A heat resistant resin is obtained by crosslinking an organic polymer having an imide bond and/or an amide bond in the main chain thereof with a compound having at least three amino groups and a phosphazene skeleton and having a specific structure.
Description

Title of Invention: HEAT RESISTANT RESIN, COMPOSITION THEREOF, RESIN/METAL LAMINATE AND CIRCUIT BOARD

Technical Field

[0001] The present invention relates to a novel polyimide resin, a polyimide resin composition, a polyimide/metal laminate and a circuit board material, which are suitably used for micro processing in manufacturing circuit boards and excellent in heat resistance and dimensional stability. The present invention relates to a novel compound, which is suitably used as a crosslinking agent for organic polymers.

Background Art

[0002] Recently, in the field of COF (chip on film), in which IC chips are directly mounted on a film type wired circuit board and which is used in liquid crystal display drivers and so on, wiring pitch is getting finer as the information processing capability is increased and the downsizing goes on. As the materials for the circuit board, a laminate comprising a resin layer and a metal layer is used, and polyimide resin is preferably used in the resin layer in view of the heat resistance and dimensional stability. (See PTL 1 for example.)

Citation List

Patent Literature

PTL 2: Japanese laid-open number; 2006-77064

Summary of Invention

[0004] Along with the shift to fine pitch as described above, the demand for circuit boards having fine pattern processability, heat resistance and dimensional stability increases. Further, high elastic modulus at high temperature is demanded for polyimides because the mounting of IC chips is carried out at a high temperature of more than 400 degrees C. Furthermore, low coefficient of thermal expansion (CTE) and low coefficient of hygroscopic expansion (CHE) are demanded. However, the conventional polyimides do not necessarily have the properties that fulfill the demands above.

[0005] Conventionally, it is proposed that various additives and structures be introduced in polyimide resins. For example, a polyimide characterized by having a phosphazene skeleton is proposed. (See PTL 2 for example.) No crosslinking structure is formed in the polyimide for the phosphazene skeleton is incorporated in the main chain of the polyimide. Also, the effect of that invention is to improve the frame flame retardancy, and no clear statement is made concerning the elastic modulus at high temperature and the dimensional stability.
The purpose of the invention is to present a heat resistant polyimide resin, which is excellent in elastic modulus at high temperature and dimensional stability. Another purpose of the invention is to prepare a polyimide/metal laminate having a layer comprising the heat resistant resin described above and thereby present a polyimide/metal laminate and a circuit board material suitable for a base material for COF.

The inventors have made extensive investigation and resultantly conceived that a resin obtainable by crosslinking an organic polymer (I) having an imide bond and/or an amide bond in the main chain thereof with a compound (C) having at least three amino groups and a phosphazene skeleton and represented by the following formula (1) can solve the problem above, and the present invention is thereby completed.

The present invention relates to:

(i) A heat resistant resin obtainable by crosslinking an organic polymer (I) having an imide bond and/or an amide bond in the main chain thereof with a compound (C) having at least three amino groups and a phosphazene skeleton and represented by the following formula (1), wherein \( m \) and \( n \) independently represents an integer provided that \( m + n \) is from 3 to 25, \( R_3, R_4, R_5 \) and \( R_6 \) independently represents a phenyl group, an amino phenyl group or a substituted phenyl group having a structure represented by the formula (2), wherein \( R_7 \) represents an organic group selected from the group consisting of an alkyl group, fluoro group, chloro group, bromo group, nitro group, cyano group, hydroxyl group, phenoxy group and a substituted group connected via an amide, imide, ester or ether bond, formula (1) has at least three amino groups, and formula (2) has at least one \( R_7 \).

[Chem.1]

![Formula 1](image1)

[Chem.2]

![Formula 2](image2)

Each of (ii) to (xiii) shown below is a preferred embodiment of the present invention.

(ii) The heat resistant resin as in (i) above, wherein the storage elastic modulus measured at 450 degrees C thereof is from 0.5 GPa to 3.0 GPa.

(iii) The heat resistant resin as in (i) or (ii) above, wherein the organic polymer (I) comprises a repeating unit derived from a tetracarboxylic dianhydride (A) and a
repeating unit derived from a diamine (B).

(iv) The heat resistant resin as in (iii) above comprising 0.01 to 80 parts by weight of the structure derived from the compound (C) based on total 100 parts by weight of the repeating unit derived from the tetracarboxylic dianhydride (A), the repeating unit derived from the diamine (B) and the compound (C)

(v) The heat resistant resin as claimed in (iv) above, wherein the molar ratio \((A)/(B)\) of the repeating unit derived from the tetracarboxylic dianhydride (A) to the repeating unit derived from the diamine (B) is not more than 1.

(vi) A heat resistant resin composition comprising the heat resistant resin as in any one of (i) to (v) above.

(vii) A resin/metal laminate having a layer (Ll) comprising the heat resistant resin as in any one of (i) to (v) above and a metal layer (L2).

(viii) A circuit board having a layer (Ll) comprising the heat resistant resin as in any one of (i) to (v) above.

(ix) The circuit board as in (viii) above characterized in that COF (chip on film) mounting process is carried out on the layer (Ll).

(x) A process for producing the heat resistant resin as in (ix) or (v) above, comprising the steps of; (1) synthesizing a polyamic acid (Ia) from a tetracarboxylic dianhydride (A) and a diamine (B), (2) preparing a solution by adding the compound (C) to the polyamic acid (Ia), and (3) heating the solution to carry out imidation, in this order.

(xi) A compound represented by the following formula (3), wherein \(R_1\) to \(R_6\) are independently fluoro group, amino group or hydrogen atom, and at least three of \(R_1\) to \(R_6\) are amino groups and at least one of \(R_1\) to \(R_6\) is fluoro group.

[0012] [Chem.3]

![Chemical Structure](image)

[0013] (xii) The compound as in (xi) above, wherein three of \(R_1\) to \(R_6\) are fluoro groups and
three of R₁ to R₆ are amino groups.

(xiii) A crosslinking agent for an organic polymer comprising the compound as in (xi) or (xii) above.

[0014] According to the present invention, a heat resistant polyimide resin, which is excellent in elastic modulus at high temperature and dimensional stability can be obtained. A polyimide/metal laminate having a layer comprising the heat resistant resin described above can cope with the high density mounting of chips, which has been accelerated recently, and effectively used as a polyimide/metal laminate for COF.

Brief Description of Drawings

[0015] [fig.1]Fig. 1 is ¹H NMR chart of FACP (tris(4-fluorophenoxy)tris(4-aminophenoxy)cyclotriphosphazene).
[fig.2]Fig. 2 is ³¹P NMR chart of FACP.
[fig.3]Fig. 3 is MALDI-TOF spectra of FACP.

Description of Embodiment

[0016] The present invention is a heat resistant resin obtainable by crosslinking an organic polymer (I) having an imide bond and/or an amide bond in the main chain thereof with a compound (C) having at least three amino groups and a phosphazene skeleton and having a specific structure.

[0017] The polyimide resin composition of the present invention preferably comprises a polyimide derived from a tetracarboxylic dianhydride (A) a diamine compound (B) and/or a precursor thereof and a compound (C) having three or more amino groups and a phosphazene skeleton wherein the composition of (C) is from 0.1 wt% to 80 wt% based on the total amount of (A) + (B) + (C).

[0018] Organic Polymer (D)

In the present invention, no particular limitation is imposed on the organic polymer (I) having an imide bond and/or an amide bond in the main chain thereof, except that the organic polymer should have at least one imide bond and/or amide bond in the main chain thereof. The polymer preferably is a polyimide precursor, more preferably a polyimide precursor comprising a polyimide polymer and/or a polyamic acid polymer.

[0019] No particular limitation is imposed on the polyimide precursor in the present invention, any polyimide precursor comprising a polyimide polymer and/or polyamic acid polymer synthesized using a known tetracarboxylic dianhydride (A) and a known diamine compound (B). The polyimide precursor preferably comprises a polyimide polymer and/or a polyamic acid polymer synthesized using at least one tetracarboxylic dianhydride (A) and at least one diamine compound (B).

[0020] The diamine compounds (B) used as the starting material of the polyimide polymer
and/or polyamic acid polymer in the present invention include, for example,  
1,3-bis(3-aminophenoxy)benzene, 4,4-bis(3-aminophenoxy)biphenyl,  
3,3'-diaminobenzophenone, 1,4-phenylenediamine, 4,4'-diaminodiphenyl ether,  
1,3-bis(3-(3-aminophenoxy)phenoxy)benzene,  
1,3-bis(3-(4-aminophenoxy)phenoxy)benzene, 5,7-diamino-1,1,4,6-tetramethylindaine, 1,3-bis(4-(3-aminophenoxy)phenoxy)benzene,  
1,3-bis(3-(2-aminophenoxy)phenoxy)benzene,  
1,3-bis(2-(2-aminophenoxy)phenoxy)benzene,  
1,3-bis(2-(3-aminophenoxy)phenoxy)benzene, 1,3-bis(2-(4-aminophenoxy)phenoxy)benzene,  
1,4-bis(3-(3-aminophenoxy)phenoxy)benzene, 1,4-bis(3-(3-aminophenoxy)phenoxy)benzene,  
1,4-bis(3-(4-aminophenoxy)phenoxy)benzene, 1,4-bis(4-(2-aminophenoxy)phenoxy)benzene,  
1,4-bis(2-(2-aminophenoxy)phenoxy)benzene,  
1,4-bis(2-(3-aminophenoxy)phenoxy)benzene, 1,4-bis(2-(4-aminophenoxy)phenoxy)benzene,  
1,2-bis(3-(3-aminophenoxy)phenoxy)benzene, 1,2-bis(3-(4-aminophenoxy)phenoxy)benzene,  
1,2-bis(3-(2-aminophenoxy)phenoxy)benzene,  
1,2-bis(4-(2-aminophenoxy)phenoxy)benzene,  
1,2-bis(4-(3-aminophenoxy)phenoxy)benzene,  
1,2-bis(4-(3-aminophenoxy)phenoxy)benzene, 1,2-bis(4-(3-aminophenoxy)phenoxy)benzene,  
1,2-bis(2-(2-aminophenoxy)phenoxy)benzene,  
1,2-bis(2-(3-aminophenoxy)phenoxy)benzene, 1,2-bis(2-(4-aminophenoxy)phenoxy)benzene,  
1,2-bis(2-(3-aminophenoxy)phenoxy)-2-methylbenzene,  
1,3-bis(3-(3-aminophenoxy)phenoxy)-4-methylbenzene,  
1,3-bis(4-(3-aminophenoxy)phenoxy)-2-ethylbenzene,  
1,3-bis(3-(2-aminophenoxy)phenoxy)-5-sec-butylbenzene,  
1,3-bis(4-(3-aminophenoxy)phenoxy)-2,5-dimethylbenzene,  
1,3-bis(4-(2-amino-6-methylphenoxy)phenoxy)benzene,  
1,3-bis(2-(2-amino-6-ethylphenoxy)phenoxy)benzene,  
1,3-bis(2-(3-aminophenoxy)-4-methylphenoxy)benzene,  
1,3-bis(2-(4-aminophenoxy)-4-tert-butylphenoxy)benzene,  
1,4-bis(3-(3-aminophenoxy)phenoxy)-2,5-di-tert-butylbenzene,  
1,4-bis(3-(4-aminophenoxy)phenoxy)-2,3 dimethylbenzene,
1,4-bis(3-(2-amino-3-propylphenoxy)phenoxy)benzene,
1,2-bis(3-(3-aminophenoxy)phenoxy)-4-methylbenzene, 1,2-bis(3-(4-aminophenoxy)phenoxy)-3-n-butyl benzene, 1,2-bis(3-(2-amino-3-propylphenoxy)phenoxy)benzene and so on. One of these compounds or two or more thereof may be used. Particularly preferable diamine compounds are 1,4-phenylenediamine, 4,4'-oxydianiline(4,4'-diaminodiphenyl ether) and 4,4-bis(3-aminophenoxy)biphenyl.

[0021] In the present invention, the tetracarboxylic dianhydrides (A) used as the starting material of the polyimide polymer and/or polyamic acid polymer are not particularly limited, and any known species can be used. The examples of the tetracarboxylic dianhydrides (A) include pyromellitic dianhydride, 3,3',4,4'-biphenyltetracarboxylic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 2,3,3',4,4'-biphenyltetra carboxylic dianhydride, bis(3,4-dicarboxyphenyl)ether dianhydride, bis(3,4-dicarboxyphenyl)sulfide dianhydride, bis(3,4-dicarboxyphenyl)sulfone dianhydride, bis(3,4-dicarboxyphenyl)methane dianhydride, 2,2-bis(3,4-dicarboxyphenyl)propane dianhydride, 2,2-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride, 1,3-bis(3,4-dicarboxyphenoxy)benzene dianhydride, 1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride, 4,4'-bis(3,4-dicarboxyphenoxy)benzhydride, 2,2-bis[(3,4-dicarboxyphenoxy)phenyl]propane dianhydride, 2,3,6,7-naphthalenetetra carboxylic dianhydride, 1,4,5,8-naphthalenetetra carboxylic anhydride, butane-1,2,3,4-tetracarboxylic dianhydride, pentane-1,2,4,5-tetracarboxylic dianhydride, cyclobutanetetracarboxylic dianhydride, cyclopentane-1,2,3,4-tetracarboxylic dianhydride, cyclohexane-1,2,4,5-tetracarboxylic dianhydride, cyclohexa-l-ene-2,3,5,6-tetracarboxylic dianhydride, 3-ethylcyclohexa-l-ene-3-(1,2),5,6-tetracarboxylic dianhydride, 1-methyl-3-ethylcyclohexane-3-(1,2),5,6-tetracarboxylic dianhydride, 1-methyl-3-ethylcyclohexa-l-ene-3-(1,2),5,6-tetracarboxylic dianhydride, 1-ethylcyclohexane-l-(1,2),3,4-tetracarboxylic dianhydride, 1-propylcyclohexane-l-(1,2),3,4-tetracarboxylic dianhydride, 1,3-dipropylcyclohexane-l-(1,2)-3,4-tetracarboxylic dianhydride, dicyclohexyl-3,4,3',4'-tetracarboxylic dianhydride, bicycle[2.2.1]heptane-2,3,5,6-tetracarboxylic dianhydride, bicycle[2.2.2]octane-2,3,5,6-tetracarboxylic dianhydride, bicycle[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride and so on. One of these tetracarboxylic dianhydrides or two or more thereof may be used. Particularly preferable tetracarboxylic dianhydrides are pyromellitic dianhydride, 3,3',4,4'-biphenyltetra carboxylic dianhydride and 3,3',4,4'-benzophenonetetra carboxylic dianhydride.

[0022] The reaction molar ratio ((A)/(B)) of tetracarboxylic dianhydride (A) to diamine
compound (B) is usually in the range of from 0.7 to 1.25, preferably not more than 1.05, more preferably not less than 0.8 and not more than 1.05. When the ratio is in the range defined above, a resin having high modulus of elasticity and excellent dimensional stability can be obtained.

In the present invention, the polyimide polymer or the polyamic acid polymer may contain any additional structural unit derived from any other component depending on the purpose of the embodiment. The purity of the starting materials is preferably high, it is particularly preferable that the diamine does not contain any impurity having the molecular weight higher than that of the diamine itself and, for this purpose, the preparative method of removing impurities by conventional means, such as distillation, can be utilized.

Further, a dicarboxylic anhydride can be added to terminate the polymer terminal. Examples of the dicarboxylic anhydride to be used include phthalic anhydride, 2,3-benzophenonedicarboxylic anhydride, 3,4-benzophenonedicarboxylic anhydride, 2,3-dicarboxyphenylphenylether anhydride, 2,3-biphenyldicarboxylic anhydride, 3,4-biphenyldicarboxylic anhydride, 2,3-dicarboxyphenylnonylsulfone anhydride, 3,4-dicarboxyphenylnonylsulfone anhydride, 2,3-dicarboxyphenylphenylsulfide anhydride, 1,2-naphthalenedicarboxylic anhydride, 2,3-naphthalenedicarboxylic anhydride, 1,8-naphthalenedicarboxylic anhydride, 1,2-anthracenedicarboxylic anhydride, 2,3-anthracenedicarboxylic anhydride, 1,9-anthracenedicarboxylic anhydride, 5-norbornene-2,3-dicarboxylic anhydride, 1-phenyl-2-(3,4-dicarboxyphenyl)acetylene anhydride, maleic anhydride and so on. These dicarboxylic anhydrides may be substituted with a group having no reactivity with an amine or a dicarboxylic anhydride.

The dicarboxylic anhydride can usually be added at a molar ratio in the range of from 0.001 moles to 0.5 moles, preferably 0.005 moles to 0.25 moles, based on 100 moles of the total amount of the specific diamines described above as the main component, other amine compounds to be used together, the specific tetracarboxylic dianhydrides described above and other tetracarboxylic dianhydrides to be used together.

Similarly, a monoamine can be added to terminate the polymer terminal. Examples of the monoamine include aniline, o-toluidine, m-toluidine, p-toluidine, 2,3-xylidine, 2,4-xylidine, 2,5-xylidine, 2,6-xylidine, 3,4-xylidine, 3,5-xylidine, o-chloroaniline, m-chloroaniline, p-chloroaniline, o-bromoaniline, m-bromoaniline, o-nitroaniline, m-nitroaniline, p-nitroaniline, o-aminophenol, m-aminophenol, p-aminophenol, o-anilidine, m-anilidine, p-anilidine, o-phenetidine, m-phenetidine, p-phenetidine, o-aminobenzaldehyde, m-aminobenzaldehyde, p-aminobenzaldehyde, o-aminobenzonitrile, m-aminobenzonitrile, p-aminobenzonitrile, 2-aminobiphenyl, 3-aminobiphenyl, 4-aminobiphenyl, 2-aminophenylphey ether, 3-aminophenylphenyl
ether, 4-aminophenylphenyl ether, 2-aminobenzophenone, 3-aminobenzophenone, 
4-aminobenzophenone, 2-aminophenylphenyl sulfd, 3-aminophenylphenyl sulfd, 
4-amino phenylphenyl sulfd, 2-aminophenylphenyl sulfone 3-aminophenylphenyl sulfone, 4-amino phenylphenyl sulfone, alpha-naphthylamine, beta-naphthylamine, 
1-amino-2-naphthol, 2-amino-1-naphthol, 4-amino-1-naphthol, 5-amino-1-naphthol, 
5-amino-2-naphthol, 7-amino-2-naphthol, 8-amino-2-naphthol, 1-aminoanthracene, 
2-aminoanthracene, 9-aminoanthracene and so on.

These monoamines can solely be used or used in combination of two or more 
species. The monoamine can usually be used at a molar ratio in the range of from 
0.001 moles to 0.5 moles, preferably 0.005 moles to 0.25 moles, based on 100 moles of 
the total amount of the specific diamine described above as the main component, other 
amine compound to be used together, the specific tetracarboxylic dianhydride 
described above and other tetracarboxylic dianhydride to be used together.

Further, it is preferable that the polymerization of the organic polymer (I) (polyimide 
and/or precursor thereof) be carried out in an organic solvent. The example of the 
solvent can be used include phenol, o-chlorophenol, m-chlorophenol, p-chlorophenol, 
o-cresol, m-cresol, p-cresol, 2,3-xylenol, 2,4-xylenol, 2,5-xylenol, 2,6-xylenol, 
3,4-xylenol, 3,5-xylenol, N,N-dimethylformamide, N,N-dimethylacetamide, 
N,N-diethylacetamide, N,N-dimethylmethoxyacetamide, N-methyl-2-pyrrolidone, 
1,3-dimethyl-2-imidazolidinone, N-methylcaprolactam, 1,2-dimethoxyethane, 
bis(2-methoxyethyl)ether, 1,2-bis(2-methoxyethoxy)ethane, 
bis(2-(2-methoxethoxy)ethyl)ether, tetrahydrofuran, 1,3-dioxane, 1,4-dioxane, 
pyridine, picoline, dimethylsulfoxide, dimethylsulfone, tetramethylene, hexamethylphosphoramide, anisole and so on, and other known solvents can also be used. 
These organic solvents can be used solely or in combination of two or more species.

There's no problem even when any of the solvents shown below further coexists. The 
examples of the solvents to coexist include p-xylene, o-chlorotoluene, m- 
chlorotoluene, p-chlorotoluene, o-bromotoluene, m-bromotoluene, p-bromotoluene, 
chlorobenzene, bromobenzene and so on.

The reaction time of the polyamic acid, which is a precursor of the polyimide, can 
roughly be from 1 hour to 48 hours, and is usually from 4 hours to 24 hours, although 
the time can vary depending on the species of the monomers to be used, the species of 
the solvent, the species of the organic base catalyst, the species and the amount of the 
solvent for azotropic dehydration and the reaction temperature. A guideline for the 
case of obtaining the polyimide by means of thermal imidization is to carry out the 
reaction until the most (usually 70 % to 90 % as not all of the distillate is recovered) of 
the theoretical amount of distillate water is obtained, which usually takes hours or tens 
of hours. In this case, it is common and useful to remove the water generated from the
imidization using an azeotropic agent such as xylene or toluene.

[0031] Although no particular limitation is imposed on the reaction pressure, the atmospheric pressure is usually sufficiently suitable.

[0032] Although no particular limitation is imposed on the reaction atmosphere, air, nitrogen, helium, neon or argon is usually used, and an inert gas such as nitrogen or argon is preferably used.

[0033] Further, an organic basic catalyst is preferably used in the preparation of the polyimide of the present invention in an organic solvent. Examples of the organic basic catalyst include, triethylamine, tributylamine, tripentylamine, N,N-dimethylaniline, pyridine, alpha-picoline, beta-picoline, gamma-picoline, 2,6-lutidine, quinoline, iso-quinoline and so on. The preferable is pyridine or picoline. No particular limitation is imposed on the amount of the catalyst to be used, provided that the polymerization reaction rate is substantially improved.

[0034] Compound (C) having at least three amino groups and a phosphazene skeleton

The heat resistant resin of the present invention is obtainable by crosslinking the above-described organic polymer (I) having an imide bond and/or an amide bond in the main chain thereof with the compound (C) having at least three amino groups and a phosphazene skeleton.

[0035] No particular limitation is imposed on the compound (C) having three or more amino groups and a phosphazene skeleton, provided that the compound is represented by the following formula (1), wherein m and n independently represents an integer provided that m + n is from 3 to 25, R₃, R₄, R₅ and R₆ independently represents a phenyl group, an amino phenyl group or a substituted phenyl group having a structure represented by the formula (2), wherein R₇ represents an organic group selected from the group consisting of an alkyl group, fluoro group, chloro group, bromo group, nitro group, cyano group, hydroxyl group, phenoxy group and a substituted group connected via an amide, imide, ester or ether bond, formula (1) has at least three amino groups, and formula (2) has at least one R₇.

[0036] [Chem.4]

[0037] [Chem.5]
The examples include hexakis(4-aminophenoxy)cyclotriphosphazene, monomethoxypentakis(4-aminophenoxy)cyclotriphosphazene, dimethoxytetrakis(4-aminophenoxy)cyclotriphosphazene, trimethoxytris(4-aminophenoxy)cyclotriphosphazene, monophenoxypentakis(4-aminophenoxy)cyclotriphosphazene, diphenoxytetrakis(4-aminophenoxy)cyclotriphosphazene, triphenoxytris(4-aminophenoxy)cyclotriphosphazene, monoocthoxypentakis(4-aminophenoxy)cyclotriphosphazene, diethoxytetrakis(4-aminophenoxy)cyclotriphosphazene, triethoxytris(4-aminophenoxy)cyclotriphosphazene, monon-propoxy pentakis(4-aminophenoxy)cyclotriphosphazene, din-propoxytetrakis(4-aminophenoxy)cyclotriphosphazene, trim-propoxytris(4-aminophenoxy)cyclotriphosphazene, monophenoxypentakis(4-aminophenoxy)cyclotriphosphazene, bis(4-(trifluoromethyl)phenoxy)tetrakis(4-aminophenoxy)cyclotriphosphazene, tris(4-chlorophenoxy)tris(4-aminophenoxy)cyclotriphosphazene, 4-bromophenoxypentakis(4-aminophenoxy)cyclotriphosphazene, bis(4-bromophenoxy)tetrakis(4-aminophenoxy)cyclotriphosphazene, tris(4-bromophenoxy)tris(4-aminophenoxy)cyclotriphosphazene, 4-ethylphenoxy pentakis(4-aminophenoxy)cyclotriphosphazene, bis(4-ethylphenoxy)tetrakis(4-aminophenoxy)cyclotriphosphazene, tris(4-ethylphenoxy)tris(4-aminophenoxy)cyclotriphosphazene, 4-n-propylphenoxy pentakis(4-aminophenoxy)cyclotriphosphazene, bis(4-n-propylphenoxy)tetrakis(4-aminophenoxy)cyclotriphosphazene, tris(4-n-propylphenoxy)tris(4-aminophenoxy)cyclotriphosphazene, 4-i-propylphenoxy pentakis(4-aminophenoxy)cyclotriphosphazene, bis(4-i-propylphenoxy)tetrakis(4-aminophenoxy)cyclotriphosphazene, tris(4-i-propylphenoxy)tris(4-aminophenoxy)cyclotriphosphazene, 4-nitrophenoxy pentakis(4-aminophenoxy)cyclotriphosphazene, bis(4-nitrophenoxy)tetrakis(4-aminophenoxy)cyclotriphosphazene, tris(4-nitrophenoxy)tris(4-aminophenoxy)cyclotriphosphazene,
bis(4-nitrophenoxy)tetrakis(4-aminophenoxy)cyclotriphosphazene, 
tris(4-nitrophenoxy)tris(4-aminophenoxy)cyclotriphosphazene, 
4-cyanophenoxypentakis(4-aminophenoxy)cyclotriphosphazene, 
bis(4-cyanophenoxy)tetrakis(4-aminophenoxy)cyclotriphosphazene, 
tris(4-cyanophenoxy)tris(4-aminophenoxy)cyclotriphosphazene, 
4-hydroxyphenoxypentakis(4-aminophenoxy)cyclotriphosphazene, 
bis(4-hydroxyphenoxy)tetrakis(4-aminophenoxy)cyclotriphosphazene, 
tris(4-hydroxyphenoxy)tris(4-aminophenoxy)cyclotriphosphazene and so on.

Although the compound (C) is usually added to a varnish comprising the tetracarboxylic dianhydride (A), the diamine (B) and the solvent described above, it can be added in any other step of the production. The crosslinking can proceed either after the polymer (I) is generated form the tetracarboxylic dianhydride (A) and the diamine (B) or simultaneously with the generation of the polymer (I). The compound (C) is preferably added 0.01 to 80 parts by weight based on total 100 parts by weight of the tetracarboxylic dianhydride (A), the diamine (B) and the compound (C).

**Novel Compound (C)**

The inventors have also conceived that a novel compound (C) represented by the following formula (3), wherein R₁ to R₆ are independently fluoro group, amino group or hydrogen atom, and at least three of R₁ to R₆ are amino groups and at least one of R₁ to R₆ is fluoro group, is particularly suitable for crosslinking the polymer (I).

The preferable examples of compound (C) includes, 4-fluorophenoxypentakis(4-aminophenoxy)cyclotriphosphazene, 
bis(4-fluorophenoxy)tetrakis(4-aminophenoxy)cyclotriphosphazene and tris(4-fluorophenoxy)tris(4-aminophenoxy)cyclotriphosphazene. In the compound (C),
three of R₁ to R₆ are preferably fluoro groups and three of R₁ to R₆ are preferably amino groups. Therefore, tris(4-fluorophenoxy)tris(4-aminophenoxy)cyclotriphosphazene is especially preferable. Compound (C) can be synthesized, for example, by reacting phosphonitrilic chloride trimer with 4-nitrophenol and 4-fluorophenol and then reducing the product. The method for synthesizing compound (C) will be explained in more detail in the examples.

[0043] **Heat Resistant Resin Composition**

The heat resistant resin composition of the invention is only required to contain a heat resistant resin obtainable by crosslinking the above-described organic polymer (I) having an imide bond and/or an amide bond in the main chain thereof with the compound (C) having at least three amino groups and a phosphazene skeleton, and may contain or does not contain any other component(s).

[0044] For example, a bismaleimide compound can be added as another component to the polyimide compound of the invention, not more than 50 wt%, in order to adjust the glass transition temperature. Specific examples of the bismaleimide compound include 4,4'-bis(4-phenyl)ethane, 1,3-bis(3-maleimidophenoxy)benzene, 1,3-bis(3-(3-maleimidophenoxy)phenoxy)benzene, 1,3-bis(3-(3-maleimidophenoxy)phenoxy)benzene, bis(4-(3-maleimidophenoxy)phenyl)methane, 1,1-bis(4-(3-maleimidophenoxy)phenyl)ethane, 1,2-bis(4-(3-maleimidophenoxy)phenyl)ethane, 2,2-bis(4-(3-maleimidophenoxy)phenyl)propane, 2,2-bis(4-(3-maleimidophenoxy)phenyl)butane, 2,2-bis(4-(3-maleimidophenoxy)phenyl)pentane, 1,1,1,3,3,3-hexafluoropropene, 4,4'-bis(3-maleimidophenoxy)biphenyl, bis(4-(3-maleimidophenoxy)phenyl)ketone, bis(4-(3-maleimidophenoxy)phenyl)sulfide, bis(4-(3-maleimidophenoxy)phenyl)sulfone, bis(4-(3-maleimidophenoxy)phenyl)ether and so on.

These bismaleimide compounds can be added solely or in combination of two or more species. The preferable is 1,3-bis(3-maleimidophenoxy)benzene.

[0045] **Heat Resistant Resin Layer**

The thickness of the polyimide layer formed from the heat resistant resin composition of the invention is preferably not less than 1 micrometer and not more than 250 micrometers, more preferably not less than 4 micrometers and not more than 50 micrometers, and further preferably not less than 10 micrometers and not more than 40 micrometers, and it is desirable that the glass transition temperature thereof be not less than 300 degrees C or no glass transition temperature thereof be observed. The linear coefficient of thermal expansion (CTE) of the layer in the temperature range of from
100 degrees C to 250 degrees C is preferably not less than 5 ppm/degrees C and not
more than 30 ppm/degrees C, more preferably not less than 10 ppm/degrees C and not
more than 20 ppm/degrees C. When the properties of the layer are in the range
described above, deformation with the temperature change is decreased, the di-
mensional stability is maintained, and thereby warpage or delamination of circuit
boards are suppressed in the mounting process, for example.

[0046] The coefficient of hygroscopic expansion (CHE) of the layer at the relative humidity
from 20 % to 60 % is preferably not less than 5 ppm/%RH and not more than 20 ppm/
%RH, and more preferably not less than 5 ppm/%RH and not more than 15 ppm/%RH.
When the layer has the said property, deformation in the drying and humidifying
processes are decreased, the dimensional stability is maintained, and thereby the circuit
board can be miniaturized and highly precise, for example.

[0047] **Resin/Metal Laminate**

The resin/metal laminate using the heat resistant resin of the present invention will be
explained below. The resin/metal laminate is a laminate, wherein a metal foil is (metal
foils are) formed on a side or both sides of a heat resistant resin layer obtained by
crosslinking a polyimide. The heat resistant resin layer is formed with one or more
layers. In case two or more layers exist, the composition of the layers can be the same
or different.

[0048] Although no particular limitation is imposed on the type of the metal in the metal foil
to be used in the invention, copper and copper alloys, stainless steels and alloys
thereof, nickel and nickel alloys, including 42 alloy, and aluminum and aluminum
alloys can be exemplified. The preferable are copper and copper alloys.

[0049] Further, a foil wherein an anti-corrosion layer or a heat resistant layer, can be formed,
for example, by plating chromium, zinc or so on, is formed or a silane coupling agent
is applied on a surface thereof can be used. The preferable is a copper alloy comprising
copper and at least one component selected from the group consisting of nickel, zinc,
iron, chromium, cobalt, molybdenum, tungsten, vanadium, beryllium, titanium, tin,
manganese, aluminum, phosphorus and silicon. The alloy is preferred in view of circuit
processing. The most preferable metal foils are copper foils formed by rolling or
electro-plating. The preferable thickness thereof is from 3 micrometers to 150 mi-
crometers, more preferably from 3 micrometers to 35 micrometers, further preferably
from 3 micrometers to 12 micrometers.

[0050] The metal foil can either be those without any surface treatment or those with
roughening treatment on one or both side(s) thereof. The preferable are low roughness
foils and foils without roughening treatment. Examples of market available foils can be
used are Fl-WS, FO-WS (manufactured by Furukawa Circuit Foil Co., Ltd., trade
name), BHY, NK120 (manufactured by Japan Energy Corporation, trade name), SLP,
USLP (manufactured by Nippon Denkai, Ltd., trade name), TQ-VLP, SQ-VLP, FQ-VLP (manufactured by Mitsui Mining & Smelting Co., Ltd., trade name), C7025, B-52 (manufactured by Dowa Olin Metal Corporation, trade name) and so on.

Also, it is desirable the ten-point mean roughness (Rz) at the side of the foil facing the heat resistant resin layer be less than 3 micrometers, preferably less than 2 micrometers, more preferably less than 1 micrometer, and those at the other side of the foil be less than 3 micrometers, preferably less than 2 micrometers, more preferably less than 1 micrometer. The ten-point mean roughness (Rz) is measured according to the method defined in JIS B-0601, wherein the cut-off value is 0.25 mm, measurement length is 2.5 mm and the measurement is carried out along the width direction of the copper foil.

Further, in view of the reliability of the circuit, it is desirable that the surface of the metal foil facing the heat resistant resin layer have 0.05 mg/dm² to 1.0 mg/dm², preferably 0.1 mg/dm² to 0.4 mg/dm², of nickel, 0.5 mg/dm² or less, preferably 0 to 0.3 mg/dm², more preferably 0 to 0.1 mg/dm², of zinc, 0.2 mg/dm² or less, preferably 0 to 0.1 mg/dm², of chromium, and 0.2 mg/dm² or less, preferably 0 to 0.1 mg/dm², of silicon. Also, the surface not facing the heat resistant resin layer preferably be plated with nickel or zinc, or chromate treatment can preferably be applied thereon.

The silicon mentioned above is derived from a silane coupling agent applied to improve the adhesion to polyimide. Generally, the silane coupling agent is dissolved in an alcohol or water, homogeneously applied to the uppermost layer of the treated surface of the metal foil, and then dried to form a layer at a temperature about from 50 degrees C to 150 degrees C. The typical types of the agent include, but not limited to, vinylsilanes such as vinyltrimethoxysilane, epoxysilanes such as and beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane and aminosilanes such as gamma-aminopropyltrimethoxysilane.

The resin layer constitutes the resin/metal laminate of the invention can either be mono-layer comprising the heat resistant resin of the present invention or be multi-layers comprising polyimides having different compositions in order to improve the warpage, the dimensional stability or the heat resistance.

The method of manufacturing polyimide/metal laminates using the heat resistant resin of the invention will be explained below.

The method for manufacturing the heat resistant resin/metal laminate can be selected, as appropriate, from so called laminate method, wherein the heat resistant resin and the metal foil are laminated by heating and pressing, cast method, wherein a varnish of heat resistant resin precursor is applied on the metal foil and dried to form the laminate, and combination thereof. In applications using a heat resistant layer having the thickness more than 25 micrometers, laminate method is preferable for it takes
shorter time for drying and thereby superior in productivity and saving costs.

Heat press method and continuous lamination method can be exemplified as the laminate method. In the heat press method, the laminate can be manufactured by stacking the metal foil(s) and heat resistant resin film(s) each cut to a dimension predetermined by the press machine and then heat pressing the stuck, for example. Although no particular limitation is imposed on the continuous lamination, the lamination can be carried out by inserting the materials between one roll and the other roll and then laminating them. The rolls can be metal roll, rubber roll and so on. Although no particular limitation is imposed on the metals, steels and stainless steels can be used. It is preferable to use rolls treated to improve the surface hardness using hard chromium plating or by forming tungsten carbide layer. A heat resistant rubber such as a silicone rubber or a fluoride rubber is preferably formed on the surface of a metal roll to form the rubber rolls. The continuous lamination can also be carried out using the method so called "belt lamination".

It is sufficient that the lamination temperature be in the range of from 200 degrees C to 400 degrees C. As preferable heating methods, conduction heating, radiant heating, such as far infrared heating, and Induction heating can be utilized. Heat annealing is preferably utilized after the heat pressing and/or heat annealing. Conventional heating furnaces, autoclaves and so on can be used as the heating equipment. The atmosphere of heating can be air, inert gas such as nitrogen or argon and so on. Both of the method of heating the film continuously and the method of putting the film rolled on a core in a heating furnace are preferable are preferable as the heating method. The preferable heating types are conduction heating, radiant heating and combination thereof. The preferable heating temperature is from 200 degrees C to 600 degrees C. The preferable heating time is from 0.05 minutes to 5000 minutes.

As the casting method, a solution containing a polyimide, which corresponds to the organic polymer (I), and/or a polyamic acid, which is a precursor thereof, and the compound (C) (hereinafter, collectively referred to as "varnish"), can be directly applied on the metal foil and dried. In view of the workability, the content of polyimide/polyamic acid in the varnish is preferably from 5 wt% to 70 wt%. A viscosity of the varnish measured with type E viscometer at 25 degrees C is preferably 1 mPas to 100000 mPas.

In the process of the application, any known apparatus such as a die coater, a comma coater, a roll coater, a gravure coater, a curtain coater or a spray coater can be utilized and selected as appropriate depending on the application thickness, varnish viscosity and so on.

The varnish can either be applied directly on the metal foil or be applied on a adhesive layer comprising a thermoplastic polyimide or so on for the purpose of
improving the adhesion to the metal foil.

The thickness of the thermoplastic polyimide layer is preferably not less than 0.1 micrometers and not more than 10 micrometers, more preferably not less than 0.2 micrometers and not more than 5 micrometers. The glass transition temperature (Tg) of the layer is preferably not less than 150 degrees C and not more than 350 degrees C, and more preferably not less than 150 degrees C and not more than 300 degrees C. The CTE of the layer in the range of from 100 degrees C to 250 degrees C is preferably not less than 20 ppm/degrees C and not more than 70 ppm/degrees C.

In the method of drying and curing the applied varnish, a conventional heat drying oven can be used. The atmosphere in the drying oven can be air, inert gases (nitrogen, argon or the like) and so on. The drying temperature can appropriately selected depending on the boiling point of the solvent and the temperature range of from 60 degrees C to 600 degrees C is preferably selected. The drying time can appropriately be selected depending on the thickness, concentration and type of the solvent and is desirably from 0.05 minutes to 500 minutes.

The thickness of the heat resistant resin layer is preferably not less than 1 micrometer and not more than 250 micrometers, more preferably not less than 5 micrometers and not more than 40 micrometers. It is preferable that the glass transition temperature (Tg) of the layer be not less than 300 degrees C or no glass transition temperature be observed. The CTE of the layer in the range of from 100 degrees C to 250 degrees C is preferably not less than 5 ppm/degrees C and not more than 30 ppm/degrees C, more preferably not more than 20 ppm/degrees C. The CHE of the layer at the relative humidity from 20 % to 60 % is preferably not less than 5 ppm/%RH and not more than 25 ppm/%RH, and more preferably not more than 20 ppm/%RH.

A protection film is preferably attached on a surface of the heat resistant resin layer of the resin/metal laminate of the invention in the production process or as a final product in view of conveyability and prevention of contamination with foreign objects or the like. A protection film having weak adhesion is preferable. When the adhesion of the protection film is too weak, delamination may take place in the rolling process and thereby the effect of preventing wrinkles, folding, lines and so on is deteriorated. When the adhesion is too strong on the other hand, the protection film is hard to remove and may thereby causes breaking of the tape, lines or wrinkles. In view of the above, the adhesion to the polyimide layer is preferably in the range of from 0.1 g/cm to 50 g/cm. The preferable thickness is from 10 micrometers to 100 micrometers.

The base film of the protection film can be a polyethylene film, a ethylene-vinyl acetate copolymer film or the like. A multi-layer film obtained by multi-layer lamination of these resins for film can be utilized. A resin having the adhesion mentioned above can be used as a single layer film. The examples of the market
available film include SUNYTECT (manufactured by Sun A Kaken Co. Ltd., trade
tame), MFl (manufactured by Sanyokasei Co. Ltd., trade neme) and so on.

[0066] A film wherein an adhesive layer having weak adhesion is formed on the single layer
or multi layer film mentioned above or a film made of a polyethersulfone, a
polyetheretherketone, a polyimide, a polyester or the like, can also preferably be used.
Although no particular limitation is imposed on the adhesive component, acrylic
adhesives, urethane adhesives, natural rubber adhesives, synthesized rubber adhesives,
polyester adhesives, silicone adhesives and so on. A polyester film laminated with an
acrylic adhesive layer is preferable.

[0067] When using the resin/metal laminate of the present invention for COF, which is used
widely in tape automated bonding (TAB) tape processing line, and the heat resistant
resin of the present invention is used in at least one layer in the resin layers, the elastic
moduli of the resin is preferably as described below in view of obtaining the effect of
the invention. The Storage Elastic Modulus E’ under Auto-Strain regulation at a
frequency of 1 Hz in a temperature range close to the mounting temperature of Au-Au
jointing or Au-Sn jointing is preferably not less than 0.5 GPa and not more than 3.0
GPa. The temperature range close to the mounting temperature means not less than 250
degrees C and not more than 500 degrees C, more preferably not less than 300 degrees
C and not more than 450 degrees C, further preferably not less than 350 degrees C and
not more than 450 degrees C.

Examples

[0068] Hereinafter, the present invention is described in more detail by reference to the
Examples, which however are not intended to limit the present invention. Abbre-
viations in the Examples mean as follows.

BPDA: 3,3′,4,4′-biphenyl tetracarboxylic dianhydride
PMDA: pyromellitic anhydride
PDA: 1,4-phenylene diamine
ODA: 4,4′-oxydianiline(4,4′-diaminodiphenyl ether)
m-BP: 4,4′-bis(3-aminophenoxy)biphenyl
NMP: N-methyl-2-pyrrolidone
DMAc: N,N-dimethyl acetamide
HACP: hexakis (4-aminophenoxy) cyclotriphosphazene
BACP: tripheoxytris(4-aminophenoxy)cyclotriphosphazene
FACP: tris(4-fluorophenoxy) tris(4-aminophenoxy)cyclotriphosphazene,

[0069] Evaluation in the Examples was conducted as follows.

[0070] (Measurement of logarithmic viscosity: eta inh)
The measurement was carried out in N-methyl-2-pyrrolidone solvent by using a
viscosity tube, Ubbelohde base on a calculation formula as below, after the solid
content of polyamic acid was adjusted to 0.5 dl/g and at 35 degrees C.
Logarithmic viscosity (eta inh) = In (Ts/T0)/Conc
Ts: Transit time of a polymer solution in the viscosity tube
TO: Transit time of a blank in the viscosity tube
Cone: Concentration of a polymer solution (0.5 g/dl)

[0071] (Viscoelasticity Measurement: Measurement of Storage Elastic Modulus (E') at 450 degrees C)
In the evaluation of viscoelasticity, temperature dispersion measurement was conducted with RSA-II (manufactured by Rheometric Scientific Inc.) in a tensile deformation mode. The measurement was conducted in the temperature range of from 30 degrees C to 500 degrees C, at a heating rate of 3 degrees C/min, under Auto-Strain regulation at a strain of 0.02 % and at a frequency of 1 Hz. A sample of 20 mm in length and 5 mm in width was used to determine the storage elastic modulus E' at 450 degrees C.

[0072] (Measurement of linear coefficient of thermal expansion (CTE))
Linear coefficient of thermal expansion was determined using a thermomechanical analyzer (TMA-50, manufactured by Shimadzu Corporation) by stretching method wherein a constant load was applied at both ends of a film and the expansion (shrinkage) was measured when the temperature was changed. The measurement was carried out in the temperature range of from 100 degrees C to 250 degrees C, and mean linear coefficient of thermal expansion (CTE) (ppm/%K) was calculated.

[0073] (Measurement of coefficient of hygroscopic expansion (CHE))
Lengths of a film at the relative humidity of 20, 40 and 60% was measured using a thermomechanical analyzer (TMA-2200S, manufactured by Shimadzu Corporation) equipped with a humidity controlling unit. The length of the film was plotted to the relative humidity and the gradient of the plotted line, which corresponds to the coefficient of hygroscopic expansion (CHE) (ppm/%RH) is calculated by linear approximation.

[0074] Synthesis and Characterization of FACP
(Step 1: Synthesis of FNCP)
To a 250 ml three-neck RBF (Round-Bottom Flask) added a solution containing 4-nitrophenol (2.224 g, 16 mmol), 4-flourophenol (1.344 g, 12 mmol), and dry THF 40 ml respectively at room temperature under argon atmosphere. Then Sodium hydride (0.912 g, 38 mmol) was added into the solution under stirrer at room temperature. Five hours later, phosphonitrilic chloride trimer (1.388 g, 4 mmol) was added into the solution. The reaction mixture was stirred for 8 hours under reflux and cooled down to room temperature. Ethyl acetate (100 ml) and water (100 ml) were added into the mixture. The organic phase was washed by water (50 ml) twice and dried under MgSO
4 for 4 hours. The product FNCP \([N_3P_3(OC_6H_4NO_2)_3(OC_6H_4F)_3]\) was obtained by removing organic solvent and dried under vacuum. Yield 86 % (3.03 g).

(Step 2: Synthesis of FACP by reduction method)

The product FNCP (4.0 g, 4.54 mmol) was dissolved in a mixed solvent containing ethyl acetate (60 ml) and methanol (20 ml). A powder Pd (5 % in C, 0.98 g) was added into the mixture. The mixture is stirred for 20 minutes under argon atmosphere.

Ammonia formate (3.6 g) was added into the reaction mixture at 60 degrees C. The mixture was stirred for 4 hours at 60 degrees C and cooled down. Ethyl (50 ml) and water (50 ml) were added to the mixture. The organic phase was washed by water twice. The product was obtained by removing solvent from organic phase. Yield 70 % (2.52 g).

\(^1\)H NMR (Acetone): delta 6.952 - 6.625 (m, 12H), 3.636 (s, 2H). \(^31\)P NMR (Acetone): 22.538, 22.363, 22.155. MALDI-TOF: 793.285. The characterization data are shown in Figures 1 to 3.

[0075]

Synthesis of Polyamic Acid A - E

(Synthesis Example 1: Synthesis of polyamic acid A)

A vessel equipped with a stirrer and a nitrogen inlet tube was charged with 110 g of NMP as solvent and then with 13.3 g of PDA, and stirred at room temperature until the sample was dissolved. Thereafter, 25.75 g of BPDA and 8.2 g of PMDA were added thereto and stirred at room temperature for 1 hour, and then 237 g of NMP was added and stirred at 50 degrees C for 3 hours and at room temperature for 20 hours to give a polyamic acid varnish A. The solid content of polyamic acid A in the resulting polyamic acid varnish A was 12% by weight, and the logarithmic viscosity was 1.3 dl/g.

(Synthesis Example 2: Synthesis of polyamic acid B)

A vessel equipped with a stirrer and a nitrogen inlet tube was charged with 123 g of NMP as solvent and then with 14.06 g of PDA, and stirred at 50 degrees C until the sample was dissolved. Thereafter, 38.82 g of BPDA and 118 g of NMP were added thereto and stirred at room temperature for 1 hour, and then 146.6 g of NMP was further added and stirred at 50 degrees C for 3 hours and at room temperature for 20 hours to give a polyamic acid varnish B. The solid content of polyamic acid B in the resulting polyamic acid varnish B was 12% by weight, and the logarithmic viscosity was 1.1 dl/g.

(Synthesis Example 3: Synthesis of polyamic acid C)

A vessel equipped with a stirrer and a nitrogen inlet tube was charged with 113 g of NMP as solvent and then with 12.26 g of PDA, and stirred at 50 degrees C until the sample was dissolved. Thereafter, 37.17 g of BPDA and 118 g of NMP were added thereto and stirred at room temperature for 1 hour, and then 102 g of NMP was further added and stirred at 50 degrees C for 3 hours and at room temperature for 20 hours to
give a polyamic acid varnish C. The solid content of polyamic acid C in the resulting polyamic acid varnish C was 12% by weight, and the logarithmic viscosity was 1.4 dl/g.

(Synthesis Example 4: Synthesis of polyamic acid D)
A vessel equipped with a stirrer and a nitrogen inlet tube was charged with 105 g of NMP as solvent and then with 12.26 g of PDA, and stirred at 50 degrees C until the sample was dissolved. Thereafter, 32.85 g of BPDA and 118 g of NMP were added thereto and stirred at room temperature for 1 hour, and then 107.1 g of NMP was further added and stirred at 50 degrees C for 3 hours and at room temperature for 20 hours to give a polyamic acid varnish D. The solid content of polyamic acid D in the resulting polyamic acid varnish D was 12% by weight, and the logarithmic viscosity was 0.90 dl/g.

(Synthesis Example 5: Synthesis of polyamic acid E)
A vessel equipped with a stirrer and a nitrogen inlet tube was charged with 261.0 g of DMAc as solvent and then with 20.44 g of ODA and 16.12 g of m-BP, and stirred at 20 - 30 degrees C until the sample was dissolved. Thereafter, 30.84 g of PMDA were added thereto, the materials adhered to the inner surface of the vessel was washed off with 11.0 g of DMAc, heated to 50 - 60 degrees C and stirred for 1 hour, and then 0.44 g of PMDA was further added and stirred while keeping the temperature at 60 degrees C for 4 hours to give a varnish (a).

Further, another vessel equipped with a stirrer and a nitrogen inlet tube was charged with 263.0 g of NMP as solvent and then with 19.62 g of PDA, and stirred at 20 - 30 degrees C until the sample was dissolved. Thereafter, 37.0 g of BPDA and 11.06 g of PMDA were added thereto, the materials adhered to the inner surface of the vessel was washed off with 10.0 g of NMP, heated to 50 - 60 degrees C and stirred for about 4 hours to give a varnish (b).

At last, another vessel equipped with a stirrer and a nitrogen inlet tube was charged with varnish (b) and varnish (a) at a weight ratio of 77:23, heated to 50 - 60 degrees C and stirred for about 4 hours to give a polyamic acid solution E. The solid content of polyamic acid E in the resulting polyamic acid solution E was 20% by weight, and the viscosity measured with type E viscometer at 25 degrees C was 30000 mPas.

(Example 1)
A 7-ml glass tube was charged with 0.046 g of HACP as C-component and 0.34 g of NMP and stirred until the sample was dissolved to give a HACP/NMP solution. Then 15 g of varnish A (polyamic acid A/NMP solution) was injected to a 100 ml reaction vessel and then the HACP/NMP solution was slowly added and stirred at room temperature for 10 minutes. The resultant polyamic acid solution (polyamic acid content: 12 wt%) was applied on a glass plate using a Baker applicator to a dry film thickness
of about 17 micrometers and dried using an inert oven under nitrogen atmosphere at 100 degrees C for 60 minutes, at 200 degrees C for 60 minutes, at 300 degrees C for 60 minutes, at 350 degrees C for 60 minutes and at 450 degrees C for 10 minutes. The obtained polyimide/glass laminate was immersed in water at a temperature of 40 degrees C to remove the polyimide film from the glass. The properties of the obtained polyimide film are shown in Table 1. As the crosslinking took place, the storage elastic modulus at high temperature was improved.

(Examples 2 to 11)

The reactions were carried out in the same manner as in Example 1 except that the compositions were changed to those shown in Table 1. The solution reacted according to the composition shown in Table 1 was applied on a glass plate using a Baker applicator to a dry film thickness of about 17 micrometers and dried using an inert oven under nitrogen atmosphere at the same condition as in Example 1 to obtain a polyimide/glass laminate. The film was prepared from the obtained polyimide/glass laminate in the same manner as in Example 1. The properties of the film are shown in Table 1. As the crosslinking took place, the storage elastic modulus at high temperature was improved.

(Examples 12 to 14)

The reactions were carried out in the same manner as in Example 1 except that the compositions were changed to those shown in Table 1. The obtained polyamic acid solution was applied on a copper foil using a Baker applicator to a dry film thickness of about 17 micrometers, dried using an inert oven under nitrogen atmosphere at from 50 degrees C to 180 degrees C at a heating rate of 3 degrees C/min, and then heat treated at from 280 degrees C to 380 degrees C using an IR reflow furnace to obtain a polyimide/metal laminate. The copper foil in the resulting laminate was treated for several minutes by spraying a ferric chloride solution (40 Baume) through a spray nozzle until the metallic foil was completely eliminated, and then the sample was washed with water and vacuum-dried at 60 degrees C thereby obtained a polyimide film. The properties of the obtained film are shown in Table 1. As the crosslinking took place, the storage elastic modulus at high temperature was improved.

(Comparative Example 1)

The polyamic acid solution (polyamic acid content: 12 wt%) obtained in Synthesis Example 1 was applied on a glass plate using a Baker applicator to a dry film thickness of about 17 micrometers and dried using an inert oven under nitrogen atmosphere at 100 degrees C for 60 minutes, at 200 degrees C for 60 minutes, at 300 degrees C for 60 minutes, at 350 degrees C for 60 minutes and at 450 degrees C for 10 minutes. The obtained polyimide/glass laminate was immersed in water at a temperature of 40 degrees C to remove the polyimide film from the glass. The properties of the obtained
polyimide film are shown in Table 1. In comparison with the Examples 1 to 7, in which similar polyamic acid solutions are used, the storage elastic modulus at high temperature is low.

[0080] (Comparative Examples 2 to 3)

The polyamic acid solutions shown in Table 1 was applied on a glass plate using a Baker applicator to a dry film thickness of about 15 micrometers and dried using an inert oven under nitrogen atmosphere at the same condition as in Comparative Example 1 to obtain a polyimide/glass laminate. A film was prepared from the obtained polyimide/glass laminate in the same manner as in as in Comparative Example 1. The properties of the obtained polyimide film are shown in Table 1. In comparison with the Examples 9 to 10, in which similar polyamic acid solutions are used, the storage elastic modulus at high temperature is low.

[0081] (Comparative Example 4)

The polyamic acid solution shown in Table 1 was applied on a copper foil using a Baker applicator to a dry film thickness of about 17 micrometers, dried using an inert oven under nitrogen atmosphere at from 50 degrees C to 180 degrees C at a heating rate of 3 degrees C/min, and then heat treated at from 280 degrees C to 380 degrees C using an IR reflow furnace to obtain a polyimide/metal laminate. The copper foil in the resulting laminate was treated for several minutes by spraying a ferric chloride solution (40 Baume) through a spray nozzle until the metallic foil was completely eliminated, and then the sample was washed with water and vacuum-dried at 60 degrees C thereby obtained a polyimide film. The properties of the obtained film are shown in Table 1. In comparison with the Examples 12 to 14, in which similar polyamic acid solutions are used, the storage elastic modulus at high temperature is low.

[0082]
<table>
<thead>
<tr>
<th>Example</th>
<th>Type</th>
<th>Component C (g)</th>
<th>NMP (g)</th>
<th>Component C Content (wt %) based on A+B+C</th>
<th>Film Thickness (µm)</th>
<th>E@450°C (GPa)</th>
<th>CTE (ppm/K) 100-250°C</th>
<th>CHE (ppm/KRH)</th>
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<tr>
<td>Example 1</td>
<td>A</td>
<td>15</td>
<td>HACP</td>
<td>0.046</td>
<td>25</td>
<td>20</td>
<td>0.9</td>
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<td>Example 2</td>
<td>A</td>
<td>15</td>
<td>HACP</td>
<td>0.065</td>
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<td>18</td>
<td>1.0</td>
<td>121</td>
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<td>Example 3</td>
<td>A</td>
<td>15</td>
<td>HACP</td>
<td>0.085</td>
<td>5</td>
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<td>Example 4</td>
<td>A</td>
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<td>FACP</td>
<td>0.200</td>
<td>10</td>
<td>16</td>
<td>1.0</td>
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<tr>
<td>Example 5</td>
<td>A</td>
<td>15</td>
<td>FACP</td>
<td>0.310</td>
<td>15</td>
<td>23</td>
<td>1.6</td>
<td>124</td>
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<tr>
<td>Example 6</td>
<td>A</td>
<td>15</td>
<td>BACP</td>
<td>0.200</td>
<td>10</td>
<td>15</td>
<td>1.0</td>
<td>157</td>
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<tr>
<td>Example 7</td>
<td>A</td>
<td>15</td>
<td>BACP</td>
<td>0.310</td>
<td>15</td>
<td>19</td>
<td>1.1</td>
<td>166</td>
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<td>Example 8</td>
<td>B</td>
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<td>HACP</td>
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<td>35</td>
<td>15</td>
<td>1.0</td>
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Industrial Applicability

According to the present invention, there can be obtained a polyimide/metal laminate having a polyimide layer excellent in modulus of elasticity at high temperatures, dimensional stability, and transparency. Using the polyimide/metal laminate, problems such as sinking, wiring deviation, release and plating soaking do not occur even in chip mounting via Au-Au jointing or Au-Sn jointing. Accordingly, the polyimide/metal laminate of the present invention can cope satisfactorily with high density mounting, which has been accelerated in recent years, and can be used effectively as a polyimide/metal laminate for COF used widely in tape automated bonding (TAB) tape processing line.
Claims

[Claim 1] A heat resistant resin obtainable by crosslinking an organic polymer (I) having an imide bond and/or an amide bond in the main chain thereof with a compound (C) having at least three amino groups and a phosphazene skeleton and represented by the following formula (1), wherein m and n independently represents an integer provided that m + n is from 3 to 25, R₃, R₄, R₅ and R₆ independently represents a phenyl group, an amino phenyl group or a substituted phenyl group having a structure represented by the formula (2), wherein R₇ represents an organic group selected from the group consisting of an alkyl group, fluoro group, chloro group, bromo group, nitro group, cyano group, hydroxyl group, phenoxy group and a substituted group connected via an amide, imide, ether or ester bond, formula (1) has at least three amino groups, and formula (2) has at least one R₇.

[Chem.1]

[Chem.2]

[Claim 2] The heat resistant resin as claimed in claim 1, wherein the storage elastic modulus measured at 450 degrees C and a frequency of 1 Hz thereof is from 0.5 GPa to 3.0 GPa.

[Claim 3] The heat resistant resin as claimed in claim 1 or 2, wherein the organic polymer (I) comprises a repeating unit derived from a tetracarboxylic dianhydride (A) and a repeating unit derived from a diamine (B).

[Claim 4] The heat resistant resin as claimed in claim 3 comprising 0.01 to 80 parts by weight of the structure derived from the compound (C) based on total 100 parts by weight of the repeating unit derived from the tetracarboxylic dianhydride (A), the repeating unit derived from the diamine (B) and the compound (C).

[Claim 5] The heat resistant resin as claimed in claim 4, wherein the molar ratio ((A)/(B)) of the repeating unit derived from the tetracarboxylic dianhydride (A) to the repeating unit derived from the diamine (B) is not
more than 1.

[Claim 6] A heat resistant resin composition comprising the heat resistant resin as claimed in any one of claims 1 to 5.

[Claim 7] A resin/metal laminate having a layer (L1) comprising the heat resistant resin as claimed in any one of the claims 1 to 5 and a metal layer (L2).

[Claim 8] A circuit board having a layer (L1) comprising the heat resistant resin as claimed in any one of the claims 1 to 5.

[Claim 9] The circuit board as claimed in claim 8 characterized in that COF (chip on film) mounting process is carried out on the layer (L1).

[Claim 10] A process for producing the heat resistant resin as claimed in claim 4 or 5, comprising the steps of: (1) synthesizing a polyamic acid (Ia) from a tetracarboxylic dianhydride (A) and a diamine (B), (2) preparing a solution by adding the compound (C) to the polyamic acid (Ia), and (3) heating the solution to carry out imidation, in this order.

[Claim 11] A compound represented by the following formula (3), wherein R1 to R6 are independently fluoro group, amino group or hydrogen atom, and at least three of R1 to R6 are amino groups and at least one of R1 to R6 is fluoro group.

[Chem.3]

[Claim 12] The compound as claimed in claim 11, wherein three of R1 to R6 are fluoro groups and three of R1 to R6 are amino groups.

[Claim 13] A crosslinking agent for an organic polymer comprising the compound claimed in claim 11 or 12.
[Fig. 2]
INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2009/003813

AClassification of Subject Matter

IntCl C08L7/09 (2006.01) i; C07F9/6593 (2006.01) i; C08K5/5399 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B.Fields Searched

Minimum documentation searched (classification system followed by classification symbols)

IntCl C08L79/08, C07F9/6593, C08K5/5399

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922 1996
Published unexamined utility model applications of Japan 1971 2009
Published registered utility model specifications of Japan 1996 2009

Electronic database consulted during the international search (name of data base and, where practicable, search terms used)

C.Documents Considered to be Relevant

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23.10.2009 | 02.11.2009

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