[Title of the document] Description

[Title of the invention] Photosensitive resin composition and method for producing photosensitive resin film

Technical field

[0001]

The invention relates to a photosensitive resin composition and a method for producing a photosensitive resin film. More specifically, it relates to a photosensitive resin composition suitable for surface protective film and interlayer dielectric film for semiconductor devices, dielectric film for organic electroluminescence (hereinafter abbreviated as EL) devices, planarization film for the substrate of thin film transistors (hereinafter abbreviated as TFT) to drive displaying components comprising organic EL devices, wiring-protecting dielectric film for circuit boards, on-chip microlens for solid imaging devices, and planarization film for various display and solid imaging devices, and also relates to a production method for the photosensitive resin composition.

[Background art]

[0002]

Resin films of polyimide, polybenzoxazole, or the like are widely used as surface protective film, interlayer dielectric film, and planarization film in semiconductor devices. Recently, they are also used as, for instance, dielectric film in organic EL devices and planarization film in TFT substrates. In these

applications, the substrates used have a very large size as compared to those used in semiconductor devices, and therefore, slit coating is generally employed to apply a resin composition. The slit coating technique uses a slit nozzle for coating, which unlike the conventional spin coating technique, does not require the rotation of the substrate to ensure a decreased consumption of resin compositions and improved safety of the process, resulting in a wide use. In performing the slit coating technique, the coating film discharged from the slit nozzle contains the solvent in large amounts, and therefore, it is commonly followed by vacuum drying to remove the solvent quickly after the coating step and subsequent heat drying using a hot plate or the like.

[0003]

As photosensitive resin compositions suitable for slit coating, some efforts have proposed those containing either a polyimide precursor or polyhydroxyamide, a photosensitive agent, and organic solvents with a boiling point of 100°C or more and 140°C or less under atmospheric pressure, the content of said organic solvent being 50 wt% or more and 100 wt% or less relative to the total quantity of the organic solvents (see, for instance, Patent document 1). With respect to positive resist compositions containing alkali-soluble resin such as phenol novolac resin, the use of a photoresist composition for slit coating containing an alkali-soluble resin, photosensitive agent, and a mixed solvent consisting of propylene glycol monomethyl ether acetate

and a cosolvent with a vapor pressure of 150 Pa or less at 1 atm and 20°C has been proposed as a technique to prevent defective patterning from being caused by a difference in the solvent evaporation speed between the surface and the interior of the coating film during the vacuum drying step after the slit coating (see, for instance, Patent document 2). In addition, the use of a photoresist composition for slit coating containing an alkali-soluble resin, a photosensitive substance and a low viscosity solvent with a viscosity of 1.1 cp or less at 20°C that account for 10 wt% or more of a solvent has been proposed as a technique to provide a coating with a decreased viscosity so that slit coating can be performed at a high speed to ensure a uniform film thickness and an improved patterned shape (see, for instance, Patent document 3).

[Prior art documents]

[Patent documents]

[0004]

Patent document 1: Japanese Unexamined Patent Publication (Kokai) No. 2004-54254

Patent document 2: Japanese Unexamined Patent Publication (Kokai) No. 2008-158281

Patent document 3: Japanese Unexamined Patent Publication (Kokai) No. 2008-70480

[Summary of the invention]

[Problems to be solved by the invention]

[0005]

The technique described in Patent document 1 actually can depress the formation of streaks due to existence of foreign objects or clogging in the slit nozzle and other defects such as indentations produced by a support device during the drying step, but it has the problem of bubble formation during the vacuum drying step after slit coating. This bubble formation takes place significantly when a photosensitive resin film with a large film thickness, particularly a photosensitive resin film with a film thickness of 5μm or more, is produced from a resin composition comprising polyimide, polybenzoxazole or their precursors, and there has been a call for a technique that can depress such bubble formation. When the techniques described in Patent documents 2 and 3 are applied to a photosensitive resin composition comprising polyimide, polybenzoxazole, or their precursors, these resins are too low in solubility in propylene glycol methyl ether acetate (boiling point 146°C) or a low viscosity solvent with a viscosity of 1.1 cp or less, causing problems such as persistence of undissolved resin components in the photosensitive resin composition and ununiform thickness of the photosensitive resin film formed by slit coating.

[0006]

There has been a call for a technique that serves to perform slit coating with a photosensitive resin composition containing polyimide, polybenzoxazole, or their precursors to form a thick

film without causing significant bubble formation during the vacuum drying step while ensuring a highly uniform film thickness after drying. Thus, the invention aims to provide a photosensitive resin composition by using a combination of organic solvents with specific characteristics to reduce bubble formation during the vacuum drying step so that an excellent photosensitive resin film with a uniform thickness is obtained after drying.

[SUMMARY]

[0006a]

In a first aspect, there is provided a photosensitive resin composition comprising at least one resin (a) selected from the group of polyimide, polybenzoxazole, a precursor of polyimide, and a precursor of polybenzoxazole; a photosensitive agent (b); an organic solvent (c) with a boiling point of 100°C or more and 130°C or less under atmospheric pressure; and an organic solvent (d) with a boiling point of 150°C or more under atmospheric pressure and a viscosity of more than 1.1 mPa·s and less than 1.5 mPa·s at 20°C, wherein the component (c) accounts for 40 wt% or more and 90 wt% or less of the total quantity of the organic solvents while the component (d) accounts for 10 wt% or more and 60 wt% or less of the total quantity of the organic solvents.

[0006b]

In a second aspect, there is provided a photosensitive resin film production method comprising the step (1) of discharging a photosensitive resin composition as defined herein from a slit nozzle onto a substrate to form a coating film and the step (2) of vacuum-drying the coating film.

[0006c]

In a third aspect, there is provided a photosensitive resin film with a film thickness of 5 μm or more and 10 μm or less produced by the production method as defined herein.

[Means of solving the problems]

[0007]

The invention provides a photosensitive resin composition comprising at least one resin (a) selected from the group of polyimide, polybenzoxazole, a precursor of polyimide, and a precursor of polybenzoxazole, a photosensitive agent (b), an organic solvent (c) with a boiling point of 100°C or more and 130°C or less under atmospheric pressure, and an organic solvent (d) with a boiling point of 150°C or more under atmospheric pressure and a viscosity of more than 1.1 mPa·s and less than 1.5 mPa·s at 20°C, wherein the component (c) accounts for 40 wt% or more and 90 wt% or less relative to the total quantity of the organic solvents while the component (d) accounts for 10 wt% or more and 60 wt% or less relative to the total quantity of the organic solvents.

[Effect of the invention]

[0008]

The invention serves to produce a photosensitive resin film having a highly uniform large thickness of 5 μm or more after drying while depressing bubble formation during the vacuum drying step after slit coating.

[Description of embodiments]

[0009]

The invention provides a photosensitive resin composition comprising at least one resin (a) selected from the group of polyimide, polybenzoxazole, a precursor of polyimide, and a precursor of polybenzoxazole, a photosensitive agent (b), an organic solvent (c) with a boiling point of 100°C or more and 130°C or less under atmospheric pressure, and an organic solvent (d) with a boiling point of 150°C or more under atmospheric pressure and a viscosity of more than 1.1 mPa·s and less than 1.5 mPa·s at 20°C, wherein the component (c) accounts for 40 wt% or more and 90 wt% or less relative to the total quantity of the organic solvents while the component (d) accounts for 10 wt% or more and 60 wt% or less relative to the total quantity of the organic solvents. Each of the components is described below.

[0010]

The photosensitive resin composition according to the invention comprises at least one resin (a) that is selected from the group of polyimide, polybenzoxazole, a precursor of polyimide, and a precursor of polybenzoxazole. Two or more of these may be

contained, and a copolymer comprising two or more of these as repeating unit may be contained.

[0011]

Polyimide and polybenzoxazole are resins having a cyclic structure, namely an imide ring or an oxazole ring, in the backbone chain structure. The number of repetitions of the structural units is preferably 10 to 100,000.

[0012]

Polyimide can be produced by reacting a tetracarboxylic acid, or a corresponding substance such as tetracarboxylic dianhydride and tetracarboxylic acid diester dichloride, with a diamine, or a corresponding substance such as diisocyanate compound and trimethylsilylated diamine, and contains a tetracarboxylic acid residue and a diamine residue. For instance, it can be produced by subjecting a polyamic acid, which is a polyimide precursor formed through reaction of a tetracarboxylic dianhydride and a diamine, to heat treatment to cause dehydration and cyclization. A solvent azeotropic with water, such as m-xylene, may be added during this heat treatment. Or, a dehydration condensation agent such as carboxylic anhydride and dicyclohexyl carbodiimide and a base such as triethyl amine may be added as a cyclization catalyst, followed by chemical heat treatment to cause dehydration and cyclization for its production. Or, it can also be produced by adding a weakly acidic carboxylic acid compound followed by heat treatment at a low temperature of 100°C or less to cause

dehydration and cyclization. The polyimide precursor will be described later.

[0013]

Polybenzoxazole can be produced by reacting a bisaminophenol compound with a dicarboxylic acid, or a corresponding substance such as dicarboxylic acid chloride and dicarboxylic acid active ester, and contains a dicarboxylic acid residue and a bisaminophenol residue. For instance, it can be produced by subjecting polyhydroxyamide, which is a polybenzoxazole precursor formed through reaction of a bisaminophenol compound and a dicarboxylic acid, to heat treatment to cause dehydration and cyclization. Or, it can also be produced by adding a phosphoric anhydride, a base, a carbodiimide compound, or the like, followed by chemical treatment to cause dehydration and cyclization. The polybenzoxazole precursor will be described later.

[0014]

For the invention, from the viewpoint of solubility in an alkali aqueous solution, it is preferable that said polyimide contains an acidic group or an acidic group derivative, such as OR^1, SO_3R^1, $CONR^1R^2$, $COOR^1$, $SO_2NR^1R^2$, more preferably the hydroxyl group, in said tetracarboxylic acid residue and/or diamine residue. Furthermore, it is preferable that said polybenzoxazole contains an acidic group or an acidic group derivative, such as OR^1, SO_3R^1, $CONR^1R^2$, $COOR^1$, $SO_2NR^1R^2$, more preferably the hydroxyl group, in said dicarboxylic acid residue and/or bisaminophenol residue.

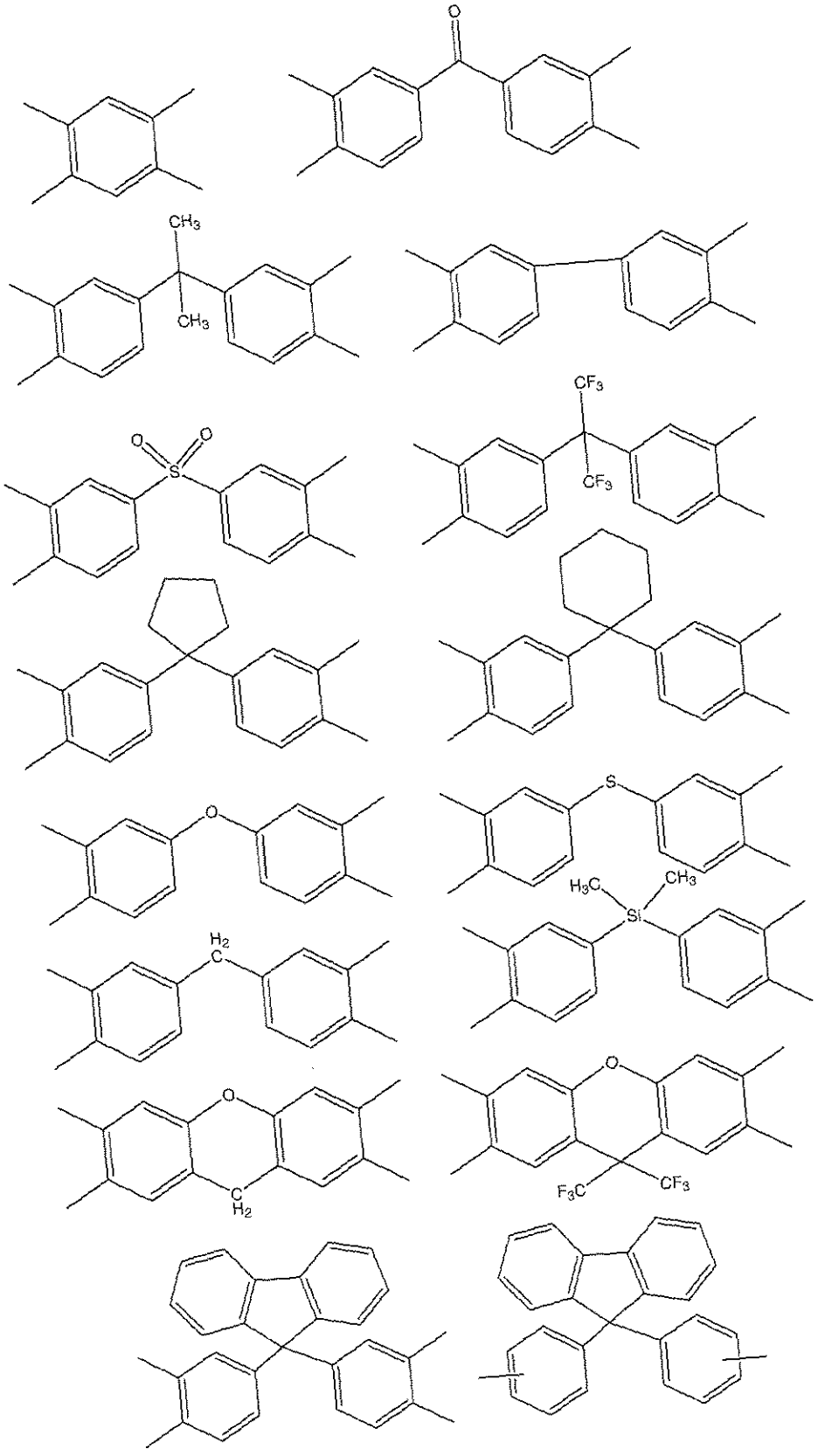
Here, R^1 and R^2 denote a hydrogen atom or a monovalent organic group with a carbon number of 1 to 20. The above component is an acidic group when both R^1 and R^2 are a hydrogen atom and it is an acidic group derivative when R^1 and R^2 contain a monovalent organic group with a carbon number of 1 to 20. Examples of said organic group include alkyl group, alkoxyl group, and ester group.

[0015]

For the invention, said tetracarboxylic acid residue in polyimide and said dicarboxylic acid residue in polybenzoxazole (hereinafter, collectively referred to as acid residues) preferably has a structure as listed below or a similar structure in which 1 to 4 of the hydrogen atoms are replaced with an alkyl group with a carbon number of 1 to 20, fluoroalkyl group, alkoxyl group, ester group, nitro group, cyano group, fluorine atom, or chlorine atom.

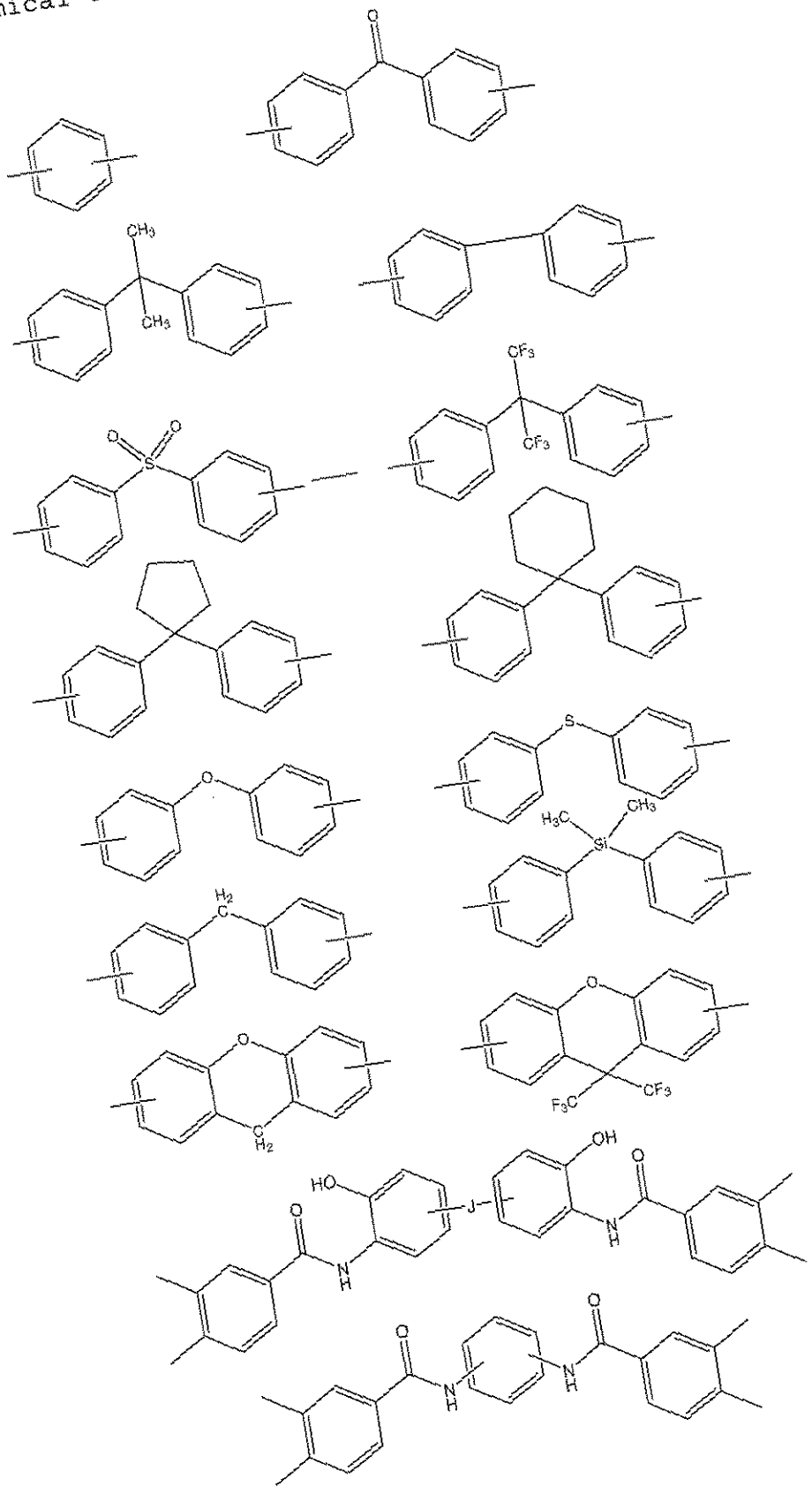
[0016]

[Chemical compound 1]



[0017]

[Chemical compound 2]



[0018]

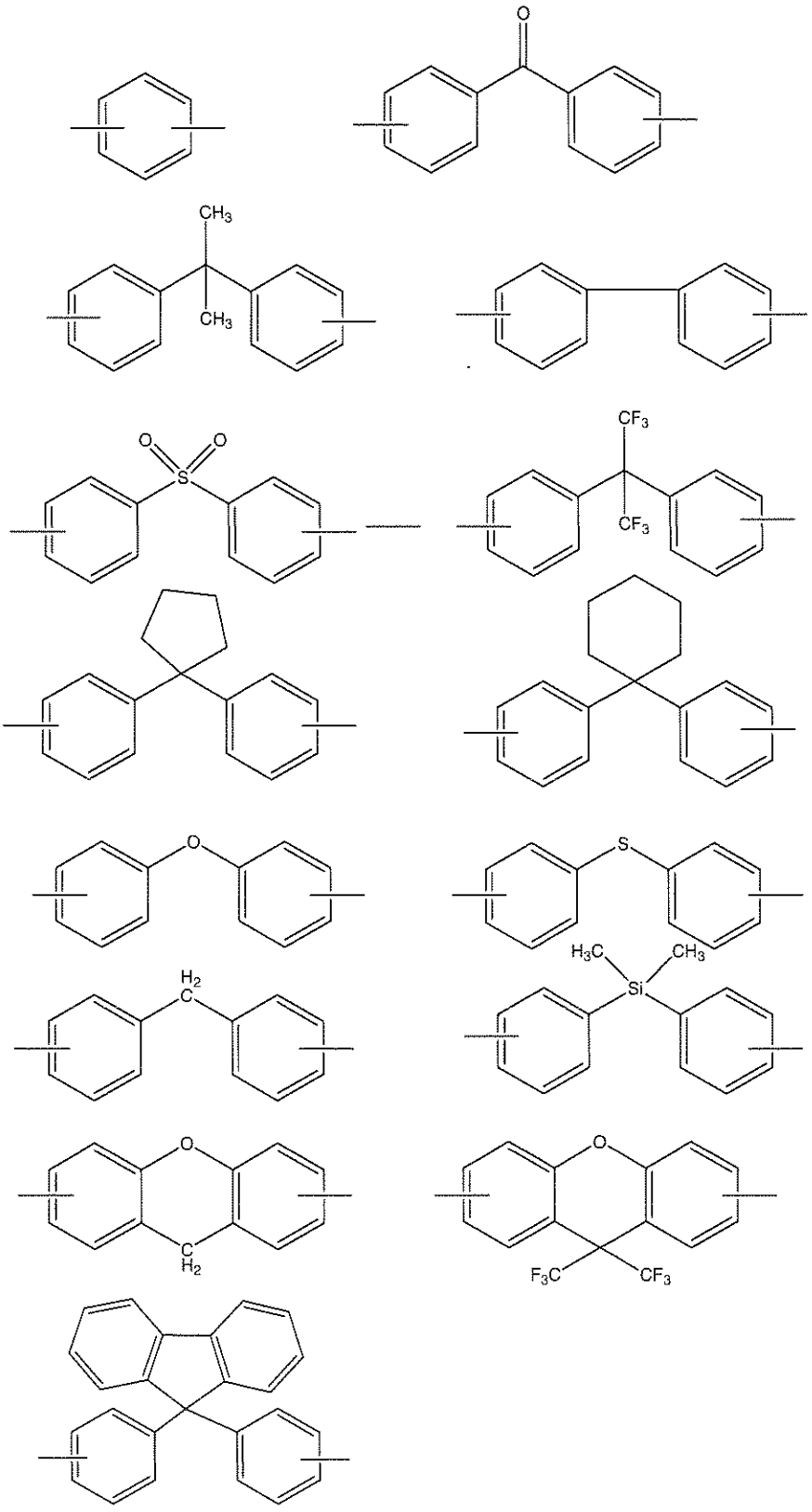
Here, "J" denotes a direct bond, -COO-, -CONH-, $-CH_2-$, $-C_2H_4-$, -O-, $-C_3H_6-$, $-C_3F_6-$, $-SO_2-$, -S-, $-Si(CH_3)_2-$, $-O-Si(CH_3)_2-O-$, $-C_6H_4-$, $-C_6H_4-O-C_6H_4-$, $-C_6H_4-C_3H_6-C_6H_4-$, or $-C_6H_4-C_3F_6-C_6H_4-$.

[0019]

For the invention, said diamine residue in polyimide and said bisaminophenol residue in polybenzoxazole (hereinafter, collectively referred to as diamine residues) preferably has a structure as listed below or a similar structure in which 1 to 4 of the hydrogen atoms are replaced with an alkyl group with a carbon number of 1 to 20, fluoroalkyl group, alkoxyl group, ester group, nitro group, cyano group, fluorine atom, or chlorine atom.

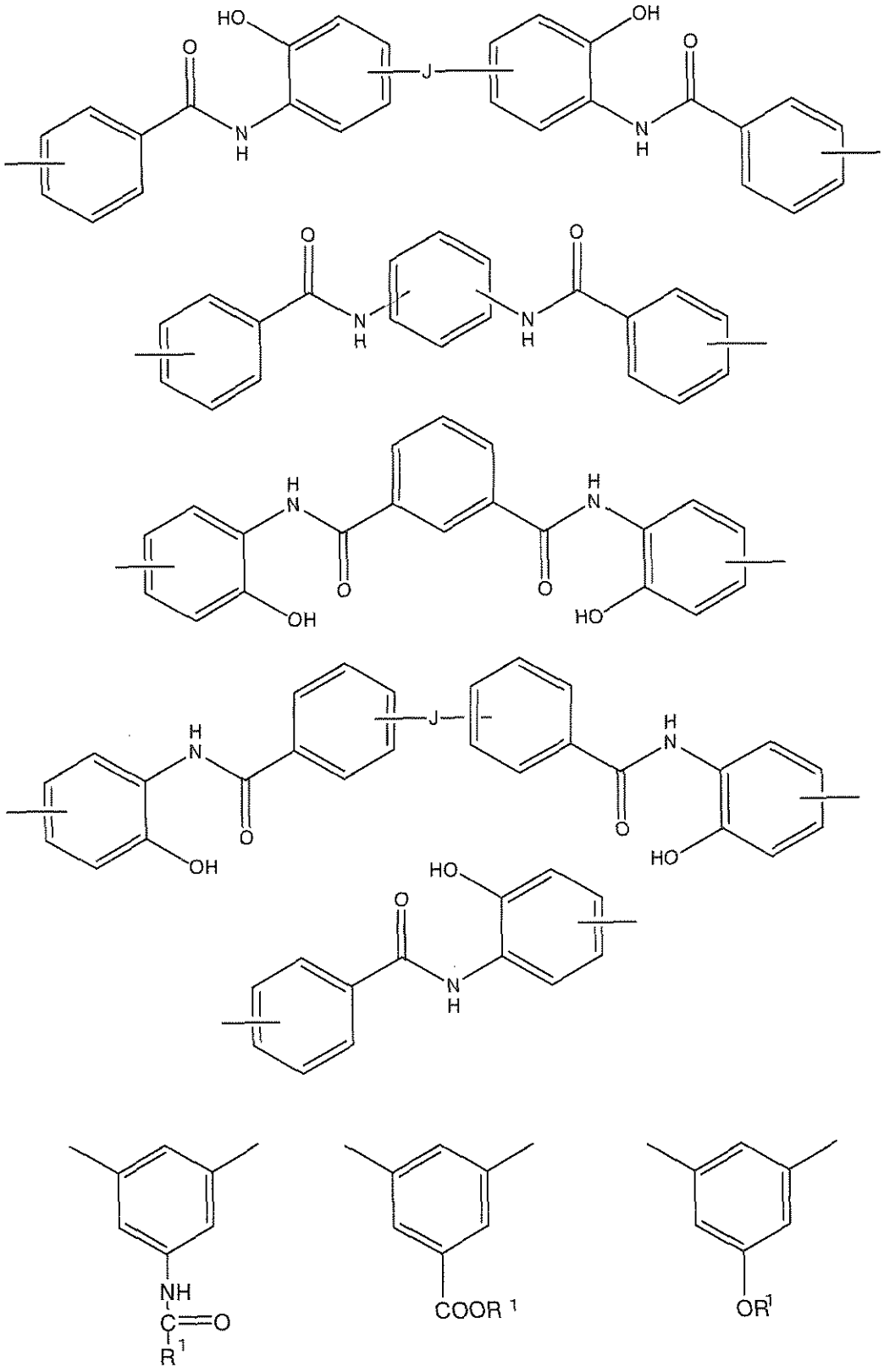
[0020]

[Chemical compound 3]



[0021]

[Chemical compound 4]



[0022]

Here, "J" denotes a direct bond, -COO-, -CONH-, $-CH_2-$, $-C_2H_4-$, -O-, $-C_3H_6-$, $-C_3F_6-$, $-SO_2-$, -S-, $-Si(CH_3)_2-$, $-O-Si(CH_3)_2-O-$, $-C_6H_4-$, $-C_6H_4-O-C_6H_4-$, $-C_6H_4-C_3H_6-C_6H_4-$, or $-C_6H_4-C_3F_6-C_6H_4-$. R^1 denotes a hydrogen atom or a monovalent organic group with a carbon number of 1 to 20.

[0023]

Of the resins of the component (a) used for the invention, said polyimide precursor and said polybenzoxazole precursor have an amide bond in their backbone chain and can be converted into said polyimide or said polybenzoxazole through dehydration and cyclization caused by heat treatment or chemical processing. The number of repetitions of the structural units is preferably 10 to 100,000. Examples of said polyimide precursor include polyamic acid, polyamic acid ester, polyamic acid amide, and polyisoimide, of which polyamic acid and polyamic acid ester are preferable. Examples of said polybenzoxazole precursor include polyhydroxyamide, polyamino amide, polyamide, and polyamide-imide, of which polyhydroxyamide is preferable.

[0024]

From the viewpoint of solubility in an alkali aqueous solution, it is preferable that said polyimide precursor and said polybenzoxazole precursor contain an acidic group or an acidic group derivative, such as OR^1, SO_3R^1, $CONR^1R^2$, $COOR^1$, $SO_2NR^1R^2$, more preferably the hydroxyl group. R^1 and R^2 denote a hydrogen

atom or a monovalent organic group with a carbon number of 1 to 20. The above component is an acidic group when both R^1 and R^2 are a hydrogen atom and it is an acidic group derivative when R^1 and R^2 contain a monovalent organic group with a carbon number of 1 to 20.

[0025]

Examples of the acid component that constitutes the acid residue in said polyimide precursor and polybenzoxazole precursor include dicarboxylic acids such as terephthalic acid, isophthalic acid, diphenyl ether dicarboxylic acid, bis(carboxyphenyl) hexafluoropropane, biphenyl dicarboxylic acid, benzophenone dicarboxylic acid, and triphenyl dicarboxylic acid; tricarboxylic acids such as trimellitic acid, trimesic acid, diphenyl ether tricarboxylic acid, and biphenyl tricarboxylic acid; and tetracarboxylic acids including aromatic tetracarboxylic acids such as pyromellitic acid, 3,3′,4,4′-biphenyl tetracarboxylic acid, 2,3,3′,4′-biphenyl tetracarboxylic acid, 2,2′,3,3′-biphenyl tetracarboxylic acid,3,3′,4,4′-benzophenone tetracarboxylic acid,2,2′,3,3′-benzophenone tetracarboxylic acid, 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane, 2,2-bis(2,3-dicarboxyphenyl) hexafluoropropane, 1,1-bis(3,4-dicarboxyphenyl) ethane, 1,1-bis(2,3-dicarboxyphenyl) ethane, bis(3,4-dicarboxyphenyl) methane, bis(2,3-dicarboxyphenyl)

methane, bis(3,4-dicarboxyphenyl) sulfone, bis(3,4-dicarboxyphenyl) ether, 1,2,5,6-naphthalene tetracarboxylic acid, 2,3,6, 7-naphthalene tetracarboxylic acid, 2,3,5,6-pyridine tetracarboxylic acid, and 3,4,9,10-perylene tetracarboxylic acid, and aliphatic tetracarboxylic acids such as butane tetracarboxylic acid, cyclobutane tetracarboxylic acid, 1,2,3,4-cyclopentane tetracarboxylic acid, cyclohexane tetracarboxylic acid, bicyclo[2.2.1.]heptane tetracarboxylic acid, bicyclo[3.3.1.]tetracarboxylic acid, bicyclo[3.1.1.]hept-2-en tetracarboxylic acid, bicyclo[2.2.2.]octane tetracarboxylic acid, adamantane tetracarboxylic acid, and 2,3,5-tri carboxycyclopentyl acetic acid. Furthermore, 1 to 4 of the hydrogen atoms in the dicarboxylic acids, tricarboxylic acids, and tetracarboxylic acids listed above may be replaced with an acidic group or acidic group derivative such as OR^1, SO_3R^1, $CONR^1R^2$, $COOR^1$, and $SO_2NR^1R^2$, preferably the hydroxyl group, sulfonic acid group, sulfonic acid amide group, or sulfonic acid ester group.

[0026]

These acids may be used in their original form or in the form of an anhydride or an active ester. Two or more of them may be used in combination.

[0027]

The use of a tetracarboxylic acid containing a silicon atom such

as dimethylsilane diphthalic acid and 1,3-bis(phthalic acid)tetramethyl disiloxane can serve to increase the adhesiveness to the substrate and the resistance to oxygen plasma used for cleaning and the like and to UV ozone processing. It is preferable that these tetracarboxylic acids containing a silicon atom account for 1 to 30 mol% of the total quantity of the acid components.

[0028]

Examples of said diamine component that constitutes the diamine residue in said polyimide precursor and polybenzoxazole precursor include diamines containing a hydroxyl group such as bis(3-amino-4-hydroxyphenyl) hexafluoropropane, bis(3-amino-4-hydroxyphenyl) sulfone, bis(3-amino-4-hydroxyphenyl) propane, bis(3-amino-4-hydroxyphenyl) methylene, bis(3-amino-4-hydroxyphenyl) ether, bis(3-amino-4-hydroxy) biphenyl, and bis(3-amino-4-hydroxyphenyl) fluorene; diamines containing a carboxyl group such as 3,5-diaminobenzoic acid and 3-carboxy-4, 4'-diaminodiphenyl ether; diamines containing a sulfonic acid such as 3-sulfonic acid-4,4'-diaminodiphenyl ether; aliphatic diamines such as dithiohydroxyphenylene diamine, 3,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl ether, 3,4'-diaminodiphenyl methane, 4,4'-diaminodiphenyl methane, 3,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl sulfone, 3,4'-diaminodiphenyl sulfide, 4,4'-diaminodiphenyl

sulfide, 1,4-bis(4-aminophenoxy) benzene, benzine, m-phenylene diamine, p-phenylene diamine, 1,5-naphthalene diamine, 2,6-naphthalene diamine, bis(4-aminophenoxy phenyl) sulfone, bis(3-aminophenoxy phenyl) sulfone, bis(4-aminophenoxy) biphenyl, bis{4-(4-aminophenoxy) phenyl} ether, 1,4-bis(4-aminophenoxy) benzene, 2, 2'-dimethyl-4,4'-diaminobiphenyl, 2, 2'-diethyl-4,4'-diaminobiphenyl, 3,3'-dimethyl-4,4'-diaminobiphenyl, 3,3'-diethyl-4,4'-diaminobiphenyl, 2,2',3,3'-tetramethyl-4,4'-diaminobiphenyl, 3,3',4,4'-tetramethyl-4,4'-diaminobiphenyl, 2,2'-di(trifluoromethyl)-4,4'-diaminobiphenyl, and compounds produced by replacing some of the hydrogen atoms of the aromatic ring in these substances with alkyl groups or halogen atoms, as well as 1,4-cyclohexyl diamine and methylene biscyclohexyl amine. In these diamines, some of the hydrogen atoms may be replaced with alkyl groups with a carbon number of 1 to 10 such as methyl groups and ethyl group, fluoroalkyl groups with a carbon number of 1 to 10 such as trifluoromethyl group, or others such as F, Cl, Br, and I. It is preferable, furthermore, that the diamines listed above contain an acidic group or an acidic group derivative, such as OR^1, SO_3R^1, $CONR^1R^2$, $COOR^1$, $SO_2NR^1R^2$, more preferably the hydroxyl group.

[0029]

These diamines may be used in their original form or in the form of a corresponding diisocyanate compound or trimethylsilylated diamine. Two or more of them may be used in combination. For uses where heat resistance is required, it is preferable that the aromatic diamines account for 50 mol% or more of the total diamines.

[0030]

The use of a diamine containing a silicon atom, such as 1,3-bis(3-aminopropyl)tetramethyl disiloxane and 1,3-bis(4-anilino)tetramethyl disiloxane, as said diamine component can serve to increase the adhesiveness to the substrate and the resistance to oxygen plasma used for cleaning and the like and to UV ozone processing. It is preferable that these diamines containing a silicon atom account for 1 to 30 mol% of the total diamines.

[0031]

It is preferable that the ends of said polyimide, polybenzoxazole, and their precursors are capped with a monoamine, acid anhydride, acid chloride or monocarboxylic acid that contain a hydroxyl group, carboxyl group, sulfonic acid group, or thiol group. Two or more of them may be used in combination. If said group exist at the end of resin molecules, the speed of dissolution of these resins in an aqueous alkali solution will be easily adjusted in a preferred range.

[0032]

Preferable examples of said monoamines include 5-amino-8-hydroxyquinoline, 1-hydroxy-7-aminonaphthalene, 1-hydroxy-6-aminonaphthalene, 1-hydroxy-5-aminonaphthalene, 1-hydroxy-4-aminonaphthalene, 2-hydroxy-7-aminonaphthalene, 2-hydroxy-6-aminonaphthalene, 2-hydroxy-5-aminonaphthalene, 2-hydroxy-3-aminonaphthalene, 1-carboxy-7-aminonaphthalene, 1-carboxy-6-aminonaphthalene, 1-carboxy-5-aminonaphthalene, 2-carboxy-7-aminonaphthalene, 2-carboxy-6-aminonaphthalene, 2-carboxy-5-aminonaphthalene, 2-aminobenzoic acid, 3-aminobenzoic acid, 4-aminobenzoic acid, 4-aminosalicylic acid, 5-aminosalicylic acid, 6-aminosalicylic acid, 2-aminobenzene sulfonic acid, 3-aminobenzene sulfonic acid, 4-aminobenzene sulfonic acid, 3-amino-4,6-dihydroxy pyrimidine, 2-aminophenol, 3-aminophenol, 4-aminophenol, 2-amino-4-terbutyl phenol, 2-aminothiophenol, 3-aminothiophenol, and 4-aminothiophenol.

[0033]

Preferable examples of said anhydrides, acid chlorides, and monocarboxylic acids include anhydrides such as phthalic anhydride, maleic anhydride, nadic acid, cyclohexanedicarboxylic anhydride, and 3-hydroxyphthalic anhydride; monocarboxylic acids such as 3-carboxyphenol, 4-carboxyphenol, 3-carboxythiophenol, 4-carboxythiophenol, 1-hydroxy-7-carboxynaphthalene, 1-hydroxy-6-carboxynaphthalene,

1-hydroxy-5-carboxynaphthalene,

1-mercapto-7-carboxynaphthalene,

1-mercapto-6-carboxynaphthalene,

1-mercapto-5-carboxynaphthalene, 3-carboxybenzene sulfonic acid, and 4-carboxybenzene sulfonic acid; those monoacid chloride compounds that can be produced from the former by converting their carboxyl group into an acid chloride group; those monoacid chloride compounds that can be produced from dicarboxylic acids such as terephthalic acid, phthalic acid, maleic acid, cyclohexanedicarboxylic acid, 1,5-dicarboxynaphthalene, 1,6-dicarboxynaphthalene, 1,7-dicarboxynaphthalene, and 2,6-dicarboxynaphthalene by converting only one of their carboxyl groups into an acid chloride group; and active ester compounds that can be produced by reacting a monoacid chloride compound with N-hydroxybenzotriazole or N-hydroxy-5-norbornene-2,3-dicarboxyimide.

[0034]

The end capping agents used for said monoamines, anhydrides, acid chlorides, or monocarboxylic acids preferably account for 0.1 to 60 mol%, more preferably 5 to 50 mol%, of the total molar quantity of the monomers for the acid components or diamine components. If their content is maintained in this range, it will be possible to produce a resin composition that can provide a solution with a suitable viscosity for coating and has good film properties.

[0035]

The resin molecules may have polymerizable functional groups at the ends. Examples of said polymerizable functional groups include ethylenically unsaturated linking groups, acetylene groups, methylol groups, and alkoxy methyl groups.

[0036]

End capping agents introduced in a resin can be detected easily by methods as described below. The resin containing an end capping agent may be dissolved in, for instance, an acidic solution to decompose it into the diamine components and acid components, that is, the constituent units of the resin, and then the end capping agent can be detected easily by gas chromatography (GC) and NMR spectroscopy. In another method, detection can be carried out by subjecting the resin containing an end capping agent directly to pyrolysis gas chromatograph (PGC), infrared spectroscopy, or ^{13}C-NMR infrared spectroscopy.

[0037]

For the invention, the component (a) is preferably a polyimide precursor or a polybenzoxazole precursor, more preferably a polyimide precursor. A polyimide precursor undergoes imidization reaction to cause cyclization of the amide acid portion when calcined at about 200°C, while a polybenzoxazole precursor undergoes oxazolation reaction to cause cyclization of the hydroxyamide portion when calcined at about 300°C, while suffering volume shrinkage. Photosensitive resin compositions

produced from these precursor resins form a pattern of a forward tapered shape when calcined after fine patterning in the exposure and development steps. When the resulting resin is used as dielectric film in an organic EL device, such a pattern of a forward tapered shape serves to provide a good cover for the upper electrode and prevent disconnection, allowing the device to have an increased reliability.

[0038]

The photosensitive resin composition according to the present invention may also contain other alkali-soluble resins in addition to the component (a). Said alkali-soluble resins are composed of molecules that have an acidic group to make them soluble in alkaline substances, and specifically, they include radical-polymerizable polymers with an acrylic acid group, phenol-novolac resin, polyhydroxystyrene, and polysiloxane. It may also be effective to control their alkali solubility by protecting the acidic groups in these resins. These resins are soluble in aqueous alkali solutions of choline, triethyl amine, dimethyl aminopyridine, monoethanol amine, diethyl aminoethanol, sodium hydroxide, potassium hydroxide, and carbonic acid sodium, as well as tetramethyl ammonium hydroxide. Two or more of these resins may be contained, but their content should preferably be 50 wt% or less of the total quantity of all resins including the component (a).

[0039]

The photosensitive resin composition according to the present invention contains a photosensitive agent (b). Said photosensitive agent may be a combination of a photoacid generating agent (b-1), photopolymerization initiator (b-2), and a compound with two or more ethylenically unsaturated bonds (b-3). The inclusion of said photoacid generating agent (b-1) works to produce an acid in the irradiated portion so that the irradiated portion increases in solubility in an aqueous alkali solution, allowing a positive relief pattern to be formed after dissolution of the irradiated portion. The inclusion of an epoxy compound or a thermal crosslinking agent as described later along with the photoacid generating agent (b-1) allows the acid formed in the irradiated portion to serve for promotion of the crosslinked reaction of the epoxy compound and the thermal crosslinking agent, leading to formation of a negative type relief pattern as a result of insolubilization of the irradiated portion. The inclusion of a photopolymerization initiator (b-2) and a compound with two or more ethylenically unsaturated bonds (b-3) allows the active radicals formed in the irradiated portion to serve for promotion of radical polymerization of ethylenically unsaturated bonds, leading to formation of a negative type relief pattern as a result of insolubilization of the irradiated portion. The photosensitive resin composition according to the present invention preferably contains a photoacid generating agent (b-1) as the photosensitive agent (b) and has positive photosensitivity.

Positive photosensitive resin compositions easily form a pattern of a forward tapered shape when calcined after fine patterning in the exposure and development steps. When the resulting resin is used as dielectric film in an organic EL device, such a pattern of a forward tapered shape serves to provide a good cover for the upper electrode and prevent disconnection, allowing the device to have an increased reliability.

[0040]

Examples of the photoacid generating agent (b-1) include quinone diazide compound, sulfonium salt, phosphonium salt, diazonium salt, and iodonium salt.

[0041]

Examples of said quinone diazide compound include polyhydroxy compounds bonded to sulfonic acid of quinone diazide through ester linkage, polyamino compounds bonded to sulfonic acid of quinone diazide through sulfonamide linkage, and polyhydroxypolyaminno compounds bonded to sulfonic acid of quinone diazide through ester linkage and/or sulfonamide linkage. It is preferable that 50 mol% or more of the functional groups in said polyhydroxy compounds and polyamino compounds are substituted by quinone diazide. It is also preferable that two or more substances corresponding to the photoacid generating agent (b-1) are contained to provide a photosensitive resin composition with high sensitivity.

[0042]

For the quinone diazide for the present invention, both 5-naphthoquinone diazide sulfonyl group and 4-naphthoquinone diazide sulfonyl group are preferred. A 4-naphthoquinone diazide sulfonyl ester compound absorbs light in the i-line range of mercury lamps, and therefore, it is suitable for i-line exposure. A 5-naphthoquinone diazide sulfonyl ester compound absorbs light in a region including the g-line of mercury lamps, and therefore, it is suitable for g-line exposure. For the present invention, it is preferable to select either a 4-naphthoquinone diazide sulfonyl ester compound or a 5-naphthoquinone diazide sulfonyl ester compound depending on the wavelength of the light used for exposure. Furthermore, the agent may contain a naphthoquinone diazide sulfonyl ester compound comprising both a 4-naphthoquinone diazide sulfonyl group and a 5-naphthoquinone diazide sulfonyl group in one molecule, or may contain both a 4-naphthoquinone diazide sulfonyl ester compound and a 5-naphthoquinone diazide sulfonyl ester compound.

[0043]

Of said examples of the photoacid generating agent (b-1), the sulfonium salt, phosphonium salt, and diazonium salt are preferable because they can stabilize moderately the acid component produced by light exposure. The sulfonium salt is particularly preferable. In addition, a sensitization agent and the like may also be contained as needed.

[0044]

Examples of the photopolymerization initiator (b-2) include diethoxy acetophenone, 2-hydroxy-2-methyl-1-phenyl propane-1-one, benzyl dimethyl ketal, 1-(4-isopropyl phenyl)-2-hydroxy-2-methyl propane-1-one, 4-(2-hydroxyethoxy) phenyl-(2-hydroxy-2-propyl) ketone, 1-hydroxycyclohexyl-phenyl ketone, 1-phenyl-1,2-propanedione-2-(o-ethoxycarbonyl) oxime, 2-methyl-[4-(methyl thio) phenyl]-2-morpholinopropane-1-one, 2-benzyl-2-dimethyl amino-1-(4-morpholinophenyl)-butanone-1, benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether, benzophenone, methyl o-benzoylbenzoate, 4-phenyl benzophenone, 4,4-dichlorobenzophenone, hydroxybenzophenone, 4-benzoyl-4′-methyl-diphenyl sulfide, alkylated benzophenone, 3,3′,4,4′-tetra(t-butylperoxy carbonyl) benzophenone, 4-benzoyl-N,N-dimethyl-N-[2-(1-oxo-2-propenyloxy) ethyl]benzene methanaminium bromide, (4-benzoyl benzyl) trimethyl-ammonium chloride, 2-hydroxy-3-(4-benzoyl phenoxy)-N,N,N-trimethyl-1-propene-aminium chloride monohydrate, 2-isopropyl thioxanthone, 2,4-dimethyl thioxanthone, 2, 4-diethyl thioxanthone, 2, 4-dichlorothioxanthone, 2-hydroxy-3-(3,4-dimethyl-9-oxo-9H-thioxanthene-2-yloxy)-N, N, N-trimethyl-1-propanaminium chloride, 2,4,6-trimethyl-benzoyl-phenyl-phosphine oxide,

1,2-octanedione-1-[4-(phenyl thio)-2-(O-benzoyloxime)], ethanone, 1-[9-ethyl-6-(2-methyl benzoyl)-9H-carbazole-3-yl]-, 1-(O-acetyl oxime), 2,2′-bis(o-chlorophenyl)-4,5,4′, 5′-tetraphenyl-1, 2-bi-imidazole, 10-butyl-2-chloroacridone, 2-ethyl anthraquinone, benzyl, 9,10-phenanthrene quinone, camphor quinone, methyl-phenyl-glyoxylic ester, η5-cyclopentadienyl-η6-cumenyl-iron(1+)-hexafluorophosphate (1-), diphenyl sulfide derivatives, bis(η5-2,4-cyclopentadiene-1-yl)-bis(2,6-difluoro-3-(1H-pyrrole-1-yl)-phenyl) titanium, 4,4-bis(dimethyl amino) benzophenone, 4,4-bis(diethyl amino) benzophenone, thioxanthone, 2-methyl thioxanthone, 2-chlorothioxanthone, 4-benzoyl-4-methyl phenyl ketone, dibenzyl ketone, fluorenone, 2,3-diethoxy acetophenone, 2,2-dimethoxy-2-phenyl-2-phenyl acetophenone, 2-hydroxy-2-methyl propiophenone, p-t-butyl dichloroacetophenone, benzyl methoxy ethyl acetal, anthraquinone, 2-t-butyl anthraquinone, 2-aminoanthraquinone, β-chloroanthraquinone, anthrone, benz-anthrone, dibenz-suberone, methylene anthrone, 4-azidobenzal acetophenone, 2,6-bis(p-azidobenzylidene) cyclohexane, 2,6-bis(p-azidobenzylidene)-4-methyl cyclohexanone, 2-phenyl-1, 2-butadione-2-(o-methoxycarbonyl) oxime, 1,3-diphenyl propanetrione-2-(o-ethoxycarbonyl) oxime, naphthalene sulfonyl chloride, quinoline sulfonyl chloride,

N-phenyl thioacridone, 4,4-azobisisobutyronitrile, benz-thiazole disulfide, triphenyl phosphine, carbon tetrabromide, tri-bromophenyl sulfone, benzoyl peroxide, and combinations of a photoreducing dye such as eosin and methylene blue and a reducing agent such as ascorbic acid and triethanol amine. Two or more thereof may be contained.

[0045]

Examples of the compound with two or more ethylenically unsaturated bonds (b-3) include acrylic monomers such as ethylene glycol dimethacrylate, ethylene glycol diacrylate, diethylene glycol dimethacrylate, trimethylolpropane triacrylate, ethoxylated bisphenol A dimethacrylate, glycerin dimethacrylate, tripropylene glycol dimethacrylate, butanediol dimethacrylate, glycerin triacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol hexaacrylate, ethoxylated pentaerythritol tetraacrylate, and ethoxylated isocyanuric acid triacrylate. Two or more thereof may be contained.

[0046]

For the present invention, the content of the photosensitive agent (b) is preferably 0.05 to 50 parts by weight per 100 parts by weight of the resins of the component (a). From the viewpoint of increasing the sensitivity, the content of the photoacid generating agent (b-1) is preferably 0.01 to 50 parts by weight per 100 parts by weight of the resins of the component (a). Of

these, said quinone diazide compound preferably accounts for 3 to 40 parts by weight. The total content of said sulfonium salt, phosphonium salt, and diazonium salt is preferably 0.5 to 20 parts by weight. The content of the photopolymerization initiator (b-2) is preferably 0.1 to 20 parts by weight per 100 parts by weight of the resins of the component (a). If it is 0.1 part by weight or more, an adequate number of radicals are formed by light irradiation to improve the sensitivity. If it is 20 parts by weight or less, on the other hand, curing in unirradiated portions due to excessive radical formation does not take place and the alkaline developer works effectively. The content of said compound with two or more ethylenically unsaturated bonds (b-3) is preferably 5 to 50 parts by weight per 100 parts by weight of the resins of the component (a).

[0047]

For solubility adjustment and the like, a compound containing only one ethylenically unsaturated bond may be added up to 1 to 50 parts by weight per 100 parts by weight of the resins of the component (a). Examples such a compound include acrylic acid, methacrylic acid, methyl acrylate, methyl methacrylate, butyl acrylate, hydroxyethyl acrylate, hydroxyethyl methacrylate, dimethyl acrylamide, dimethylaminoethyl methacrylate, acryloyl morpholine, 1-hydroxyethyl α-chloroacrylate, 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl α-chloroacrylate, 1-hydroxypropyl methacrylate,

1-hydroxypropyl acrylate, 1-hydroxypropyl α-chloroacrylate, 2-hydroxypropyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl α-chloroacrylate, 3-hydroxypropyl methacrylate, 3-hydroxypropyl acrylate, 3-hydroxypropyl α-chloroacrylate, 1-hydroxy-1-methylethyl methacrylate, 1-hydroxy-1-methylethyl acrylate, 1-hydroxy-1-methylethyl α-chloroacrylate, 2-hydroxy-1-methylethyl methacrylate, 2-hydroxy-1-methylethyl acrylate, 2-hydroxy-1-methylethyl α-chloroacrylate, 1-hydroxybutyl methacrylate, 1-hydroxybutyl acrylate, 1-hydroxybutyl α-chloroacrylate, 2-hydroxybutyl methacrylate, 2-hydroxybutyl acrylate, 2-hydroxybutyl α-chloroacrylate, 3-hydroxybutyl methacrylate, 3-hydroxybutyl acrylate, 3-hydroxybutyl α-chloroacrylate, 4-hydroxybutyl methacrylate, 4-hydroxybutyl acrylate, 4-hydroxybutyl α-chloroacrylate, 1-hydroxy-1-methylpropyl methacrylate, 1-hydroxy-1-methylpropyl acrylate, 1-hydroxy-1-methylpropyl α-chloroacrylate, 2-hydroxy-1-methylpropyl methacrylate, 2-hydroxy-1-methylpropyl acrylate, 2-hydroxy-1-methylpropyl α-chloroacrylate, 1-hydroxy-2-methylpropyl methacrylate, 1-hydroxy-2-methylpropyl acrylate, 1-hydroxy-2-methylpropyl α-chloroacrylate, 2-hydroxy-2-methylpropyl methacrylate, 2-hydroxy-2-methylpropyl acrylate, 2-hydroxy-2-methylpropyl α-chloroacrylate, 2-hydroxy-1, 1-dimethylethyl methacrylate, 2-hydroxy-1, 1-dimethylethyl acrylate, 2-hydroxy-1, 1-dimethylethyl α-chloroacrylate, 1,2-dihydroxypropyl

methacrylate, 1,2-dihydroxypropyl acrylate, 1,2-dihydroxypropyl α-chloroacrylate, 2,3-dihydroxypropyl methacrylate, 2,3-dihydroxypropyl acrylate, 2,3-dihydroxypropyl α-chloroacrylate, 2,3-dihydroxybutyl methacrylate, 2,3-dihydroxybutyl acrylate, 2,3-dihydroxybutyl α-chloroacrylate, p-hydroxystyrene, p-isopropenyl phenol, phenethyl methacrylate, phenethyl acrylate, phenethyl α-chloroacrylate, N-methylol acrylamide, N-methylol methacrylamide, α-chloroacrylic acid, crotonic acid, 4-pentene acid, 5-hexene acid, 6-heptene acid, 7-octene acid, 8-nonane acid, 9-decanoic acid, 10-undecylenic acid, brassidic acid, ricinoleic acid, 2-(methacryloyloxy)ethyl isocyanate, 2-(acryloyloxy)ethyl isocyanate, and 2-(α-chloroacryloyloxy)ethyl isocyanate.

[0048]

The photosensitive resin composition according to the present invention contains an organic solvent (c) with a boiling point of 100°C or more and 130°C or less under atmospheric pressure. If the boiling point is less than 100°C under atmospheric pressure, said components (a) and (b) can suffer a decrease in solubility to cause precipitation of solid material. This allows streaks (streak-like irregularities in thickness) on the coating film to be caused by foreign objects adhered in the slit nozzle, leading to deterioration in the uniformity of the thickness of the photosensitive resin film. With a boiling point of 130°C or less

under atmospheric pressure, on the other hand, it has s high volatility and it is possible to remove the organic solvent from the coating film quickly. It is also possible to prevent the formation of transferred marks such as traces of pins during the vacuum drying and heat drying steps.

[0049]

For the present invention, the content of the component (C) is 40 wt% or more and 90 wt% or less of the total quantity of the organic solvents. If the content of the component (C) is less than 40 wt%, streaks and transferred marks can take place in the coating film or the photosensitive resin film after being dried, leading to deterioration in the uniformity of the thickness of the photosensitive resin film. It can also cause an increase in the required processing time in the vacuum drying step. It is more preferably 60 wt% or more. If the content of the component (C) is more than 90 wt%, on the other hand, the content of the component (d) described later decreases relatively, resulting in insufficient effect for depressing the bubble formation during the vacuum drying step. It is preferably 80 wt% or less.

[0050]

Said organic solvent (c) with a boiling point of 100°C or more and 130°C or less under atmospheric pressure should preferably be able to dissolve the resin of said component (a). Specifically, examples include alkylene glycol monoalkyl ethers such as

ethylene glycol monomethyl ether (boiling point 124°C) and propylene glycol monomethyl ether (boiling point 120°C); alkyl acetates such as propyl acetate (boiling point 102°C), butyl acetate (boiling point 125°C), and isobutyl acetate (boiling point 118°C); ketones such as methylbutyl ketone (boiling point 116°C), methyl isobutyl ketone (boiling point 116°C), and methylpropyl ketone (boiling point 102°C); and alcohols such as n-butyl alcohol (boiling point 117°C) and isobutyl alcohol (boiling point 108°C). From the viewpoint of storage stability and viscosity stability of the photosensitive resin composition, the use of propylene glycol monomethyl ether is more preferable.

[0051]

The photosensitive resin composition according to the present invention contains an organic solvent (d) with a boiling point of 150°C or more under atmospheric pressure and a viscosity of more than 1.1 mPa·s and less than 1.5 mPa·s at 20°C. The existence of contains an organic solvent with a boiling point of 150°C or more under atmospheric pressure in addition to said organic solvent (c) with a boiling point of 100°C or more and 130°C or less under atmospheric pressure allows the development of a photosensitive resin film to be performed easily during patterning. Furthermore, it is also possible to depress the bubble formation during the vacuum drying step. It is preferable, on the other hand, that the boiling point is 230°C or less to prevent organic solvents from remaining in the film after the

curing step. The organic solvent of the component (d) has a viscosity of more than 1.1 mPa·s and less than 1.5 mPa·s at 20°C. If the viscosity is 1.1 mPa·s or less at 20°C, said polyimide, polybenzoxazole and their precursor resins can be insufficient in solubility, leading to deterioration in the uniformity in the thickness of the photosensitive resin film and a decrease in the stability of the photosensitive resin composition. If it is 1.5 mPa·s or more, on the other hand, the viscosity of the photosensitive resin composition can be too high, and when it is applied by slit coating to form a film with a film thickness of 5 μm or more in particular, unstable discharge from the orifice often takes place. Bubble formation also tends to take place during the vacuum drying step. In the vacuum drying step, the component (c), which has a lower boiling point, is removed more easily, leaving an increased content of the component (d), but if its viscosity at 20°C is less than 1.5 mPa, it serves to maintain a moderate flowability, and serves to produce a photosensitive resin film with a highly uniform film thickness while depressing bubble formation. If the photosensitive resin film has a large thickness in particular, it is necessary to increase the amount of the coating liquid, often resulting in decreased film thickness uniformity. Furthermore, a larger amount of the organic solvent has to be removed in the vacuum drying step, which tends to increase the bubble formation, but the use of a specific combination of the component (c) and the component (d), which

comprise organic solvents, works very effectively to depress the bubble formation during the vacuum drying step and improve the thickness uniformity of the photosensitive resin film. Some of the bubbles resulting from vacuum drying here will be left in the photosensitive resin film after the drying step in the form of bubbles with a diameter of 1 mm or less, which can be detected visually when observing the surface of the photosensitive resin film irradiated by a sodium lamp.

[0052]

The component (d) should account for 10 wt% or more and 60 wt% or less of the total quantity of the organic solvents used for the present invention. If the content of the component (d) is less than 10 wt%, the bubble formation during the vacuum drying step will not be depressed sufficiently. If it is more than 60 wt%, on the other hand, the photosensitive resin film can suffer from transferred marks, and the photosensitive resin film can decrease in thickness uniformity. It is preferably 40 wt% or less, and more preferably 20 wt% or less.

[0053]

Said organic solvent (d) with a boiling point of 150°C or more under atmospheric pressure and a viscosity of more than 1.1 mPa·s and less than 1.5 mPa·s at 20°C should preferably be able to dissolve the resin of said component (a). Specifically, its examples include dialkylene glycol dialkyl ethers such as dipropylene glycol dimethyl ether (boiling point 171°C,

viscosity 1.27 mPa·s), diethylene glycol dimethyl ether (boiling point 162°C, viscosity 1.17 mPa·s), diethylene glycol ethyl methyl ether (boiling point 176°C, viscosity 1.27 mPa·s), diethylene glycol diethyl ether (boiling point 189°C, viscosity 1.47 mPa·s); and acetates such as 3-methoxy butyl acetate (boiling point 171°C, viscosity 1.21 mPa·s) and ethylene glycol monoethyl ether acetate (boiling point 160°C, viscosity 1.25 mPa·s). Of these, diethylene glycol dimethyl ether, diethylene glycol ethyl methyl ether, and diethylene glycol diethyl ether are preferable, and diethylene glycol dimethyl ether and diethylene glycol ethyl methyl ether are more preferable, from the viewpoint of storage stability and viscosity stability of the photosensitive resin composition.

[0054]

The boiling points of these organic solvents under atmospheric pressure are listed in, for instance, "CRC Handbook of Chemistry and Physics" and "Aldrich Handbook of Fine Chemical and Laboratory Equipment." If not available in generally known reference documents, the boiling point of an organic solvent can be determined with commercial boiling point measuring equipment such as FP81HT/FP81C (supplied by Mettler Toledo International Inc.). The viscosity of an organic solvent at 20°C can be measured with a Ubbelohde viscometer.

[0055]

The viscosity at 25°C of the photosensitive resin composition

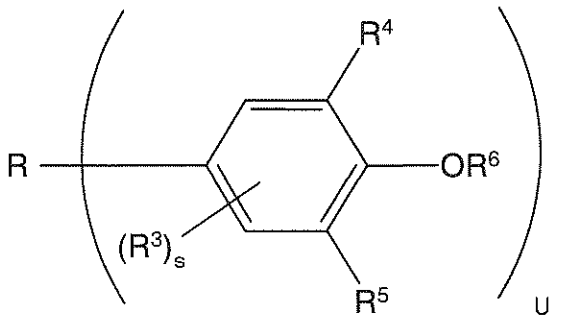
according to the present invention can be adjusted to a suitable range for slit coating by the combined used of said component (c) and said component (d), and it is preferably 10 mPa·s or less when the solids content is, for instance, 15 wt%, for effective prevention of streaks during slit coating. It is more preferably 8 mPa·s or less to further improve the thickness uniformity during thick film coating to produce a film with a thickness of 5 μm or more. Here, the viscosity of the photosensitive resin composition solution can be measured with an E type viscometer.

[0056]

The photosensitive resin composition according to the present invention may contain a thermal crosslinking agent as represented by general formula (1) given below or a thermal crosslinking agent as represented by general formula (2) given below (hereinafter, collectively referred to as thermal crosslinking agents (e)). These thermal crosslinking agents (e) acts to crosslink between resins of said photosensitive resin composition comprising at least one resin (a) selected from the group of polyimide, polybenzoxazole, a precursor of polyimide, and a precursor of polybenzoxazole or between them and other added substances so that the thermally cured film will have an increased chemical resistance and hardness.

[0057]

[Chemical compound 5]



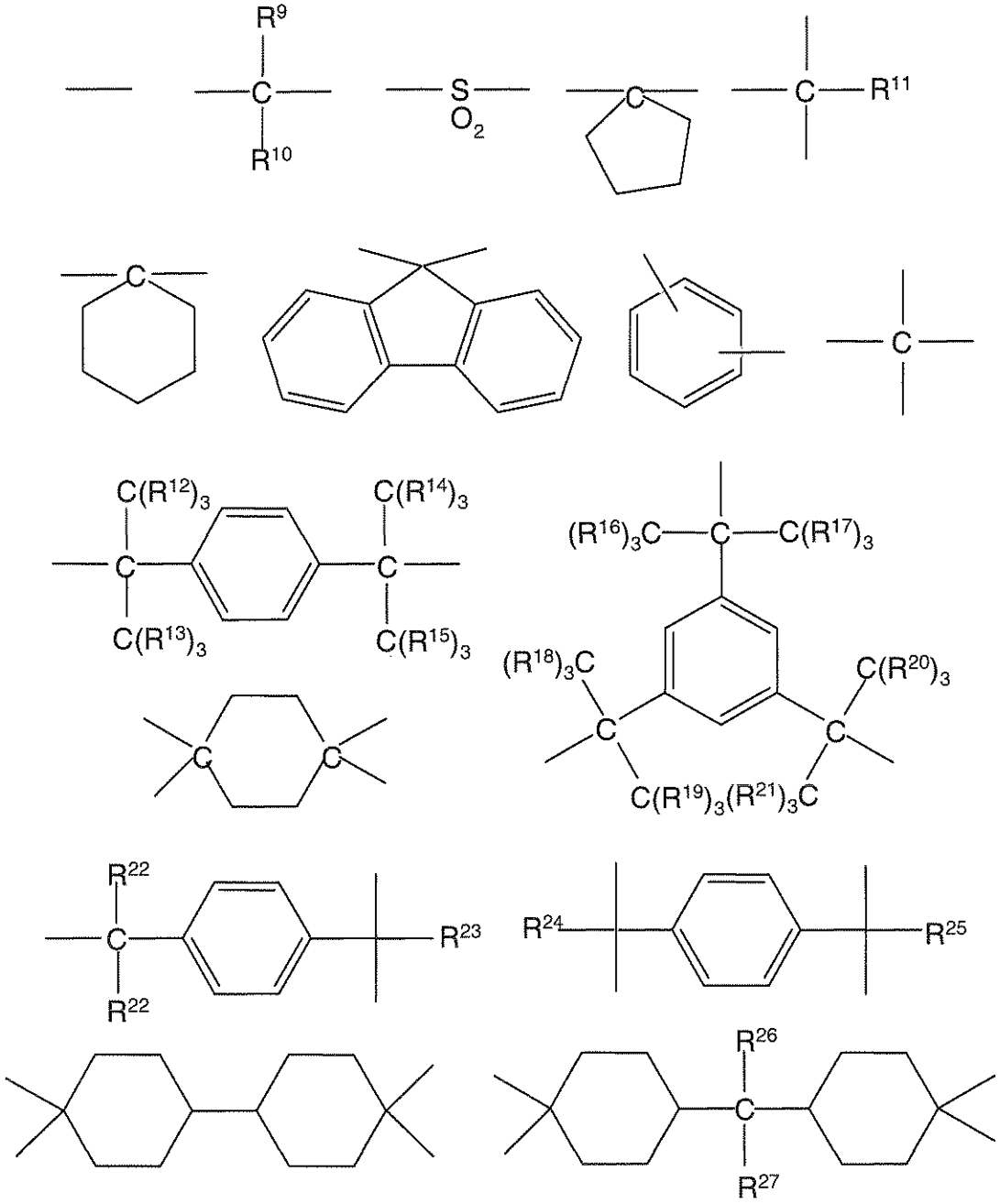
(1)

[0058]

In said general formula (1), R denotes a divalent to tetravalent linking group. R^3 denotes a monovalent organic group with a carbon number of 1 to 20, Cl, Br, I, or F. R^4 and R^5 represent CH_2OR^7 (R^7 is a hydrogen atom or a monovalent hydrocarbon group with a carbon number of 1 to 6). R^6 denotes a hydrogen atom, methyl group, or ethyl group. Furthermore, s represents an integer of 0 to 2, and u an integer of 2 to 4. The few groups of R^3 to R^6 may be identical to or different from each other. Examples of said linking groups R's are listed below.

[0059]

[Chemical compound 6]



[0060]

In the above formulae, R^9 to R^{27} represent a hydrogen atom, monovalent organic group with a carbon number of 1 to 20, Cl, Br, I, or F.

[0061]

$-N(CH_2OR^8)_t(H)_v$ (2)

In the above general formula (2), R^8 denotes a hydrogen atom or a monovalent hydrocarbon group with a carbon number of 1 to 6. Furthermore, t denotes 1 or 2, and v denotes 0 or 1. Here, t+v equals to 1 or 2.

[0062]

In said general formula (1), R^4 and R^5 represent the thermal crosslinkable group CH_2OR^7 (R^7 is a hydrogen atom or monovalent hydrocarbon group with a carbon number of 1 to 6). To maintain a moderate reactivity and storage stability, R^7 is preferably a monovalent hydrocarbon group with a carbon number of 1 to 4. For a photosensitive resin composition that contains a photoacid generating agent or photopolymerization initiator, R^7 is preferably the methyl group or the ethyl group.

[0063]

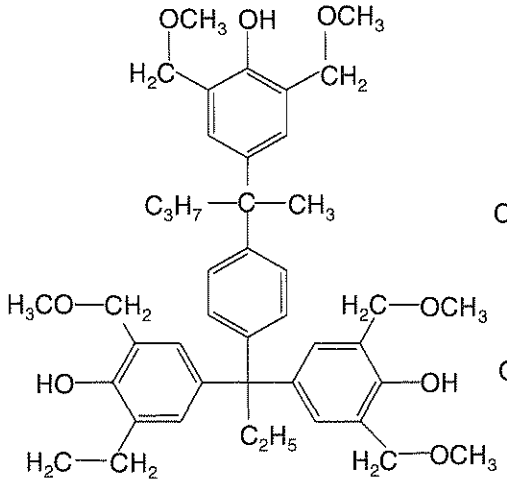
A thermal crosslinking agent having a structure as represented by general formula (1) preferably has a purity of 85% or more. If the purity is 85% or more, the agent is high in storage stability and leaves a less amount of unreacted groups that work as water absorbing groups, serving to produce a photosensitive resin composition with an increased water absorption rate. A thermal crosslinking agent with high purity can be produced by recrystallization, distillation, and the like. The purity of a thermal crosslinking agent can be determined by liquid chromatography.

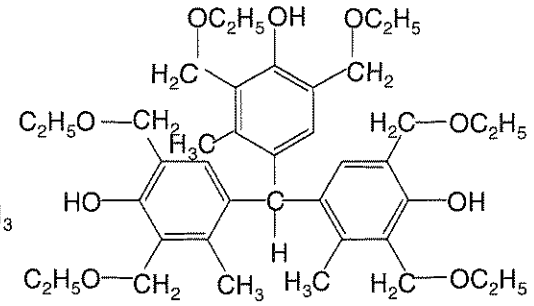
[0064]

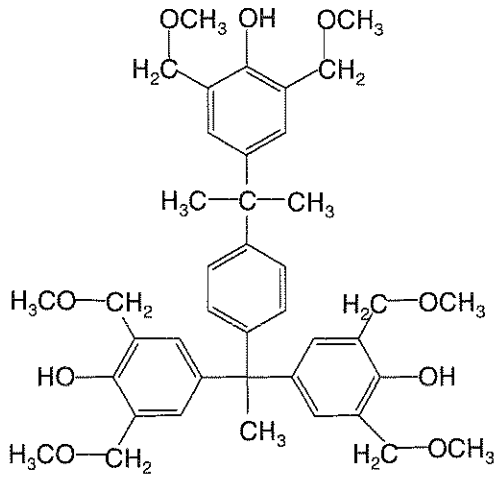
Preferable examples of said thermal crosslinking agents having a structure as represented by general formula (1) are listed below.

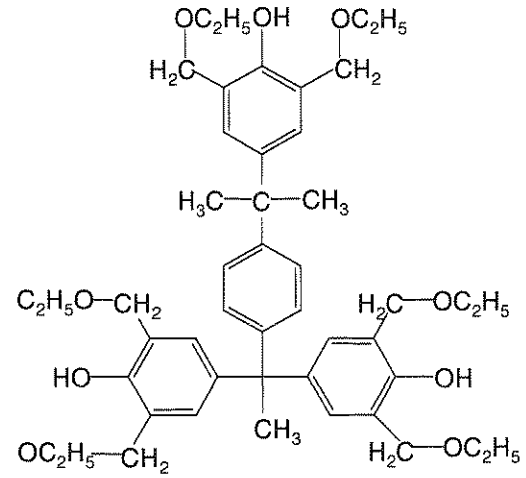
[0065]

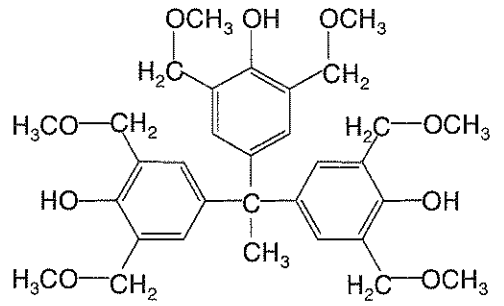
[Chemical compound 7]

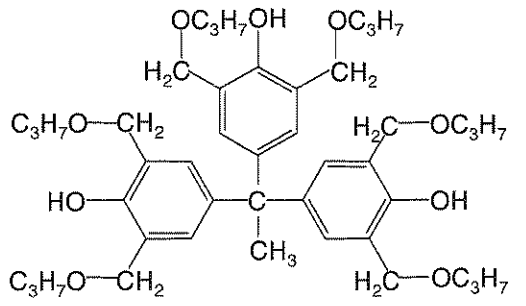


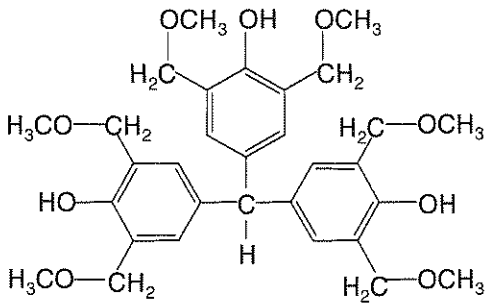


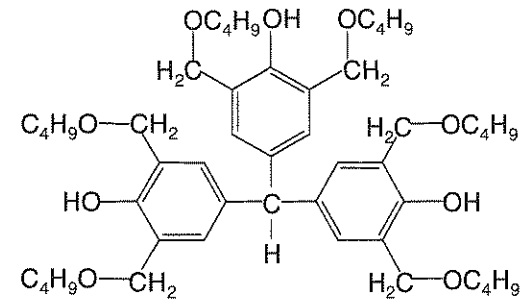












[0066]

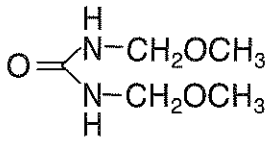
In general formula (2), R^8 denotes a hydrogen atom or a monovalent hydrocarbon group with a carbon number of 1 to 6, of which a monovalent hydrocarbon group with a carbon number of 1 to 4 is referable. In a photosensitive resin composition that contains a photoacid generating agent, photopolymerization initiator, or the like, furthermore, R^8 is preferably the methyl group or the ethyl group and the number of (CH_2OR^8) groups contained in the compound is preferably 8 or less, from the viewpoint of the stability of the compound and the storage stability of the resin composition.

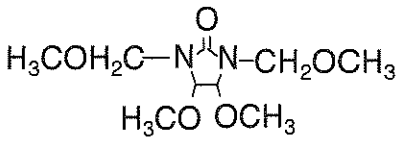
[0067]

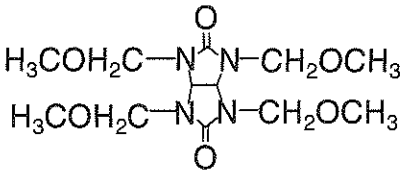
Preferable examples of said thermal crosslinking agents having a group as represented by general formula (2) are listed below.

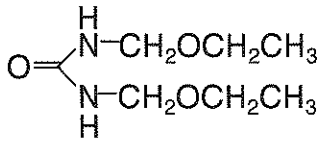
[0068]

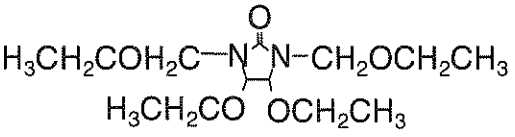
[Chemical compound 8]

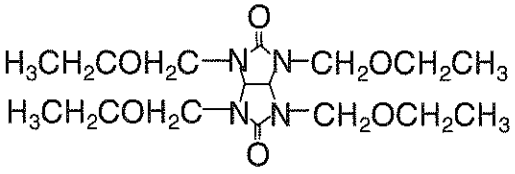


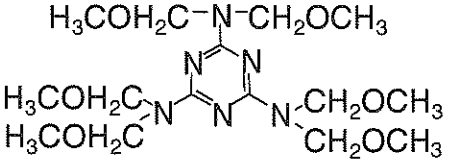


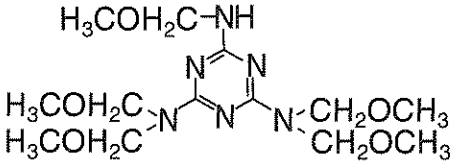


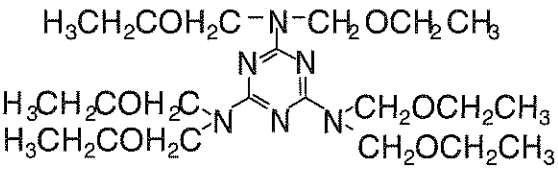












[0069]

The content of the thermal crosslinking agent (e) is preferably 10 parts by weight or more and 100 parts by weight or less per 100 parts by weight of the resins of the component (a). If the thermal crosslinking agent (e) accounts for 10 parts by weight or more and 100 parts by weight or less, the thermally cured film will have high strength, and the photosensitive resin composition will have high storage stability.

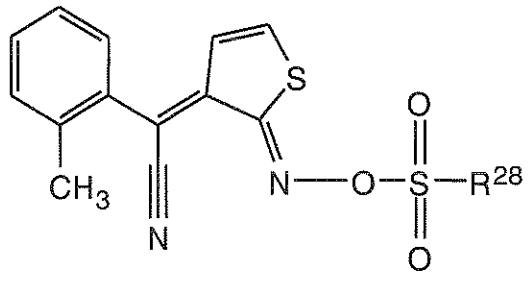
[0070]

The resin composition according to the present invention may further contain a thermal acid-forming agent (f). Said thermal acid-forming agent (f) works to generate an acid when heated after development as described later, promote the crosslinking

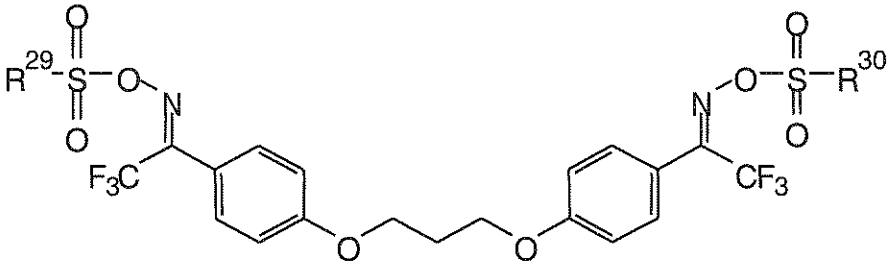
reaction involving the resins of the component (a), the component (e) and the thermal crosslinking agent, and promote the cyclization of imide rings and oxazole rings in the resins of the component (a). This serves to provide a calcined film with improved chemical resistance and reduce the film loss. The acid generated from said thermal acid-forming agent (f) is preferably a strong acid, which is, for instance, preferably an aryl sulfonic acid such as p-toluene sulfonic acid and benzene sulfonic acid or an alkyl sulfonic acid such as methane sulfonic acid, ethane sulfonic acid, and butane sulfonic acid. For the present invention, said thermal acid-forming agent is preferably an aliphatic sulfonic acid compound as represented by general formula (3) or (4), and two or more of such compounds may be contained.

[0071]

[Chemical compound 9]



(3)



(4)

[0072]

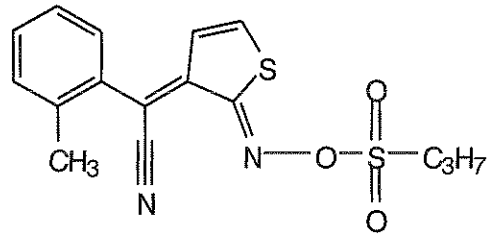
In said general formulae (3) and (4), R^{28} to R^{30} denote an alkyl group with a carbon number of 1 to 10 or a monovalent aromatic group with a carbon number of 7 to 12. The alkyl group and aromatic group may be substituted by a substituent group such as alkyl group and carbonyl group.

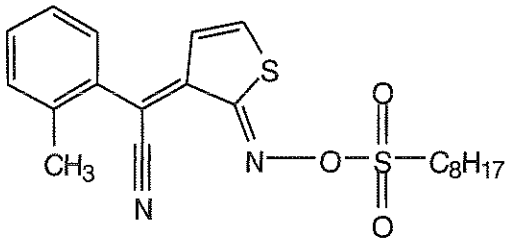
[0073]

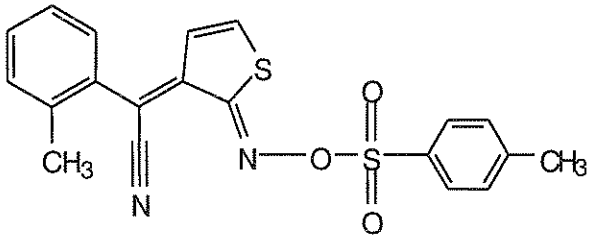
Specific examples of said compound represented by general formula (3) are listed below.

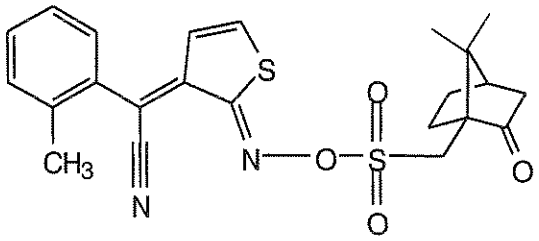
[0074]

[Chemical compound 10]







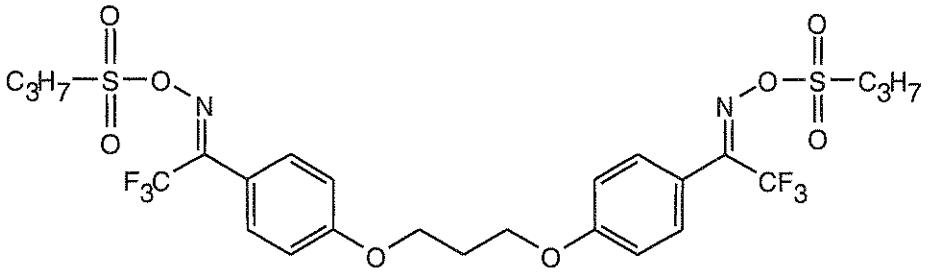


[0075]

Specific examples of said compound represented by general formula (4) are listed below.

[0076]

[Chemical compound 11]



[0077]

The content of said thermal acid-forming agent (f) is preferably 0.5 parts by weight or more, more preferably 10 parts by weight or less, per 100 parts by weight of the resins of the component (a) from the viewpoint of promoting the crosslinking reaction.

[0078]

It may contain a compound having a phenolic hydroxyl group as needed to help the alkaline developer in developing the photosensitive resin composition. Examples of said compound with a phenolic hydroxyl group include, for instance, Bis-Z, BisOC-Z, BisOPP-Z, BisP-CP, Bis26X-Z, BisOTBP-Z, BisOCHP-Z, BisOCR-CP, BisP-MZ, BisP-EZ, Bis26X-CP, BisP-PZ, BisP-IPZ, BisCR-IPZ, BisOCP-IPZ, BisOIPP-CP, Bis26X-IPZ, BisOTBP-CP, TekP-4HBPA (tetrakis P-DO-BPA), TrisP-HAP, TrisP-PA, TrisP-PHBA, TrisP-SA, TrisOCR-PA, BisOFP-Z, BisRS-2P, BisPG-26X, BisRS-3P, BisOC-OCHP, BisPC-OCHP, Bis25X-OCHP, Bis26X-OCHP, BisOCHP-OC, Bis236T-OCHP, methylenetris-FR-CR, BisRS-26X, BisRS-OCHP, (trade names, supplied by Honshu Chemical Industry Co., Ltd.), BIR-OC, BIP-PC, BIR-PC, BIR-PTBP, BIR-PCHP, BIP-BIOC-F, 4PC, BIR-BIPC-F, TEP-BIP-A (trade names, supplied by Asahi Organic Chemicals Industry Co., Ltd.), 1,4-dihydroxy naphthalene,

1,5-dihydroxy naphthalene, 1,6-dihydroxy naphthalene, 1,7-dihydroxy naphthalene, 2,3-dihydroxy naphthalene, 2,6-dihydroxy naphthalene, 2,7-dihydroxy naphthalene, 2,4-dihydroxy quinoline, 2,6-dihydroxy quinoline, 2,3-dihydroxy quinoxaline, anthracene-1,2,10-triol, anthracene-1,8,9-triol, and 8-quinolinol. If such a compound with a phenolic hydroxyl group is contained, the resulting photosensitive resin composition will not be dissolved significantly in an alkaline developer before exposure, but will be easily dissolved in an alkaline developer after exposure, leading to a decreased film loss during development and easy development in a short time. Accordingly, the sensitivity will improve.

[0079]

Such a compound with a phenolic hydroxyl group preferably accounts for 3 parts by weight or more and 40 parts by weight or less per 100 parts by weight of the resins of the component (a).

[0080]

The photosensitive resin composition according to the present invention may contain a thermo-coloring compound that develops a color when heated and that shows an absorption maximum at 350 nm or more and 700 nm or less and an organic dyes or dye that shows no absorption maximum at 350 nm or more and 500 nm or less but shows an absorption maximum at 500 nm or more and 750 nm

or less. Said thermo-coloring compound preferably works for coloration at a temperature of 120°C or more, more preferably 150°C or more. As the thermo-coloring compound has a higher coloration temperature, the heat resistance under high temperature conditions increases and the light resistant also increases to prevent color degradation during prolonged ultraviolet-visible light irradiation.

[0081]

Examples of said thermo-coloring compound include thermosensitive dyes, pressure-sensitive dyes, and hydroxyl-containing compounds with a triaryl methane backbone.

[0082]

The photosensitive resin composition according to the present invention may contain a contact improving agent. Examples of said contact improving agent include silane coupling agents such as vinyl trimethoxysilane, vinyl triethoxysilane, epoxy cyclohexyl ethyl trimethoxysilane, 3-glycidoxy propyl trimethoxysilane, 3-glycidoxypropyl triethoxysilane, p-styryl trimethoxysilane, 3-aminopropyl trimethoxysilane, 3-aminopropyl triethoxysilane, and N-phenyl-3-aminopropyl trimethoxysilane, as well as titanium chelate agents and aluminum chelate agents. Two or more thereof may be contained. If these contact improving agents are contained, the photosensitive resin film can come in stronger contact with the substrate material such as silicon wafer, ITO, SiO_2, and nitride silicon during

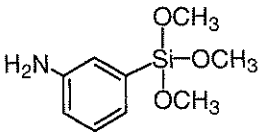
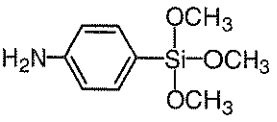
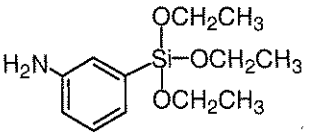
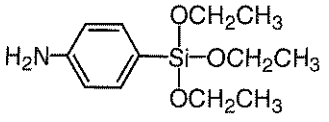
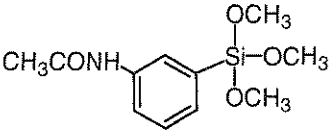
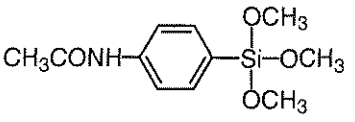
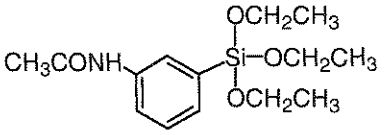
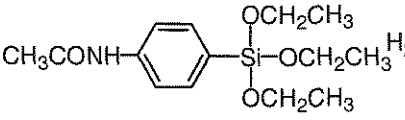
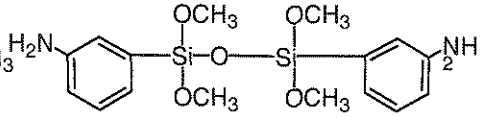
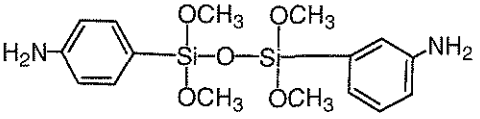
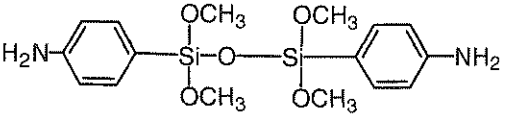
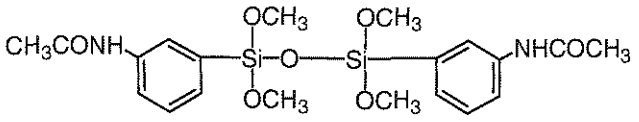
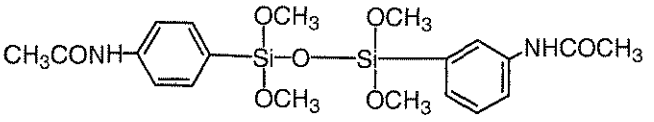
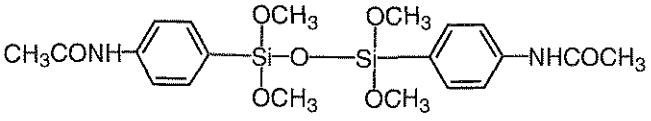
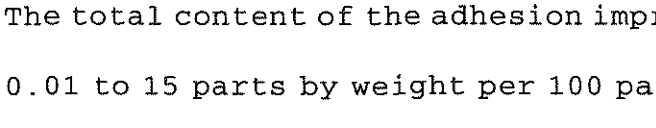
the development step. They also serve to improve the resistance to oxygen plasma used for cleaning and to UV ozone processing. The content of the contact improving agent is preferably 0.1 to 10 parts by weight per 100 parts by weight of the resins of the component (a).

[0083]

The photosensitive resin composition according to the present invention may contain an adhesion improving agent. Examples of said adhesion improving agent include alkoxysilane-containing aromatic amine compounds, aromatic amide compounds, and non-aromatic silane compounds. Two or more thereof may be contained. If these compounds are contained, the thermally cured film will be able to achieve improved adhesion with the base material. Specific examples of said alkoxysilane-containing aromatic amine compounds and aromatic amide compounds are described below. In addition, they also include compounds produced through a reaction between an aromatic amine compound and an alkoxyl-containing silicon compound, such as, for instance, compounds produced through a reaction between an aromatic amine compound and an alkoxysilane compound having an epoxy group, chloromethyl group, or the like that reacts with an amino group.

[0084]

[Chemical compound 12]

[0085]

The total content of the adhesion improving agents is preferably 0.01 to 15 parts by weight per 100 parts by weight of the resins of the component (a).

[0086]

The photosensitive resin composition according to the present invention may contain a surface active agent to improve the wettability with the substrate.

[0087]

Examples of said surface active agent include fluorine-based surface active agents such as Fluorad (trade name, supplied by

Sumitomo 3M), Megafac (registered trademark) (supplied by DIC Corporation), and Surflon (trade name, supplied by Asahi Glass Co., Ltd.); organic siloxane surface active agents such as KP341 (trade name, supplied by Shin-Etsu Chemical Co., Ltd.), DBE (trade name, supplied by Chisso Corporation), Glanol (trade name, supplied by Kyoeisha Chemical Co., Ltd.), and BYK (supplied by BYK-Chemie GmbH); and acrylic polymer surface active agents such as Polyflow (trade name, supplied by Kyoeisha Chemical Co., Ltd.).

[0088]

Described below is the production method for the photosensitive resin composition according to the present invention. For instance, a photosensitive resin composition can be produced by dissolving said components (a) to (d), along with the components (e) to (f) component, a dissolution adjusting agent, a thermo-coloring agent, a contact improving agent, an adhesion improving agent and a surface active agent as necessary. This dissolution can be carried out by stirring and heating. When heating is performed, an appropriate heating temperature is selected preferably in a range, commonly from room temperature to 80°C, where a photosensitive resin composition with unimpaired performance is obtained. There are no specific limitations on the order of dissolving these components, and for instance, the compound with the lowest solubility may be dissolved first followed by others in the order of solubility. Or, the dissolution

of those components that are likely to form bubbles when dissolved by stirring, such as surface active agents and some contact improving agents, may be postponed to the other components so that the dissolution of the latter will not be hindered by bubble formation.

[0089]

It is preferable that the resulting photosensitive resin composition is filtrated through a filter to remove dust and particles. Filters with a pore size of, for instance, 0.5 μm, 0.2 μm, 0.1 μm, 0.07 μm, or 0.05 μm are available, though there are no specific limitations on the size. The filter to be used for filtration may be of such a material as polypropylene (PP), polyethylene (PE), nylon (NY), and polytetrafluoroethylene (PTFE), of which polyethylene and nylon are preferable.

[0090]

Described below is a method to produce a photosensitive resin film from the photosensitive resin composition according to the present invention. The available coating techniques for the photosensitive resin composition include spin coating, slit coating, dip coating, spray coating, printing, and combinations thereof, of which slit coating can serve most effectively for the photosensitive resin composition according to the present. Conventionally, slit coating has some problems such as easily causing defective appearance with transferred marks and streaks and poor thickness uniformity of the resulting photosensitive

resin film after drying, but the use of the photosensitive resin composition according to the present invention serves to produce a photosensitive resin film with good appearance and high film thickness uniformity even when the slit coating technique is employed. Furthermore, it is also possible to depress the bubble formation during the vacuum drying step. The photosensitive resin film production method according to the invention includes the step (1) of discharging the photosensitive resin composition according to the present invention from a slit nozzle onto a substrate to form a coating film and the step (2) of vacuum-drying the coating film.

[0091]

First, in the step (1), the photosensitive resin composition according to the present invention is discharged from a slit nozzle onto a substrate to form a coating film. There are no specific limitations on the slit nozzle to be used for the coating, and several ones supplied from different manufacturers may be used. Specific examples include Linear Coater supplied by Dainippon Screen Mfg. Co., Ltd., Spinless supplied by Tokyo Ohka Kogyo Co., Ltd., TS Coater supplied by Toray Engineering Co., Ltd., Table Coater supplied by Chugai Ro Co., Ltd., CS series and CL series supplied by Tokyo Electron Ltd., In-line Slit Coater supplied by Cermatronics Boeki Co., Ltd., and Head Coater HC series supplied by Hirata Corporation. The coating is performed commonly in the speed range of 10 mm/sec to 400 mm/sec. Depending

on the solid content and the viscosity of the photosensitive resin composition, coating is commonly performed to form a film with a thickness of 0.1 to 20 μm, preferably 0.3 to 10 μm, after being dried. The photosensitive resin composition according to the present invention can form a thick photosensitive resin film of 5 μm or more with high thickness uniformity.

[0092]

Prior to the coating step, the substrate may be pre-treated in advance with said contact improving agent. For instance, a contact improving agent may be dissolved up to 0.5 to 20 wt% in a solvent such as isopropanol, ethanol, methanol, water, tetrahydrofuran, propylene glycol monomethyl ether acetate, propylene glycol monomethyl ether, ethyl lactate, and adipic acid diethyl to prepare a solution, which is then used to treat the substrate surface by an appropriate technique such as spin coating, slit die coating, bar coating, dip coating, spray coating, and steam processing. Vacuum drying may be carried out as needed, followed by heat treatment at 50°C to 300°C to accelerate the reaction between the substrate and the contact improving agent.

[0093]

Then, in the step (2), the coating film is vacuum-dried to provide a photosensitive resin film. Commonly, the coating film is subjected to the vacuum drying step together with the substrate that carries it. For instance, a substrate with a coating film

formed on it is placed on proxy pins arranged in a vacuum chamber, followed by reducing the pressure in the vacuum chamber to carry out vacuum drying. If there is a large distance between the substrate and the ceiling of the vacuum chamber, the large volume of air existing in the space between the substrate and the ceiling of the vacuum chamber can move significantly during the vacuum drying step to cause drying marks. It is preferable, therefore, to adjust the height of the proxy pins to decrease the distance. The distance between the substrate and the ceiling of the vacuum chamber is preferably 2 to 20 mm, more preferably 2 to 10 mm.

[0094]

Depending on the volume of the vacuum chamber, capacity of the vacuum pump, and diameter of the pipe connecting the chamber to the pump, the rate of vacuum drying may be set, for instance, so that the pressure in the vacuum chamber containing no coated substrate is reduced to 40 Pa in 60 seconds. Commonly, the vacuum drying time may be set to about 60 to 100 seconds, and the final pressure in the vacuum chamber containing a coated substrate may be 60 Pa or less at the end of the vacuum drying step. A final pressure maintained at or below 60 Pa allows the coating film surface to be in a nonsticky, dry state, serving to prevent surface contamination and particle formation from taking place during the subsequent substrate conveyance step. A lower final pressure, however, can allow bubbles to form more easily on the coating film surface. The photosensitive resin composition

according to the present invention can form a thick photosensitive resin film of 5 μm or more without suffering significant bubble formation in the vacuum drying step.

[0095]

Commonly, the coating film is dried by heating after the vacuum drying step. This step is referred to as pre-baking. Drying is carried out by using a hot plate, oven, infrared ray, and the like. When using a hot plate, the coating film is put directly on the plate or held on jigs such as proxy pins fixed on the plate while heating. There are various proxy pins of different materials including metals such as aluminum and stainless steel and synthetic resins such as polyimide resin and Teflon (registered trademark), but any types of proxy pins may work effectively if they have heat resistance. Depending on the size of the substrate, type of the coating film, and purpose of the heating, the height of the proxy pins is preferably in the range of about 0.1 to 10 mm. Depending on the type and purpose of the coating film, heating is performed preferably at a temperature in the range of room temperature to 180°C for 1 minute to several hours.

[0096]

Described below is the method for forming a pattern from the resulting photosensitive resin film. An actinic ray is applied to the photosensitive resin film through a mask of an intended pattern. Actinic rays available for exposure include ultraviolet

ray, visible light, electron beam, and X-ray, of which the i-line (365 nm), h-line (405 nm), and g-line (436 nm) of mercury lamp are preferred for the invention. If positively photosensitive, the exposed portions are dissolved by the developer. If negatively photosensitive, the exposed portions are cured and become insoluble in the developer.

[0097]

After the exposure step, a developer is used to remove the exposed portions of a positive film or unexposed portions of a negative film to form an intended pattern. Regardless of whether the film is positive or negative, preferable developers include an aqueous solution of tetramethyl ammonium and aqueous solutions of alkaline compounds such as diethanol amine, diethyl aminoethanol, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, trimethyl amine, diethyl amine, methyl amine, dimethyl amine, dimethylaminoethyl acetate, dimethyl aminoethanol, dimethylaminoethyl methacrylate, cyclohexyl amine, ethylene diamine, and hexamethylene diamine. In some cases, polar solvents such as N-methyl-2-pyrolidone, N,N-dimethyl formamide, N,N-dimethyl acetamide, dimethyl sulfoxide, γ-butyrolactone, and dimethyl acrylamide; alcohols such as methanol, ethanol and isopropanol; esters such as ethyl lactate and propylene glycol monomethyl ether acetate; and ketones such as cyclopentanone, cyclohexaone, isobutyl ketone, and methyl isobutyl ketone may be added singly or in combination to these

aqueous alkali solution. For negative films, it is also possible to use said polar solvents that contain no aqueous alkali solution, or alcohols, esters, or ketones, which may be added singly or in combination. Commonly, rinsing in water is performed after the development step. Here again, the water used for rinsing may contain an alcohol such as ethanol and isopropyl alcohol, and an ester such as ethyl lactate and propylene glycol monomethyl ether acetate.

[0098]

The resulting patterned photosensitive resin film is heat-treated for curing of the photosensitive resin film. The available methods include, for instance, heat treatment at 230°C for 60 minutes, heat treatment at 120 to 400°C for 1 minute to 10 hours, heat treatment at a low temperature in the range from room temperature to about 100°C after adding a curing catalyst and the like, and curing at a low temperature in the range from room temperature to about 100°C by applying ultrasonic waves or electromagnetic waves.

[0099]

Films produced by calcining the photosensitive resin composition according to the present invention can be used preferably as surface protective film and interlayer dielectric film for semiconductor devices such as LSI, dielectric film for organic EL devices, planarization film for TFT panels of displaying devices, wiring protective film for circuit boards, on-chip

microlens for solid imaging devices, and planarization film for various displaying devices and solid imaging devices.

[Examples]

[0100]

The present invention will be illustrated below in greater detail with reference to Examples, but it should be understood that the invention is not construed as being limited thereto. The evaluations of photosensitive resin composition samples described in Example are carried out with the following methods.

[0101]

(1) Preparation of photosensitive resin film

A photosensitive resin composition was applied over a chromed substrate with a size of 1,100 mm × 960 mm with a slit coater (TS Coater, supplied by Toray Engineering Co., Ltd.) in such a manner that the film thickness would be 4 μm, 5 μm, or 6 μm after being dried. The coating speed was 50 mm/sec. After the coating, the film was placed in a vacuum chamber for vacuum drying for 100 seconds. The chamber was controlled so that the inner pressure would reach 30 Pa in 100 seconds. In the vacuum drying step, the height of the proxy pins was 30 mm, and the distance between the substrate and the ceiling of the chamber was 6 mm. Subsequently, a hot plate was used for pre-baking at 120°C for 120 seconds to prepare a photosensitive resin film. In the pre-baking step, the height of the proxy pins was 0.5 mm.

[0102]

(2) Appearance evaluation of photosensitive resin film

The photosensitive resin film prepared by the procedure described in paragraph (1) was observed visually using a sodium lamp and evaluated in terms of streaks caused by the slit nozzle, marks of proxy pins (VCD pin marks) formed during the vacuum drying step, marks of hot plate proxy pins (HP pin marks), drying marks, and bubbles in three ranks. A sample was evaluated as rank 1 if they are clearly visible, rank 2 if they are slightly visible, and rank 3 if they are not visible.

[0103]

(3) Thickness uniformity evaluation of photosensitive resin film

The thickness of the photosensitive resin film prepared by the procedure described in paragraph (1) was measured using a FTM film thickness gauge supplied by Toray Engineering Co., Ltd. Measurements were made at 100 positions defined by eliminating the 10 mm wide peripheral portions along the edges and dividing the remaining film sample into 100 parts. The uniformity in film thickness was calculated by the following equation. The uniformity should preferably be 3.5% or less and more preferably 3% or less.

[0104]

Average film thickness = total of 100 film thickness measurements / 100

Film thickness uniformity (%) = [{(maximum film thickness - minimum film thickness) / 2} / average film thickness] × 100

[0105]

(4) Method for calculation of boiling point of organic solvent

The boiling points of the organic solvents used in Examples and Comparative examples of the invention are cited from "CRC Handbook of Chemistry and Physics" and "Aldrich Handbook of Fine Chemical and Laboratory Equipment."

[0106]

(5) Method for calculation of viscosity

The viscosity of the organic solvents used in Examples and Comparative examples was measured using a Ubbelohde viscometer at 20°C. The viscosity of varnish of the photosensitive resin compositions prepared in Examples and Comparative examples of the invention was measured using an E-type viscometer at 25°C.

[0107]

Synthesis example 1: synthesis of hydroxyl-containing diamine compound (HFHA)

First, 18.3 g (0.05 mole) of 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane (BAHF, supplied by Central Glass Co., Ltd.) was dissolved in acetone 100 mL and 17.4 g (0.3 mole) of propylene oxide (supplied by Tokyo Chemical Industry Co., Ltd.), and cooled to -15°C. Then, a solution of 20.4 g (0.11 mole) of 3-nitrobenzoyl chloride (supplied by Tokyo Chemical Industry Co., Ltd.) dissolved in 100 mL of acetone was added in drops. After the end of dropwise addition, the solution was stirred at -15°C for 4 hours, followed by leaving it to return to room temperature.

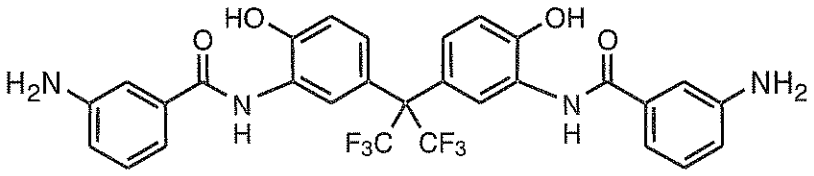
The white solid precipitate was separated out by filtration and vacuum-dried at 50°C.

[0108]

A 30 g portion of the resulting white solid was placed in a 300 mL stainless steel autoclave and dispersed in 250 mL of methyl cellosolve, followed by adding 2 g of 5% palladium-carbon (supplied by Wako Pure Chemical Industries, Ltd.). Then, a balloon was used to introduce hydrogen into the solution to cause reduction reaction at room temperature. In about 2 hours, the reaction was finished after checking that the balloon would be deflated no more. After the end of the reaction, the solution was filtrated to remove the palladium compound used as catalyst and concentrated with a rotary evaporator to provide hydroxyl-containing diamine compound (HFHA) as represented by the formula given below.

[0109]

[Chemical compound 13]



[0110]

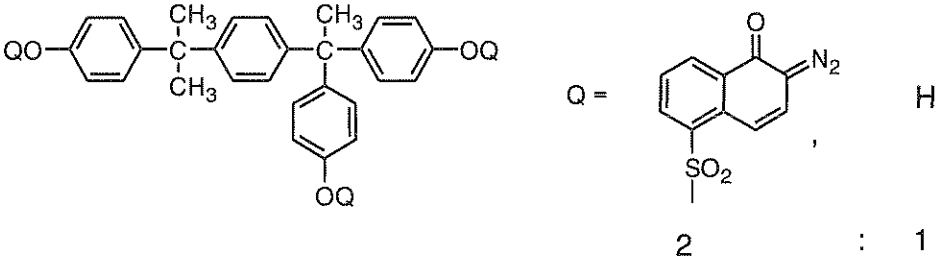
Synthesis example 2: synthesis of quinone diazide compound

In a dry nitrogen flow, 21.22 g (0.05 mole) of TrisP-PA (trade name, supplied by Honshu Chemical Industry Co., Ltd.) and 26.8 g (0.1 mole) of 5-naphthoquinone diazide sulfonic acid chloride

(NAC-5, supplied by Toyo Gosei Co., Ltd.) are dissolved in 450 g of 1,4-dioxane and maintained at room temperature. To this solution, 12.65 g of triethyl amine mixed with 50 g of 1,4-dioxane was added in droplets while maintaining the system below 35°C. After the dripping step, it was stirred at 40°C for 2 hours. The triethylamine salt was filtered and the filtrate was put in water. Subsequently, the resulting precipitate was collected by filtration, and then washed in 1 L of 1% hydrochloric acid solution. In addition, washing in 2 L of water was carried out twice. The resulting precipitate was dried in a vacuum dryer to provide a quinone diazide compound as represented by the following formula.

[0111]

[Chemical compound 14]



[0112]

Synthesis example 3: synthesis of alkoxymethyl-containing compound (A-1)

An 103.2 g (0.4 mole) amount of 1,1,1-tris-(4-hydroxyphenyl) ethane (TrisP-HAP, supplied by Honshu Chemical Industry Co., Ltd.) was dissolved in a solution of 80 g (2.0 moles) of sodium hydroxide in 800 g of pure water. After confirming complete

dissolution, 686 g of a 36 to 38 wt% aqueous formalin solution was added dropwise at 20 to 25°C during 2 hours. Subsequently, it was stirred at 20 to 25°C for 17 hours. It was neutralized by adding 98 g of sulfuric acid and 552 g of water, and left to stand for 2 days. After the standing period, the needle-like white crystal formed in the solution was collected by filtration and washed in 100 mL of water. This white crystal was vacuum-dried at 50°C for 48 hours. The white crystal dried was analyzed with a high speed liquid chromatograph supplied by Shimadzu Corporation at 254 nm using ODS as column and an acetonitrile/water (70/ 30) solution as developing solvent, and results showed that the starting materials had completely disappeared and the crystal had a purity of 92%. It was analyzed further using NMR equipment (GX-270, supplied by JEOL Ltd.) with a DMSO-d6 deuterated solvent, and results showed that it was hexamethylolated TrisP-HAP.

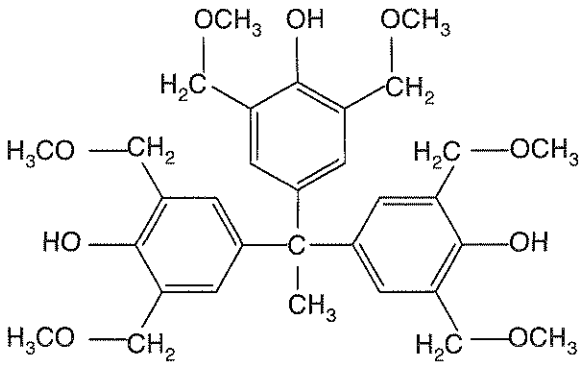
[0113]

Then, the compound thus obtained was dissolve in 300 mL of methanol, and 2 g of sulfuric acid was added, followed by stirring at room temperature. To this solution, 15 g of an anion exchange resin (Amberlyst IRA96SB, supplied by Rohm and Haas) was added and stirred for 1 hour, followed by filtering out the ion exchange resin. Subsequently, 500 mL of ethyl lactate was added and methanol was removed with a rotary evaporator to provide an ethyl lactate solution. This solution was left to stand at room

temperature for 2 days to produce white crystal. The white crystal obtained was analyzed by high speed liquid chromatography and results showed that it was hexamethoxy-methylated TrisP-HAP as represented by the following formula (alkoxymethyl-containing compound (A-1)) with a purity of 99%.

[0114]

[Chemical compound 15]

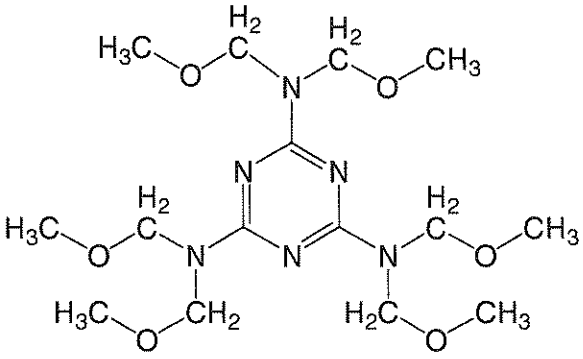


[0115]

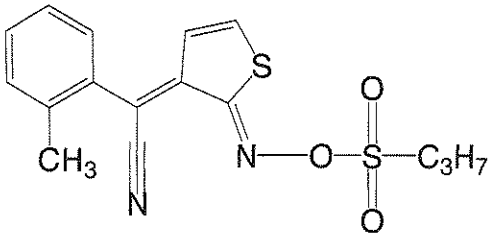
Other substances including thermal crosslinking agents and acid generating agents used in Examples were as listed below.

[0116]

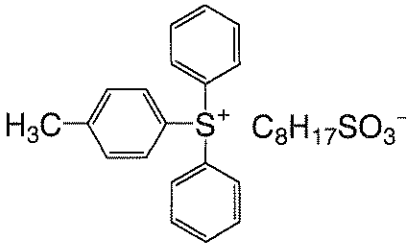
[Chemical compound 16]



MW－30HM



PAG-103



WPAG-314

[0117]

Example 1

In a dry nitrogen flow, 51.3 g (0.085 mole) of the hydroxyl-containing diamine prepared in Synthesis example 1, 1.24 g (0.005 mole) of 1,3-bis(3-aminopropyl) tetramethyl disiloxane (SiDA, supplied by Shin-Etsu Chemical Co., Ltd.), 2.18 g (0.02 mole) of 3-aminophenol (supplied by Tokyo Chemical Industry Co., Ltd.) were dissolved in 200 g of N-methyl pyrolidone (NMP). To this, 31.0 g (0.1 mole) of 3,3',4,4'-diphenyl ether tetracarboxylic dianhydride (ODPA, supplied by Manac Incorporated) was added and stirred at 40°C for 2 hours. Subsequently, a solution prepared by diluting 7.14 g (0.06 mole) of dimethyl formamide dimethyl acetal (DFA, supplied by Mitsubishi Rayon Co., Ltd.) with 5 g of NMP was added dropwise over 10 minutes. After the dripping step, it was stirred at 40°C

for 2 hours. After the stirring step, the solution was poured in 2 L of water, and the resulting polymer solid precipitate was collected by filtration. In addition, washing in 2 L of water was repeated three times, and the collected polymer solid material was dried at 50°C in a vacuum dryer for 72 hours to provide a polyimide precursor.

[0118]

Then, 10 g of this polyimide precursor, 3 g of the quinone diazide compound prepared in Synthesis example 2, 2 g of TrisP-PHBA (supplied by Honshu Chemical Industry Co., Ltd.) as dissolution adjusting agent, and 0.04 g of BYK333 (supplied by BYK-Chemie GmbH) as surface active agent were added to 68 g of propylene glycol monomethyl ether (boiling point 120°C) and 17 g of diethylene glycol ethyl methyl ether (boiling point 176°C, viscosity 1.27 mPa·s) and stirred to provide varnish of a positive photosensitive polyimide precursor composition. The varnish had a viscosity of 7.3 mPa·s. The resulting varnish was applied by slit coating according to the procedure described in said paragraph (1) so that the film thickness would be 4 μm after drying, to provide a photosensitive resin film.

[0119]

In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks, marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, drying marks, and bubbles and rated as rank 3. The film thickness

uniformity was 1.9%.

[0120]

Example 2

The varnish prepared in Example 1 was applied by slit coating so that the film thickness would be 5 μm after drying, to provide a photosensitive resin film. In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks, marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, drying marks, and bubbles, and rated as rank 3. The film thickness uniformity was 2.5%.

[0121]

Example 3

The varnish prepared in Example 1 was applied by slit coating so that the film thickness would be 6 μm after drying, to provide a photosensitive resin film. In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks, marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, and drying marks, and rated as rank 3. For bubbles, slight bubble formation was observed and the rating was rank 2. The film thickness uniformity was 2.9%.

[0122]

Example 4

Except that 68 g of propylene glycol monomethyl ether (boiling point 120°C) and 17 g of diethylene glycol dimethyl ether (boiling point 162°C, viscosity 1.17 mPa·s) were used as solvent

components, the same procedure as in Example 2 was carried out to prepare a photosensitive resin film. The varnish had a viscosity of 7.1 mPa·s. In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks, marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, and drying marks, and rated as rank 3. For bubbles, slight bubble formation was observed and the rating was rank 2. The film thickness uniformity was 2.4%.

[0123]

Example 5

Except that 68 g of propylene glycol monomethyl ether (boiling point 120°C) and 17 g of diethylene glycol diethyl ether (boiling point 189°C, viscosity 1.47 mPa·s) were used as solvent components, the same procedure as in Example 2 was carried out to prepare a photosensitive resin film. The varnish had a viscosity of 7.6 mPa·s. In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks, marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, drying marks, and bubbles and rated as rank 3. The film thickness uniformity was 2.9%.

[0124]

Example 6

Then, 10 g of the polyimide precursor prepared in Example 1, 2.5 g of the quinone diazide compound prepared in Synthesis example 2, 1 g of the alkoxymethyl-containing compound (A-1)

prepared in Synthesis example 3, 1.5 g of TrisP-PHBA (supplied by Honshu Chemical Industry Co., Ltd.) as dissolution adjusting agent, and 0.04 g of BYK333 (supplied by BYK-Chemie GmbH) as surface active agent were added to 59.5 g of propylene glycol monomethyl ether (boiling point 120°C), 17 g of diethylene glycol ethyl methyl ether (boiling point 176°C, viscosity 1.27 mPa·s), and 8.5 g of γ-butyrolactone (boiling point 203°C, viscosity 1.90 mPa·s), and stirred to provide varnish of a positive photosensitive polyimide precursor composition. The varnish had a viscosity of 7.4 mPa·s. The resulting varnish was applied by slit coating according to the procedure described in said paragraph (1) so that the film thickness would be 5 μm after drying, to provide a photosensitive resin film.

[0125]

In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks, marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, drying marks, and bubbles, and rated as rank 3. The film thickness uniformity was 2.8%.

[0126]

Example 7

Except that 51 g of propylene glycol monomethyl ether (boiling point 120°C) and 34 g of diethylene glycol dimethyl ether (boiling point 176°C, viscosity 1.27 mPa·s) were used as solvent components, the same procedure as in Example 2 was carried out

to prepare a photosensitive resin film. The varnish had a viscosity of 6.8 mPa·s. In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks and bubbles, and rated as rank 3. A few marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, and drying marks were found and the film was rated as rank 2. The film thickness uniformity was 3.5%.

[0127]

Example 8

Except that 51 g of propylene glycol monomethyl ether (boiling point 120°C) and 34 g of diethylene glycol dimethyl ether (boiling point 162°C, viscosity 1.17 mPa·s) were used as solvent components, the same procedure as in Example 2 was carried out to prepare a photosensitive resin film. The varnish had a viscosity of 6.5 mPa·s. In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks, marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, and drying marks, and rated as rank 3. For bubbles, slight bubble formation was observed and the rating was rank 2. The film thickness uniformity was 3.4%.

Example 9

Except that 51 g of propylene glycol monomethyl ether (boiling point 120°C), 17 g of diethylene glycol diethyl methyl ether (boiling point 176°C, viscosity 1.27 mPa·s), and 17 g of γ-butyrolactone (boiling point 203°C, viscosity 1.90 mPa·s) were

used as solvent components, the same procedure as in Example 2 was carried out to prepare a photosensitive resin film. The varnish had a viscosity of 7.3 mPa·s. In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks, marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, drying marks, and bubbles, and rated as rank 3. The film thickness uniformity was 2.9%.

[0128]

Example 10

Except that 76.5 g of propylene glycol monomethyl ether (boiling point 120°C) and 8.5 g of diethylene glycol ethyl methyl ether (boiling point 176°C, viscosity 1.27 mPa·s) were used as solvent components, the same procedure as in Example 2 was carried out to prepare a photosensitive resin film. The varnish had a viscosity of 7.9 mPa·s. In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks, marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, and drying marks, and rated as rank 3. Slight bubble formation was observed and the rating was rank 2. The film thickness uniformity was 2.9%.

[0129]

Example 11

In a dry nitrogen flow, 18.3 g (0.05 mole) of BAHF was dissolved in 50 g of NMP and 26.4 g (0.3 mole) of glycidyl methyl ether, and the temperature of the solution was decreased to -15°C. Then

a solution prepared by dissolving 7.4 g (0.025 mole) of diphenyl ether dicarboxylic acid dichloride (supplied by Nihon Nohyaku Co., Ltd.) and 5.1 g (0.025 mole) of isophthalic acid chloride (supplied by Tokyo Chemical Industry Co., Ltd.) in 25 g of γ-butyrolactone (GBL) was added dropwise while maintaining the internal temperature at or below 0°C. After the dripping step, it was stirred at -15°C for 6 hours. After the end of the reaction, the solution was poured in 3 L of water containing 10 wt% methanol and white precipitate was collected. The precipitate was collected by filtration, washed in water three times, and dried at 50°C in a vacuum dryer for 72 hours to provide a polybenzoxazole precursor.

[0130]

Then, 10 g of this polybenzoxazole precursor, 3 g of the quinone diazide compound prepared in Synthesis example 2, 2 g of TrisP-PHBA (supplied by Honshu Chemical Industry Co., Ltd.) as dissolution adjusting agent, and 0.04 g of BYK333 (supplied by BYK-Chemie GmbH) as surface active agent were added to 51 g of propylene glycol monomethyl ether (boiling point 120°C) and 34 g of diethylene glycol ethyl methyl ether (boiling point 176°C, viscosity 1.27 mPa·s) and stirred to provide varnish of a positive photosensitive polybenzoxazole precursor composition. The varnish had a viscosity of 7.1 mPa·s. The resulting varnish was applied by slit coating according to the procedure described in said paragraph (1) so that the film thickness would be 5 μm

after drying, to provide a photosensitive resin film.

[0131]

In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks and bubbles, and rated as rank 3. A few marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, and drying marks were found and the film was rated as rank 2. The film thickness uniformity was 3.5%.

[0132]

Example 12

In a dry nitrogen flow, 32.9 g (0.09 mole) of BAHF was dissolved in 500 g of NMP. To this solution, 31.0 g (0.1 mole) of ODPA was added together with 50 g of NMP and stirred at 30°C for 2 hours. Then, 2.18 g (0.02 mole) of 3-aminophenol (supplied by Tokyo Chemical Industry Co., Ltd.) was added, and stirring was continued at 40°C for 2 hours. Furthermore, 5 g of pyridine (supplied by Tokyo Chemical Industry Co., Ltd.) was diluted with 30 g of toluene (supplied by Tokyo Chemical Industry Co., Ltd.) and added to the solution, which was then heated for reaction at 120°C for 2 hours and subsequently at 180°C for 2 hours, with a cooling pipe provided to remove water out of the reaction system by azeotropy with toluene. The solution was cooled down to room temperature and poured in 3 L of water to provide white powder. This powder was collected by filtration and washed in water three times. After the washing step, the white powder was dried at

50°C in a vacuum dryer for 72 hours to provide polyimide.

[0133]

Then, 10 g of this polyimide, 3 g of the quinone diazide compound prepared in Synthesis example 2, 2 g of TrisP-PHBA (supplied by Honshu Chemical Industry Co., Ltd.) as dissolution adjusting agent, and 0.04 g of BYK333 (supplied by BYK-Chemie GmbH) as surface active agent were added to 51 g of propylene glycol monomethyl ether (boiling point 120°C) and 34 g of diethylene glycol ethyl methyl ether (boiling point 176°C, viscosity 1.27 mPa·s) and stirred to provide varnish of a positive photosensitive polyimide composition. The varnish had a viscosity of 6.5 mPa·s. The resulting varnish was applied by slit coating according to the procedure described in said paragraph (1) so that the film thickness would be 5 μm after drying, to provide a photosensitive resin film.

[0134]

In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks and bubbles, and rated as rank 3. A few marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, and drying marks were found and the film was rated as rank 2. The film thickness uniformity was 3.3%.

[0135]

Example 13

A 10 g portion of the polyimide prepared in Example 12, 2.4 g

of the alkoxymethyl-containing compound (A-1) prepared in Synthesis example 3, 2 g of ethylene oxide modified bisphenol A dimethacrylate (NK Ester BPE-100, supplied by Shin-Nakamura Chemical Co., Lid.), 0.5 g of trimethylolpropane triacrylate, 0.1 g of 1,2-octanedione-1-[4-(phenyl thio)-2-(O-benzoyloxime)] (supplied by Ciba Specialty Chemicals), and 0.04 g of BYK333 (supplied by BYK-Chemie GmbH) as surface active agent were added to 68 g of propylene glycol monomethyl ether (boiling point 120°C) and 17 g of diethylene glycol ethyl methyl ether (boiling point 176°C, viscosity 1.27 mPa·s) and stirred to provide varnish of a negative photosensitive polyimide composition. The varnish had a viscosity of 7.9 mPa·s. The resulting varnish was applied by slit coating according to the procedure described in said paragraph (1) so that the film thickness would be 5 μm after drying, to provide a photosensitive resin film.

[0136]

In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks, marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, drying marks, and bubbles, and rated as rank 3. The film thickness uniformity was 2.8%.

[0137]

Example 14

A 10 g portion of the polybenzoxazole precursor prepared in

Example 11, 0.5 g of WPAG-314 (trade name, supplied by Wako Pure Chemical Industries, Ltd.), 0.5 g of 5-propylsulfonyloxyimino-5H-thiophene-2-methylphenyl-acetonitrile (trade name PAG-103, supplied by Ciba Specialty Chemicals Inc.) as thermal acid-forming agent, 4 g of MW-30HM (supplied by Sanwa Chemical Co., Ltd.), 0.04 g of BYK333 (supplied by BYK-Chemie GmbH) as surface active agent were added to 68 g of propylene glycol monomethyl ether (boiling point 120°C) and 17 g of diethylene glycol ethyl methyl ether (boiling point 176°C, viscosity 1.27 mPa·s) and stirred to provide varnish of a negative photosensitive polybenzoxazole precursor composition. The varnish had a viscosity of 7.6 mPa·s. The resulting varnish was applied by slit coating according to the procedure described in said paragraph (1) so that the film thickness would be 5 μm after drying, to provide a photosensitive resin film.

[0138]

In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks, marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, drying marks, and bubbles, and rated as rank 3. The film thickness uniformity was 2.8%.

[0139]

Example 15

Except that 68 g of ethylene glycol monomethyl ether (boiling point 124°C and 17 g of diethylene glycol ethyl methyl ether

(boiling point 176°C, viscosity 1.27 mPa·s) were used as solvent components, the same procedure as in Example 2 was carried out to prepare a photosensitive resin film. The varnish had a viscosity of 7.0 mPa·s. In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks, marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, drying marks, and bubbles, and rated as rank 3. The film thickness uniformity was 2.3%.

[0140]

Example 16

Except that 51 g of ethylene glycol monomethyl ether (boiling point 124°C) and 34 g of diethylene glycol ethyl methyl ether (boiling point 176°C, viscosity 1.27 mPa·s) were used as solvent components, the same procedure as in Example 2 was carried out to prepare a photosensitive resin film. The varnish had a viscosity of 6.8 mPa·s. In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks and bubbles, and rated as rank 3. A few marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, and drying marks were found and the film was rated as rank 2. The film thickness uniformity was 2.5%.

[0141]

Example 17

Except that 42.5 g of propylene glycol monomethyl ether (boiling point 120°C) and 42.5 g of diethylene glycol ethyl methyl ether

(boiling point 176°C, viscosity 1.27 mPa·s) were used as solvent components, the same procedure as in Example 2 was carried out to prepare a photosensitive resin film. The varnish had a viscosity of 6.6 mPa·s. In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks and bubbles, and rated as rank 3. A few marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, and drying marks were found and the film was rated as rank 2. The film thickness uniformity was 3.3%.

[0142]

Example 18

Except that 68 g of n-butyl alcohol (boiling point 117°C) and 17 g of diethylene glycol ethyl methyl ether (boiling point 176°C, viscosity 1.27 mPa·s) were used as solvent components, the same procedure as in Example 2 was carried out to prepare a photosensitive resin film. The varnish had a viscosity of 7.6 mPa·s. In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks, marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, drying marks, and bubbles, and rated as rank 3. The film thickness uniformity was 3.5%.

[0143]

Example 19

Except that 51 g of butyl acetate (boiling point 125°C) and 34 g of diethylene glycol ethyl methyl ether (boiling point 176°C,

viscosity 1.27 mPa·s) were used as solvent components, the same procedure as in Example 12 was carried out to prepare a photosensitive resin film. The varnish had a viscosity of 6.1 mPa·s. In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks and bubbles, and rated as rank 3. A few marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, and drying marks were found and the film was rated as rank 2. The film thickness uniformity was 2.5%.

[0144]

Example 20

Except that 51 g of isobutyl alcohol (boiling point 108°C) and 34 g of diethylene glycol ethyl methyl ether (boiling point 176°C, viscosity 1.27 mPa·s) were used as solvent components, the same procedure as in Example 12 was carried out to prepare a photosensitive resin film. The varnish had a viscosity of 6.7 mPa·s. In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks and bubbles, and rated as rank 3. A few marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, and drying marks were found and the film was rated as rank 2. The film thickness uniformity was 2.7%.

[0145]

Comparative example 1

Except that 68 g of propylene glycol monomethyl ether (boiling

point 120°C) and 17 g of ethyl lactate (boiling point 154°C, viscosity 2.61 mPa·s) were used as solvent components, the same procedure as in Example 1 was carried out to prepare a photosensitive resin film. The varnish had a viscosity of 10.2 mPa·s. In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks, marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, and drying marks, and rated as rank 3. For bubbles, slight bubble formation was observed and the rating was rank 2. The film thickness uniformity was 4.1%.

[0146]

Comparative example 2

The varnish prepared in Comparative example 1 was applied by slit coating so that the film thickness would be 5 μm after drying, to provide a photosensitive resin film. In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks, marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, and drying marks, and rated as rank 3. Bubble formation was observed distinctly and the rating was rank 1. The film thickness uniformity was 6.4%.

[0147]

Comparative example 3

The varnish prepared in Comparative example 1 was applied by slit coating so that the film thickness would be 6 μm after drying,

to provide a photosensitive resin film. In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks (rank 3), but suffer slightly from marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, and drying marks (rank 2). Bubble formation was observed distinctly and the rating was rank 1. The film thickness uniformity was 8.1%.

[0148]

Comparative example 4

Except that 68 g of propylene glycol monomethyl ether (boiling point 120°C) and 17 g of N-methyl-2-pyrolidone (boiling point 204°C, viscosity 1.65 mPa·s) were used as solvent components, the same procedure as in Example 2 was carried out to prepare a photosensitive resin film. The varnish had a viscosity of 9.5 mPa·s. In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks (rank 3), but suffer slightly from marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, drying marks, and bubbles (rank 2). The film thickness uniformity was 6.8%.

Comparative example 5

Except that 59.5 g of propylene glycol monomethyl ether (boiling point 120°C) and 25.5 g of γ-butyrolactone (boiling point 203°C, viscosity 1.90 mPa·s) were used as solvent components, the same procedure as in Example 2 was carried out to prepare a photosensitive resin film. The varnish had a viscosity of 9.2

mPa·s. In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks (rank 3), but suffer slightly from marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, drying marks, and bubbles (rank 2). The film thickness uniformity was 5.1%.

[0149]

Comparative example 6

Except that 51 g of propylene glycol monomethyl ether (boiling point 120°C) and 34 g of γ-butyrolactone (boiling point 203°C, viscosity 1.90 mPa·s) were used as solvent components, the same procedure as in Example 2 was carried out to prepare a photosensitive resin film. The varnish had a viscosity of 9.4 mPa·s. In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks (rank 3), but suffer slightly from marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, drying marks, and bubbles (rank 2). The film thickness uniformity was 5.3%.

[0150]

Comparative example 7

Except that 76.5 g of propylene glycol monomethyl ether (boiling point 120°C) and 8.5 g of γ-butyrolactone (boiling point 203°C, viscosity 1.90 mPa·s) were used as solvent components, the same procedure as in Example 2 was carried out to prepare a photosensitive resin film. The varnish ha d a viscosity of 8.3 mPa·s. In the appearance evaluation, the resulting

photosensitive resin film was found to be free from streaks, marks of proxy pins used in the vacuum drying step, and marks of hot plate proxy pins (rank 3), but suffer slightly from drying marks (rank 2) and distinctly from bubbles (rank 1). The film thickness uniformity was 6.6%.

[0151]

Comparative example 8

Except that 25.5 g of propylene glycol monomethyl ether (boiling point 120°C) and 59.5 g of diethylene glycol ethyl methyl ether (boiling point 176°C, viscosity 1.27 mPa·s) were used as solvent components, the same procedure as in Example 2 was carried out to prepare a photosensitive resin film. The varnish had a viscosity of 6.7 mPa·s. In the appearance evaluation, the resulting photosensitive resin film was found to suffer slightly from streaks, marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, drying marks, and bubbles (rank 2). The film thickness uniformity was 4.0%.

[0152]

Comparative example 9

Except that 25.5 g of propylene glycol monomethyl ether (boiling point 120°C) and 59.5 g of diethylene glycol diethyl ether (boiling point 189°C, viscosity 1.47 mPa·s) were used as solvent components, the same procedure as in Example 2 was carried out to prepare a photosensitive resin film. The varnish had a viscosity of 8.1 mPa·s. In the appearance evaluation, the

resulting photosensitive resin film was found to suffer slightly from streaks, marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, drying marks, and bubbles (rank 2). The film thickness uniformity was 4.3%.

[0153]

Comparative example 10

Except that 68 g of propylene glycol monomethyl ether (boiling point 120°C) and 17 g of γ-butyrolactone (boiling point 203°C, viscosity 1.90 mPa·s) were used as solvent components, the same procedure as in Example 11 was carried out to prepare a photosensitive resin film. The varnish had a viscosity of 8.1 mPa·s. In the appearance evaluation, the resulting photosensitive resin film was found to be free from streaks (rank 3), but suffer slightly from marks of proxy pins used in the vacuum drying step, marks of hot plate proxy pins, and drying marks (rank 2) and distinctly from bubbles (rank 1). The film thickness uniformity was 5.5%.

[0154]

Comparative example 11

Except that 59.5 g of propylene glycol monomethyl ether acetate (boiling point 146°C, 1.18 mPa·s) and 25.5 g of ethylene glycol n-butyl ether acetate (boiling point 188°C, 1.70 mPa·s) were used as solvent components, the same procedure as in Example 1 was carried out to prepare varnish of a positive photosensitive polyimide precursor composition. The varnish contained resin

components left undissolved, and its coatability evaluation could not be performed.

[0155]

Comparative example 12

Except that 51.0 g of butyl acetate (boiling point 125°C) and 34.0 g of acetylacetone (boiling point 141°C, viscosity 0.75 mPa·s) were used as solvent components, the same procedure as in Example 1 was carried out to prepare varnish of a positive photosensitive polyimide precursor composition. The varnish contained resin components left undissolved, and its coatability evaluation could not be performed.

[0156]

Comparative example 13

Except that 51.0 g of butyl acetate (boiling point 125°C) and 34.0 g of acetylacetone (boiling point 141°C, viscosity 0.75 mPa·s) were used as solvent components, the same procedure as in Example 12 was carried out to prepare a photosensitive resin film. The varnish had a viscosity of 5.2 mPa·s. In the appearance evaluation, the resulting photosensitive resin film was found to be free from marks of proxy pins used in the vacuum drying step and marks of hot plate proxy pins (rank 3), but suffer slightly from streaks and drying marks (rank 2) and distinctly from bubbles (rank 1). The film thickness uniformity was 4.8%.

[0157]

The components used in Examples 1 to 20 and Comparative examples

1 to 13 are listed in Tables 1 to 3, and evaluation results are given in Table 4.

[0158]

Table 1

	(a) Resin	(b) Photosensitive agent	(c) Organic solvent with boiling point of 100°C or more and 130°C or less		(d) Organic solvent with boiling point of 150°C or more and viscosity of more than 1.1 mpa·s and less than 1.5 mpa·s		Other solvents		Other components	Coating thickness
			Boiling point	Content	Boiling point/viscosity	Content	Boiling point·viscosity	Content		
Example 1	Polyimide precursor	Synthesis example 2	Propylene glycol monomethyl ether		Diethylene glycol ethyl methyl ether		—		Trisp-PHBA BYK333	4 μm
			120°C	80wt%	176°C/1.27mpa·s	20wt%				
Example 2	Polyimide precursor	Synthesis example 2	Propylene glycol monomethyl ether		Diethylene glycol ethyl methyl ether		—		Trisp-PHBA BYK333	5 μm
			120°C	80wt%	176°C/1.27mpa·s	20wt%				
Example 3	Polyimide precursor	Synthesis example 2	Propylene glycol monomethyl ether		Diethylene glycol ethyl methyl ether		—		Trisp-PHBA BYK333	6 μm
			120°C	80wt%	176°C/1.27mpa·s	20wt%				
Example 4	Polyimide precursor	Synthesis example 2	Propylene glycol monomethyl ether		Diethylene glycol dimethyl ether		—		Trisp-PHBA BYK333	5 μm
			120°C	80wt%	162°C/1.17mpa·s	20wt%				
Example 5	Polyimide precursor	Synthesis example 2	Propylene glycol monomethyl ether		Diethylene glycol diethyl ether		—		Trisp-PHBA BYK333	5 μm
			120°C	80wt%	189°C/1.47mpa·s	20wt%				
Example 6	Polyimide precursor	Synthesis example 2	Propylene glycol monomethyl ether		Diethylene glycol ethyl methyl ether		γ-butyrolactone		Trisp-PHBA SBYK333	5 μm
			120°C	70wt%	176°C/1.27mpa·s	20wt%	203°C/1.90mpa·s	10wt%		
Example 7	Polyimide precursor	Synthesis example 2	Propylene glycol monomethyl ether		Diethylene glycol ethyl methyl ether		—		Trisp-PHBA BYK333	5 μm
			120°C	60wt%	176°C/1.27mpa·s	40wt%				
Example 8	Polyimide precursor	Synthesis example 2	Propylene glycol monomethyl ether		Diethylene glycol dimethyl ether		—		Trisp-PHBA BYK333	5 μm
			120°C	60wt%	162°C/1.17mpa·s	40wt%				
Example 9	Polyimide precursor	Synthesis example 2	Propylene glycol monomethyl ether		Diethylene glycol ethyl methyl ether		γ-butyrolactone		Trisp-PHBA BYK333	5 μm
			120°C	60wt%	176°C/1.27mpa·s	20wt%	203°C/1.90mpa·s	20wt%		
Example 10	Polyimide precursor	Synthesis example 2	Propylene glycol monomethyl ether		Diethylene glycol ethyl methyl ether		—		Trisp-PHBA BYK333	5 μm
			120°C	90wt%	176°C/1.27mpa·s	10wt%				
Example 11	Polybenzoxazole precursor	Synthesis example 2	Propylene glycol monomethyl ether		Diethylene glycol ethyl methyl ether		—		Trisp-PHBA BYK333	5 μm
			120°C	60wt%	176°C/1.27mpa·s	40wt%				
Example 12	Polyimide resin	Synthesis example 2	Propylene glycol monomethyl ether		Diethylene glycol ethyl methyl ether		—		Trisp-PHBA BYK333	5 μm
			120°C	60wt%	176°C/1.27mpa·s	40wt%				

[0159]

[Table 2-1]

	(a) Resin	(b) Photosensitive agent	(c) Organic solvent with boiling point of 100°C or more and 130°C or less		(d) Organic solvent with boiling point of 150°C or more and viscosity of more than 1.1 mpa·s and less than 1.5 mpa·s		Other solvents		Other components	Coating thickness
			Boiling point	Content	Boiling point/viscosity	Content	Boiling point·viscosity	Content		
Example 13	Polyimide resin	1,2-octanedione-1-[4-(phenylthio) phenyl]-2-(o-benzoyloxime) BPE-100, trimethylolpropane triacrylate	Propylene glycol monomethyl ether		Diethylene glycol ethyl methyl ether		—		Synthesis example 3 BYK333	5 μm
			120°C	80wt%	176°C/1.27mpa·s	20wt%				
Example 14	Polybenzoxazole precursor	WPAG-314	Propylene glycol monomethyl ether		Diethylene glycol ethyl methyl ether		—		PAG103, MW-30HM BYK333	5 μm
			120°C	80wt%	176°C/1.27mpa·s	20wt%				
Example 15	Polyimide precursor	Synthesis example 2	Ethylene glycol monomethyl ether		Diethylene glycol ethyl methyl ether		—		Trisp-PHBA BYK333	5 μm
			124°C	80wt%	176°C/1.27mpa·s	20wt%				
Example 16	Polyimide precursor	Synthesis example 2	Ethylene glycol monomethyl ether		Diethylene glycol ethyl methyl ether		—		Trisp-PHBA BYK333	5 μm
			124°C	60wt%	176°C/1.27mpa·s	40wt%				
Example 17	Polyimide precursor	Synthesis example 2	Propylene glycol monomethyl ether		Diethylene glycol ethyl methyl ether		—		Trisp-PHBA BYK333	5 μm
			120°C	50wt%	176°C/1.27mpa·s	50wt%				
Example 18	Polyimide precursor	Synthesis example 2	n-butyl alcohol		Diethylene glycol ethyl methyl ether		—		Trisp-PHBA BYK333	5 μm
			117°C	80wt%	176°C/1.27mpa·s	20wt%				
Example 19	Polyimide resin	Synthesis example 2	Butyl acetate		Diethylene glycol ethyl methyl ether		—		Trisp-PHBA BYK333	5 μm
			125°C	60wt%	176°C/1.27mpa·s	40wt%				
Example 20	Polyimide resin	Synthesis example 2	iso-butyl alcohol		Diethylene glycol ethyl methyl ether		—		Trisp-PHBA BYK333	5 μm
			108°C	60wt%	176°C/1.27mpa·s	40wt%				

[0160]

[Table 2-2]

	(a) Resin	(b) Photosensitive agent	(c) Organic solvent with boiling point of 100°C or more and 130°C or less		(d) Organic solvent with boiling point of 150°C or more and viscosity of more than 1.1 mPa·s and less than 1.5 mPa·s		Other solvents		Other components	Coating thickness
			Boiling point	Content	Boiling point/viscosity	Content	Boiling point·viscosity	Content		
Comparative example 1	Polyimide precursor	Synthesis example 2	Propylene glycol monomethyl ether		—		Ethyl lactate		TrisP-PHBA BYK333	4 μm
			120°c	80wt%			154°C/2.61mPa·s	20wt%		
Comparative example 2	Polyimide precursor	Synthesis example 2	Propylene glycol monomethyl ether		—		Ethyl lactate		TrisP-PHBA BYK333	5 μm
			120°c	80wt%			154°C/2.61mPa·s	20wt%		
Comparative example 3	Polyimide precursor	Synthesis example 2	Propylene glycol monomethyl ether		—		Ethyl lactate		TrisP-PHBA BYK333	6 μm
			120°c	80wt%			154°C/2.61mPa·s	20wt%		
Comparative example 4	Polyimide precursor	Synthesis example 2	Propylene glycol monomethyl ether		—		N-methyl-2-pyrrolidone		TrisP-PHBA BYK333	5 μm
			120°c	80wt%			204°C/1.65mPa·s	20wt%		
Comparative example 5	Polyimide precursor	Synthesis example 2	Propylene glycol monomethyl ether		—		γ-butyrolactone		TrisP-PHBA BYK333	5 μm
			120°c	70wt%			203°C/1.90mPa·s	30wt%		
Comparative example 6	Polyimide precursor	Synthesis example 2	Propylene glycol monomethyl ether		—		γ-butyrolactone		TrisP-PHBA BYK333	5 μm
			120°c	60wt%			203°C/1.90mPa·s	40wt%		
Comparative example 7	Polyimide precursor	Synthesis example 2	Propylene glycol monomethyl ether		—		γ-butyrolactone		TrisP-PHBA BYK333	5 μm
			120°c	90wt%			203°C/1.90mPa·s	10wt%		
Comparative example 8	Polyimide precursor	Synthesis example 2	Propylene glycol monomethyl ether		Diethylene glycol ethyl methyl ether		—		TrisP-PHBA BYK333	5 μm
			120°c	30wt%	176°C/1.27mPa·s	70wt%				

[0161]

[Table 3]

	(a) Resin	(b) Photosensitive agent	(c) Organic solvent with boiling point of 100°C or more and 130°C or less		(d) Organic solvent with boiling point of 150°C or more and viscosity of more than 1.1 mPa·s and less than 1.5 mPa·s		Other solvents		Other components	Coating thickness
			Boiling point	Content	Boiling point/viscosity	Content	Boiling point·viscosity	Content		
Comparative example 9	Polyimide precursor	Synthesis example 2	Propylene glycol monomethyl ether		Diethylene glycol diethyl ether		—		TrisP-PHBA BYK333	5 μm
			120°C	30wt%	189°C/1.47mPa·s	70wt%				
Comparative example 10	Polybenzoxazole precursor	Synthesis example 2	Propylene glycol monomethyl ether		—		γ-butyrolactone		TrisP-PHBA BYK333	5 μm
			120°C	80wt%			203°C/1.90mPa·s	20wt%		
Comparative example 11	Polyimide precursor	Synthesis example 2	—		—		Propylene glycol monomethyl ether acetate, ethylene glycol n-butyl ether acetate		TrisP-PHBA BYK333	-
							146°C/1.18mPa·s	70wt%		
							188°C/1.70mPa·s	30wt%		
Comparative example 12	Polyimide precursor	Synthesis example 2	Butyl acetate		—		Acetylacetone		TrisP-PHBA BYK333	-
			125°C	60wt%			141°C/0.75mPa·s	40wt%		
Comparative example 13	Polyimide resin	Synthesis example 2	Butyl acetate		—		Acetylacetone		TrisP-PHBA BYK333	5 μm
			125°C	60wt%			141°C/0.75mPa·s	40wt%		

[0162]

[Table 4]

	Viscosity of varnish (mPa·s)	Streak	VCD pin mark	HP pin mark	Drying mark	Bubble	Film thickness uniformity (%)
Example 1	7.3	3	3	3	3	3	1.9
Example 2	7.3	3	3	3	3	3	2.5
Example 3	7.3	3	3	3	3	2	2.9
Example 4	7.1	3	3	3	3	2	2.4
Example 5	7.6	3	3	3	3	3	2.9
Example 6	7.4	3	3	3	3	3	2.8
Example 7	6.8	3	2	2	2	3	3.5
Example 8	6.5	3	3	3	3	2	3.4
Example 9	7.3	3	3	3	3	3	2.9
Example 10	7.9	3	3	3	3	2	2.9
Example 11	7.1	3	2	2	2	3	3.5
Example 12	6.5	3	2	2	2	3	3.3
Example 13	7.9	3	3	3	3	3	2.8
Example 14	7.6	3	3	3	3	3	2.8
Example 15	7.0	3	3	3	3	3	2.3
Example 16	6.8	3	2	2	2	3	2.5
Example 17	6.6	3	2	2	2	3	3.3
Example 18	7.6	3	3	3	3	3	3.5
Example 19	6.1	3	2	2	2	3	2.5

Example 20	6.7	3	2	2	2	3	2.7
Comparative example 1	10.2	3	3	3	3	2	4.1
Comparative example 2	10.2	3	3	3	3	1	6.4
Comparative example 3	10.2	3	2	2	2	1	8.1
Comparative example 4	9.5	3	2	2	2	2	6.8
Comparative example 5	9.2	3	2	2	2	2	5.1
Comparative example 6	9.4	3	2	2	2	2	5.3
Comparative example 7	8.3	3	3	3	2	1	6.6
Comparative example 8	6.7	2	2	2	2	2	4.0
Comparative example 9	8.1	2	2	2	2	2	4.3
Comparative example 10	8.1	3	2	2	2	1	5.5
Comparative example 11	Not dissolved	—	—	—	—	—	—
Comparative example 12	Not dissolved	—	—	—	—	—	—
Comparative example 13	5.2	2	3	3	2	1	4.8

[Industrial applicability]

[0163]

The photosensitive resin composition according to the present invention can be used for applications including surface protective film and interlayer dielectric film for semiconductor devices, dielectric film for organic electroluminescence (hereinafter abbreviated as EL) devices, planarization film for the substrate of thin film transistors (hereinafter abbreviated as TFT) to drive displaying components comprising organic EL devices, wiring-protecting dielectric film for circuit boards, on-chip microlens for solid imaging devices, and planarization film for various display and solid imaging devices.

[Title of the document] Claims

[Claim 1] A photosensitive resin composition comprising at least one resin (a) selected from the group of polyimide, polybenzoxazole, a precursor of polyimide, and a precursor of polybenzoxazole; a photosensitive agent (b); an organic solvent (c) with a boiling point of 100°C or more and 130°C or less under atmospheric pressure; and an organic solvent (d) with a boiling point of 150°C or more under atmospheric pressure and a viscosity of more than 1.1 mPa·s and less than 1.5 mPa·s at 20°C, wherein the component (c) accounts for 40 wt% or more and 90 wt% or less of the total quantity of the organic solvents while the component

(d) accounts for 10 wt% or more and 60 wt% or less of the total quantity of the organic solvents.

[Claim 2] A photosensitive resin composition as described in Claim 1 wherein said component (d) is at least one selected from the group of diethylene glycol dimethyl ether, diethylene glycol ethyl methyl ether, and diethylene glycol diethyl ether.

[Claim 3] A photosensitive resin composition as described in Claim 1 wherein the content of said component (d) is 10 wt% or more and 20 wt% or less of the total quantity of the organic solvents.

[Claim 4] A photosensitive resin film production method comprising the step (1) of discharging a photosensitive resin composition as claimed in any of Claims 1 to 3 from a slit nozzle onto a substrate to form a coating film and the step (2) of vacuum-drying the coating film.

[Claim 5] A photosensitive resin film with a film thickness of 5 μm or more and 10 μm or less produced by the production method claimed in Claim 4.

PHOTOSENSITIVE RESIN COMPOSITION AND METHOD FOR PRODUCING PHOTOSENSITIVE RESIN FILM

Abstract

The invention provides a photosensitive resin composition that does not suffer significant bubble formation during the vacuum drying step and that can form a photosensitive resin film with high thickness uniformity after being dried.

It is a photosensitive resin composition comprising at least one resin (a) selected from the group of polyimide, polybenzoxazole, a precursor of polyimide, and a precursor of polybenzoxazole, a photosensitive agent (b), an organic solvent (c) with a boiling point of 100°C or more and 130°C or less under atmospheric pressure, and an organic solvent (d) with a boiling point of 150°C or more under atmospheric pressure and a viscosity of more than 1.1 mPa·s and less than 1.5 mPa·s at 20°C, wherein the component (c) accounts for 40 wt% or more and 90 wt% or less relative to the total quantity of the organic solvents while the component (d) accounts for 10wt% or more and 60wt% or less relative to the total quantity of the organic solvents.

No suitable figure.