236

Dinuclear containing ratio, trinuclear containing ratio, tetranuclear containing ratio, pentanuclear or more containing ratio, number average molecular weight (M_n) and degree of dispersion (M_w/M_n): Molecular distribution is measured by gel permeation chromatography, then dinuclear

containing ratio, trinuclear containing ratio, tetranuclear containing ratio, pentanuclear or more containing ratio are obtained by area % of peaks, number average molecular weight, weight-average molecular weight and degree of dispersion are converted from calibration curve prepared by using standard monodispersed polystyrene (product of Toso Co., Ltd.; A-500, A-1000, A-2500, A-5000, F-1, F-2, F-4, F-10, F-20, F-40). Actually, columns (product of Toso Co., Ltd.; TSKgelG4000HXL, TSKgelG3000HXL, TSKgelG2000HXL) are connected to main body (product of Toso Co., Ltd.; HLC-8220GPC) in series and column temperature is set to 40 °C. Tetrahydrofuran is used as an eluate, flow rate is set up to 1ml/min and as a detector, RI (differential refractometer) detector is used.

Phosphorus-containing ratio: Sulfuric acid, hydrochloric acid and perchloric acid are added to specimen, make wet ashing by heating and all phosphorus atoms reduced to orthophosphoric acid. The obtained ortho-phosphoric acid is reacted with metavanadate and molybdate in sulfuric acid acidic solution so as to form phosphovanademolybdic acid complex. Absorbancy of the obtained phosphovanademolybdic acid complex is measured and according to previously prepared calibration curve using potassium dihydrogenphosphate, phosphorus atom containing ratio is obtained and indicated by %. Phosphorus-containing ratio of laminated board is indicated as containing ratio to resin component in the laminated board.

Copper foil peeling strength and phase boundary bonding strength: Measured according to JIS C 6481 and phase boundary bonding strength is measured by peeling 7th layer and 8th layer.

Flammability: Conformed to UL94 (Safety Certified Standard of Underwriters Laboratories Inc.). Tests are made on 5 specimens. A flame is applied to each specimen for 2 times (2 times to 5 specimens, total 10 times) and total flame combustion time after 1st and 2nd flame application is measured and indicated by seconds.

Glass transition point DSC: Differential scanning calorimeter (Product of SII Nano Technology Co., Ltd.; EXTAR6000 DSC6200) is used. Measured by 10°C/min temperature-programmed condition, and indicated by DSC extrapolated temperature.

Glass transition point TMA: Thermomechanical analyzer (Product of SII Nano Technology Co., Ltd.; EXTAR6000 TMA/SS120U) is used. Measured

by 5°C/min temperature-programmed condition, and indicated by TMA extrapolated temperature.

Epoxy resins which are used in Examples and Comparative Examples are shown as follows.

Epotohto YDPN-638 (product of Nippon Steel Chemical Co., Ltd.; general phenol novolac epoxy resins, dinuclear containing ratio is 22 area %, trinuclear containing ratio is 15 area %, sum total containing ratio of trinuclear and tetranuclear is 25 area %, pentanuclear or more containing ratio is 53 area %, number average molecular weight is 528, weight-average molecular weight is 1127, degree of dispersion is 2.13 and epoxy equivalent weight is 176g/eq) (refer to Fig.1)

Epotohto YDF-170 (product of Nippon Steel Chemical Co., Ltd.; bis phenol F epoxy resins, epoxy equivalent weight is 170g/eq)

Synthesis Example 1 (synthesis of phenol novolac resin)

2500 parts of phenol and 7.5 parts of oxalic acid dehydrate are put into a four-neck glass separable flask to which stirrer, thermometer, condenser and N₂ gas introduction apparatus are provided. Temperature is elevated by heating under N₂ gas flow with constant stirring. 474.1 parts of 37.4% formalin is dropped by 30 minutes at 80°C. Further, temperature is kept at 92°C and reacted for 3 hours. Temperature is elevated to 110°C so as to remove water which is a react formed by reaction out of system of reaction. Remained phenol is recovered by vacuum distillation at 160°C, and phenol novolac resin is obtained. Further, temperature is elevated and a part of dinuclear is recovered. Dinuclear containing ratio and trinuclear containing ratio are measured by gel permeation chromatography and are 10 area % and 38 area % respectively.

Synthesis Example 2 (synthesis of phenol novolac epoxy resin)

Same apparatus as to Synthesis Example 1 is used. 665.8 parts of phenol novolac resin obtained in Synthesis Example 1, 2110.8 parts of epichlorohydrine and 17 parts of water are put into 4-neck separable flask and temperature is elevated to 50°C with constant stirring. 14.2 parts of 49% sodium hydroxide aqueous solution is added and reacted for 3 hours. Temperature is elevated to 64°C, and vacuumed so as to cause water reflux, then 457.7 parts of 49% sodium hydroxide aqueous is dropped by 3 hours

and reacted. Temperature is elevated to 70°C and dehydration is carried out, then temperature is elevated to 135°C so as to recover remained epichlorohydrine. Pressure is put back to atmospheric pressure, after that 1232 parts of MIBK is added and dissolved. 1200 parts of ion-exchange water is added, stirred and stood so as to remove common salt, which is byproduct, by dissolving it in water. Then 37.4 parts of 49% sodium hydroxide is added and purifying reaction is carried out by stirred for 90 minutes at 80°C. MIBK is added, and washing with water is repeated several times and ionic impurity is removed. Solvent is recovered and novolac epoxy resin is obtained. Dinuclear containing ratio is 9 area %, trinuclear containing ratio is 36 area %, total of containing ratio of trinuclear and tetranuclear is 53 area %, pentanuclear or more containing ratio is 38 area %, number average molecular weight is 513, weight-average molecular weight is 713, degree of dispersion is 1.39 and epoxy equivalent weight is 174g/eq (refer to Fig.2)

Example 1

127 parts of HCA (product of Sanko Co., Ltd.; 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, phosphorus-containing ratio is 14.2%), 270 parts of toluene are put into same apparatus as to Synthetic Example 1, heated and dissolved. Then 1,4-naphthoxinone (product of Tokyo Kasei Co., Ltd; purity is more than 98%) is added by anxiously exotherm and maintained for 30 minutes keeping temperature less than 90°C. Further temperature elevated gradually and maintained for 2 hours at refluxing temperature. After a part of toluene is recovered, 804 parts of phenol novolac epoxy resin of Synthesis Example 2 is added and elevate temperature to 130°C with constant stirring under N₂ gas flow. 0.20 parts of triphenylphosphine is added as catalyst and reacted 3 hours at 160°C. Epoxy equivalent weight of the obtained epoxy resin is 276g/eq and phosphorus-containing ratio is 1.8%. Results are summarized in Table 1.

Example 2

Same process as to Example 1 is carried out except changing parts of HCA to 141 parts, parts of 1,4-naphthoxinone to 77 parts, parts of phenol novolac resin of Synthesis Example 2 to 782 parts and parts of triphenylphosphine to 0.22 parts. Epoxy equivalent weight of the obtained

epoxy resin is 294g/eq and phosphorus-containing ratio is 2.0%. Results are summarized in Table1.

Example 3

Same process as to Example 1 is carried out except changing parts of HCA to 155 parts, parts of 1,4-naphthoxinone to 85 parts, parts of phenol novolac resin of Synthesis Example 2 to 760 parts and parts of triphenylphosphine to 0.24 parts. Epoxy equivalent weight of the obtained epoxy resin is 317g/eq and phosphorus-containing ratio is 2.2%. Results are summarized in Table1.

Example 4

Same process as to Example 1 is carried out except changing parts of HCA to 141 parts, parts of 1,4-naphthoxinone to 83 parts, parts of phenol novolac resin of Synthesis Example 2 to 726 parts, parts of triphenylphosphine to 0.22 parts and further adding 50 parts of YDF-170B together with phenol novolac epoxy resin. Epoxy equivalent weight of the obtained epoxy resin is 297g/eq and phosphorus-containing ratio is 2.0%. Results are summarized in Table1.

Example 5

Same process as to Example 1 is carried out except changing parts of HCA to 155 parts, parts of 1,4-naphthoxinone to 57 parts, parts of phenol novolac resin of Synthesis Example 2 to 638 parts, parts of triphenylphosphine to 0.21 parts and further adding 150 parts of YDF-170 together with phenol novolac epoxy resin. Epoxy equivalent weight of the obtained epoxy resin is 286g/eq and phosphorus-containing ratio is 2.2%. Results are summarized in Table1.

Example 6

Same process as to Example 1 is carried out except changing parts of HCA to 155 parts, parts of 1,4-naphthoxinone to 34 parts, parts of phenol novolac resin of Synthesis Example 2 to 777 parts, parts of triphenylphosphine to 0.19 parts and further adding 34 parts of BRG-555 (product of Syowa Denko Co., Ltd.; phenol novolac resin) together with phenol novolac epoxy resin. Epoxy equivalent weight of the obtained epoxy

resin is 310g/eq and phosphorus-containing ratio is 2.2%. Results are summarized in Table1.

Example 7

Same process as to Example 1 is carried out except changing parts of HCA to 155 parts, parts of 1,4-naphthoxinone to 23 parts, parts of phenol novolac resin of Synthesis Example 2 to 779 parts, parts of triphenylphosphine to 0.18 parts and further adding 43 parts of BRG-555 together with phenol novolac epoxy resin. Epoxy equivalent weight of the obtained epoxy resin is 310g/eq and phosphorus-containing ratio is 2.2%. Results are summarized in Table1.

Table 1

YDF-170			
YDPN-638			
epoxy resin of Synthesis Example 2	804	782	76
BRG-555			
triphenylphosphine	0.20	0.22	0.2
epoxy equivalent weight (g/eq)	276	294	31
phosphorus containing ratio (%)	1.8	2.0	2.0
non volatile matter (%)	75.0	75.0	75
viscosity (mPa · s)	2470	3420	41

Comparative Example 1

824 parts of YDPN-638 and 176 parts of HCA are put into same apparatus used in Synthesis Example 1, and temperature is elevated by heating under N₂ gas flow with constant stirring. 0.18 parts of triphenylphosphine is added as a catalyst and reacted at 160°C for 3 hours. Epoxy equivalent weight of the obtained epoxy resin is 263g/eq and phosphorus-containing ratio is 2.5%. Results are summarized in Table1.

Comparative Example 2

Same process as to Comparative Example 1 is carried out except changing parts of phenol novolac resin of Synthesis Example 2 to 824 parts and parts of HCA to 176 parts. Epoxy equivalent weight of the obtained epoxy resin is 266g/eq and phosphorus-containing ratio is 2.5%. Results are summarized in Table1.

Comparative Example 3

Same process as to Example 1 is carried out except changing parts of HCA to 141 parts, parts of 1,4-naphthoxinone to 77 parts, parts of YDPN-638 to 782 parts and parts of triphenylphosphine to 0.22 parts. Epoxy equivalent weight of the obtained epoxy resin is 303g/eq and phosphorus-containing ratio is 2.0%. Results are summarized in Table1.

Comparative Example 4

Same process as to Example 1 is carried out except changing parts of HCA to 155 parts, parts of 1,4-naphthoxinone to 80 parts, parts of YDPN-638 to 465 parts, parts of triphenylphosphine to 0.23 parts and further adding 300 parts YDF-177 together with phenol novolac epoxy resin. Epoxy equivalent weight of the obtained epoxy resin is 311g/eq and phosphorus-containing ratio is 2.2%. Results are summarized in Table1.

Examples 8-14 and Comparative Examples 5-8

Epoxy resins of Example 1 to Example 7 and Comparative Example 1 to Comparative Example 4, and dicyandiamine as curing agent are blended according to recipes shown in Table 2, dissolved into mixed solvent consisting of methyl ethyl ketone, propylene glycol monomethyl ether and N,N-dimethylformamide and epoxy resin composition varnishes are

obtained.

Obtained epoxy resin composition varnish is impregnated in glass cloth WEA 7627 XS13 (product of Nitto Boseki Co., Ltd.; 0.18mm thickness). The glass cloth in which varnish is impregnated is dried in a hot-air circulation oven at 150°C, and a prepreg is obtained. 8 sheets of obtained prepreg are piled up, and copper foil (product of Mitsui Kinzoku Mining Co., Ltd.; 3EC) is piled up on upper surface and lower surface of the piled prepregs, then, heated at 130°C for 15 minutes, heat pressed at 170°C × 20kg/cm² for 70 minutes and a laminated board is obtained. Glass transition point by TMA, DSC and DMS, copper foil peeling strength, phase boundary bonding strength and flammability are measured and measuring results of the laminated board are summarized in Table2.

Table 2

	Co. Exp. 2			
	Co. Exp. 3			
	Co. Exp. 4			
DICY		3.80	3.57	
2E4MZ				
phosphorus containing ratio		1.7	1.9	
flammability: UL-94		V-0	V-0	
flammability: flame remaining time (sec)		45	30	
copper foil peeling strength (kN/m)		1.7	1.7	
phase boundary bonding strength (kN/m)		0.9	1.0	
glass transition point	DSC °C	174	174	
	TMA °C	167	167	
	DMS °C	179	181	

Co. Exp.: Comparative Example

As shown in Tables 1 and 2, when a phosphorus-containing epoxy resin (A) which is obtained by reaction of phosphorus compound represented by general formula (1), quinone compound and epoxy resin (a) having specific molecular weight distribution is compared with an epoxy resins which do not use an epoxy resin not reacted with a quinone compound or a phenol novolac epoxy resin not having specific molecular weight distribution, said epoxy resin (A) performs higher glass transition point and better adhering feature maintaining lower viscosity, further performs better flammability by lower phosphorus-containing ratio.

INDUSTRIAL APPLICABILITY

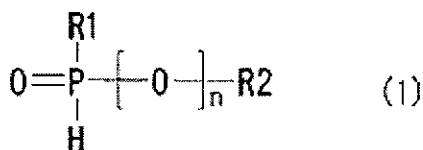
The present invention relates to a phosphorus-containing epoxy resin (A) obtained by reaction of specific phosphorus compound, quinone compound and epoxy resin (a) having specific molecular weight distribution, and can be used as an epoxy resin usable for an electronic circuit board which is excellent in flammability, heat resistance and adhering feature.

CLAIMS

1. A phosphorus-containing epoxy resin (A) which is obtained by reacting a phosphorus compound represented by general formula (1), a quinone compound and an epoxy resin (a) as essential components, and which is characterized in that the epoxy resin (a) is a novolac epoxy resin that has a molecular weight distribution having a dinuclear component content of 15 area % or less, a trinuclear component content of 15-60 area %, and a number average molecular weight of 350-700 as determined by gel permeation chromatography.

(Measuring condition of gel permeation chromatography)

TSKgel G4000HXL, TAKgel G3000HXL and TSKgel 2000HXL, which are the products of Toso Co., Ltd., are placed in series, column temperature is set up to 40°C. Tetrahydrofuran is used as an eluate, flowing rate is set up to 1ml/min, and RI (differential refractometer) is used as a detector. 0.1g of specimen is dissolved in 10ml of tetrahydrofuran, thus a sample solution is prepared. From obtained chromatogram, containing ratio of the dinuclear component and the trinuclear component are calculated and a number average molecular weight is measured from calibration curve prepared by using standard polystyrene.



(in the formula, R1 and R2 represents hydrocarbon group and can be same or can be different, further, R1 and R2 can be cyclic structure with phosphorus atom, and n indicates 0 or 1)

2. A phosphorus-containing epoxy resin composition comprising the phosphorus-containing epoxy resin (A) of claim 1 and a curing agent, as essential components, wherein active group of the curing agent is 0.3-1.5 equivalent weight per 1 equivalent weight of epoxy group of the phosphorus-containing epoxy resin (A).

3. An epoxy resin cured product obtained by curing of the phosphorus-containing epoxy resin composition of claim 2.

4. A prepreg prepared by impregnating the phosphorus-containing epoxy resin composition of claim 2 into a substrate.
5. A laminated board prepared by curing the phosphorus-containing epoxy resin composition of claim 2.
6. An electronic printed circuit board prepared by curing the phosphorus-containing epoxy resin composition of claim 2.