

- 1 -

EPOXY RESIN COMPOSITION AND COPPER-CLAD LAMINATE

The present invention relates to an epoxy resin composition and a copper-clad laminate and particularly to an epoxy resin composition superior in low dielectric constant and a copper-clad laminate made therefrom.

Hitherto, among epoxy resins utilized for electrical and electronic uses, bisphenol type epoxy resins and dicyandiamide have been mainly used in combination as the materials of substrates for printed circuit boards. Recently, resins of low dielectric constant have been demanded mainly for the purpose of improving signal speed with increase in the number of layers of printed circuit boards and it has been proposed to combine low dielectric thermoplastic resins with conventional epoxy resins. The proposals are, for example, to modify epoxy resins with reactive polybutadiene resins, to disperse powders of polytetrafluoroethylene resins and to use aramid fibers as a substrate. Another proposal is use of D-glass or quartz lower in dielectric constant than the conventionally used E-glass as a substrate.

However, according to these conventional methods the proportion of the thermoplastic resins combined with epoxy resins must be increased for attaining the desired dielectric constant because the dielectric constant of the base epoxy resins is high. Thus, heat resistance, dimensional stability and chemical resistance which are features of epoxy resins are lost. Use of aramid fibers or quartz suffers from the problem that the drill used at the time of drilling to make holes through the substrate wears out. When D-glass is used, there is no problem in drilling, but production cost is high.

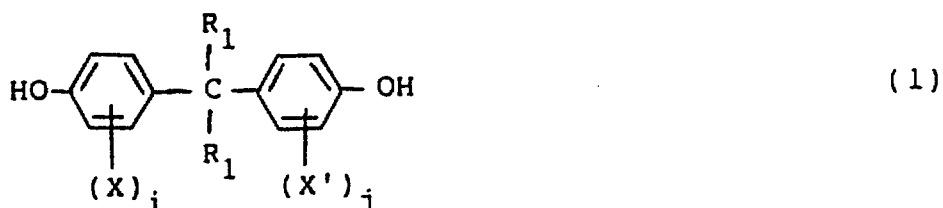
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Under these circumstances, epoxy resins of low dielectric constant from which substrates for printed circuit boards which have low dielectric constant can be obtained in the same manner as by conventional methods have been earnestly desired. The object of the present invention is to provide epoxy resin compositions excellent in heat resistance and low in dielectric constant and copper-clad laminates made by molding the compositions.

The above object could be solved after investigating the matrix structure of epoxy resins and characteristics of laminates obtained therefrom by the finding that a specific composition has both the excellent heat resistance and the low dielectric constant.

That is, the invention relates in a first embodiment to an epoxy resin composition comprising:

(1) a compound obtainable by previously reacting (A) an epoxy resin obtainable by glycidyl etherifying a 3-methyl-6-(C₁-C₈)alkylphenol novolak with (B) a halogen-containing bisphenol compound represented by the following formula (1):



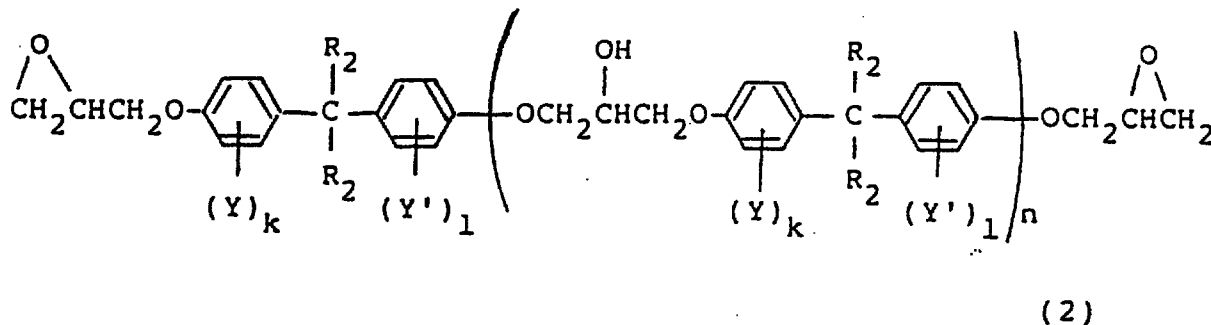
wherein R₁ represents a hydrogen atom or a methyl group and the two R₁ may be identical or different, X and X' represent halogen atom and may be identical or

different, and i and j independently of one another are integers of 1 to 4, and

(2) an epoxy hardener.

The invention relates in a second embodiment to an epoxy resin composition comprising:

(1) a compound obtainable by previously reacting (A) the epoxy resin used in the first embodiment of this invention, (B) the halogen-containing bisphenol compound used in the first embodiment of this invention and (C) a glycidyl etherified product of a halogen-containing bisphenol compound which is represented by the following formula (2):



wherein R_2 represents a hydrogen atom or a methyl group and the two R_2 may be identical or different, Y and Y' represent halogen atom and may be identical or different, n represents an average recurring unit number and is 0 to 10 and k and l independently of one another are integers of 1 to 4, and

(2) an epoxy hardener.

The invention in a third embodiment relates to an epoxy resin copper-clad laminate made by heat molding a copper foil and a prepreg obtained by impregnating a substrate with a solution of the epoxy resin composition of the first or second embodiment of the invention in an organic solvent.

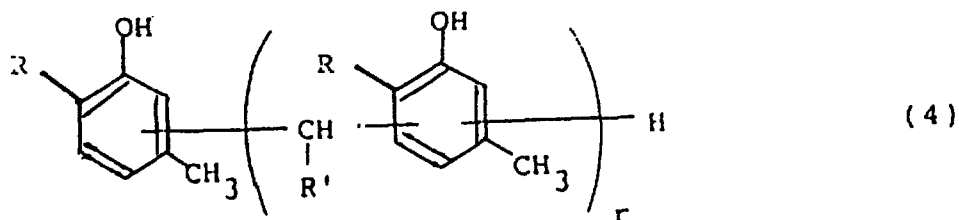
The epoxy resin of the component (A) used in the present invention is obtainable by glycidyl etherification of a 3-methyl-6-(C₄-C₈)alkylphenol novolak.

The 3-methyl-6-(C₄-C₈)alkylphenol novolak is prepared by the process ordinarily used for preparing novolak type phenolic resins. For example, it is prepared by polycondensation of a 3-methyl-6-(C₄-C₈)-alkylphenol with an aldehyde using as a catalyst an inorganic acid such as hydrochloric acid, phosphoric acid or sulfuric acid, an organic acid such as benzenesulfonic acid, toluenesulfonic acid or oxalic acid or a metallic salt such as zinc acetate.

The alkyl group of the 3-methyl-6-(C₄-C₈)-alkylphenol includes, for example, various isomers of butyl group, pentyl group, hexyl group, heptyl group and octyl group. Among them, preferred are t-butyl group and sec-butyl group from the economical viewpoints such as easiness in availability of starting materials.

Examples of the aldehyde are formaldehyde, acetaldehyde and propionaldehyde and formaldehyde is preferred from the economical viewpoint.

The recurring unit number of the phenol component and the aldehyde of the 3-methyl-6-(C₄-C₈)alkylphenol novolak is defined by r in the following formula (4):



wherein R represents a C₁-C₈ alkyl group and R' represents an aldehyde residue.

The value r is preferably 1-5, more preferably 1.1-3 on an average. If the recurring unit number exceeds 5 on an average, viscosity of the epoxy resin increases and workability at the time of making the laminate deteriorates. If it is less than 1 on an average, heat resistance of the laminate made using the resin decreases.

The glycidyl etherification of 3-methyl-6-(C₁-C₈)alkylphenol novolak is carried out by known processes. For example, it is carried out by allowing this novolak to react with epichlorohydrin in the presence of an alkali such as sodium hydroxide.

Examples of the halogen-containing bisphenol compound used in the present invention as the component (B) which is represented by the formula (1) are tetrabromobisphenol A, tetrachlorobisphenol A, tetraiodobisphenol A, tetrabromobisphenol F, tetrachlorobisphenol F, tribromobisphenol A and 2,2'-dibromobisphenol A and among them, tetrabromobisphenol A is preferred from the economical viewpoint and for obtaining efficient flame retardance.

Examples of the glycidyl etherification product of halogen-containing bisphenol compound used in the present invention as the component (C) which is represented by the formula (2) are those which are obtained by glycidyl etherifying the above-mentioned halogen-containing bisphenol compounds and glycidyl ether of tetrabromobisphenol A is preferred from the economical viewpoint and for obtaining efficient flame retardance.

The reaction of the epoxy resin (A) with the halogen-containing bisphenol compound (B) or the reaction of the (A) and the (B) with the glycidyl etherification product (C) of the halogen-containing bisphenol compound can be carried out by known processes.

For example, the above components can be allowed to react in the presence of a basic catalyst such as triphenylphosphine or imidazole. By the reaction, control of glass transition temperature owing to the change of distance between crosslinking points and impartation of flame retardance using the halogen-containing compound can be performed without causing volatilization of low molecular weight materials at the time of hardening.

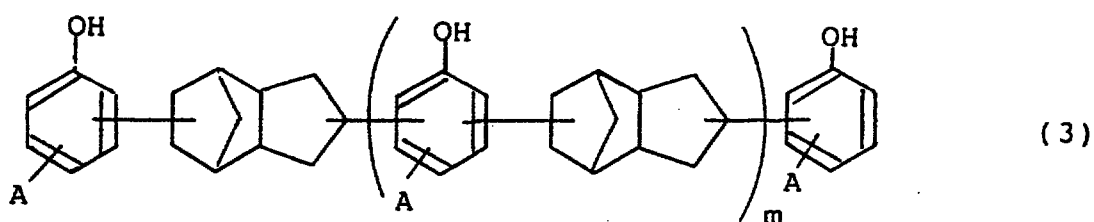
The components (A) and (B) or (A), (B) and (C) can be allowed to react at optional ratios. Preferably, the epoxy resin (A) is used in an amount 30-95% by weight based on the whole resin for maintaining the low dielectric constant. Amount of the halogen-containing bisphenol compound (B) or that of the glycidyl etherification product (C) of halogen-containing bisphenol compound is desirably adjusted so that content of the halogen atom is within such range as being able to attain V-0 in UL flame retardancy rating. For example, for bromine atom, it is desirable to determine the amount of these components so that bromine atom is contained in an amount of 15-30% by weight in the epoxy resin composition.

The reaction of the above components may be carried out with or without using solvents. If solvents are used, they may be general-purpose solvents. Examples of the solvents are ketones such

as acetone, methyl ethyl ketone and methyl isobutyl ketone, hydrocarbons such as benzene, toluene and xylene, ethers such as tetrahydrofuran, dioxane and diethylene glycol dimethyl ether and alcohols such as methyl cellosolve and butyl cellosolve. Preferred are methyl ethyl ketone, toluene, xylene, butyl cellosolve, dioxane and diethylene glycol dimethyl ether.

The reaction temperature can be in the range of 50-200° C, but preferably in the range of 80-150° C for carrying out the reaction efficiently and inhibiting side reactions.

The epoxy hardeners used in the present invention may be known ones, but polybutadiene compounds modified with phenolic compounds and the dicyclopentadiene-phenol compounds represented by the following formula (3) are preferred for obtaining hardened resins of low dielectric constant. Amount of the hardener is preferably such that content of phenolic hydroxyl group is 0.3-1.2 equivalent per 1 equivalent of epoxy group in the epoxy resin.



wherein m represents an average recurring unit number and is a numeral in the range of 0 to 10 and A represents a hydrogen atom or an alkyl group of 1 to 8 carbon atoms.

The polybutadiene compounds modified with

phenolic compounds are obtained by allowing homo-polymers of butadiene having a number-average molecular weight of 500-10000 or copolymers of butadiene with vinyl monomers such as styrene or diolefins such as isoprene to react with phenols. Examples of catalysts used are sulfuric acid, perchloric acid, aluminum chloride, boron trifluoride, boron trifluoride-ether complex and boron trifluoride-phenol complex. The phenols include, for example, monohydric phenols, polyhydric phenols and alkyl-substituted phenols.

General processes for producing the dicyclopentadiene-phenol compounds represented by the formula (3) include a process which comprises allowing phenols to react with dicyclopentadiene in the presence of an acid catalyst for Friedel-Craft's reaction (Japanese Patent Application Kokai No. 63-99224).

Furthermore, as far as the effects of the present invention are not damaged, there may be additionally used known bifunctional epoxy resins, polyfunctional epoxy resins, other thermosetting resins, thermoplastic resins having functional group and others. Examples thereof are glycidyl ether of bisphenol A, glycidyl ether of phenolic novolak, glycidyl ether of cresol novolak, glycidyl ether of brominated phenol novolak, unsaturated polyester resins, cyanate resins, maleimide resins, glycidyl-modified polybutadienes and maleic anhydride-modified polyethylenes.

These resins may be used by incorporating into the epoxy resin compositions of the present invention or by previously allowing them to react with the epoxy resins used in the present invention.

Known additives such as curing accelerator, flame retardant and surface treating agent may be added to the compositions depending on the object.

Examples of the curing accelerator are imidazoles, tertiary amines and phosphorus compounds, those of the flame retardants are antimony trioxide, aluminum hydroxide and red phosphorus, and those of the surface treating agent are silane coupling agents.

The copper-clad laminate of the present invention can be produced by known methods. That is, a substrate is impregnated with a resin varnish prepared by dissolving the epoxy resin composition of the present invention in an organic solvent and then the impregnated substrate is heat treated to obtain a prepreg. Thereafter, the prepreg and a copper foil are laminated and heat molded to make a copper-clad laminate.

The organic solvent used is selected from one or mixtures of acetone, methyl ethyl ketone, methyl isobutyl ketone, ethylene glycol monomethyl ether, propylene glycol monomethyl ether, toluene, xylene, N,N-dimethylformamide, dioxane, tetrahydrofuran and the like.

The substrate to be impregnated with resin varnish includes, for example, woven or nonwoven fabrics or mats comprising inorganic fibers or organic fibers such as glass fibers, polyester fibers and polyamide fibers and papers. These may be used each alone or in combination of two or more.

The heat treating conditions for making the prepreg can be optionally selected depending on the

kinds of solvents, catalysts and additives used and amounts thereof, but usually the conditions of 80-220° C for 3-30 minutes are employed.

The heat molding conditions include, for example, hot press molding conducted at 150-300° C, under a molding pressure of 10-100 kg/cm² for 20-300 minutes.

In the following examples, "epoxy equivalent" is defined to be molecular weight of epoxy resin per one epoxy group; "OH equivalent" is defined to be molecular weight of OH compound per one OH group; and "Br content" is defined to be % by weight based on solid content of the resin.

Preparation Example 1

This example concerns with preparation of a novolak resin which is a starting material for epoxy resin (A) as a constituting component of the resin composition of the present invention.

2-t-Butyl-5-methylphenol (2231.0 g, 13.58 mol), p-toluenesulfonic acid (12.9 g, 0.068 mol) and deionized water (223.2 g) were charged in a 5 liter four-necked round flask equipped with a thermometer, a stirrer and a condenser and heated to 100° C. Formaldehyde (218.4 g, 2.715 mol) was added dropwise thereto using a dropping tube over a period of 2 hours and then kept at 100° C for 2 hours to carry out the reaction for preparing a novolak. Thereafter, the reaction mixture was cooled to 80° C and neutralized with 10% aqueous NaOH solution (27.7 g, 0.069 mol). The organic layer obtained by separation was washed twice with deionized water (700 g). The organic layer

after washed was subjected to concentration under reduced pressure (180 ° C/10 mmHg/1 hour) to obtain a resinous product (857.2 g). OH equivalent of the resulting resinous product was 176.0 g/eq. The recurring unit number (r in the formula (3)) of this novolak resin was 1.25 on an average.

Preparation Example 2

This example concerns with preparation of an epoxy resin by the reaction of the novolak resin obtained in Preparation Example 1 with epichlorohydrin.

The novolak resin obtained in Preparation Example 1 (246.4 g, 1.4 equivalent), epichlorohydrin (906.5 g, 9.8 mol), dimethyl sulfoxide (453.3 g) and deionized water (14.0 g) were charged in a 2 liter four-necked round flask equipped with a thermometer, a stirrer and a condenser with a separating pipe and 48.6% aqueous sodium hydroxide solution (108.31 g, 1.316 mol) was added dropwise thereto over a period of 5 hours under the conditions of 49° C, 42 Torr, during which the reaction was allowed to proceed with keeping the temperature at 49 ° C and with cooling and liquefying the azeotropic epichlorohydrin and water and with returning the organic layer to the reaction system.

After completion of the reaction, unreacted epichlorohydrin was removed by concentration under reduced pressure and the epoxidized product containing by-produced salts and dimethyl sulfoxide was dissolved in methyl isobutyl ketone and the by-produced salts and dimethyl sulfoxide were removed by washing with warm water. The solvent was removed under reduced pressure to obtain an epoxy resin (304.9 g).

Epoxy equivalent of the resulting epoxy resin was 256 g/eq. It was confirmed by infrared absorption spectrum that absorption 3200-3600 cm^{-1} of phenolic OH disappeared and there were absorptions of 1240, 910 cm^{-1} of epoxide.

Preparation Example 3

This example relates to preparation of a terminal epoxy resin having a bromine content of 20% by addition reaction of the epoxy resin obtained in Preparation Example 2 with diglycidyl ether of tetrabromobisphenol A and tetrabromobisphenol A.

The epoxy resin obtained in Preparation Example 2 (62.0 g), diglycidyl ether of tetrabromobisphenol A (Sumiepoxy ESB-400 having an epoxy equivalent of 403 g/eq manufactured by Sumitomo Chemical Co., Ltd., 25.3 g) and tetrabromobisphenol A (12.7 g) were charged in a 300 ml four-necked round flask equipped with a thermometer, a stirrer, a condenser tube and molten by heating at 110° C. Thereafter, a solution prepared by dissolving triphenylphosphine (40 mg, 4×10^{-4} wt% based on resin) in methyl ethyl ketone (2.25 g) was added and the mixture was kept at 110 ° C for 4 hours to carry out the addition reaction between the epoxy group and the phenolic hydroxyl group. After completion of the reaction, the reaction system was cooled to 90° C and methyl ethyl ketone (22.75 g) was added dropwise to obtain a resin solution (123.9 g, resin solid content 80.62 wt%). Epoxy equivalent of the resulting resin adduct was 399.0 g/eq.

Preparation Example 4

This example relates to preparation of a terminal epoxy resin having a bromine content of 27% by the addition reaction of the epoxy resin obtained in

Preparation Example 2 with diglycidyl ether of tetrabromobisphenol A and tetrabromobisphenol A.

The epoxy resin obtained in Preparation Example 2 (132.6 g), diglycidyl ether of tetrabromobisphenol A (Sumiepoxy ESB-400 having an epoxy equivalent of 403 g/eq manufactured by Sumitomo Chemical Co., Ltd., 119.5 g) and tetrabromobisphenol A (279.0 g) were charged in a 500 ml four-necked round flask equipped with a thermometer, a stirrer and a condenser tube and molten by heating at 110° C. Thereafter, a solution prepared by dissolving triphenylphosphine (112 mg, 4×10^{-4} wt% based on resin) in methyl ethyl ketone (0.30 g) was added and the mixture was kept at 110° C for 4 hours to carry out the addition reaction between the epoxy group and the phenolic hydroxyl group. After completion of the reaction, the reaction system was cooled to 90° C and methyl ethyl ketone (73.5 g) was added dropwise to obtain a resin solution (349.2 g, resin solid content 79.80 wt%). Epoxy equivalent of the resulting resin adduct was 388.0 g/eq.

Example 1

The epoxy resin obtained in Preparation Example 3, dicyandiamide and 2-ethyl-4-methylimidazole were mixed at the ratio as shown in Table 1 and the mixture was dissolved in a mixed solvent of methyl ethyl ketone and ethylene glycol monomethyl ether to prepare a homogeneous resin varnish. A glass cloth (KS-1600S962LP manufactured by Kanebo Ltd.) was impregnated with the varnish and treated at 150° C for 5-10 minutes by a hot-air dryer to obtain a prepreg. Five prepreps and a copper foil (subjected to TSTO treatment; 35 μ thick, manufactured by Furukawa Circuit Foil Co.) were stacked and hot press molded under the conditions of 170° C $\times$ 50 kg/cm² $\times$

120 minutes to obtain a copper-clad laminate of 1 mm thick. Peeling strength of the copper foil of the laminate and solder resistance were measured in accordance with JIS-C-6481. Glass transition temperature (T_g) was obtained from the inflexion point of an expansion curve using a thermal apparatus DT-30 manufactured by Shimadzu Seisakusho Ltd. Dielectric constant and dissipation factor at room temperature were measured using 4275 Multi-Frequency LCR meter manufactured by Yokogawa Hurett Packard Co. and the value of dielectric constant was calculated from electric capacity. The results are shown in Table 1.

Example 2

The epoxy resin obtained in Preparation Example 4, a phenol novolak resin (Tamanol 758 manufactured by Arakawa Chemical Co., Ltd.) and 2-ethyl-4-methylimidazole were mixed at the ratio as shown in Table 1 and the mixture was dissolved in methyl ethyl ketone to prepare a homogeneous resin varnish. A copper-clad laminate of 1 mm thick was obtained using the resulting varnish in the same manner as in Example 1. The properties of the laminate were also measured in the same manner as in Example 1. The results are shown in Table 1.

Example 3

The epoxy resin obtained in Preparation Example 4, diglycidyl ether of tetrabromobisphenol A (Sumiepoxy ESB-400 manufactured by Sumitomo Chemical Co., Ltd.; epoxy equivalent: 403 g/eq), a phenol-modified polybutadieneresin (PP-700-300 manufactured by Nippon Oil Chemical Co., Ltd.; OH equivalent: 317 g/eq, softening point: 149 °C) and 2-ethyl-4-methylimidazole were mixed at the ratio as shown in Table 1 and the

mixture was dissolved in methyl ethyl ketone to prepare a homogeneous resin varnish. A copper-clad laminate of 1 mm thick was obtained using the resulting varnish in the same manner as in Example 1. The properties of the laminate were also measured in the same manner as in Example 1. The results are shown in Table 1.

Example 4

The epoxy resin obtained in Preparation Example 4, diglycidyl ether of tetrabromobisphenol A (Sumiepoxy ESB-400 manufactured by Sumitomo Chemical Co., Ltd.; epoxy equivalent: 403 g/eq), a dicyclopentadiene-phenol resin (DPP-600M manufactured by Nippon Oil Chemical Co., Ltd.; OH equivalent: 168 g/eq, softening point: 96 °C) and 2-ethyl-4-methylimidazole were mixed at the ratio as shown in Table 1 and the mixture was dissolved in methyl ethyl ketone to prepare a homogeneous resin varnish. A copper-clad laminate of 1 mm thick was obtained using the resulting varnish in the same manner as in Example 1. The properties of the laminate were also measured in the same manner as in Example 1. The results are shown in Table 1.

Comparative Example 1

Brominated epoxy resin (Sumiepoxy ESB-500 manufactured by Sumitomo Chemical Co., Ltd.; epoxy equivalent: 472 g/eq) and a cresol novolak type epoxy resin (Sumiepoxy ESCN-220 manufactured by Sumitomo Chemical Co., Ltd.; epoxy equivalent: 215 g/eq) as the epoxy resins, dicyandiamide and 2-ethyl-4-methylimidazole were mixed at the ratio as shown in Table 1 and the mixture was dissolved in a mixed solvent of methyl ethyl ketone and ethylene glycol monomethyl ether to prepare a homogeneous resin varnish. A glass cloth (KS-1600S962LP manufactured by Kanebo Ltd.) was

impregnated with the varnish and treated at 150 ° C for 5-10 minutes by a hot-air dryer to obtain a prepreg. Five prepregs and a copper foil (subjected to TSTO treatment; 35 μ thick, manufactured by Furukawa Circuit Foil Co.) were stacked and hot press molded under the conditions of 160 ° C $\times$ 50 kg/cm² $\times$ 90 minutes to obtain a copper-clad laminate of 1 mm thick.

The properties of the laminate were measured in the same manner as in Example 1 and the results are shown in Table 1.

Table 1

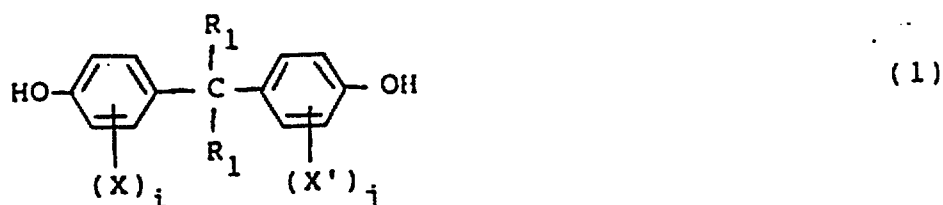
		Example 1	Example 2	Example 3	Example 4	Compar- ative Example 1
Epoxy resin of Preparation Example 3 (solid content)		100				
Epoxy resin of Preparation Example 4 (solid content)			78.6	32.3	84.7	
Suniepoxy ESB-400				22.7	5.1	
Suniepoxy ESB-500						90
Suniepoxy ESCN-220						10
Dicyandiamide		2.63				2.49
Tamanol 758			21.4			
PP-700-300				45.0		
DPP-600M					30.2	
2-Ethyl-4-methylimidazole		0.2	0.2	0.2	0.2	0.1
Copper foil peeling strength	kg/cm	2.0	1.8	1.7	1.8	2.0
Solder resistance (260°C x 3 min.)		No blister	No blister	No blister	No blister	No blister
Glass transition temperature	°C	159	150	178	157	135
Dielectric constant (1MHz)		4.23	4.29	4.05	4.12	4.91
Dissipation factor (1MHz)		0.01	0.01	0.01	0.01	0.02

The cured resin of the epoxy resin composition of the present invention was excellent in heat resistance and low in dielectric and the copper-clad laminate obtained by molding it is suitable for multi-layer printed circuit boards for high-speed operational processing because of these excellent properties.

CLAIMS:

1. An epoxy resin composition which comprises:

(1) a compound obtainable by previously reacting (A) an epoxy resin obtainable by glycidyl etherifying a 3-methyl-6-(C₁-C₄)alkylphenol novolak with (B) a halogen-containing bisphenol compound represented by the following formula (1):

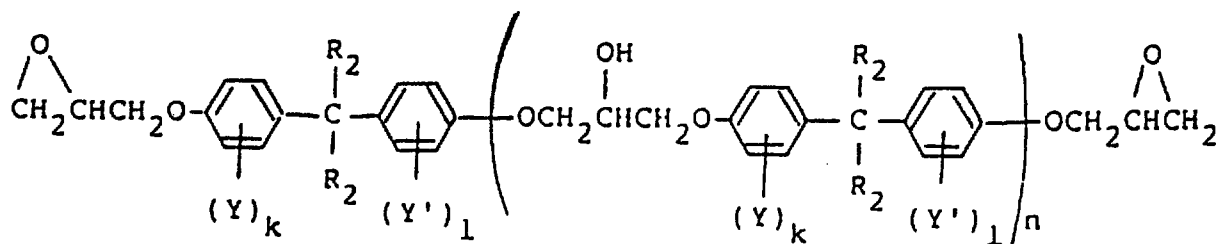


wherein R₁ represents a hydrogen atom or a methyl group and the two R₁ may be identical or different, X and X' represent halogen atom and may be identical or different, and i and j independently of one another are integers of 1 to 4 and

(2) an epoxy hardener.

2. An epoxy resin composition which comprises:

(1) a compound obtainable by previously reacting (A) the epoxy resin defined in claim 1, (B) the halogen-containing bisphenol compound defined in claim 1 and (C) a glycidyl etherification product of a halogen-containing bisphenol compound which is represented by the following formula (2):



(2)

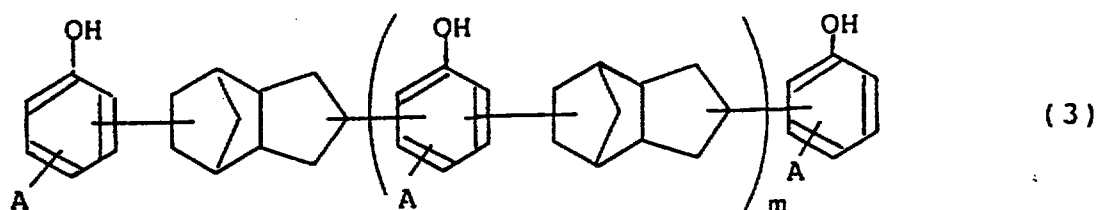


wherein R_2 represents a hydrogen atom or a methyl group and the two R_2 may be identical or different, Y and Y' represent halogen atom and may be identical or different, n represents an average recurring unit number and is 0 to 10 and k and l independently of one another are integers of 1 to 4 and

(2) an epoxy hardener.

3. An epoxy resin composition according to claim 1 or 2, wherein the epoxy hardener is a polybutadiene compound modified with a phenolic compound.

4. An epoxy resin composition according to claim 1 or 2, wherein the epoxy hardener is a dicyclopentadiene-phenol compound represented by the following formula (3):



wherein m represents an average recurring unit number and is a numeral in the range of 0 to 10 and A represents a hydrogen atom or an alkyl group of 1 to 8 carbon atoms.

5. An epoxy resin copper-clad laminate obtained by heat molding a copper foil and a prepreg obtained by impregnating a substrate with a solution prepared by dissolving the epoxy resin composition of claim 1, 2, 3 or 4 in an organic solvent.

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