

SPECIFICATION
PHOTOSENSITIVE RESIN COMPOSITION AND METHOD OF PRODUCING
PRINTED WIRING BOARD

BACKGROUND OF THE INVENTION

Field of the Invention

[0001]

The present invention relates to a photosensitive resin composition, and particularly to a photosensitive resin composition to be suitably used for the formation of a solder resist. Furthermore, the present invention also relates to a method of producing a printed wiring board using the photosensitive resin composition.

Background Art

[0002]

In general, when electronic components are mounted on a printed wiring board to be used for electronic devices, a solder resist layer is formed in an area other than connection holes on the board with a circuit pattern formed thereon, in order that soldering can be prevented from adhering to portions that need no soldering.

[0003]

In recent years, printed wiring boards have become more precise and denser as electronic devices have become lighter, thinner, shorter, and smaller. Associated with this, it is currently mainstream that a solder resist layer is formed with what is called a photosolder resist, wherein a photosensitive resin composition is applied onto a board, and dried; pattern formation is carried out by exposure and development; and then the resin after the pattern formation is subjected to final curing by heating or light irradiation. Furthermore, from the viewpoint of productivity, recent interest has focused on a coating method such as a spray coating method and a curtain coating method. A spray coating method, a curtain coating method, or the like requires a low viscosity material, considering the characteristics of such a method.

[0004]

Hitherto, there is a technical problem in that, when a board is coated with a photosensitive resin composition containing an organic solvent, the coating of the photosensitive resin composition, even if seemingly without any unevenness, causes cissing and sagging after

coating or during drying, failing to form a uniform dried coating film after drying. What is proposed for such a technical problem is using diethylene glycol monoethyl ether acetate, dipropylene glycol monomethyl ether, or propylene glycol monomethyl ether acetate as an organic solvent for a low-viscosity photosensitive resin composition containing a carboxyl group-containing resin, thermosetting resin, photosensitive monomer, and organic solvent (see Patent Literature 1).

Citation List

Patent Literature

[0005]

Patent Literature 1: Japanese Patent Application Laid-Open Publication No. 2019-174788

SUMMARY OF THE INVENTION

Technical Problem

[0006]

However, a technical problem has been discovered in that, when a low-viscosity photosensitive resin composition disclosed in Patent Literature 1 is applied, a resin layer having a sufficient film thickness cannot be formed at an edge portion of a circuit on a printed wiring board.

[0007]

Accordingly, an object of the present invention is to provide a photosensitive resin composition that, even if adjusted to a low viscosity, achieves an excellent developability and covering property at an edge portion of a circuit printed wiring board during coating. Another object of the present invention is to provide a method of producing a printed wiring board, in which method, the above-described photosensitive resin composition is used for coating in a low viscosity range, thus enabling a solder resist layer having a sufficient thickness to be formed at an edge portion of a circuit on a printed wiring board.

Solution to Problem

[0008]

The present inventors have made studies vigorously, and consequently discovered that, when a photosensitive resin composition containing a carboxyl group-containing resin, thermosetting resin, photosensitive monomer, and organic solvent is adjusted to a low viscosity,

and applied, the above-described problems can be solved by regulating the viscosity and volume-specific resistance value of the photosensitive resin composition so that the viscosity and the resistance value can satisfy a specific relational formula. That is, the present inventors have discovered that the viscosity and volume-specific resistance value of a photosensitive resin composition stand in a straight-line relationship, have considered a balance between the coating properties of the photosensitive resin composition in a low viscosity range and the developability of the photosensitive resin composition, and have consequently made a discovery that bringing the slope of the straight line within a specific range can solve the above-described problems. The present invention is based on such a discovery.

[0009]

That is, a photosensitive resin composition according to the present invention is a photosensitive resin composition containing a carboxyl group-containing resin, a thermosetting resin, a photosensitive monomer, and an organic solvent, and characterized in that,

when it is assumed that the viscosity of the photosensitive resin composition at 25°C is A (dPa·s), and that the volume-specific resistance value of the photosensitive resin composition at 25°C is B (MΩ), and when the viscosity of the photosensitive resin composition is adjusted to $A_1 = 5.0$ (dPa·s) and $A_2 = 1.5$ (dPa·s) using propylene glycol monomethyl ether, the volume-specific resistance value B_1 (MΩ) given at A_1 and the volume-specific resistance value B_2 (MΩ) given at A_2 satisfy the following formula:

$$1.4 \leq (A_1 - A_2)/(B_1 - B_2) \leq 40.$$

[0010]

In an aspect of the present invention, the photosensitive resin composition preferably further contains a quaternary ammonium salt compound.

[0011]

In an aspect of the present invention, the quaternary ammonium salt compound is preferably at least one selected from tetrabutylammonium bromide and tetrapropylammonium bromide.

[0012]

In an aspect of the present invention, the organic solvent is preferably at least one selected from the group consisting of diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether

acetate, propylene glycol monomethyl ether acetate, dipropylene glycol monomethyl ether, and propylene glycol monoethyl ether acetate.

[0013]

In an aspect of the present invention, the photosensitive resin composition is preferably for use in the coating with a spray coater, more preferably for use in the coating by electrostatic spraying in particular.

[0014]

In an aspect of the present invention, the photosensitive resin composition is preferably for use in the formation of a solder resist.

[0015]

Another aspect of the present invention provides a method of producing a printed wiring board including a solder resist layer, characterized by including: applying the photosensitive resin composition to a board using a spray coater; exposing the composition; and curing the composition under at least any one of light and heat to form the solder resist layer.

Advantageous Effects of Invention

[0016]

The present invention can provide a photosensitive resin composition that, even if adjusted to a low viscosity and applied, achieves an excellent covering property at an edge portion of a circuit printed wiring board during coating. Furthermore, a photosensitive resin composition according to the present invention is enabled to have an excellent developability. In addition, another embodiment of the present invention can provide a method of producing a printed wiring board, in which method, the above-described photosensitive resin composition in a low viscosity range is used for coating so that a solder resist layer having a sufficient thickness can be formed also at an edge portion of a circuit on a printed wiring board.

DETAILED DESCRIPTION OF THE INVENTION

[0017]

[Photosensitive Resin Composition]

A photosensitive resin composition according to the present invention will be described. A photosensitive resin composition according to the present invention contains at least a carboxyl group-containing resin, thermosetting resin, photosensitive monomer (reactive diluent), and

organic solvent (unreactive diluent), and may further contain another component such as a quaternary ammonium salt compound, photoinitiator, colorant, curing catalyst, inorganic filler, and additive.

[0018]

In the present invention, the viscosity of the photosensitive resin composition can be regulated using the above-described organic solvent, and, if desired, an inorganic filler or the like. Without any particular limitation, the viscosity of the photosensitive resin composition can be diluted suitably with propylene glycol monomethyl ether, and thereby regulated to a suitable viscosity. A photosensitive resin composition usually has a viscosity at 25°C of 300 dPa·s or less, preferably 200 dPa·s or less, as measured as a value based on 25°C, 5 rpm, and 30 seconds in accordance with Viscosity Measurement Method Using Cone-Plate Rotational Viscometer in JIS Z8803:2011, Part 10, using a cone-plate viscometer (TVE-33H, manufactured by Toki Sangyo Co., Ltd.) with a 1°34' × R24 cone rotor. The photosensitive resin composition is usually regulated to 1.3 dPa·s or more and 5.0 dPa·s or less, preferably regulated to 1.5 dPa·s or more and 4.5 dPa·s or less, when used for the coating by electrostatic spraying. Using the photosensitive resin composition diluted in the above-described range of viscosity enables a resin layer having a sufficient film thickness to be formed at an edge portion of a circuit on a printed wiring board during coating in a low-viscosity range, thus making it possible to enhance the solder dip resistance and the plating resistance.

[0019]

In the present invention, when it is assumed that the viscosity of the photosensitive resin composition at 25°C is A (dPa·s), and that the volume-specific resistance value of the photosensitive resin composition at 25°C is B (MΩ), and when the viscosity of the photosensitive resin composition is adjusted to $A_1 = 5.0$ (dPa·s) and $A_2 = 1.5$ (dPa·s) using propylene glycol monomethyl ether, the volume-specific resistance value B_1 (MΩ) given at A_1 and the volume-specific resistance value B_2 (MΩ) given at A_2 satisfy

the following formula:

$$1.4 \leq (A_1 - A_2)/(B_1 - B_2) \leq 40,$$

preferably satisfy

$$2.0 \leq (A_1 - A_2)/(B_1 - B_2) \leq 35,$$

more preferably satisfy

$$3.0 \leq (A_1 - A_2)/(B_1 - B_2) \leq 30,$$

still more preferably satisfy

$$5.0 \leq (A_1 - A_2)/(B_1 - B_2) \leq 25,$$

still more preferably satisfy

$$10 \leq (A_1 - A_2)/(B_1 - B_2) \leq 20.$$

In the present invention, using the photosensitive resin composition that gives 1.4 or more and 40 or less as $(A_1 - A_2)/(B_1 - B_2)$ in the above-described formula provides developability and achieves an excellent covering property at an edge portion of a circuit on a printed wiring board during coating in a low-viscosity range, thus making it possible to decrease unevenness in the higher and lower portions on a board, and to prevent a circuit on the underlying material from being uncovered. This reason is not necessarily clear, but is inferred as follows. The formula $(A_1 - A_2)/(B_1 - B_2)$ represents a change in the volume-specific resistance value of the photosensitive resin composition diluted in a viscosity range suitable for coating. It is considered that the photosensitive resin composition that gives less than 1.4 as the $(A_1 - A_2)/(B_1 - B_2)$ causes too large an increase in the volume-specific resistance value when increased in the viscosity, and thus that the photosensitive resin composition is decreased in adhesion when adjusted to a low viscosity, and applied. On the other hand, it is considered that the photosensitive resin composition that gives more than 40 causes too small an increase in the volume-specific resistance value when increased in the viscosity, and thus that the photosensitive resin composition is decreased in developability.

In addition, the value of B_2 is usually 0.01 to 5.0, preferably 0.03 to 2.0, more preferably 0.05 to 1.2, still more preferably 0.07 to 1.1, still more preferably 0.1 to 1.0. Bringing the value of B_2 within these ranges provides developability and achieves an excellent covering property at an edge portion of a circuit on a printed wiring board during coating in a low-viscosity range, thus making it possible to decrease unevenness in the higher and lower portions on a board, and to prevent a circuit on the underlying material from being uncovered. In the present invention, the volume-specific resistance value of the photosensitive resin composition at 25°C is a volume-specific resistance value ($M\Omega$) given when an electrode (the electrode area: 1 cm², and the electrode-to-electrode distance: 1 cm) of an electrostatic tester (tradename: EM-IV, manufactured by Asahi Sunac Corporation) is immersed in the photosensitive composition. Each of the components constituting the photosensitive resin composition according to the present invention will now be described.

[0020]

[Carboxyl Group-containing Resin]

A carboxyl group-containing resin that can be used is any kind of conventionally known resin having a carboxyl group in the molecule. Allowing the photosensitive resin composition to contain a carboxyl group-containing resin makes it possible to afford alkali developability to the photosensitive resin composition. In particular, a carboxyl group-containing photosensitive resin having an ethylenically unsaturated double bond in the molecule is preferable from viewpoints of photo-curability and development resistance. As the ethylenically unsaturated double bond, preferred is one derived from acrylic acid or methacrylic acid or a derivative thereof. In cases where only a carboxyl group-containing resin having no ethylenically unsaturated double bond is used, making the composition photo-curable involves using, in combination, the below-described compound having a plurality of ethylenically unsaturated groups in the molecule, that is, a photosensitive monomer to make the composition photosensitive.

Specific examples of the carboxyl group-containing resin include such compounds as below-described (may be either oligomers or polymers).

[0021]

(1) A carboxyl group-containing resin obtained by copolymerization of an unsaturated carboxylic acid such as (meth)acrylic acid with an unsaturated group-containing compound such as styrene, α -methylstyrene, lower alkyl (meth)acrylate, or isobutylene.

[0022]

(2) A carboxyl group-containing urethane resin obtained by a polyaddition reaction of a diisocyanate such as an aliphatic diisocyanate, branched aliphatic diisocyanate, alicyclic diisocyanate, or aromatic diisocyanate with a carboxyl group-containing dialcohol compound such as dimethylol propionic acid or dimethylol butanoic acid and a diol compound such as polycarbonate polyol, polyether polyol, polyester polyol, polyolefin polyol, acrylic polyol, bisphenol A alkylene oxide adduct diol, or a compound having a phenolic hydroxyl group and an alcoholic hydroxyl group.

[0023]

(3) A carboxyl group-containing photosensitive urethane resin obtained by a polyaddition reaction of the following: a partial acid

anhydride-modified product as a reaction product of a diisocyanate, a bifunctional epoxy resin such as a bisphenol A-type epoxy resin, hydrogenated bisphenol A-type epoxy resin, bisphenol F-type epoxy resin, bisphenol S-type epoxy resin, bixylenol-type epoxy resin, or biphenol-type epoxy resin, and a carboxylic acid compound having an ethylenically unsaturated double bond, such as a (meth)acrylic acid; a carboxyl group-containing dialcohol compound; and a diol compound.

[0024]

(4) A carboxyl group-containing photosensitive urethane resin obtained by adding a compound having one hydroxyl group and one or more (meth)acryloyl groups in the molecule, such as hydroxyalkyl (meth)acrylate, during synthesis of a resin in the above-described (2) or (3) to make the resin terminally (meth)acrylated.

[0025]

(5) A carboxyl group-containing photosensitive urethane resin obtained by adding a compound having one isocyanate group and one or more (meth)acryloyl groups in the molecule, such as an equimolar reaction product of isophorone diisocyanate and pentaerythritol triacrylate, during synthesis of a resin in the above-described (2) or (3) to make the resin terminally (meth)acrylated.

[0026]

(6) A carboxyl group-containing photosensitive resin obtained by bringing a bifunctional or more polyfunctional (solid) epoxy resin into reaction with (meth)acrylic acid, and adding a dibasic acid anhydride to the hydroxyl group present in a side chain.

[0027]

(7) A carboxyl group-containing photosensitive resin obtained by bringing a polyfunctional epoxy resin into reaction with (meth)acrylic acid, and adding a dibasic acid anhydride to the hydroxyl group generated, in which the polyfunctional epoxy resin is obtained by further epoxidation of a hydroxyl group of bifunctional (solid) epoxy resin with epichlorohydrin.

[0028]

(8) A carboxyl group-containing polyester resin obtained by bringing a bifunctional oxetane resin into reaction with a dicarboxylic acid such as adipic acid, phthalic acid, or hexahydrophthalic acid, and adding a dibasic acid anhydride such as phthalic anhydride, tetrahydrophthalic anhydride, or hexahydrophthalic anhydride to the primary hydroxyl group generated.

[0029]

(9) A carboxyl group-containing photosensitive resin obtained by bringing an epoxy compound having a plurality of epoxy groups in one molecule into reaction with a compound having at least one alcoholic hydroxyl group and one phenolic hydroxyl group in one molecule, such as *p*-hydroxyphenethyl alcohol, and an unsaturated group-containing monocarboxylic acid such as (meth)acrylic acid, and bringing the alcoholic hydroxyl group of the resulting reaction product into reaction with a polybasic anhydride such as maleic anhydride, tetrahydrophthalic anhydride, trimellitic anhydride, pyromellitic anhydride, or adipic acid.

[0030]

(10) A carboxyl group-containing photosensitive resin obtained by bringing a compound having a plurality of phenolic hydroxyl groups in one molecule into reaction with an alkylene oxide such as ethylene oxide or propylene oxide, bringing the resulting reaction product into reaction with an unsaturated group-containing monocarboxylic acid, and bringing the resulting reaction product into reaction with a polybasic anhydride.

[0031]

(11) A carboxyl group-containing photosensitive resin obtained by bringing a compound having a plurality of phenolic hydroxyl groups in one molecule into reaction with a cyclic carbonate compound such as ethylene carbonate or propylene carbonate, bringing the resulting reaction product into reaction with an unsaturated group-containing monocarboxylic acid, and bringing the resulting reaction product into reaction with a polybasic anhydride.

[0032]

(12) A carboxyl group-containing photosensitive resin obtained by further adding a compound having one epoxy group and one or more (meth)acryloyl groups in one molecule to a resin in the above-described (1) to (11).

It is to be noted that the term (meth)acrylate, as used herein, is a generic term of an acrylate, a methacrylate, and a mixture thereof; and the same applies to other similar expressions.

[0033]

The acid value of the carboxyl group-containing resin is preferably 40 to 150 mg KOH/g. Bringing the acid value of the carboxyl group-containing resin to 40 mg KOH/g or more makes the alkaline development good. In addition, bringing the acid value to 150 mg KOH/g or less can

make it easier to draw a good resist pattern. The acid value is more preferably 50 to 130 mg KOH/g.

[0034]

The weight average molecular weight of the carboxyl group-containing resin varies depending on the backbone of the resin, and in general, is preferably 2,000 to 150,000. Bringing the weight average molecular weight to 2,000 or more makes it possible to enhance the tack-free performance and resolution. In addition, bringing the weight average molecular weight to 150,000 or less makes it possible to enhance the developability and storage stability. The weight average molecular weight is more preferably 5,000 to 100,000.

[0035]

The blending amount of the carboxyl group-containing resin is preferably 20 mass% or more and 60 mass% or less in terms of the solid concentration in the photosensitive resin composition. Bringing the amount to 20 mass% or more makes it possible to enhance the strength of the cured coating film. In addition, the amount of 60 mass% or less makes the viscosity suitable, and enhances the covering property at an edge portion of a circuit on a printed wiring board during coating with a spray coater. The amount is more preferably 30 mass% or more and 50 mass% or less.

[0036]

[Thermosetting Resin]

Examples of a thermosetting resin to be used in the present invention include a commonly used known thermosetting resin such as an amino resin, a maleimide compound, a benzoxazine resin, a carbodiimide resin, a cyclocarbonate compound, an epoxy compound, an oxetane compound, or an episulfide resin. A thermosetting resin preferable among these is an epoxy resin.

[0037]

Examples of an epoxy resin that can be used include bisphenol A-type epoxy resins, bisphenol F-type epoxy resins, hydrogenated bisphenol A-type epoxy resins, brominated bisphenol A-type epoxy resins, bisphenol S-type epoxy resins, phenol novolak-type epoxy resins, cresol novolak-type epoxy resins, bisphenol A novolak-type epoxy resins, biphenyl-type epoxy resins, naphthalene epoxy resins, dicyclopentadiene-type epoxy resins, triphenylmethane-type epoxy resins, and the like. These epoxy resins may be used singly or in combination of two or more kinds thereof.

[0038]

Examples of commercially available epoxy resins include: jER 828, 806, 807, 834, YX8000, and 8034 manufactured by Mitsubishi Chemical Corporation; YD-128, YDF-170, ZX-1059, and ST-3000 manufactured by Nippon Steel Chemical & Material Co., Ltd.; EPICLON 830, 840, 850, and N-695 manufactured by DIC Corporation; and RE-310S manufactured by Nippon Kayaku Co., Ltd.; and the like.

[0039]

The equivalent of an epoxy group of an epoxy resin in the photosensitive resin composition is preferably 0.3 to 3.0 in terms of the solid concentration with respect to 1 as the equivalent of a carboxyl group of a carboxyl group-containing resin. Bringing the equivalent to 0.3 or more makes it possible to prevent the carboxyl group from remaining in the cured coating film, and to obtain good heat resistance, alkaline resistance, electrical insulation property, and the like. On the other hand, bringing the blending amount to 3.0 equivalents or less makes it possible to prevent a low molecular weight cyclic (thio)ether group from remaining in the dried coating film, and to sufficiently secure the strength of the cured coating film, and the like.

[0040]

[Heat-curing Catalyst]

A photosensitive resin composition according to the present invention can have a heat-curing catalyst blended therein. Examples of such a heat-curing catalyst include: imidazole; imidazole derivatives such as 2-methylimidazole, 2-ethylimidazole, 2-ethyl-4-methylimidazole, 2-phenylimidazole, 4-phenylimidazole, 1-cyanoethyl-2-phenylimidazole, and 1-(2-cyanoethyl)-2-ethyl-4-methylimidazole; dicyandiamide; amine compounds such as benzyldimethylamine, 4-(dimethylamino)-N,N-dimethylbenzylamine, 4-methoxy-N,N-dimethylbenzylamine, and 4-methyl-N,N-dimethylbenzylamine; hydrazine compounds such as adipic dihydrazide and sebacic dihydrazide; and phosphorus compounds such as triphenylphosphine. In addition, examples of commercially available heat-curing catalysts include 2MZ-A, 2MZ-OK, 2PHZ, 2P4BHZ, and 2P4MHZ (which are all tradenames of imidazole-based compounds), which are manufactured by Shikoku International Corporation; and U-CAT 3513N (the tradename of a dimethyl amine-based compound), DBU, DBN, and U-CAT SA 102 (which are all amidine compounds and salts thereof) which are manufactured by San-Apro Ltd. The catalyst is not limited particularly

to these; and can be a heat-curing catalyst for an epoxy resin or an oxetane compound, or one that promotes a reaction of at least any one of an epoxy group and an oxetanyl group with a carboxyl group. The catalysts may be used singly or in mixture of two or more kinds thereof. In addition, guanamine, acetoguanamine, benzoguanamine, melamine, and S-triazine derivatives such as 2,4-diamino-6-methacryloyloxyethyl-S-triazine, 2-vinyl-2,4-diamino-S-triazine, and 2-vinyl-4,6-diamino-S-triazine-isocyanuric acid adduct, and a 2,4-diamino-6-methacryloyloxyethyl-S-triazine-isocyanuric acid adduct can be used.

[0041]

In cases where the photosensitive resin composition contains a thermosetting component having a cyclic (thio)ether group in the molecule of the epoxy resin or the like, the blending amount of the heat-curing catalyst is preferably 0.1 parts by mass or more and 20 parts by mass or less, more preferably 0.5 parts by mass or more and 15.0 parts by mass or less, in terms of the solid concentration, with respect to 100 parts by mass of the thermosetting component having a cyclic (thio)ether group in the molecule.

[0042]

[Photosensitive Monomer]

A photosensitive resin composition according to the present invention contains a photosensitive monomer. The photosensitive monomer is a monomer having an ethylenically unsaturated double bond. Examples of the photosensitive monomer include commonly-used known polyester (meth)acrylate, polyether (meth)acrylate, urethane (meth)acrylate, carbonate (meth)acrylate, and epoxy (meth)acrylate. Specifically, a photosensitive monomer that can be used is at least one selected suitably from the following: hydroxyalkyl acrylates such as 2-hydroxyethyl acrylate or 2-hydroxy propyl acrylate; diacrylates of glycol such as ethylene glycol, methoxytetra ethylene glycol, polyethylene glycol, or propylene glycol; acrylamides such as N,N-dimethyl acrylamide, N-methylolacrylamide, or N,N-dimethylamino propyl acrylamide; aminoalkyl acrylates such as N,N-dimethylamino ethyl acrylate or N,N-dimethylamino propyl acrylate; polyacrylates such as polyalcohol such as hexanediol, trimethylolpropane, pentaerythritol, dipentaerythritol, or tris-hydroxyethyl isocyanurate, or an ethylene oxide adduct, propylene oxide adduct, or ϵ -caprolactone adduct thereof; polyacrylates such as phenoxy acrylate, bisphenol A diacrylate, and an ethylene oxide adduct or

propylene oxide adduct of those phenols; polyacrylates of glycidyl ether such as glycerin diglycidyl ether, glycerin triglycidyl ether, trimethylolpropane triglycidyl ether, or triglycidyl isocyanurate; and, besides the above, acrylates obtained by subjecting polyols such as polyether polyol, polycarbonate diol, hydroxyl-terminated polybutadiene, or polyester polyol to direct acrylation or urethane acrylation via diisocyanate, and melamine acrylates; and each of methacrylates corresponding to the above-described acrylates. Such a photosensitive monomer can be used also as a reactive diluent.

[0043]

An epoxy acrylate resin obtained by bringing a polyfunctional epoxy resin such as a cresol novolak-type epoxy resin into reaction with acrylic acid, an epoxyurethane acrylate compound obtained by further bringing the hydroxyl group of the epoxy acrylate resin into reaction with a hydroxy acrylate such as pentaerythritol triacrylate and a halfurethane compound of diisocyanate such as isophorone diisocyanate, or the like may be used as the photosensitive monomer. Such an epoxy acrylate-based resin can enhance the photo-curability without decreasing the dry-to-touch property.

[0044]

The blending amount of the photosensitive monomer is preferably 1 part by mass or more and 50 parts by mass or less, more preferably 5 parts by mass or more and 40 parts by mass or less, with respect to 100 parts by mass of the carboxyl group-containing resin in terms of the solid concentration in the photosensitive resin composition. Bringing the blending amount of the photosensitive monomer to 1 part by mass or more enhances the photo-curability of the photosensitive resin composition. In addition, bringing the blending amount to 50 parts by mass or less makes it possible to enhance the hardness of the cured coating film.

[0045]

In particular, in cases where a carboxyl group-containing non-photosensitive resin having no ethylenically unsaturated double bond is used, a photosensitive monomer is effective because a photosensitive monomer needs to be used in combination to make the composition photo-curable.

[0046]

[Organic Solvent]

Examples of organic solvents to be used in the present invention include: ketones such as methyl ethyl ketone and cyclohexanone; aromatic

hydrocarbons such as toluene, xylene, and tetramethylbenzene; glycol ethers such as cellosolve, methyl cellosolve, butyl cellosolve, carbitol, methyl carbitol, butyl carbitol, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, dipropylene glycol diethyl ether, and tripropylene glycol monomethyl ether; esters such as ethyl acetate, butyl acetate, butyl lactate, cellosolve acetate, butyl cellosolve acetate, diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, butyl carbitol acetate, propylene glycol monomethyl ether acetate, dipropylene glycol monomethyl ether acetate, and propylene carbonate; aliphatic hydrocarbons such as octane and decane; petroleum solvents such as petroleum ether, petroleum naphtha, and solvent naphtha; and the like. Among these organic solvents, esters are preferable. Diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether acetate, dipropylene glycol monomethyl ether, propylene glycol monomethyl ether, and the like are more preferable. Propylene glycol monomethyl ether acetate, dipropylene glycol monomethyl ether, and propylene glycol monomethyl ether are still more preferable. These organic solvents may be used singly or in combination of two or more kinds thereof. The blending amount of the organic solvent can be set suitably in accordance with the target viscosity of the photosensitive resin composition. It is preferable that, when used, these organic solvents industrially provided are taken out in a necessary amount immediately after the container is opened, and that, after use, these organic solvents are stored in a hermetically sealed container in a cool and dark place.

[0047]

[Quaternary Ammonium Salt Compound]

A photosensitive resin composition according to the present invention can further have a quaternary ammonium salt compound blended therein. Examples of the quaternary ammonium salt compound include a tetraalkyl (or aryl) ammonium compound. Specific examples include tetraalkylammonium halide, tetraalkylammonium acetate, tetraalkylammonium hydrogen sulfate, tetraalkylammonium hydrogen sulfate, tetramethylammonium hydroxide, and the like. Among these, tetraalkylammonium halide is preferably used from the viewpoint of enhancing the covering property at an edge portion of a circuit on a printed wiring board during coating with a spray coater. Besides a quaternary ammonium salt compound, a quaternary phosphonium salt compound or

a tertiary sulfonium salt compound may be used. The quaternary ammonium salt compound can be used singly or in combination of two or more kinds thereof.

[0048]

Specific examples of the tetraalkylammonium halide include: tetramethylammonium bromide, tetraethylammonium bromide, tetrapropylammonium bromide, tetrabutylammonium bromide, tetradecylammonium bromide, trimethylcetylammmonium bromide, triethylcetylammmonium bromide, triethylmethylammmonium bromide, lauryltrimethylammmonium bromide, trioctylmethylammmonium bromide, benzyltrimethylammmonium bromide, benzyltriethylammmonium bromide, benzyltributylammmonium bromide, phenyltrimethylammmonium bromide, phenyltriethylammmonium bromide, hexyltrimethylammmonium bromide, octyltrimethylammmonium bromide, decyltrimethylammmonium bromide, dodecyltrimethylammmonium bromide, tetradecyltrimethylammmonium bromide, hexadecyltrimethylammmonium bromide, octadecyltrimethylammmonium bromide, docosenyloctadecyltrimethylammmonium bromide, dilauryldimethylammmonium bromide, distearyldimethylammmonium bromide, and the like; and

ethyltrimethylammmonium iodide, ethyltri-*n*-propylammmonium iodide, phenyltriethylammmonium iodide, phenyltrimethylammmonium iodide, tetra-*n*-amylammmonium iodide, tetra-*n*-butylammmonium iodide, tetraethylammmonium iodide, tetrabutylammmonium iodide, tetra-*n*-octylammmonium iodide, tetra-*n*-propylammmonium iodide, triethylbenzylammmonium iodide, and the like.

[0049]

Specific examples of the tetraalkylammonium acetate include tetramethylammmonium acetate, tetraethylammmonium acetate, tetrabutylammmonium acetate, benzyltrimethylammmonium acetate, benzyltriethylammmonium acetate, benzyltributylammmonium acetate, and the like.

[0050]

Specific examples of the tetraalkylammonium hydrogen sulfate include tetramethylammmonium hydrogen sulfate, tetraethylammmonium hydrogen sulfate, tetrabutylammmonium hydrogen sulfate, and the like.

[0051]

Specific examples of the tetramethylammmonium hydroxide include

tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, benzyltrimethylammonium hydroxide, monohydroxyethyl trimethylammonium hydroxide, and the like.

[0052]

Examples of the quaternary ammonium salt compound include di-hardened tallow alkyldimethylammonium acetate, benzyldimethylammonium perchlorate, and the like, besides the above-described compounds.

[0053]

As the quaternary ammonium salt compound, tetrabutylammonium bromide, tetrapropylammonium bromide, and the like are particularly preferable.

[0054]

The blending amount of the quaternary ammonium salt compound is preferably 0.1 parts by mass or more and 5 parts by mass or less, more preferably 0.5 parts by mass or more and 3 parts by mass or less, with respect to 100 parts by mass of the carboxyl group-containing resin in terms of the solid concentration in the photosensitive resin composition. Bringing the blending amount of the inorganic filler within the above-described range makes it possible to enhance the characteristics of the cured product, such as adhesion, mechanical strength, a coefficient of linear expansion, along with regulation to a desired viscosity.

[0055]

[Photoinitiator]

In the present invention, a known photoinitiator can be used to photopolymerize the above-described photosensitive resin composition. Examples of the photoinitiator include; an oxime ester photoinitiator having an oxime ester group, a titanocene photoinitiator, an α -aminoacetophenone photoinitiator, an acylphosphine oxide photoinitiator, and the like. Among these, an α -aminoacetophenone photoinitiator and an acylphosphine oxide photoinitiator are preferable. Such photoinitiators may be used singly or in combination of two or more kinds thereof.

[0056]

Specific examples of the α -aminoacetophenone photoinitiator include 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-1-propanone, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butane-1-one, 2-

(dimethylamino)-2-[(4-methylphenyl)methyl]-1-[4-(4-morpholinyl)phenyl]-1-butanone, *N,N*-dimethylaminoacetophenone, and the like. Examples of commercially available products of such a photoinitiator include: Omnirad 369, Omnirad 379, and Omnirad 907 manufactured by IGM Resins B.V.; and the like.

[0057]

Specific examples of the acylphosphine oxide photoinitiator include 2,4,6-trimethylbenzoyl diphenylphosphine oxide, bis (2,4,6-trimethylbenzoyl)-phenylphosphine oxide, bis(2,6-dimethoxybenzoyl)-2,4,4-trimethyl-pentylphosphine oxide, and the like. Examples of commercially available products of such a photoinitiator include: Omnirad 819 manufactured by IGM Resins B.V.; and the like.

[0058]

In combination with the above-described photoinitiator, a photoinitiation auxiliary agent or a sensitizer may be used. Examples of the photoinitiation auxiliary agent or the sensitizer include a benzoin compound, an anthraquinone compound, a thioxanthone compound, a ketal compound, a benzophenone compound, a tertiary amine compound, a xanthone compound, and the like. In particular, a thioxanthone compound such as 2,4-dimethyl thioxanthone, 2,4-diethyl thioxanthone, 2-chlorothioxanthone, 2-isopropyl thioxanthone, or 4-isopropyl thioxanthone is preferably used. Containing such a thioxanthone compound makes it possible to enhance the curability in the deep portions. Examples of commercially available products of the thioxanthone compound include: DETX and ITX manufactured by Lambson Ltd.; and the like. These compounds can be used as the photoinitiator in some cases, but are preferably used in combination with the photoinitiator. Further, the photoinitiation auxiliary agents or the sensitizers may be used singly or in combination of two or more kinds thereof.

[0059]

It is to be noted that, because these photoinitiator, photoinitiation auxiliary agent, and sensitizer absorb a specific wavelength, there are some cases in which they have lower sensitivity and function as ultraviolet absorbents. However, these are not used only for the purpose of enhancing the sensitivity of the composition. Light having a specific wavelength is absorbed if desired, and thereby, the photoreactivity of the surface can be increased. Thus, the line shape and opening of the resist can be changed to a vertical shape, a tapered shape, or a reversed tapered

shape. Besides, the accuracy of the width of the line and the accuracy of the diameter of the opening can be enhanced.

[0060]

[Inorganic Filler]

A photosensitive resin composition according to the present invention can further have an inorganic filler blended therein. Examples of the inorganic filler include barium sulfate, barium titanate, silicon oxide powder, fine silicon oxide powder, amorphous silica, talc, clay, magnesium carbonate, calcium carbonate, aluminum oxide, aluminum hydroxide, mica powder, and the like.

[0061]

The blending amount of the inorganic filler is preferably 10 parts by mass or more and 200 parts by mass or less, more preferably 20 parts by mass or more and 150 parts by mass or less, with respect to 100 parts by mass of the carboxyl group-containing resin in terms of the solid concentration in the photosensitive resin composition. Bringing the blending amount of the inorganic filler within the above-described range makes it possible to enhance the characteristics of the cured product, such as adhesion, mechanical strength, and a coefficient of linear expansion, along with regulation to a desired viscosity.

[0062]

[Colorant]

A photosensitive resin composition according to the present invention can further have a colorant blended therein. As the colorant, a known colorant such as of red, blue, green, or yellow can be used; and any one of pigment, dye, and coloring matter may be used. Note that it is preferable not to contain halogens from the viewpoint of reduction of an environmental burden and an influence on the human body.

[0063]

As the red color colorant, monoazo-based, disazo-based, azo lake-based, benzimidazolone-based, perylene-based, diketopyrrolopyrrole-based, condensed azo-based, anthraquinone-based, quinacridone-based red color colorants, and the like are available; and specific examples thereof include those given Colour Index International (C.I.; published by The Society of Dyers and Colourists) numbers as shown below.

[0064]

Examples of the monoazo-based red color colorant include Pigment Red 1, 2, 3, 4, 5, 6, 8, 9, 12, 14, 15, 16, 17, 21, 22, 23, 31, 32, 112, 114,

146, 147, 151, 170, 184, 187, 188, 193, 210, 245, 253, 258, 266, 267, 268, and 269. Further, examples of the disazo-based red color colorant include Pigment Red 37, 38, and 41. Further, examples of the monoazo lake-based red color colorant include Pigment Red 48:1, 48:2, 48:3, 48:4, 49:1, 49:2, 50:1, 52:1, 52:2, 53:1, 53:2, 57:1, 58:4, 63:1, 63:2, 64:1, and 68. Further, examples of the benzimidazolone-based red color colorant include Pigment Red 171, 175, 176, 185, and 208. Further, examples of the perylene-based red color colorant include Solvent Red 135, 179, Pigment Red 123, 149, 166, 178, 179, 190, 194, and 224. Further, examples of the diketopyrrolopyrrole-based red color colorant include Pigment Red 254, 255, 264, 270, and 272. Further, examples of the condensed azo-based red color colorant include Pigment Red 220, 144, 166, 214, 220, 221, and 242. Further, examples of the anthraquinone-based red color colorant include Pigment Red 168, 177, and 216, Solvent Red 149, 150, 52, and 207. Further, examples of the quinacridone-based red color colorant include Pigment Red 122, 202, 206, 207, and 209.

[0065]

As the blue color colorant, phthalocyanine-based and anthraquinone-based colorants are available. Examples of the pigment-based colorant include compounds classified as Pigment, for example, Pigment Blue 15, 15:1, 15:2, 15:3, 15:4, 15:6, 16, and 60. Examples of a dye-based colorant that can be used include Solvent Blue 35, 63, 68, 70, 83, 87, 94, 97, 122, 136, 67, and the like. Besides these, metal-substituted or unsubstituted phthalocyanine compounds can be used as well.

[0066]

As the yellow color colorant, monoazo-based, disazo-based, condensed azo-based, benzimidazolone-based, isoindolinone-based, anthraquinone-based yellow color colorants, and the like are available; and examples of the anthraquinone-based yellow color colorant include Solvent Yellow 163, and Pigment Yellow 24, 108, 193, 147, 199, and 202. Examples of the isoindolinone-based yellow color colorant include Pigment Yellow 110, 109, 139, 179, and 185. Examples of the condensed azo-based yellow color colorant include Pigment Yellow 93, 94, 95, 128, 155, 166, and 180. Examples of the benzimidazolone-based yellow color colorant include Pigment Yellow 120, 151, 154, 156, 175, and 181. Further, examples of the monoazo-based yellow color colorant include Pigment Yellow 1, 2, 3, 4, 5, 6, 9, 10, 12, 61, 62, 62:1, 65, 73, 74, 75,

97, 100, 104, 105, 111, 116, 167, 168, 169, 182, and 183. Further, examples of the disazo-based yellow color colorant include Pigment Yellow 12, 13, 14, 16, 17, 55, 63, 81, 83, 87, 126, 127, 152, 170, 172, 174, 176, 188, and 198.

[0067]

Besides, a colorant of violet, orange, brown, black, white, or the like may be added. Specific examples thereof include: Pigment Black 1, 6, 7, 8, 9, 10, 11, 12, 13, 18, 20, 25, 26, 28, 29, 30, 31, and 32; Pigment Violet 19, 23, 29, 32, 36, 38, and 42; Solvent Violet 13 and 36; C.I. Pigment Orange 1, 5, 13, 14, 16, 17, 24, 34, 36, 38, 40, 43, 46, 49, 51, 61, 63, 64, 71, and 73; Pigment Brown 23 and 25; carbon black; titanium oxide; and the like.

[0068]

[Other Components]

A photosensitive resin composition according to the present invention can further have, blended therein, a component such as an antifoaming agent, flame retardant, adhesion promoter, antioxidant, ultraviolet absorbent, and dispersant, if desired. As such a component, a product known in the field of electronic materials can be used. In addition, the composition can have, blended therein, at least one kind of commonly-used known additives such as: at least any one kind of antifoaming agents and leveling agents based on silicone, fluorine, polymer, and the like; and silane coupling agents, anti-rust agents, and fluorescent brightening agents based on imidazole, thiazole, triazole, and the like.

[0069]

A base material containing a board with a circuit formed thereon is coated with a photosensitive resin composition according to the present invention by a method such as a dip coating method, flow coating method, roll coating method, bar coater method, spray coating method, screen printing method, or curtain coating method. Among these, a spray coating method can be suitably used for coating. In particular, an electrostatic spray coating method can be more suitably used for coating.

[0070]

A photosensitive resin composition according to the present invention can be suitably used to form a cured film in particular on a printed wiring board, and to form a solder resist, interlayer insulating agent, marking ink, cover lay, or solder dam. To form a solder resist among others, the composition can be used suitably. In addition, a

photosensitive resin composition according to the present invention may be one-component or multi-component composition.

[0071]

[Method of Producing Printed Wiring Board]

A method of producing a printed wiring board includes: applying the photosensitive resin composition to a board using a spray coater; exposing the composition; and curing the composition under at least any one of light and heat to form a solder resist layer. One example of a method of forming a solder resist layer will now be described.

[0072]

As a solder resist layer, a tack-free dry coating film can be formed by adjusting the photosensitive resin composition to a viscosity suitable for a coating method, applying, with a spray coater, the composition to the whole face of a board with a circuit formed thereon, and allowing the organic solvent contained in the composition to be volatilized for drying (temporary drying) at a temperature of approximately 60 to 100°C. The film thickness achieved after the drying is preferably 30 to 50 μm . Using a photosensitive resin composition according to the present invention makes it possible to provide a solder resist layer having a sufficient film thickness at an edge portion of a circuit. Then, using a contact method (or noncontact method), the layer is selectively exposed to active energy rays applied through a photomask having a pattern formed therein, and the unexposed portions are developed with an aqueous solution of dilute alkali (for example, an aqueous solution of 0.3 to 3% sodium carbonate) to form a resist pattern. Furthermore, for example, heat-curing by heating at a temperature of approximately 140 to 180°C makes it possible to form a cured coating film having various excellent characteristics such as heat resistance, chemical resistance, hygroscopicity resistance, adhesion, and electrical characteristics.

[0073]

Examples of the base material to be used for a board with a circuit formed thereon include: all grades (FR-4 and the like) of copper clad laminates produced using a material to be used for a copper clad laminate for high frequency circuit, the material being paper phenol, paper epoxy, glass cloth epoxy, glass polyimide, glass cloth/non-woven fabric epoxy, glass cloth/paper epoxy, synthetic fiber epoxy, fluorine/polyethylene/PPO/cyanate ester, or the like; and beside, polyimide films, PET films, glass boards, ceramic boards, and wafer boards.

[0074]

In addition, examples of a suitable irradiation light source to be used for active energy ray irradiation include a low-pressure mercury lamp, medium-pressure mercury lamp, high-pressure mercury lamp, ultrahigh-pressure mercury lamp, xenon lamp, metal halide lamp, or the like. Besides, a laser beam or the like can be utilized as active energy rays.

[0075]

Examples of the development method include a dipping method, shower method, spray method, and brush method. Examples of developing solutions that can be used include aqueous solutions of dilute alkali such as potassium hydroxide, sodium hydroxide, sodium carbonate, potassium carbonate, sodium phosphate, sodium silicate, ammonia, or amine.

EXAMPLES

[0076]

The present invention will now be described in detail with reference to Examples. However, the present invention is not limited to these Examples. The following adjustments, measurements, and evaluations were all performed in an environment at a temperature of 25°C and a relative humidity of 50%.

[0077]

<Preparation of Carboxyl Group-containing Resin>

Into a four-necked flask with a stirrer and a reflux condenser, 220 parts of cresol novolak-type epoxy resin (EPICLON N-695, manufactured by DIC Corporation, the epoxy equivalent: 220) was added, and 214 parts of carbitol acetate was added and dissolved under heating. Next, 0.1 parts of hydroquinone as a polymerization inhibitor and 2.0 parts of dimethyl benzyl amine as a reaction catalyst were added. This mixture was heated to 95 to 105°C, and to the mixture, 72 parts of acrylic acid was gradually added dropwise. The resulting mixture was allowed to react for 16 hours. This reaction product was cooled to 80 to 90°C, 106 parts of tetrahydrophthalic anhydride was added to the product, and the resulting mixture was allowed to react for 8 hours, cooled, and then taken out. The carboxyl group-containing resin obtained in this manner had a solid concentration of 65%, a solid acid value of 100 mg KOH/g, and a weight average molecular weight M_w of approximately 3,500. In this regard, the weight average molecular weight of the resin obtained was

measured by GPC.

[0078]

<Preparation of Photosensitive Resin Compositions>

[Examples 1 to 6 and Comparative Examples 1 to 3]

The components were blended in a flask in accordance with the formulations shown in the following Tables 1 and 2, and dispersed with a stirrer for 30 minutes to prepare each photosensitive resin composition. The blending amounts in Tables are expressed in part(s) by mass. The photosensitive resin composition prepared was used for the following evaluations.

[0079]

[Table 1]

Components of Photosensitive Resin Composition	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Carboxyl Group-containing Resin *1	100.0	100.0	100.0	100.0	100.0	100.0
Thermosetting Resin *2	20.0	20.0	20.0	20.0	20.0	20.0
Thermosetting Resin *3	20.0	20.0	20.0	20.0	20.0	20.0
Heat-curing Catalyst *4	0.3	0.3	0.3	0.3	0.3	0.3
Heat-curing Catalyst *5	3.0	3.0	3.0	3.0	3.0	3.0
Photosensitive Monomer *6	25.0	25.0	25.0	25.0	25.0	25.0
Photoinitiator *7	15.0	15.0	15.0	15.0	15.0	15.0
Sensitizer *8	0.9	0.9	0.9	0.9	0.9	0.9
Quaternary Ammonium Salt Compound *9	0.5	0.2	0.3	0	0.4	0.5
Quaternary Ammonium Salt Compound *10	0	0	0	0.3	0	0
Inorganic Filler *11	120.0	120.0	120.0	120.0	120.0	120.0
Colorant *12	1.5	1.5	1.5	1.5	1.5	1.5
Antifoaming Agent *13	0.3	0.3	0.3	0.3	0.3	0.3
Organic Solvent *14	56.0	56.0	56.0	56.0	56.0	56.0
Organic Solvent *15	20.0	20.0	20.0	20.0	20.0	0
Organic Solvent *16	0	0	0	0	0	20.0
Total	382.5	382.2	382.3	382.3	382.4	382.5

[0080]

[Table 2]

Components of Photosensitive Resin Composition	Comparative Example 1	Comparative Example 2	Comparative Example 3
Carboxyl Group-containing Resin *1	100.0	100.0	100.0
Thermosetting Resin *2	20.0	20.0	20.0
Thermosetting Resin *3	20.0	20.0	20.0
Heat-curing Catalyst *4	0.3	0.3	0.3
Heat-curing Catalyst *5	3.0	3.0	3.0

Photosensitive Monomer *6	25.0	25.0	25.0
Photoinitiator *7	15.0	15.0	15.0
Sensitizer *8	0.9	0.9	0.9
Quaternary Ammonium Salt Compound *9	0	0	3.0
Quaternary Ammonium Salt Compound *10	0	0	0
Inorganic Filler *11	120.0	120.0	120.0
Colorant *12	1.5	1.5	1.5
Antifoaming Agent *13	0.3	0.3	0.3
Organic Solvent *14	56.0	56.0	56.0
Organic Solvent *15	20.0	0	20.0
Organic Solvent *16	0	20.0	0
Total	382.0	382.0	385.0

[0081]

The details of each component in Tables 1 and 2 are as below-described.

*1: the carboxyl group-containing resin synthesized as above-described

*2: a bisphenol A-type epoxy resin (tradename: jER 828, manufactured by Mitsubishi Chemical Corporation)

*3: a triazine ring epoxy resin (tradename: TEPIC-S, manufactured by Nissan Chemical Corporation)

*4: dicyandiamide (tradename: Dicyandiamide, manufactured by Nippon Carbide Industries Co., Inc.)

*5: melamine (tradename: Melamine, manufactured by MCC Trading Co., Ltd.)

*6: dipentaerythritol hexaacrylate (tradename: KAYARAD DPHA, manufactured by Nippon Kayaku Co., Ltd.)

*7: 2-[4-(methylthio)benzoyl]-2-(4-morpholinyl)propane (tradename: Omnirad 907, manufactured by IGM Resins B.V.)

*8: 2,4-diethylthioxanthone (tradename: KAYACURE DETX-S, manufactured by Nippon Kayaku Co., Ltd.)

*9: tetrabutylammonium bromide (tradename: Tetrabutylammonium Bromide, manufactured by Fujifilm Wako Pure Chemical Corporation)

*10: tetrapropylammonium bromide (tradename: Tetrapropylammonium Bromide, manufactured by Fujifilm Wako Pure Chemical Corporation)

*11: barium sulfate (tradename: B-100, manufactured by Sakai Chemical Industry Co., Ltd.)

*12: phthalocyanine green (tradename: FASTOGEN GREEN S, manufactured by DIC Corporation)

*13: antifoaming agent (tradename: KS-66, manufactured by Shin-Etsu

Chemical Co., Ltd.)

*14: propylene glycol monomethyl ether acetate

*15: dipropylene glycol monomethyl ether

*16: toluene

[0082]

<Adjustment of Viscosity>

The photosensitive resin composition prepared in each of the above-described Examples and Comparative Examples was diluted with propylene glycol monomethyl ether. Then, two kinds of photosensitive resin compositions were prepared, one having a viscosity (dPa·s) $A_1 = 5.0$ (dPa·s) and the other having a viscosity $A_2 = 1.5$ (dPa·s), as measured as a value based on 25°C, 5 rpm, and 30 seconds at 5 rpm in accordance with Viscosity Measurement Method Using Cone-Plate Rotational Viscometer in JIS Z8803:2011, Part 10, using a cone-plate viscometer (TVE-33H, manufactured by Toki Sangyo Co., Ltd.) with a 1°34' × R24 cone rotor. The work for viscosity adjustment was completed within 60 minutes. The photosensitive resin composition diluted was placed in a polyethylene container, which was then sealed hermetically.

[0083]

<Measurement of Volume-specific Resistance Value>

The temperature of each of the two kinds of photosensitive resin compositions diluted to $A_1 = 5.0$ (dPa·s) and $A_2 = 1.5$ (dPa·s) respectively, and prepared as above-described was adjusted to 25°C, and an electrode (the electrode area: 1 cm², and the electrode-to-electrode distance: 1 cm) of an electrostatic tester (tradename: EM-IV, manufactured by Asahi Sunac Corporation) was immersed in the composition to measure the volume-specific resistance value B (MΩ). In this regard, the volume-specific resistance value at the viscosity A_1 was represented by B_1 (MΩ), and the volume-specific resistance value at the viscosity A_2 was represented by B_2 (MΩ). Furthermore, the value of " $(A_1 - A_2)/(B_1 - B_2)$ " was calculated. The measurement results and calculation results are shown in Tables 3 and 4. The measurement of the volume-specific resistance value was completed within 20 minutes.

[0084]

<Covering Property at Edge Portion of Circuit>

The photosensitive resin composition diluted to $A_2 = 1.5$ (dPa·s) and prepared in each of the above-described Examples and Comparative Examples was applied, by electrostatic spraying, to an FR-4 copper clad

laminated board that was buffed to have a length of 15 cm, a width of 9.5 cm, and a thickness of 1.6 mm, and had a circuit having a thickness of 35 μm (the discharge condition: wet. 90 g/m²). This was dried using a hot air circulation drying furnace under conditions at 80°C for 30 minutes to volatilize the solvent, and then exposed at a cumulative amount of light of 300 mJ/cm². Next, the resulting composition was developed with an aqueous solution of 1% sodium carbonate to remove the photosensitive resin composition of the unexposed portions. Then, the photosensitive resin composition was heat-cured using a hot air circulation drying furnace under conditions at 150°C for 60 minutes to produce an evaluation board. The covering property at the edge portion of the circuit was evaluated on the following criteria, and the evaluation results are shown in Tables 3 and 4.

[Evaluation Criteria]

- ◎: The circuit was very well covered with the resist.
- : The circuit was sufficiently covered with the resist.
- △: The resist on the circuit had a thinner portion.
- ×: The resist on the circuit had an extremely thin portion.

[0085]

<Developability>

The residue of the resist on the evaluation board produced in <Covering Property at Edge Portion of Circuit> was evaluated on the following criteria, and the evaluation results are shown in Tables 3 and 4.

- ◎: No development residue was found.
- : A slight development residue was found, but not problematic for practical use.
- ×: Some development residues were found.

[0086]

<Solder Dip Resistance>

The evaluation board produced in <Covering Property at Edge Portion of Circuit> was tested in a solder flow test, using a rosin-based flux at 260°C for 30 seconds. The solder dip resistance was evaluated on the following criteria. The evaluation results are shown in Tables 3 and 4. In this regard, the board the developability of which was evaluated as "×" was not evaluated, and the evaluation result was represented by "-".

[Evaluation Criteria]

- : No peeling was found.

△: Slight peeling was found.

×: Some peeling was found.

[0087]

<Electroless Plating Resistance>

Using the evaluation board produced in <Covering Property at Edge Portion of Circuit>, the electroless plating resistance was evaluated on the following criteria, and the evaluation results are shown in Tables 3 and 4. In this regard, the board the developability of which was evaluated as "×" was not evaluated, and the evaluation result was represented by "-".

[Evaluation Criteria]

○: No peeling was found.

△: Slight peeling was found.

×: Some peeling was found.

[0088]

[Table 3]

Evaluation	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Viscosity A ₁ (dPa·s)	5.0	5.0	5.0	5.0	5.0	5.0
Viscosity A ₂ (dPa·s)	1.5	1.5	1.5	1.5	1.5	1.5
Volume-specific Resistance Value B ₁ (MΩ)	0.2	3.5	0.5	0.5	0.3	0.4
Volume-specific Resistance Value B ₂ (MΩ)	0.1	1.0	0.2	0.2	0.1	0.2
(A ₁ - A ₂)/(B ₁ - B ₂)	35	1.4	12	12	18	18
Covering Property	◎	○	◎	◎	◎	○
Developability	○	◎	◎	◎	◎	○
Solder Dip Resistance	○	○	○	○	○	○
Plating Resistance	○	○	○	○	○	○

[0089]

[Table 4]

Evaluation	Comparative Example 1	Comparative Example 2	Comparative Example 3
Viscosity A ₁ (dPa·s)	5.0	5.0	5
Viscosity A ₂ (dPa·s)	1.5	1.5	1.5
Volume-specific Resistance Value B ₁ (MΩ)	4.0	7.0	0.05
Volume-specific Resistance Value B ₂ (MΩ)	1.3	2,1	0.02
(A ₁ - A ₂)/(B ₁ - B ₂)	1.3	0.71	1.2 × 10 ²
Covering Property	△	×	◎
Developability	◎	◎	×
Solder Dip Resistance	△	×	-
Plating Resistance	△	×	-

[0090]

As evident from the evaluation results in Tables 3 and 4, the photosensitive resin composition (Examples 1 to 6) had an excellent covering property, developability, solder dip resistance, and plating resistance, wherein, when it is assumed that the viscosity of the photosensitive resin composition at 25°C is A (dPa·s), and that the volume-specific resistance value of the photosensitive resin composition at 25°C is B (MΩ), and when the viscosity of the photosensitive resin composition was adjusted to A₁ = 5.0 (dPa·s) and A₂ = 1.5 (dPa·s) using propylene glycol monomethyl ether, the volume-specific resistance value B₁ (MΩ) given at A₁ and the volume-specific resistance value B₂ (MΩ) given at A₂

satisfy the formula: $1.4 \leq (A_1 - A_2)/(B_1 - B_2) \leq 40$.

On the other hand, the photosensitive resin compositions (Comparative Examples 1 to 3) that did not satisfy the above-described formula were found to be unable to enhance each of the covering property, developability, solder dip resistance, and plating resistance in a well-balanced manner.

CLAIMS

1. A photosensitive resin composition comprising a carboxyl group-containing resin, a thermosetting resin, a photosensitive monomer, and an organic solvent, wherein,

when it is assumed that the viscosity of the photosensitive resin composition at 25°C is A (dPa·s), and that the volume-specific resistance value of the photosensitive resin composition at 25°C is B (MΩ), and when the viscosity of the photosensitive resin composition is adjusted to $A_1 = 5.0$ (dPa·s) and $A_2 = 1.5$ (dPa·s) using propylene glycol monomethyl ether, the volume-specific resistance value B_1 (MΩ) given at A_1 and the volume-specific resistance value B_2 (MΩ) given at A_2 satisfy the following formula:

$$1.4 \leq (A_1 - A_2)/(B_1 - B_2) \leq 40.$$

2. The photosensitive resin composition according to claim 1, further comprising a quaternary ammonium salt compound.

3. The photosensitive resin composition according to claim 2, wherein the quaternary ammonium salt compound is at least one selected from tetrabutylammonium bromide and tetrapropylammonium bromide.

4. The photosensitive resin composition according any one of claims 1 to 3, wherein the organic solvent is at least one selected from the group consisting of diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether acetate, dipropylene glycol monomethyl ether, and propylene glycol monomethyl ether.

5. The photosensitive resin composition according to any one of claims 1 to 4, for use in the coating with a spray coater.

6. The photosensitive resin composition according to any one of claims 1 to 5, for use in the formation of a solder resist.

7. A method of producing a printed wiring board comprising a solder resist layer, comprising:

applying the photosensitive resin composition according to any one of claims 1 to 6 to a board using a spray coater; exposing the composition; and curing the composition under at least any one of light and heat to form the solder resist layer.