DESCRIPTION

TITLE OF THE INVENTION: RESIN, PHOTOSENSITIVE RESIN COMPOSITION, ELECTRONIC COMPONENT AND DISPLAY DEVICE USING THE SAME

TECHNICAL FIELD

[0001]

The present invention relates to a resin containing a specific structure. More specifically, this invention relates to a resin suited for applications such as a surface protective film or interlayer insulating film of an electronic component or circuit board, a solder resist for a circuit board, an insulating layer of an organic electroluminescent element, a flattening film of a driving thin film transistor substrate of a display device using an organic electroluminescent element, an interlayer insulating film of a thin film transistor, an on-chip microlens of a solid-state image pickup element, various displays, and a flattening film for a solid state image pickup device, and a photosensitive resin composition using the resin.

[0002]

This invention further relates to 5,5'-dihydroxyl-4,4'-diaminobiphenyl derivatives which can be used for these resins, resin compositions and pharmaceutical intermediates, a process for producing the same, and a method for synthesizing dibromobiphenyl derivatives used therein.

BACKGROUND ART

[0003]

Resins having excellent insulating characteristics and made of organic polymers are applied to a flattening film of a driving thin film transistor substrate of a display device using a surface protective film or an interlayer insulating film of an electronic part or circuit board, an insulating layer of an organic electroluminescent element, and the organic electroluminescent element. Polyimide resins and polybenzoxazole resins which are particularly excellent in heat resistance, chemical resistance, mechanical properties and the like have been widely used.

[0004]

In recent years, with the miniaturization and thinning of a device, deterioration of the process yield due to warpage of a device substrate and adverse effect on the reliability of the device are concerned. For this reason, it is also required to impart resins with the property of reducing the warpage of the substrate.

[0005]

Examples of a method for reducing the warpage of the device substrate include a method of reducing a difference in coefficient of linear thermal expansion between a resin film-formed on the substrate and the substrate itself to reduce

stress produced by a difference in thermal expansion. Since the linear thermal expansion coefficient of ordinary resins is larger by 10 ppm or more than the linear thermal expansion coefficient of a substrate, it is effective to reduce the linear thermal expansion coefficient of the resin in order to reduce the stress. In order to attain this object, polyimide resins including a rigid structure in the main chain and having a small linear thermal expansion coefficient (see, for example, Patent Documents 1 to 6), polyimide-polybenzoxazole resins (see, for example, Patent Document 7) and the like have been reported.

[0006]

In a resin film formed using the resin, it is necessary to form a pattern such as a through hole in an opening of an electrode portion or the like. In the prior art, a pattern has been formed by forming a positive type photoresist film or the like on a resin film having no photosensitivity and etching the film. However, with this method, it is difficult to miniaturize the pattern due to high density and high speed and large capacity of a device, and therefore, resins having photosensitivity have been studied.

[0007]

For example, regarding a positive type photosensitive resin composition, a composition containing a polyamide acid ester containing a phenolic hydroxyl group and an o-quinonediazide compound (see, for example, Patent Document

8), a composition containing a solvent-soluble ring-closing-type polyimide and naphthoquinonediazide compound (see, for example, Patent Document 9), and a composition containing a polybenzoxazole precursor and a naphthoquinonediazide compound (see, for example, Patent Document 10) have been reported. Regarding a negative type photosensitive resin composition, a polyimide precursor in which an acrylic compound is bonded to a side chain (see, for example, Patent Document 11) and a mixture of polyimide with an acrylic compound (see, for example, Patent Document 12) have been reported.

[0008]

In addition, monomers for synthesizing these polyimides have a very important role in the performance of a polyimide polymer. A monomer of polyimide mainly has two kinds of monomers including a diamine monomer and a diacid anhydride monomer. When structures of the two kinds of monomers are changed, it is possible to remarkably improve the performance in each field of polyimide, such as the coefficient of thermal expansion, light transmittance, or elastic modulus. As a result of study, it is disclosed that introducing a hydroxyl group into a monomer can remarkably change the coefficient of thermal expansion, light transmittance or modulus of elasticity of polyimide (see, for example, Non-Patent Document 1). In an industrial production process, in order to reduce the cost of

a polymer monomer, it is very important to obtain a low-cost hydroxyl group-containing diamine monomer. On the other hand, 4,4'-diaminobiphenyl derivative monomers have already been widely used for the synthesis of polyimides, and the cost is very low (see, for example, Patent Documents 13 and 14).

[0009]

A dibromobiphenyl derivative used for this is a commonly used chemical raw material, pharmaceutical intermediate, or electronic material. At the same time, since a bromine group in a dibromobiphenyl compound can be further converted into a hydroxyl group, an amino group, a cyano group, an alkoxy group, a double bond, a triple bond, an organometallic compound, or etc., the bromine group finds very wide application in the fields of refinement, polymer intermediates, and the like. Commonly used methods for synthesizing dibromobiphenyl derivatives are as follows. That is, a biphenyl compound is used as a raw material, and a dibromobiphenyl derivative can be obtained under the action of a bromination reagent. However, there is a possibility that a plurality of positions on a benzene ring of a biphenyl derivative are substituted with bromine, and selectivity is poor, so that the yield of reaction is low. In order to solve this problem, a bromination reaction using liquid bromine and protic solvent ethanol alone is disclosed (see, for example, Patent Document 15). It is also disclosed to promote the reaction by using liquid bromine as a bromination reagent

and acetic acid as a solvent and adding sodium acetate (see, for example, Non-Patent Document 2).

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0010]

Patent Document 1: Japanese Patent Laid-open Publication No. H2-283762

Patent Document 2: Japanese Patent Laid-open Publication No. H8-48773

Patent Document 3: Japanese Patent Laid-open Publication No. H8-253584

Patent Document 4: Japanese Patent Laid-open Publication No. H11-158279

Patent Document 5: Japanese Patent Laid-open Publication No. 2002-363283

Patent Document 6: Japanese Patent Laid-open Publication No. 2003-212996

Patent Document 7: Japanese Patent Laid-open Publication No. 2007-177117

Patent Document 8: Japanese Patent Laid-open Publication No. H4-204945

Patent Document 9: Japanese Patent Laid-open Publication No. H3-209478

Patent Document 10: International Publication No.

WO10/092824

Patent Document 11: Japanese Patent Laid-open Publication No. 2011-191749

Patent Document 12: International Publication No. WO04/109403

Patent Document 13: Japanese Patent Laid-open Publication No. 2007-106859

Patent Document 14: US Patent No. 5,378,420

Patent Document 15: Chinese Patent Application Publication No. 200780002686.6

NON-PATENT DOCUMENTS

[0011]

Non-Patent Document 1: Progress in Polymer Science (2012), 37(7), 907-974

Non-Patent Document 2: Synthesis, 2000, 383-388

SUMMARY

PROBLEMS TO BE SOLVED

[0012]

However, in the above resin having a small linear thermal expansion coefficient, there is a problem that due to the rigid skeleton introduced into the main chain, the absorbance, particularly the absorbance of an i-line (light having a wavelength of 365 nm) currently widely used for pattern processing a photosensitive resin, is high, and it is difficult

to impart good photosensitive characteristics due to energy loss caused by absorption of the resin itself.

[0013]

A further object is to produce, as a monomer for synthesizing polyimide, a low-cost hydroxyl group-containing diamine monomer in which a hydroxyl group is introduced into a 4,4'-diaminobiphenyl derivative monomer.

[0014]

Further, regarding a dibromobiphenyl derivative used for this, the yield is very low according to the method disclosed in Patent Document 15, and there is a problem that it is not suitable for mass production. Furthermore, according to the method disclosed in Non-Patent Document 2, the degree of corrosion to equipment is relatively large due to use of acidic solvent and salt, recovery of solvent is difficult, difficulty in post-treatment is increased, and there is a problem of environmental pollution.

[0015]

In view of the above-described problems of the prior art, an object of the embodiments disclosed hereinis to provide a resin having a small linear thermal expansion coefficient and a low absorbance.

[0016]

A further object is to provide a production process including highly selectively introducing a bromine atom into

a 5,5'-dihydroxyl-4,4'-diaminobiphenyl derivative used in these resins and a 5,5' position, at the same time, simplifying a process for post-treating a bromination reaction, obtaining a 5,5'-dibromo-4,4'-diaminobiphenyl derivative, and then converting the bromine atom into a hydroxyl group by a reaction of an oxazole ring and a ring opening reaction. A furthermore object is to provide a method for synthesizing dibromobiphenyl derivatives used for this, easily achieving high yield, low cost, and mass production, and hardly polluting the environment.

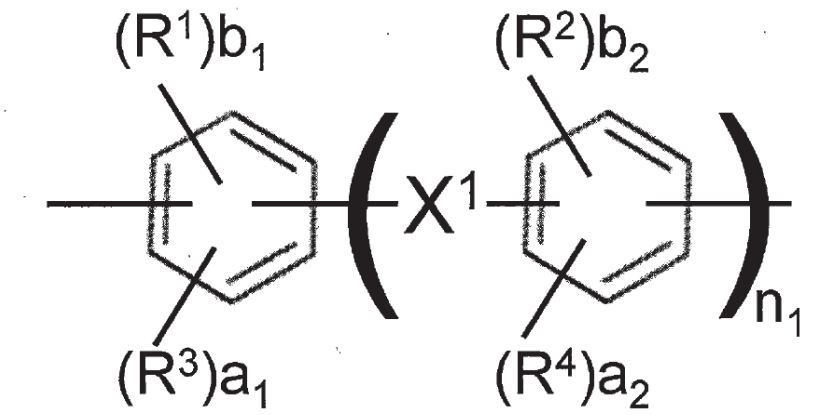
SOLUTIONS TO THE PROBLEMS

[0017]

As a result of intensive studies to solve the above problems, the inventors have found the present disclosure. That is, there is provided a resin comprising at least one structure selected from the structures represented by the following general formulae (1) and (2).

[0018]

[Chemical Formula 1]



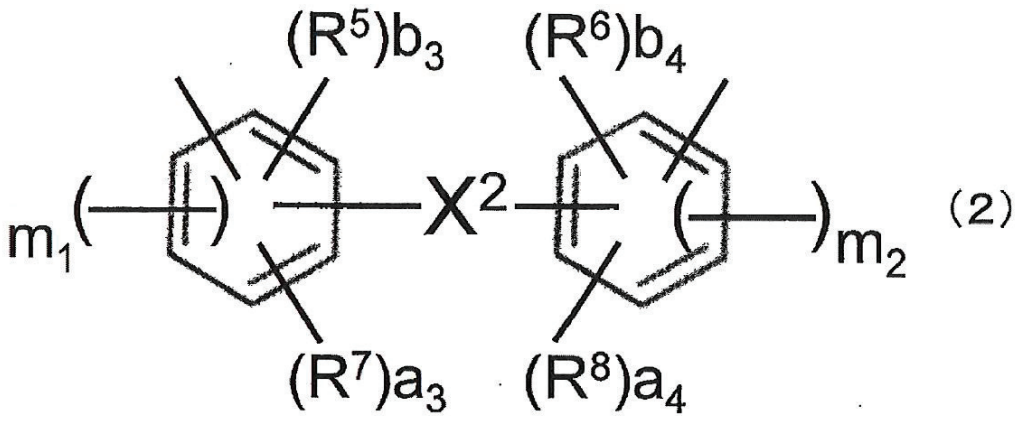
(1)

[0019]

(The general formula (1) is a divalent organic group, and R^1 and R^2 each independently represent a halogen atom or a monovalent organic group having 1 to 3 carbon atoms. R^3 and R^4 each represent an organic group selected from a hydroxyl group, a carboxyl group and a sulfonic acid group. X^1 is a single bond, O, S, NH, SO_2, CO or a divalent organic group having 1 to 3 carbon atoms or a divalent crosslinked structure formed by linking two or more of them. n_1 is 0 or 1. When $n_1 = 0$, a_1 is an integer of 1 to 3, b_1 is an integer of 1 to 3, and $a_1 + b_1$ is an integer of 2 to 4. When $n_1 = 1$, a_1 is an integer of 1 to 4, b_1 is an integer of 0 to 3, a_2 is an integer of 0 to 4, b_2 is an integer of 0 to 4, $a_1 + b_1$ is an integer of 1 to 4, $a_2 + b_2$ is an integer of 0 to 4, and at least one of b_1 and b_2 is an integer of 1 or more.)

[0020]

[Chemical Formula 2]



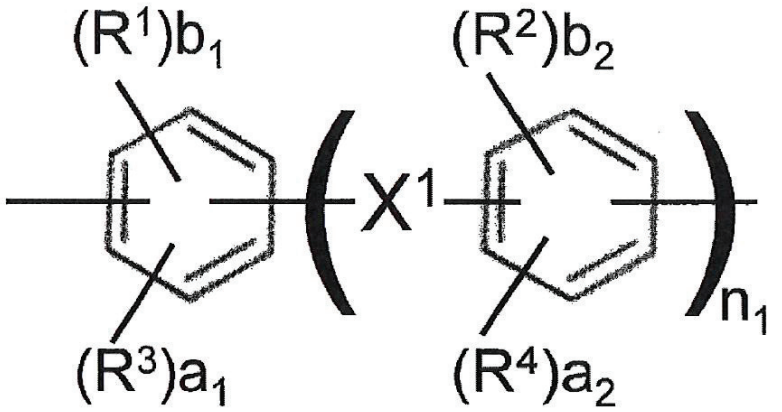
(2)

[0021]

(The general formula (2) is a trivalent or tetravalent organic group, and R^5 and R^6 each independently represent a halogen atom or a monovalent organic group having 1 to 3 carbon atoms. R^7 and R^8 each represent an organic group selected from a hydroxyl group, a carboxyl group and a sulfonic acid group. X^2 is a single bond, O, S, NH, SO_2, CO or a divalent organic group having 1 to 3 carbon atoms or a divalent crosslinked structure formed by linking two or more of these. a_3, a_4, b_3 and b_4 are integers of 0 to 3, $a_3 + b_3$ is an integer of 0 to 3, $a_4 + b_4$ is an integer of 0 to 3, at least one of a_3 and a_4 is an integer of 1 or more, and at least one of b_3 and b_4 is an integer of 1 or more. m_1 and m_2 are integers of 0 or 1, and $m_1 + m_2$ is an integer of 1 or 2.)

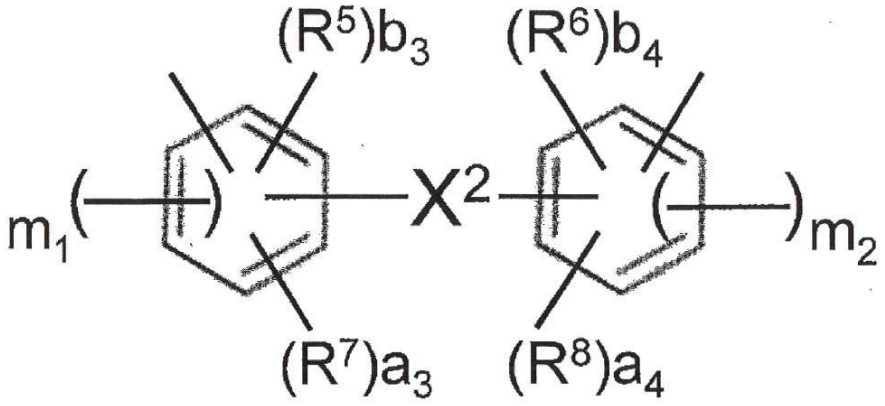
[0021a] In an aspect, there is provided a resin comprising at least one structure selected from structures represented by the following general formulae (1) and (2), wherein the resin comprises at least one selected from polyimide, polyamideimide, polyimide precursor, and a copolymer thereof, and wherein the

resin comprises at least one selectd from structures represented by the following general formulae (3) or (4) or a copolymer thereof:



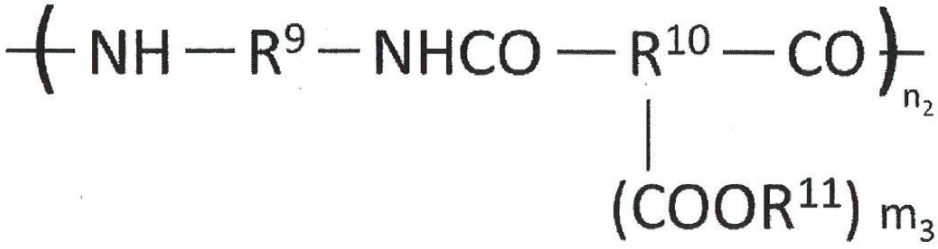
(1)

wherein the general formula (1) is a divalent organic group, and R^1 and R^2 each independently represent a halogen atom or a monovalent organic group having 1 to 3 carbon atoms and are bonded to positions 2 and 2'; R^3 and R^4 each represent an organic group selected from a hydroxyl group, and a carboxyl group; X^1 is a single bond; n_1 is 0 or 1; when $n_1 = 0$, a_1 is an integer of 1 to 3, b_1 is an integer of 1 to 3, and $a_1 + b_1$ is an integer of 2 to 4; when $n_1 = 1$, a_1 is an integer of 1 to 4, b_1 is an integer of 0 to 3, a_2 is an integer of 0 to 4, b_2 is an integer of 0 to 4, $a_1 + b_1$ is an integer of 1 to 4, $a_2 + b_2$ is an integer of 0 to 4, and at least one of b_1 and b_2 is an integer of 1 or more;



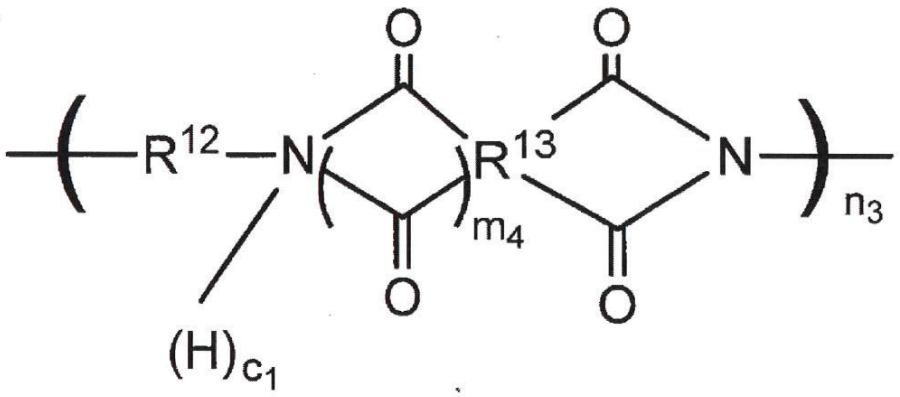
(2)

wherein the general formula (2) is a trivalent or tetravalent organic group, and R^5 and R^6 each independently represent a halogen atom or a monovalent organic group having 1 to 3 carbon atoms; R^7 and R^8 each represent an organic group selected from a hydroxyl group, a carboxyl group and a sulfonic acid group; X^2 is a single bond, O, S, NH, SO_2, CO or a divalent organic group having 1 to 3 carbon atoms or a divalent crosslinked structure formed by linking two or more of these; a_3, a_4, b_3 and b_4 are integers of 0 to 3, $a_3 + b_3$ is an integer of 0 to 3, $a_4 + b_4$ is an integer of 0 to 3, at least one of a_3 and a_4 is an integer of 1 or more, and at least one of b_3 and b_4 is an integer of 1 or more; m_1 and m_2 are integers of 0 or 1, and $m_1 + m_2$ is an integer of 1 or 2;



(3)

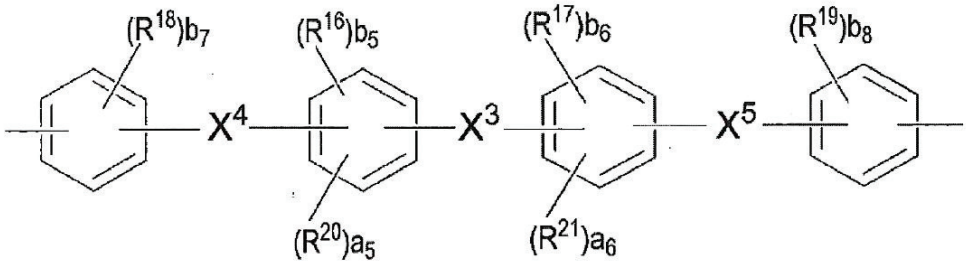
wherein R^9 represents a divalent organic group having 2 to 50 carbon atoms; R^{10} represents a trivalent or tetravalent organic group having 2 to 50 carbon atoms; R^9 represents a structure selected from the general formula (1) or (6), and/or R^{10} represents a structure selected from the general formula (2) or (7); R^{11} represents hydrogen or an organic group having 1 to 10 carbon atoms; m_3 is an integer of 1 or 2; and n_2 represents a range of 10 to 100,000;



(4)

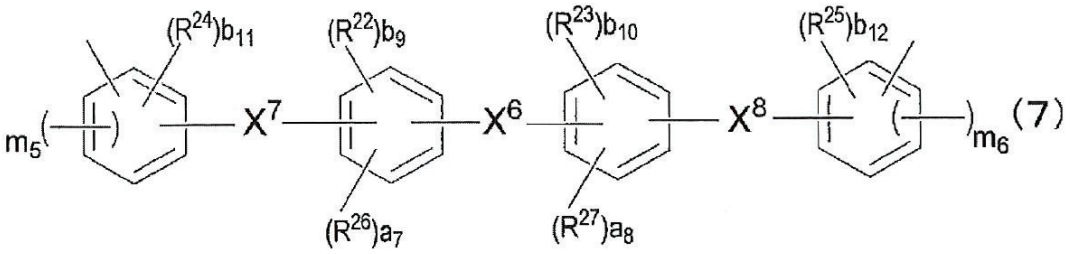
wherein R^{12} represents a divalent organic group having 2 to 50 carbon atoms; R^{13} represents a trivalent or tetravalent organic group having 2 to 50 carbon atoms; R^{12} represents a structure selected from the general formula (1) or (6), and/or R^{13} represents a structure selected from the general formula (2)

or (7); m_4 is an integer of 0 or 1, c_1 is an integer of 0 or 1, $c_1 = 1$ when $m_4 = 0$, and $c_1 = 0$ when $m_4 = 1$; and n_3 represents a range of 10 to 100,000;



(6)

wherein the general formula (6) is a divalent organic group, and R^{16} to R^{19} each independently represent a halogen atom or a monovalent organic group having 1 to 3 carbon atoms; R^{20} and R^{21} each represent an organic group selected from a hydroxyl group, a carboxyl group, and a sulfonic acid group; X^3 is a single bond, O, S, NH, SO_2, CO or a divalent organic group having 1 to 3 carbon atoms or a divalent crosslinked structure formed by linking two or more of these; X^4 and X^5 each represent a structure selected from an amide bond and an azomethine bond; a_5 is an integer of 1 to 4, b_5 is an integer of 0 to 3, a_6 is an integer of 0 to 4, b_6 is an integer of 0 to 4, b_7 and b_8 are integers of 0 to 4, $a_5 + b_5$ is an integer of 1 to 4, $a_6 + b_6$ is an integer of 0 to 4, and at least one of b_5 and b_6 is an integer of 1 or more;



wherein the general formula (7) is a trivalent or tetravalent organic group, and R^{22} to R^{25} each independently represent a halogen atom or a monovalent organic group having 1 to 3 carbon atoms; R^{26} and R^{27} each represent an organic group selected from a hydroxyl group, a carboxyl group, and a sulfonic acid group; X^6 is a single bond, O, S, NH, SO_2, CO or a divalent organic group having 1 to 3 carbon atoms or a divalent crosslinked structure formed by linking two or more of these; X^7 and X^8 each represent a structure selected from an amide bond and an azomethine bond; a_7 is an integer of 1 to 4, b_9 is an integer of 0 to 3, a_8 is an integer of 0 to 4, b_{10} is an integer of 0 to 4, b_{11} and b_{12} are integers of 0 to 3, $a_7 + b_9$ is an integer of 1 to 4, $a_8 + b_{10}$ is an integer of 0 to 4, and at least one of b_9 and b_{10} is an integer of 1 or more; m_5 and m_6 are integers of 0 or 1, and $m_5 + m_6$ is an integer of 1 or 2.

[0021b]

In another aspect, there is provided a resin composition comprising the resin as defined above.

[0021c]

In another aspect, there is provided a process for producing

a heat resistance coating film, comprising: coating the resin composition as defined above onto a support substrate to form a coating film; drying the coating film to form a resin film; exposing the resin film; developing the exposed resin film; and applying heat treatment to the developed resin film.

[0021d]

In another aspect, there is provided a process for producing a heat resistance coating film, comprising: coating the resin composition as defined above onto a support substrate using a slit nozzle to form a coating film; drying the coating film under reduced pressure to form a resin film; exposing the resin film; developing the exposed resin film; and applying heat treatment to the developed resin film.

[0021e]

In another aspect, there is provided an electronic component mounted in such a state that one or a plurality of structures comprising a substrate and a coating film provided on one or both surfaces of the substrate are stacked, the coating film is a heat resistance coating film obtained by the production process as defined above.

[0021f]

In another aspect, there is provided an electronic component comprising a substrate, a rewiring structure comprising a coating film layer and a wiring layer alternately formed on the substrate, or a multilayer wiring structure, wherein the

coating film layer is a heat resistance coating film obtained by the production process as defined above.

[0021g]

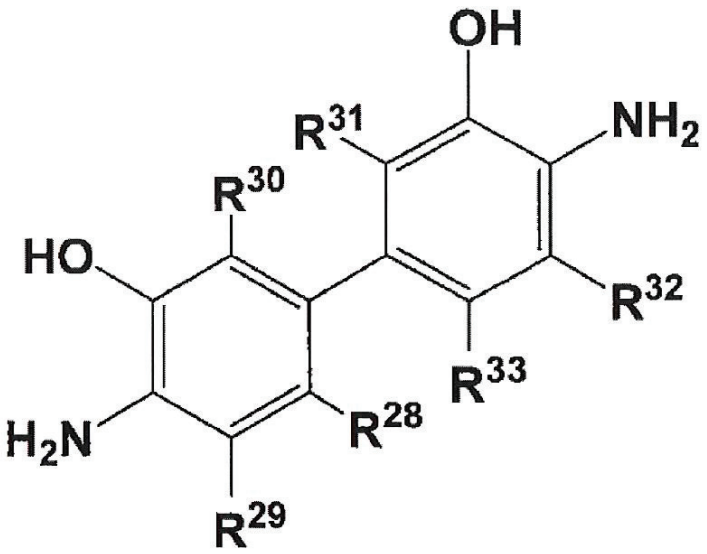
In another aspect, there is provided a display device comprising a first electrode provided on a substrate, an insulating layer provided on the first electrode such that the first electrode is partially exposed, and a second electrode provided facing the first electrode, wherein the insulating layer is a heat resistance coating film obtained by the production process as defined above.

[0021h]

In another aspect, there is provided a display element comprising a flattening film provided to cover concavoconvexes on a substrate comprising a thin film transistor (TFT) and a display element provided on the flattening film, wherein the flattening film is a heat resistance coating film obtained by the production process as defined above.

[0021i]

In another aspect, there is provided a 5,5'-dihydroxyl-4,4'-diaminobiphenyl derivative represented by the following general formula (8):



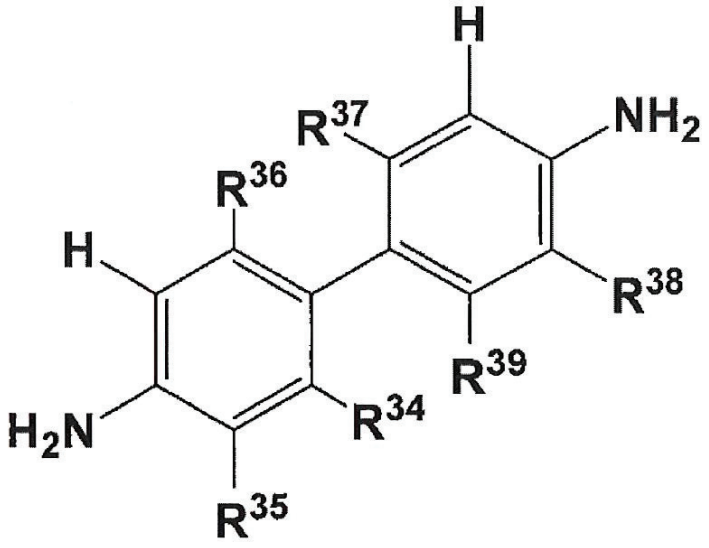
(8)

wherein R^{28} and R^{33} are the same and independently one kind selected from the group consisting of a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group; R^{29} and R^{32} are the same, R^{30} and R^{31} are the same, and they are each one kind selected from the group consisting of hydrogen, halogen, a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or

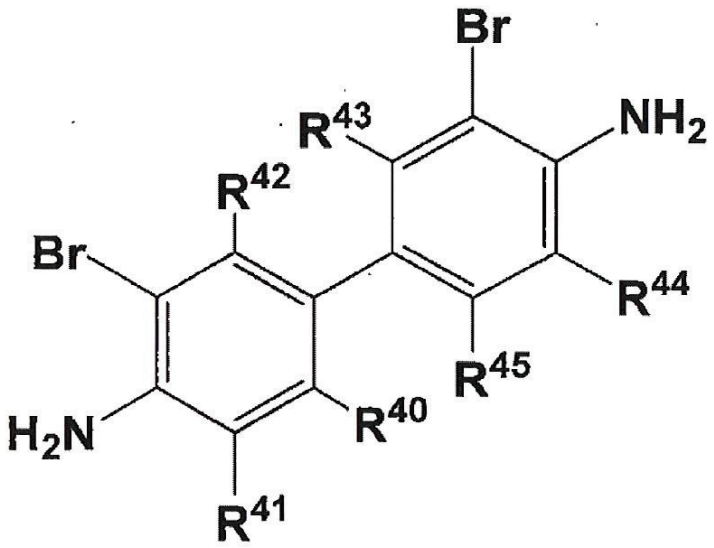
unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group; and wherein among them, the substituents may be the same or different and represent one or more of halogen, trifluoromethyl, trimethylsilyl, a C_1 to C_6 alkoxyl group, a C_1 to C_6 alkyl group, an aryl alkoxyl group, a C_6 to C_{30} aryl group, and a C_4 to C_{30} heterocyclic group.

[0021j]

In another aspect, there is provided a process for producing a 5,5'-dihydroxy-4,4'-diaminobiphenyl derivative, comprising a production process for obtaining a 5,5'-dibromo-4,4'-diaminobiphenyl derivative of the general formula (10) by bromination reaction of 4,4'-diaminobiphenyl of the general formula (9):



(9)



(10)

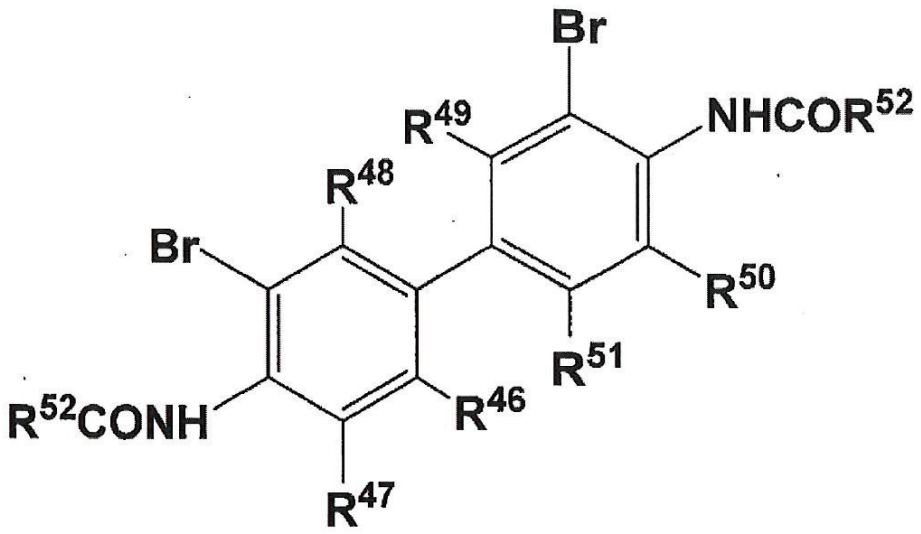
wherein R^{34} and R^{39} are the same and each independently one kind selected from the group consisting of a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino

group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group; R^{35} and R^{38} are the same, R^{36} and R^{37} are the same, and they are each independently one kind selected from the group consisting of hydrogen, halogen, a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group; R^{40} and R^{45} are the same and each independently one kind selected from the group consisting of a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group; R^{41} and R^{44} are the same, R^{42} and R^{43} are the same, and they are each independently one kind selected from the group consisting of hydrogen, halogen, a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a

halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group; wherein the substituents may be the same or different and each independently represent one or more of halogen, trifluoromethyl, trimethylsilyl, a C_1 to C_6 alkoxyl group, a C_1 to C_6 alkyl group, an aryl alkoxyl group, a C_6 to C_{30} aryl group, and a C_4 to C_{30} heterocyclic group.

[0021k]

In another aspect, there is provided a process for producing a 5,5'-dihydroxy-4,4'-diaminobiphenyl derivative, comprising a production process for obtaining a 5,5'-dibromo-4,4'-diamidebiphenyl derivative of the general formula (11) by amidation reaction of a 5,5'-dibromo-4,4'-diaminobiphenyl derivative using acid anhydride or acyl chloride:



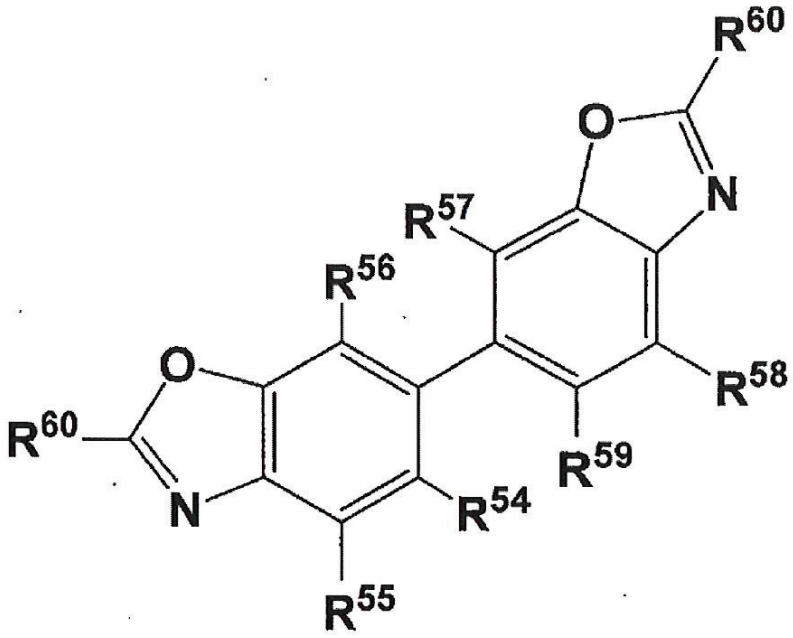
(11)

wherein R^{46} and R^{51} are the same and each independently one kind selected from the group consisting of a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group; R^{47} and R^{50} are the same, R^{48} and R^{49} are the same, and they are each independently one kind selected from the group consisting of hydrogen, halogen, a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group,

an ester group and a nitro group; wherein among them, the substituents may be the same or different and each independently represent one or more of halogen, trifluoromethyl, trimethylsilyl, a C_1 to C_6 alkoxyl group, a C_1 to C_6 alkyl group, an aryl alkoxyl group, a C_6 to C_{30} aryl group, and a C_4 to C_{30} heterocyclic group, and R^{52} is one kind selected from the group consisting of a substituted or unsubstituted C_1 to C_6 alkyl group or a substituted or unsubstituted aryl group; and wherein the substituent in R^{52} is one or more of a methyl group, a sulfo group, a fluorine atom, an amino group, and a methoxy group.

[00211]

In another aspect, there is provided a process for producing a 5,5'-dihydroxy-4,4'-diaminobiphenyl derivative, comprising a production process for obtaining a 6,6'-dibenzoxazole derivative represented by the general formula (12) by reaction of a 5,5'-dibromo-4,4'-diamidobiphenyl derivative under the action of a catalyst and inorganic alkali:



(12)

wherein R^{54} and R^{59} are the same and each independently one kind selected from the group consisting of a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group; R^{55} and R^{58} are the same, R^{56} and R^{57} are the same, and they are each independently one kind selected from the group consisting of hydrogen, halogen, a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide

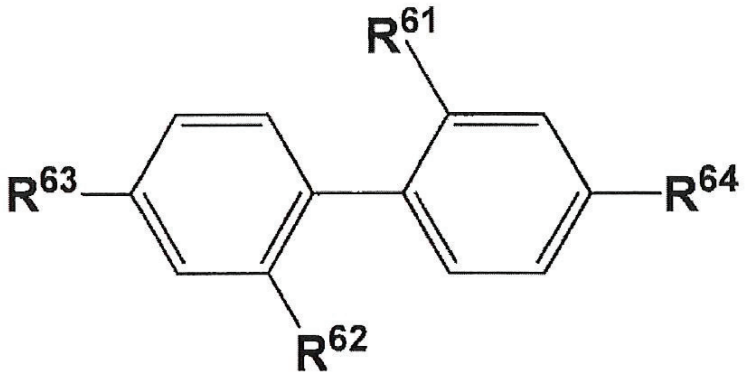
group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group; wherein one or more substituents among them may be the same or different and are each independently represent one or more of halogen, trifluoromethyl, trimethylsilyl, a C_1 to C_6 alkoxyl group, a C_1 to C_6 alkyl group, an arylalkoxyl group, a C_6 to C_{30} aryl group, and a C_4 to C_{30} heterocyclic group; R^{60} is one kind selected from the group consisting of a substitutable C_1 to C_6 alkyl group and a substitutable aryl group; and wherein the substituent in R^{60} is one or more of a methyl group, a sulfo group, a fluorine atom, an amino group, and a methoxy group.

[0021m]

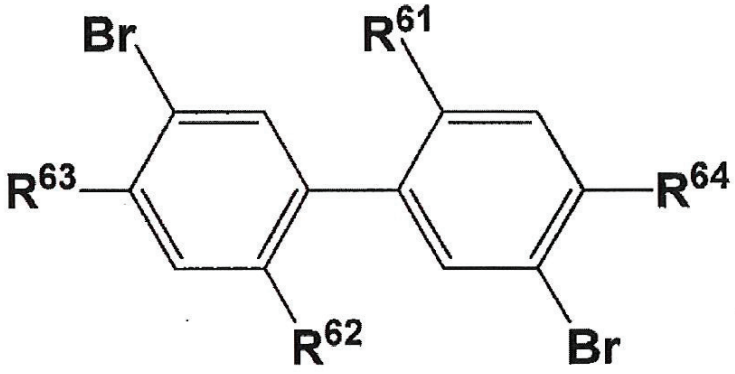
In another aspect, there is provided a process for producing a 5,5'-dihydroxy-4,4'-diaminobiphenyl derivative characterized by obtaining a 6,6'-dibenzoxazole derivative by ring-opening reaction under an inorganic strong acid.

[0021n]

In another aspect, there is provided a process for producing a 5,5'-dibromobiphenyl derivative characterized by obtaining a 5,5'-dibromobiphenyl derivative having a structure represented by the general formula (14) under the action of an aprotic solvent and a bromination reagent, using a biphenyl compound having a structure represented by the general formula (13) as a raw material:



(13)



(14)

wherein R^{61} and R^{62} may be the same or different and are each one kind selected from the group consisting of halogen, a C_1 to C_6 alkyl group, a halogenated alkyl group, an ester group and a nitro group; R^{63} and R^{64} may be the same or different and are each one kind selected from the group consisting of a C_1 to C_6 alkyl group, a C_1 to C_6 alkoxyl group, a hydroxyl group, a

substituted or unsubstituted aryl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted imide group, a substituted or unsubstituted sulfamine group, a substituted or unsubstituted sulfinamide group, and a substituted or unsubstituted aromatic heterocyclic group; and wherein among them, the substituents may be the same or different and represent one or more of trifluoromethyl, trimethylsilyl, a C_1 to C_6 alkoxyl group, a C_1 to C_6 alkyl group, an aryl alkoxyl group, a C_6 to C_{30} aryl group, and a heterocyclic group.

EFFECTS [0022]

According to the present disclosure, it is possible to obtain a resin having a low linear thermal expansion coefficient

and a low absorbance.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023]

Fig. 1 is an enlarged cross-sectional view of a pad portion of a semiconductor device having a bump.

Fig. 2 is a view showing a detailed method for producing the semiconductor device having the bump.

Fig. 3 is an enlarged cross-sectional view of an electrode portion of a chip stacked type semiconductor device.

Fig. 4 is an enlarged cross-sectional view of an electrode portion of a chip stacked type semiconductor device.

Fig. 5 is a view showing a detailed method for producing the chip stacked type semiconductor device.

Fig. 6 is a view showing a detailed method for producing the chip stacked type semiconductor device.

Fig. 7 is a cross-sectional view of a TFT substrate.

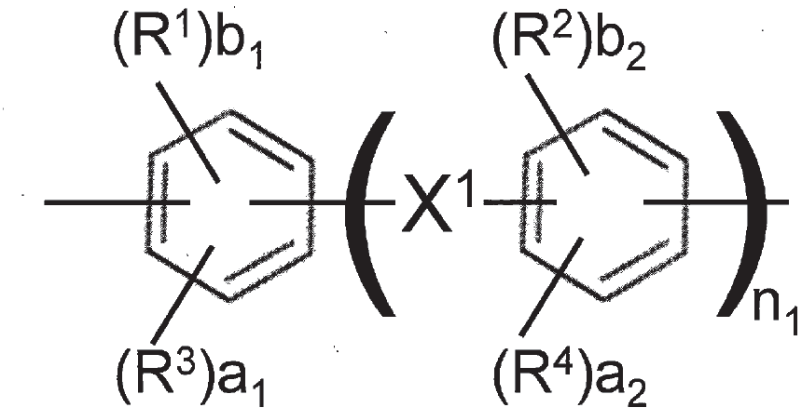
EMBODIMENTS OF THE INVENTION

[0024]

The present invention is a resin characterized by including at least one structure selected from the structures represented by the following general formulae (1) and (2).

[0025]

[Chemical Formula 3]



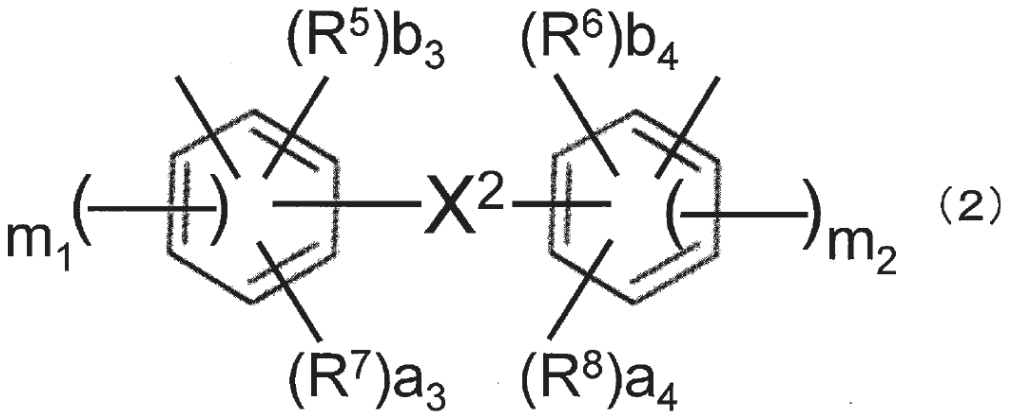
(1)

[0026]

(The general formula (1) is a divalent organic group, and R^1 and R^2 each independently represent a halogen atom or a monovalent organic group having 1 to 3 carbon atoms. R^3 and R^4 each represent an organic group selected from a hydroxyl group, a carboxyl group and a sulfonic acid group. X^1 is a single bond, O, S, NH, SO_2, CO or a divalent organic group having 1 to 3 carbon atoms or a divalent crosslinked structure formed by linking two or more of them. n_1 is 0 or 1. When $n_1 = 0$, a_1 is an integer of 1 to 3, b_1 is an integer of 1 to 3, and $a_1 + b_1$ is an integer of 2 to 4. When $n_1 = 1$, a_1 is an integer of 1 to 4, b_1 is an integer of 0 to 3, a_2 is an integer of 0 to 4, b_2 is an integer of 0 to 4, $a_1 + b_1$ is an integer of 1 to 4, $a_2 + b_2$ is an integer of 0 to 4, and at least one of b_1 and b_2 is an integer of 1 or more.)

[0027]

[Chemical Formula 4]



(2)

[0028]

(The general formula (2) is a trivalent or tetravalent organic group, and R^5 and R^6 each independently represent a halogen atom or a monovalent organic group having 1 to 3 carbon atoms. R^7 and R^8 each represent an organic group selected from a hydroxyl group, a carboxyl group and a sulfonic acid group. X^2 is a single bond, O, S, NH, SO_2, CO or a divalent organic group having 1 to 3 carbon atoms or a divalent crosslinked structure formed by linking two or more of these. a_3, a_4, b_3 and b_4 are integers of 0 to 3, $a_3 + b_3$ is an integer of 0 to 3, $a_4 + b_4$ is an integer of 0 to 3, at least one of a_3 and a_4 is an integer of 1 or more, and at least one of b_3 and b_4 is an integer of 1 or more. m_1 and m_2 are integers of 0 or 1, and $m_1 + m_2$ is an integer of 1 or 2.)

The general formula (1) is a divalent organic group, and R^1 and R^2 each independently represent a halogen atom or a monovalent organic group having 1 to 3 carbon atoms. From the viewpoint of heat resistance of the resultant resin, preferred

specific examples include a methyl group, a methoxy group, an ethyl group, an ethoxy group, a fluoro group, a trifluoromethyl group, a pentafluoroethyl group, a trifluoromethoxy group, and a pentafluoroethoxy group, but the present invention is not limited thereto. Further, from the viewpoint that absorbance of the resultant resin can be reduced, a fluoro group, a trifluoromethyl group, a pentafluoroethyl group, a trifluoromethoxy group and a pentafluoroethoxy group are more preferable, and a trifluoromethyl group and a pentafluoroethyl group are most preferable. Further, from the viewpoint that the absorbance of the resultant resin can be reduced, R^1 and R^2 are preferably in the ortho position relative to a polymer chain. Furthermore, from the viewpoint that a linear thermal expansion coefficient of the resultant resin can be reduced, R^1 and R^2 are more preferably bonded to positions 2 and 2'.

[0029]

R^3 and R^4 each represent an organic group selected from a hydroxyl group, a carboxyl group and a sulfonic acid group. The organic group is preferably a hydroxyl group. From the viewpoint that the absorbance of the resultant resin can be reduced, R^3 and R^4 are preferably in the ortho position relative to a polymer chain. X^1 is a single bond, O, S, NH, SO_2, CO or a divalent organic group having 1 to 3 carbon atoms or a divalent crosslinked structure formed by linking two or more of them. From the viewpoint that the linear thermal expansion

coefficient of the resultant resin can be reduced, X^1 is preferably a single bond.

[0030]

n_1 is 0 or 1. From the viewpoint that the absorbance of the resultant resin can be reduced, n_1 is preferably 1. When $n_1 = 0$, a_1 is an integer of 1 to 3, b_1 is an integer of 1 to 3, and $a_1 + b_1$ is an integer of 2 to 4. When $n_1 = 1$, a_1 is an integer of 1 to 4, b_1 is an integer of 0 to 3, a_2 is an integer of 0 to 4, b_2 is an integer of 0 to 4, $a_1 + b_1$ is an integer of 1 to 4, $a_2 + b_2$ is an integer of 0 to 4, and at least one of b_1 and b_2 is an integer of 1 or more. From the viewpoint that the linear thermal expansion coefficient of the resultant resin can be reduced, when $n_1 = 0$, it is preferable that a_1 and b_1 are 1 or 2, and it is more preferable that $a_1 = b_1 = 2$. Similarly, from the viewpoint that the linear thermal expansion coefficient of the resultant resin can be reduced, when $n_1 = 1$, it is preferable that $a_1 = a_2 = 1$ and b_1 and b_2 are 1 or 2, and it is more preferable that $a_1 = a_2 = b_1 = b_2 = 1$. Further, from the viewpoint that the linear thermal expansion coefficient of the resultant resin can be reduced, it is preferable that all aromatic rings having a structure represented by the general formula (1) are bonded to a polymer main chain at the para positions.

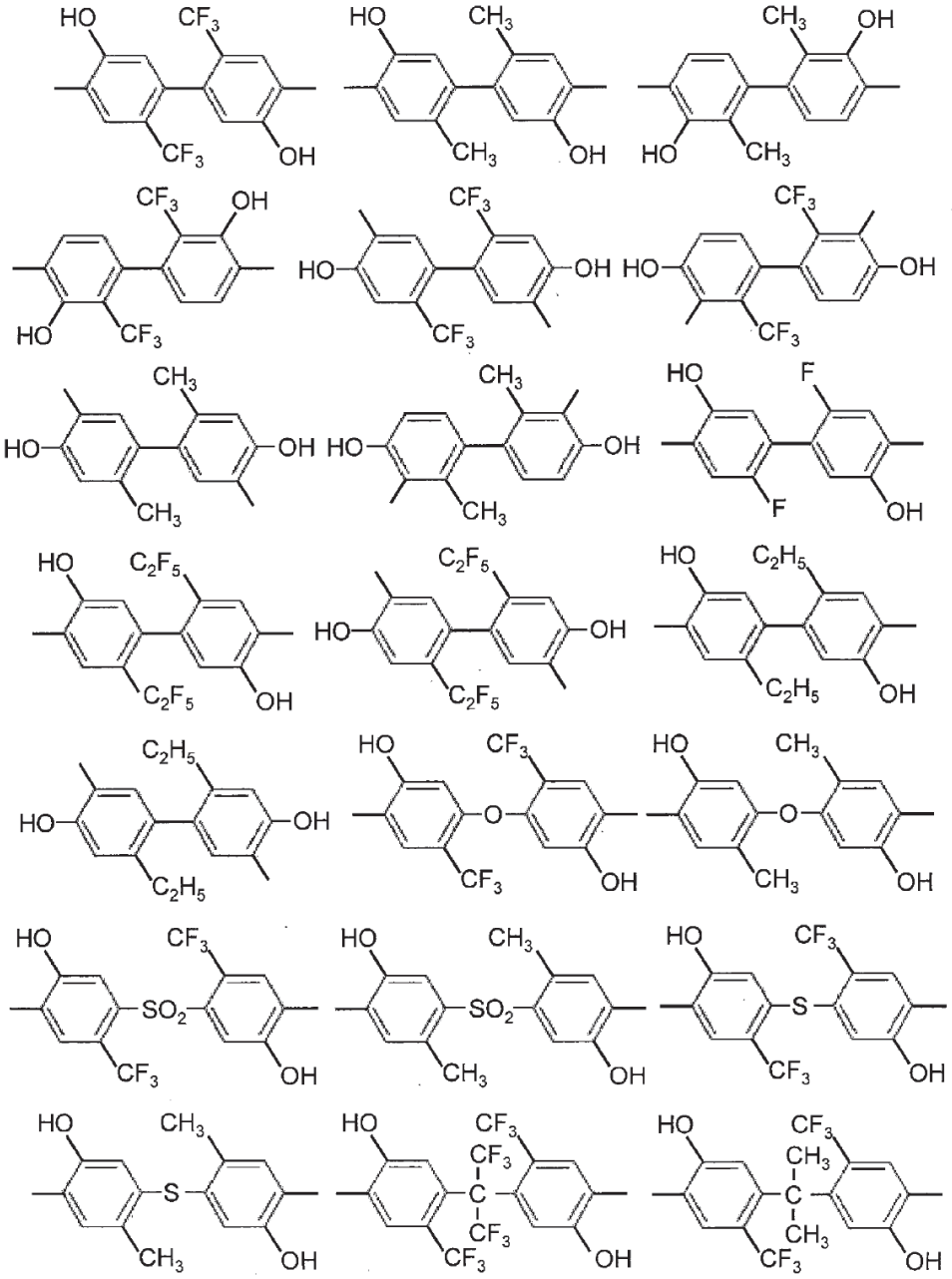
[0031]

In the present invention, examples of preferred structures represented by the general formula (1) include the

following structures, but the structures are not limited thereto.

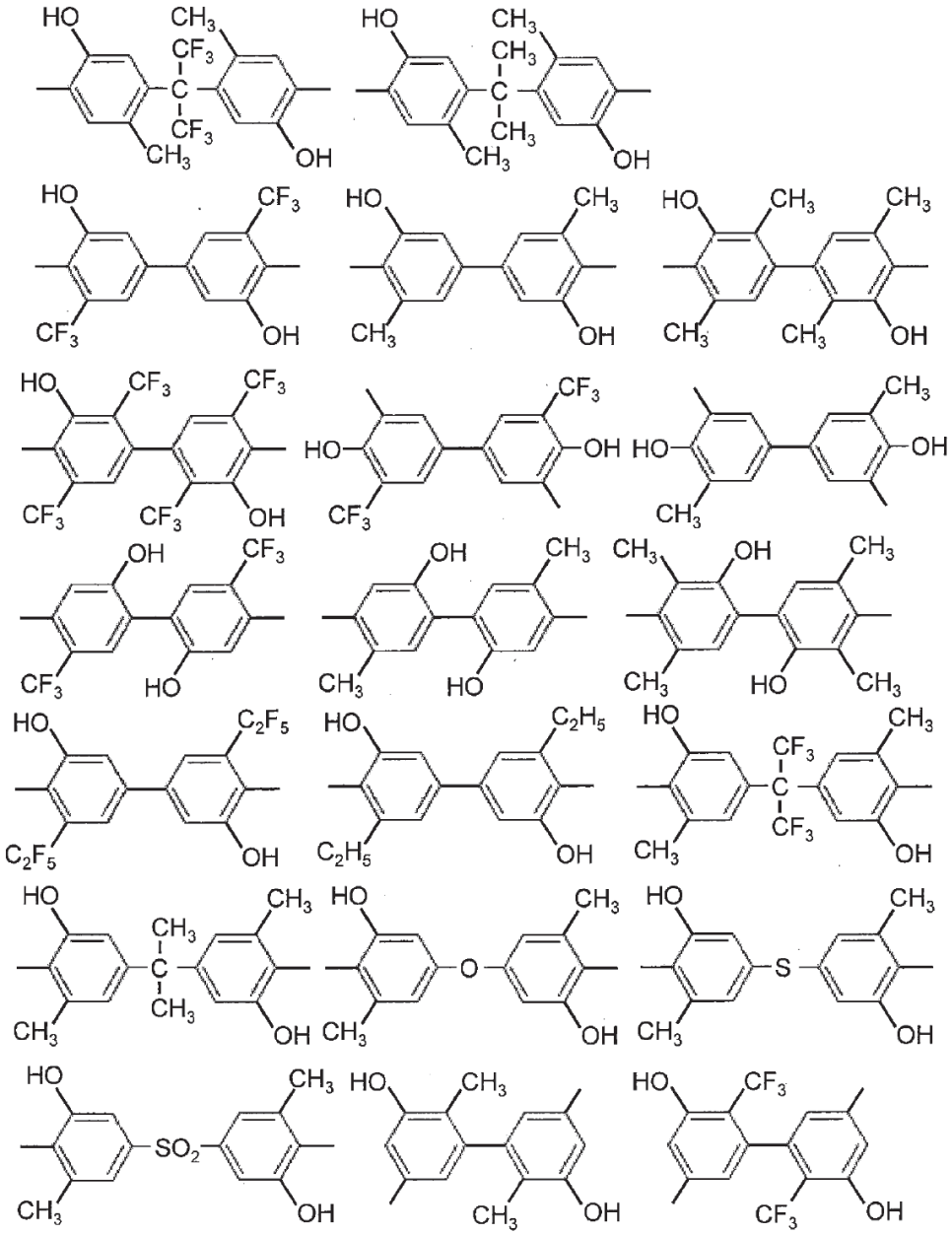
[0032]

[Chemical Formula 5]



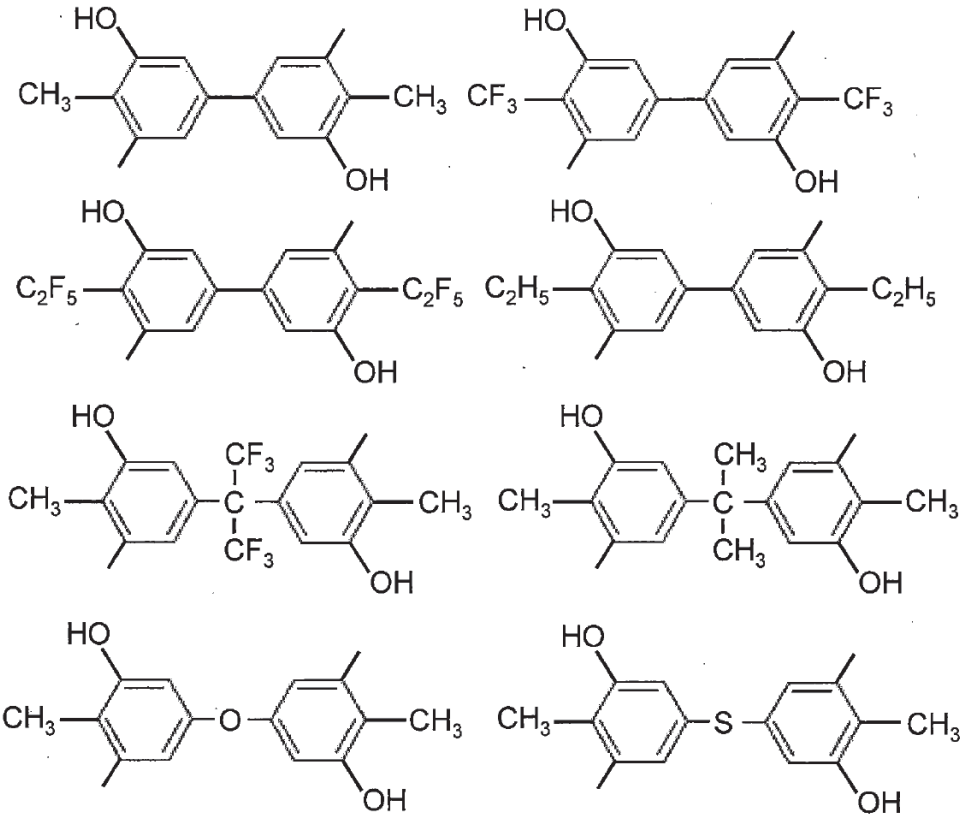
[0033]

[Chemical Formula 6]



[0034]

[Chemical Formula 7]



[0035]

In the general formula (2), R^5 and R^6 each independently represent a halogen atom or a monovalent organic group having 1 to 3 carbon atoms. From the viewpoint of the heat resistance of the resultant resin, preferred specific examples include a methyl group, a methoxy group, an ethyl group, an ethoxy group, a fluoro group, a trifluoromethyl group, a pentafluoroethyl group, a trifluoromethoxy group, and a pentafluoroethoxy group, but the present invention is not limited thereto. Further, from the viewpoint that absorbance of the resultant resin can be reduced, a fluoro group, a trifluoromethyl group, a pentafluoroethyl group, a trifluoromethoxy group and a

pentafluoroethoxy group are more preferable, and a trifluoromethyl group and a pentafluoroethyl group are most preferable.

[0036]

Further, from the viewpoint that the absorbance of the resultant resin can be reduced, R^5 and R^6 are preferably in the ortho position relative to the polymer chain. Furthermore, from the viewpoint that the linear thermal expansion coefficient of the resultant resin can be reduced, R^5 and R^6 are more preferably bonded to positions 2 and 2'. R^7 and R^8 each represent an organic group selected from a hydroxyl group, a carboxyl group and a sulfonic acid group. The organic group is preferably a hydroxyl group. From the viewpoint that the absorbance of the resultant resin can be reduced, R^7 and R^8 are preferably in the ortho position relative to the polymer chain. X^2 is a single bond, O, S, NH, SO_2, CO or a divalent organic group having 1 to 3 carbon atoms or a divalent crosslinked structure formed by linking two or more of these. From the viewpoint that the linear thermal expansion coefficient of the resultant resin can be reduced, X^1 is preferably a single bond.

[0037]

a_3, a_4, b_3 and b_4 are integers of 0 to 3, $a_3 + b_3$ is an integer of 0 to 3, $a_4 + b_4$ is an integer of 0 to 3, at least one of a_3 and a_4 is an integer of 1 or more, and at least one of b_3 and b_4 is an integer of 1 or more. From the viewpoint that the linear

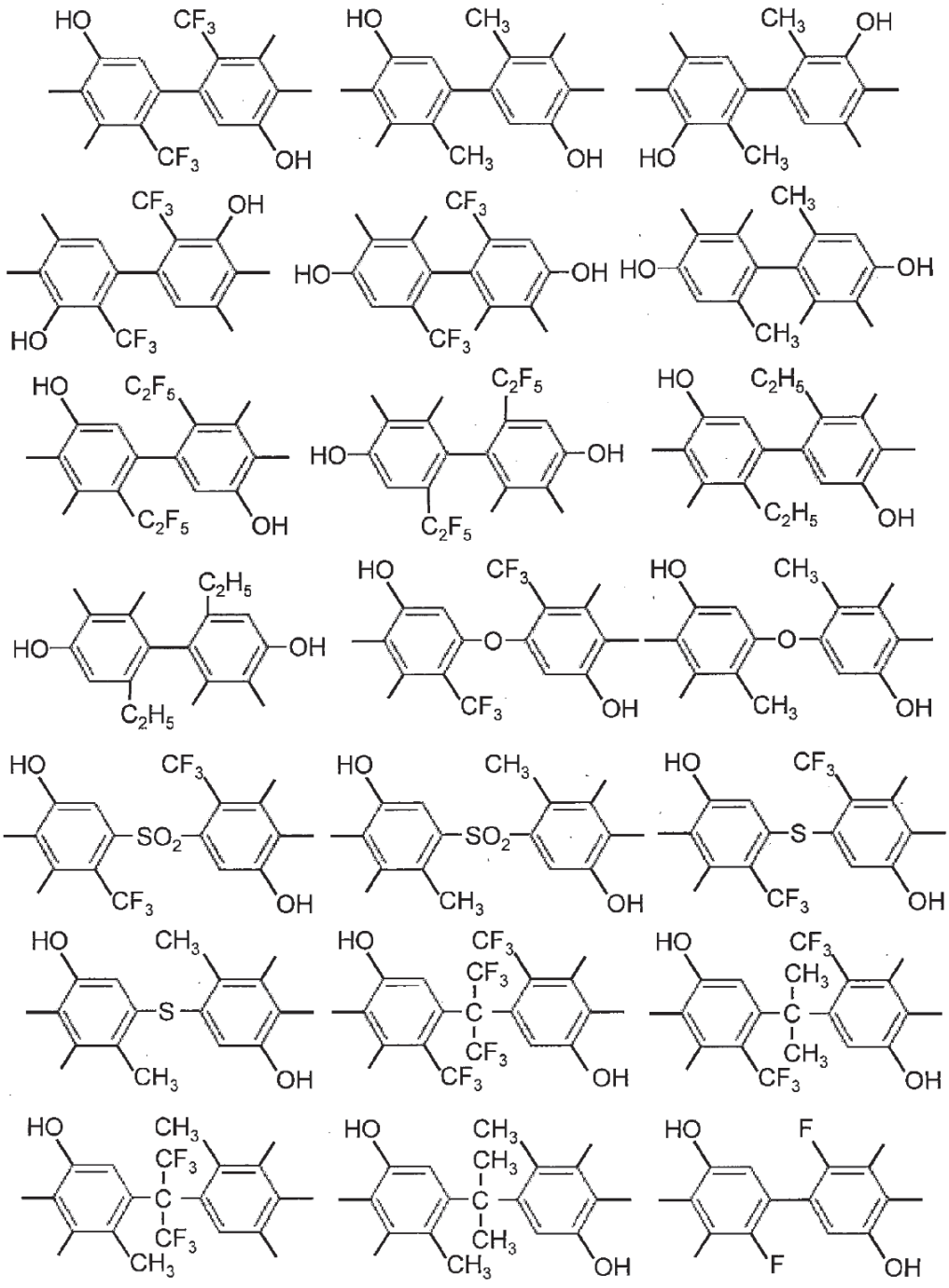
thermal expansion coefficient of the resultant resin can be reduced, it is preferable that $a_3 = a_4 = 1$ and b_3 and b_4 are 1 or 2, and it is more preferable that $a_3 = a_4 = b_3 = b_4 = 1$. m_1 and m_2 are integers of 0 or 1, and $m_1 + m_2$ is an integer of 1 or 2. Preferably, $m_1 = m_2 = 1$.

[0038]

In the present invention, examples of preferred structures represented by the general formula (2) include the following structures.

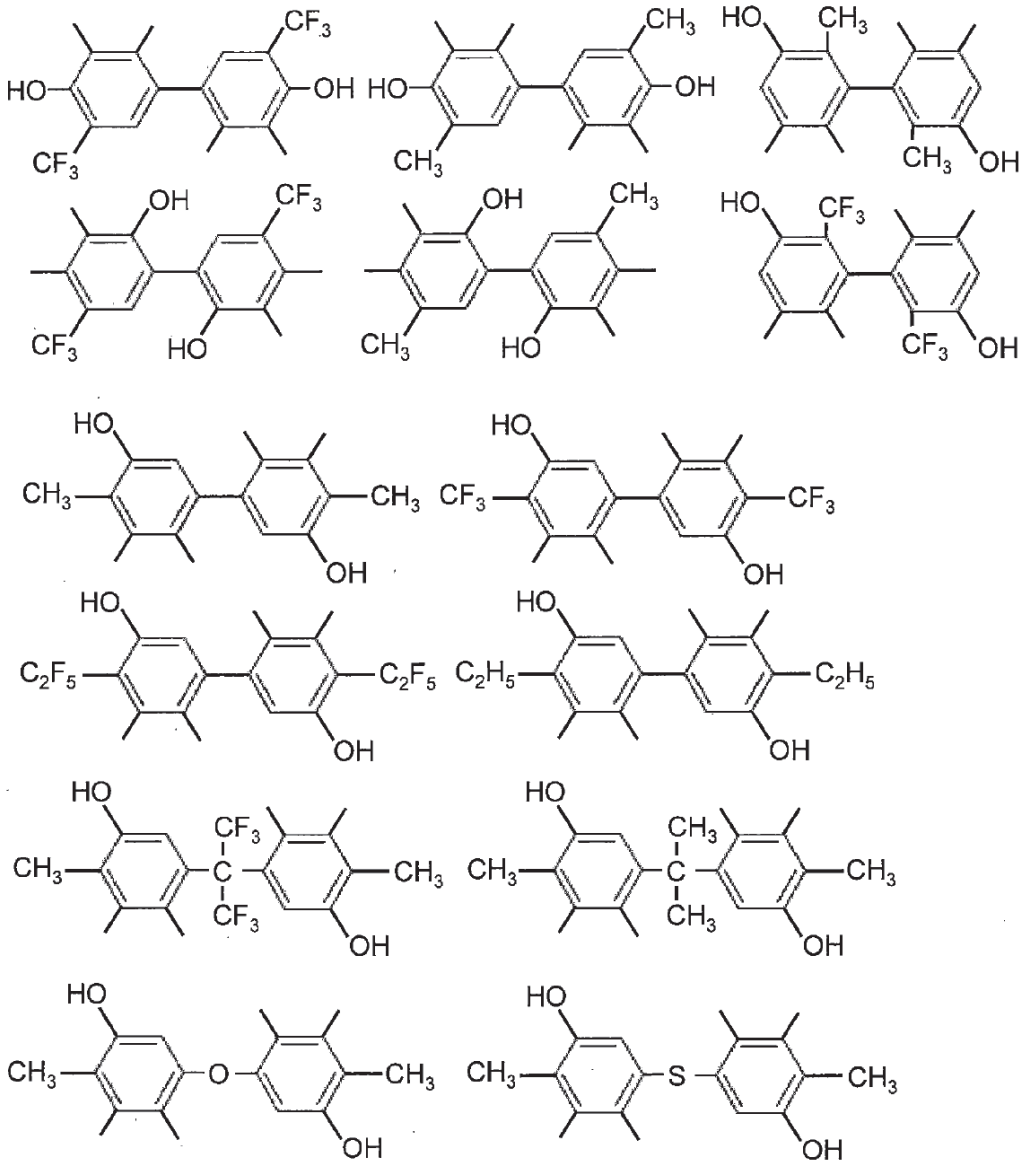
[0039]

[Chemical Formula 8]



[0040]

[Chemical Formula 9]



[0041]

Examples of the resin having at least one structure selected from the structures represented by the general formulae (1) and (2) include, but are not limited to, polyurethane, polyurea, polyester, polycarbonate, polyamine, polyazomethine, polyamide, polyamideimide, polyamideimide precursor, polyimide, polyimide precursor, polybenzoxazole,

polybenzoxazole precursor, polybenzothiazole, polybenzothiazole precursor, polybenzimidazole, polybenzimidazole precursor, polyether ketone, polyphenylene oxide, polyphenylene sulfide, polyether ether ketone, polyethersulfone, random copolymers thereof, and block copolymers thereof. From the viewpoints of heat resistance, chemical resistance and mechanical properties of a film obtained after heat treatment, the resin is preferably at least one selected from polyimide, polyamideimide, polybenzoxazole, polyimide precursor, polyamideimide precursor, polybenzoxazole precursor, random copolymers thereof, and block copolymers thereof. From the viewpoint that a heat treatment temperature can be lowered, polyimide and polyamideimide are more preferable, and from the viewpoint of heat resistance, polyimide is most preferable.

[0042]

Such a resin can be synthesized, for example, by reacting dicarboxylic acid, tricarboxylic acid, tetracarboxylic acid or a derivative or anhydride thereof with diamine, diisocyanate, or a compound obtained by substituting these with a hydroxyl group or a carboxyl group or a derivative thereof, at a temperature in a range of −30°C to 300°C. For example, a polyimide precursor or polyimide can be obtained by reacting tetracarboxylic acid, a tetracarboxylic acid derivative or tetracarboxylic dianhydride with diamine. A polyamide-imide

precursor or polyamide-imide can be obtained by reacting tricarboxylic acid, a tricarboxylic acid derivative or a tricarboxylic anhydride with diamine. A polybenzoxazole precursor and polybenzoxazole can be obtained by reacting bisaminophenol with a dicarboxylic acid derivative such as dicarboxylic acid or hydroxybenzotriazole ester thereof and an imidazolide compound thereof.

[0043]

The kind of a polymerization solvent is not particularly limited as long as it can dissolve a produced resin. Examples of the polymerization solvent include polar aprotic solvents such as N-methyl-2-pyrrolidone, γ-butyrolactone, N, N-dimethylformamide, N, N-dimethylacetamide, 1,3-dimethyl-2-imidazolidinone, and dimethylsulfoxide; glycol ethers such as tetrahydrofuran, dioxane, propylene glycol monomethyl ether, propyleneglycolmonoethylether, diethyleneglycoldimethylether, diethyleneglycoldiethylether, and diethyleneglycolethylmethylether; ketones such as acetone, methyl ethyl ketone, diisobutyl ketone, and diacetone alcohol; esters such as ethyl acetate, butyl acetate, isobutyl acetate, propyl acetate, propylene glycol monomethyl ether acetate, glycol ether acetate, and 3-methyl-3-methoxybutylacetate; alcohols such as ethyl lactate, methyl lactate, diacetone alcohol, and 3-methyl-3-methoxybutanol; and aromatic hydrocarbons such as toluene and xylene. Two or more of those

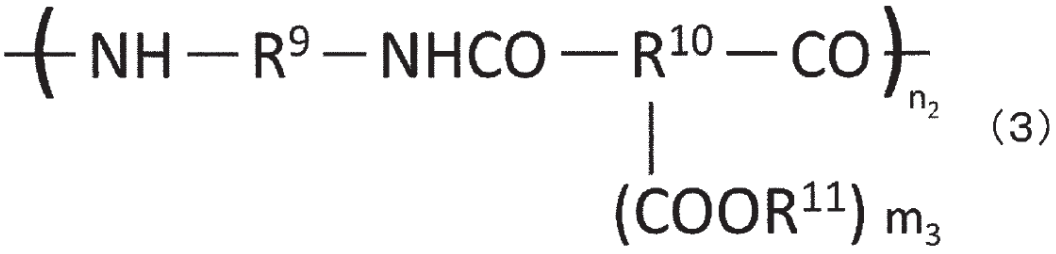
polymerization solvents may be contained. The polymerization solvent is preferably used in an amount of from 100 to 1900 parts by weight, more preferably from 150 to 950 parts by weight, based on 100 parts by weight of the resultant resin. When the amount of the polymerization solvent is within this range, the solution after polymerization has an easily handled viscosity.

[0044]

Examples of the specific structure of the resin in the present invention include the resins listed in the following general formulae (3) to (5).

[0045]

[Chemical Formula 10]



(3)

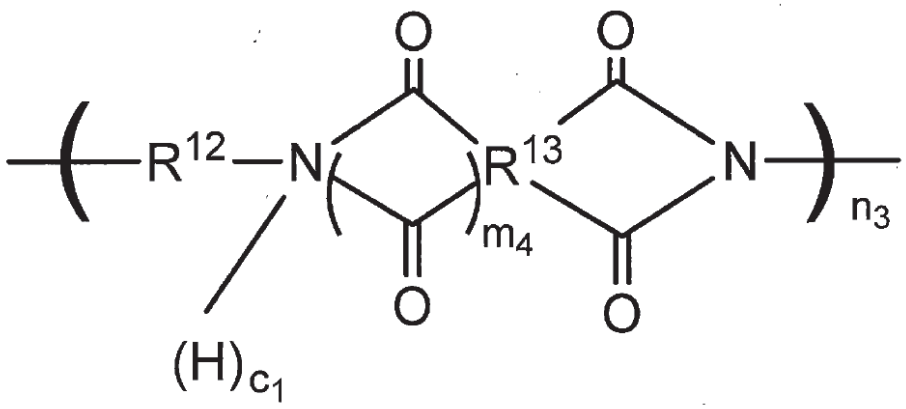
[0046]

(In the general formula (3), R^9 represents a divalent organic group having 2 to 50 carbon atoms. R^{10} represents a trivalent or tetravalent organic group having 2 to 50 carbon atoms. R^9 represents a structure selected from the general formula (1) or the following general formula (6), and/or R^{10} represents a structure selected from the general formula (2) or the following general formula (7). R^{11} represents hydrogen or an organic

group having 1 to 10 carbon atoms. m_3 represents an integer of 1 or 2. n_2 represents a range of 10 to 100,000.)

[0047]

[Chemical Formula 11]



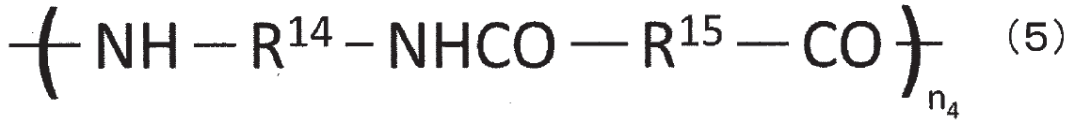
(4)

[0048]

(In the general formula (4), R^{12} represents a divalent organic group having 2 to 50 carbon atoms. R^{13} represents a trivalent or tetravalent organic group having 2 to 50 carbon atoms. R^{12} represents a structure selected from the general formula (1) or the following general formula (6), and/or R^{13} represents a structure selected from the general formula (2) or the following general formula (7). m_4 is an integer of 0 or 1, c_1 is an integer of 0 or 1, $c_1 = 1$ when $m_4 = 0$, and $c_1 = 0$ when $m_4 = 1$. n_3 represents a range of 10 to 100,000.)

[0049]

[Chemical Formula 12]



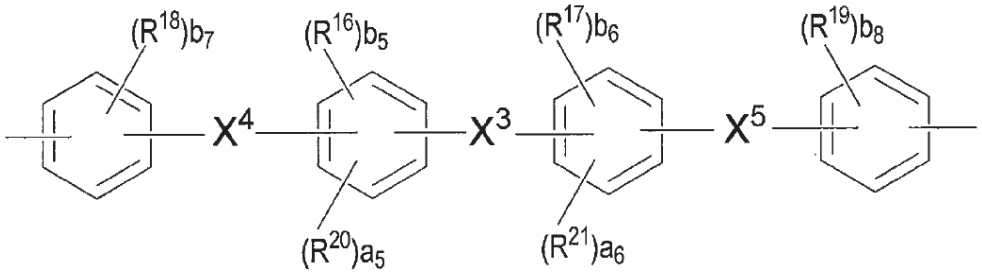
(5)

[0050]

(In the above general formula (5), R^{14} and R^{15} each represent a tetravalent organic group having 2 to 50 carbon atoms, R^{14} and/or R^{15} represents a structure selected from the general formula (1) or the following general formula (6). n_4 represents a range of 10 to 100,000.)

[0051]

[Chemical Formula 13]



(6)

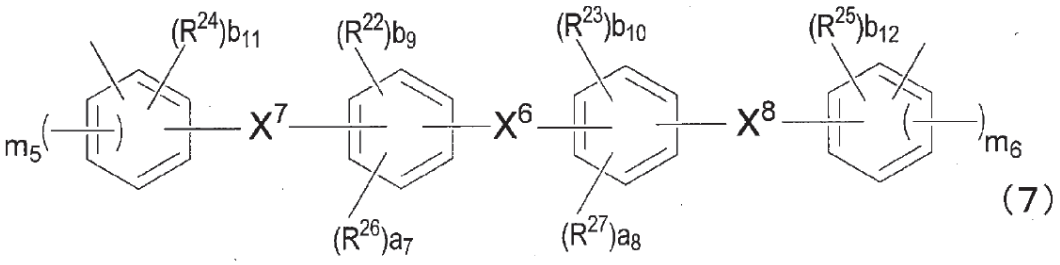
[0052]

(The general formula (6) is a divalent organic group, and R^{16} to R^{19} each independently represent a halogen atom or a monovalent organic group having 1 to 3 carbon atoms. R^{20} and R^{21} each represent an organic group selected from a hydroxyl group, a carboxyl group, and a sulfonic acid group. X^3 is a single bond, O, S, NH, SO_2, CO or a divalent organic group having 1 to 3 carbon atoms or a divalent crosslinked structure formed by linking two or more of these. X^4 and X^5 each represent a

structure selected from an amide bond and an azomethine bond. a_5 is an integer of 1 to 4, b_5 is an integer of 0 to 3, a_6 is an integer of 0 to 4, b_6 is an integer of 0 to 4, b_7 and b_8 are integers of 0 to 4, $a_5 + b_5$ is an integer of 1 to 4, $a_6 + b_6$ is an integer of 0 to 4, and at least one of b_5 and b_6 is an integer of 1 or more.)

[0053]

[Chemical Formula 14]



(7)

[0054]

(The general formula (7) is a trivalent or tetravalent organic group, and R^{22} to R^{25} each independently represent a halogen atom or a monovalent organic group having 1 to 3 carbon atoms. R^{26} and R^{27} each represent an organic group selected from a hydroxyl group, a carboxyl group, and a sulfonic acid group. X^6 is a single bond, O, S, NH, SO_2, CO or a divalent organic group having 1 to 3 carbon atoms or a divalent crosslinked structure formed by linking two or more of these. X^7 and X^8 each represent a structure selected from an amide bond and an azomethine bond. a_7 is an integer of 1 to 4, b_9 is an integer of 0 to 3, a_8 is an integer of 0 to 4, b_{10} is an integer of 0 to 4, b_{11} and b_{12}

are integers of 0 to 3, $a_7 + b_9$ is an integer of 1 to 4, $a_8 + b_{10}$ is an integer of 0 to 4, and at least one of b_9 and b_{10} is an integer of 1 or more. m_5 and m_6 are integers of 0 or 1, and $m_5 + m_6$ is an integer of 1 or 2.)

In the general formulae (3), (4) and (5), R^9, R^{12} and R^{14} each represent a residue of diamine, silylated diamine, or diisocyanate and represent a divalent organic group having 2 to 50 carbon atoms. Among them, an organic group containing an aromatic ring or a cyclic aliphatic group and having 5 to 40 carbon atoms is preferable. Preferred specific examples include 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, bis(3-amino-4-hydroxyphenyl)fluorene, 3,5-diaminobenzoic acid, 3-carboxy-4,4'-diaminodiphenyl ether, 3-sulfonic acid-4,4'-diaminodiphenyl ether, dithiohydroxyphenylenediamine, 3,4'-diaminodiphenyl ether, 4,4'-diamino diphenyl ether, 3,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, 3,4'-diaminodiphenylsulfone, 4,4'-diaminodiphenylsulfone, 3,4'-diaminodiphenylsulfide, 4,4'-diaminodiphenylsulfide, 1,4-bis (4-aminophenoxy)benzene, 1,3-bis (4-aminophenoxy)benzene, benzidine,

m-phenylenediamine, p-phenylenediamine,
1,5-naphthalenediamine, 2,6-naphthalenediamine,
bis(4-aminophenoxyphenyl)sulfone,
bis(3-aminophenoxyphenyl)sulfone,
bis(4-aminophenoxy)biphenyl,
bis{4-(4-aminophenoxy)phenyl}ether,
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, a residue of 9,9-bis(4-aminophenyl)fluorene, residues of compounds in which aromatic rings of these compounds are substituted with alkyl groups or halogen atoms, residues of hydrogenated products of these compounds, and the structures represented by the general formulae (1) and (6). These may be used alone or in combination of two or more.

[0055]

In the general formulae (3) and (4), R^{10} and R^{13} each represent a residue of tetracarboxylic acid, tricarboxylic acid, tetracarboxylic acid dianhydride or tricarboxylic acid anhydride, and a trivalent or tetravalent organic group having 2 to 50 carbon atoms. Among them, an organic group containing

an aromatic ring or a cyclic aliphatic group and having 5 to 40 carbon atoms is preferable. Preferred specific examples include pyromellitic anhydride,

3,3',4,4'-biphenyltetracarboxylic dianhydride,

2,3,3',4'-biphenyltetracarboxylic dianhydride,

2,2',3,3'-biphenyltetracarboxylic dianhydride,

3,3',4,4'-benzophenonetetracarboxylic dianhydride,

2,2',3,3'-benzophenonetetracarboxylic dianhydride,

2,2-bis(3,4-dicarboxyphenyl)propane dianhydride,

2,2-bis(2,3-dicarboxyphenyl)propane dianhydride,

1,1-bis(3,4-dicarboxyphenyl)ethane dianhydride,

1,1-bis(2,3-dicarboxyphenyl)ethane dianhydride,

bis(3,4-dicarboxyphenyl)methane dianhydride,

bis(2,3-dicarboxyphenyl)methane dianhydride,

bis(3,4-dicarboxyphenyl)sulfone dianhydride,

bis(3,4-dicarboxyphenyl)ether dianhydride,

2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride,

2,2-bis(2,3-dicarboxyphenyl)hexafluoropropane dianhydride,

9,9-bis(3,4-dicarboxyphenyl)fluorenic acid dianhydride,

9,9-bis{4-(3,4-dicarboxyphenoxy)phenyl}fluorenic acid dianhydride, 1,2,5,6-naphthalenetetracarboxylic dianhydride,

2,3,6,7-naphthalenetetracarboxylic dianhydride,

3,4,9,10-perylenetetracarboxylic dianhydride,

2,3,5,6-pyridinetetracarboxylic acid dianhydride,

trimellitic anhydride, trimesic anhydride,

diphenylethertricarboxylic acid anhydride, a residue of a biphenyltricarboxylic anhydride, a residue of a compound in which these aromatic rings are substituted with alkyl groups or halogen atoms,
1,2-dimethyl-1,2,3,4-cyclobutanetetracarboxylic acid dianhydride,
1,2,3,4-tetramethyl-1,2,3,4-cyclobutanetetracarboxylic dianhydride, 1,2,4,5-cyclohexane tetracarboxylic dianhydride, 3,4-dicarboxy-1,2,3,4-tetrahydro-1-naphthalene succinic dianhydride,
5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic dianhydride, 2,3,5-tricarboxy-2-cyclopentane acetic acid dianhydride, bicyclo [2.2.2] oct-7-ene-2,3,5,6-tetracarboxylic dianhydride,
2,3,4,5-tetrahydrofuran tetracarboxylic dianhydride, a residue of 3,5,6- tricarboxy-2-norbornane acetic acid dianhydride, and structures represented by the general formulae (2) and (7). These may be used alone or in combination of two or more.

[0056]

From the viewpoint that the linear thermal expansion coefficient of the resultant resin can be reduced, it is preferable that R^{10} and R^{13} contain residues derived from pyromellitic anhydride. Further, from the viewpoint that the absorbance can be reduced while reducing the linear thermal

expansion coefficient, it is more preferable that the contained pyromellitic anhydride is 30 mol% to 80 mol% in acid anhydride.

[0057]

In the general formula (5), R^{15} represents a residue derived from dicarboxylic acid and represents a divalent organic group having 2 to 50 carbon atoms. Specific examples of preferred dicarboxylic acids include terephthalic acid, isophthalic acid, diphenyl ether dicarboxylic acid, naphthalene dicarboxylic acid, bis(carboxyphenyl)propane, bis(carboxyphenyl)hexafluoropropane, biphenyl dicarboxylic acid, benzophenonedicarboxylic acid, residues of aromatic dicarboxylic acids such as terphenydicarboxylic acid, residues of aliphatic dicarboxylic acids such as cyclohexanedicarboxylic acid, adipic acid, sebacic acid, and dodecanedioic acid, or residues of a compound in which these aromatic rings are substituted with alkyl groups or halogen atoms, and the structures represented by the general formulae (1) and (6). These may be used alone or in combination of two or more.

[0058]

In the general formulae (3) and (4), it is preferable that R^9 and R^{12} represent a structure selected from the general formulae (1) and (6), and/or R^{10} and R^{13} represent a structure selected from the general formulae (2) and (7).

[0059]

In the general formula (5), at least one of R^{14} and R^{15} preferably represents the structure selected from the general formulae (1) and (6).

[0060]

In the general formulae (3), (4) and (5), in order to improve adhesion between a heat resistance coating film after heat treatment and a silicon-based substrate or a glass substrate, or in order to increase resistance to oxygen plasma used for cleaning or UV ozone treatment, a siloxane structure may be copolymerized with R^{9}, R^{10}, R^{12}, R^{13} and R^{14} within a range not lowering heat resistance. Specific examples of R^{9}, R^{12} and R^{14} include residues of bis(3-aminopropyl)tetramethyldisiloxane, bis(p-amino-phenyl)octamethylpentasiloxane, and the like. These are preferably copolymerized in an amount of 1 mol% to 10 mol% relative to the whole of R^{9}, R^{12} and R^{14}. Specific examples of R^{10} and R^{13} include residues of dimethylsilanediphthalic acid dianhydride, 1,3-bis(phthalic acid)tetramethyldisiloxane dianhydride, and the like. These may be used alone or in combination of two or more, and it is preferable that 1 mol% to 10 mol% relative to the whole of R^{10} and R^{13} is copolymerized.

[0061]

In the general formulae (3), (4) and (5), in order to improve adhesion between a heat resistance coating film after

heat treatment and a metal substrate, an aliphatic structure having a polyalkyleneoxide group may be copolymerized with R^9, R^{12}, and R^{14} within a range not lowering heat resistance. Examples of specific structures include residues of Jeffamine (registered trademark) KH-511, Jeffamine ED-600, Jeffamine ED-900, Jeffamine ED-2003, Jeffamine EDR-148, Jeffamine EDR-176, Jeffamine D-200, Jeffamine D-400, Jeffamine D-2000, Jeffamine D-4000 (trade names, manufactured by HUNTSMAN Co., Ltd.), and the like. These may be used alone or in combination of two or more, and it is preferable that 1 mol% to 30 mol% relative to the whole of R^9, R^{12}, and R^{14} is copolymerized.

[0062]

In the general formula (3), R^{11} represents hydrogen or an organic group having 1 to 10 carbon atoms. From the viewpoint of stability of the resultant photosensitive resin composition solution, R^{11} is preferably an organic group, but hydrogen is preferable from the viewpoint of solubility of an alkaline aqueous solution. In the present invention, a hydrogen atom and an alkyl group can be mixed. By adjusting the amounts of hydrogen and an organic group in R^{11}, the dissolution rate in an alkaline aqueous solution is changed, so that a photosensitive resin composition having an appropriate dissolution rate can be obtained by this adjustment. In a preferable range, 10 mol% to 90 mol% of each R^{11} is a hydrogen atom. If the carbon number of R^{11} is 20 or less, a sufficient

alkali solubility can be obtained. From the above, it is preferable that R^{11} contains at least one hydrocarbon group having 1 to 20 carbon atoms, and the others are hydrogen atoms. Preferred examples of situations when R^{11} is a hydrocarbon group include a methyl group, an ethyl group, a propyl group, and a butyl group. m_3 represents an integer of 1 or 2. m_3 is preferably 2.

[0063]

In the general formula (4), m_4 is an integer of 0 or 1, c_1 is an integer of 0 or 1, $c_1 = 1$ when $m_4 = 0$, and $c_1 = 0$ when $m_4 = 1$. From the viewpoint that the linear thermal expansion coefficient of the resultant resin can be reduced, it is preferable that $m_4 = 1$ and $c_1 = 0$.

[0064]

The general formula (6) is a divalent organic group, and R^{16} to R^{19} each independently represent a halogen atom or a monovalent organic group having 1 to 3 carbon atoms. From the viewpoint of the heat resistance of the resultant resin, preferred specific examples include, but are not limited to, a methyl group, a methoxy group, an ethyl group, an ethoxy group, a fluoro group, a trifluoromethyl group, a pentafluoroethyl group, a trifluoromethoxy group, and a pentafluoroethoxy group. Further, from the viewpoint that absorbance of the resultant resin can be reduced, a fluoro group, a trifluoromethyl group, a pentafluoroethyl group, a trifluoromethoxy group and a

pentafluoroethoxy group are more preferable, and a trifluoromethyl group and a pentafluoroethyl group are most preferable. Further, from the viewpoint that the absorbance of the resultant resin can be reduced, R^{16} to R^{19} are preferably in the ortho position relative to the polymer chain. Furthermore, from the viewpoint that the linear thermal expansion coefficient of the resultant resin can be reduced, R^{16} to R^{19} are more preferably bonded to positions 2 and 2'.

[0065]

R^{20} and R^{21} each represent an organic group selected from a hydroxyl group, a carboxyl group, and a sulfonic acid group. The organic group is preferably a hydroxyl group. Further, from the viewpoint that the absorbance of the resultant resin can be reduced, R^{20} and R^{21} are preferably in the ortho position relative to the polymer chain.

[0066]

X^3 is a single bond, O, S, NH, SO_2, CO or a divalent organic group having 1 to 3 carbon atoms or a divalent crosslinked structure formed by linking two or more of these. From the viewpoint that the linear thermal expansion coefficient of the resultant resin can be reduced, X^3 is preferably a single bond. X^4 and X^5 each represent a structure selected from an amide bond and an azomethine bond. From the viewpoint that the absorbance of the resultant resin can be reduced, it is preferably an amide bond.

[0067]

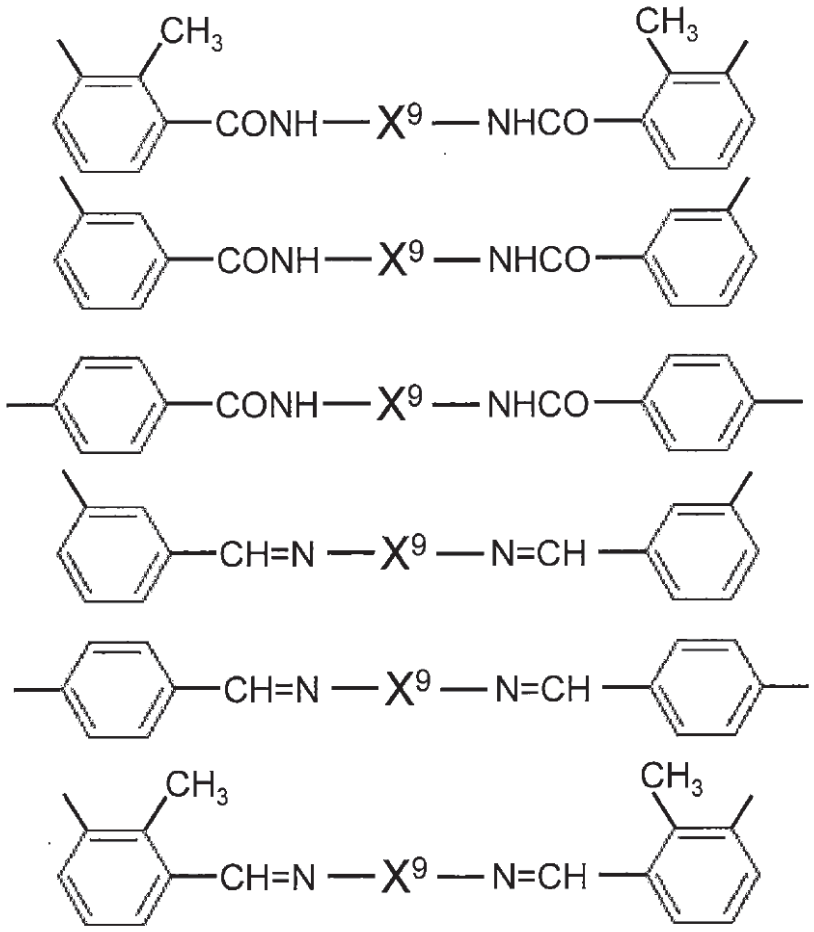
a_5 is an integer of 1 to 4, b_5 is an integer of 0 to 3, a_6 is an integer of 0 to 4, b_6 is an integer of 0 to 4, b_7 and b_8 are integers of 0 to 4, $a_5 + b_5$ is an integer of 1 to 4, $a_6 + b_6$ is an integer of 0 to 4, and at least one of b_5 and b_6 is an integer of 1 or more. From the viewpoint that the linear thermal expansion coefficient of the resultant resin can be reduced, it is preferable that $a_5 = a_6 = 1$, b_5 and b_6 are 1 or 2, and b_7 and b_8 are 0 to 2, it is more preferable that $a_1 = a_2 = b_5 = b_6 = 1$, and b_7 and b_8 are 0 to 2, and it is most preferable that $a_1 = a_2 = b_5 = b_6 = 1$, and $b_7 = b_8 = 0$. Further, from the viewpoint that the linear thermal expansion coefficient of the resultant resin can be reduced, it is preferable that all aromatic rings having a structure represented by the general formula (6) are bonded to a polymer main chain at the para positions.

[0068]

In the present invention, examples of preferred structures represented by the general formula (6) include the following structures, but the structures are not limited thereto.

[0069]

[Chemical Formula 15]



(8)

[0070]

(In the general formula (8), X^9 represents a structure represented by [Chemical Formula 5] to [Chemical Formula 7].)

The general formula (7) is a trivalent or tetravalent organic group, and R^{22} to R^{25} each independently represent a halogen atom or a monovalent organic group having 1 to 3 carbon atoms. From the viewpoint of the heat resistance of the resultant resin, preferred specific examples include a methyl group, a methoxy group, an ethyl group, an ethoxy group, a fluoro group, a trifluoromethyl group, a pentafluoroethyl group, a

trifluoromethoxy group, and a pentafluoroethoxy group, but the present invention is not limited thereto. Further, from the viewpoint that absorbance of the resultant resin can be reduced, a fluoro group, a trifluoromethyl group, a pentafluoroethyl group, a trifluoromethoxy group and a pentafluoroethoxy group are more preferable, and a trifluoromethyl group and a pentafluoroethyl group are most preferable. Further, from the viewpoint that the absorbance of the resultant resin can be reduced, R^{22} to R^{25} are preferably in the ortho position relative to the polymer chain. Furthermore, from the viewpoint that the linear thermal expansion coefficient of the resultant resin can be reduced, R^{22} to R^{25} are more preferably bonded to positions 2 and 2'.

[0071]

R^{26} and R^{27} each represent an organic group selected from a hydroxyl group, a carboxyl group, and a sulfonic acid group. The organic group is preferably a hydroxyl group. Further, from the viewpoint that the absorbance of the resultant resin can be reduced, R^{26} and R^{27} are preferably in the ortho position relative to the polymer chain. X^6 is a single bond, O, S, NH, SO_2, CO or a divalent organic group having 1 to 3 carbon atoms or a divalent crosslinked structure formed by linking two or more of these. From the viewpoint that the linear thermal expansion coefficient of the resultant resin can be reduced, X^6 is preferably a single bond. X^7 and X^8 each represent a

structure selected from an amide bond and an azomethine bond. From the viewpoint that the absorbance of the resultant resin can be reduced, it is preferably an amide bond.

[0072]

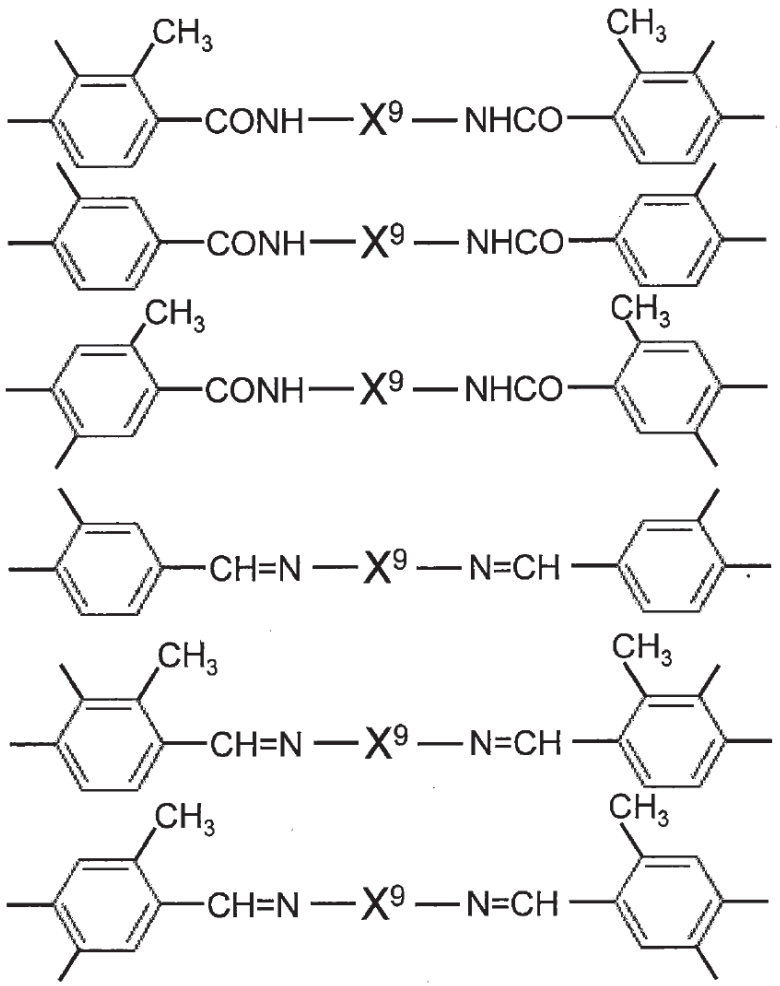
a_7 is an integer of 1 to 4, b_9 is an integer of 0 to 3, a_8 is an integer of 0 to 4, b_{10} is an integer of 0 to 4, b_{11} and b_{12} are integers of 0 to 3, $a_7 + b_9$ is an integer of 1 to 4, $a_8 + b_{10}$ is an integer of 0 to 4, and at least one of b_9 and b_{10} is an integer of 1 or more. From the viewpoint that the linear thermal expansion coefficient of the resultant resin can be reduced, it is preferable that $a_7 = a_8 = 1$, b_9 and b_{10} are 1 or 2, and b_{11} and b_{12} are 0 or 1, it is more preferable that $a_7 = a_8 = b_9 = b_{10} = 1$, and b_{11} and b_{12} are 0 or 1, and it is most preferable that $a_7 = a_8 = b_9 = b_{10} = 1$, and $b_{11} = b_{12} = 0$. m_5 and m_6 are integers of 0 or 1, and $m_5 + m_6$ is an integer of 1 or 2. Preferably, $m_5 = m_6 = 1$.

[0073]

In the present invention, examples of preferred structures represented by the general formula (7) include the following structures, but the structures are not limited thereto.

[0074]

[Chemical Formula 16]



(9)

[0075]

(In the general formula (9), X^9 each independently represents a structure represented by [Chemical Formula 5] to [Chemical Formula 7].)

In the general formulae (3), (4) and (5), n_2, n_3 and n_4 represent a range of 10 to 100,000.

[0076]

In order to further improve adhesion properties between a heat resistance coating film and a substrate after heat

treatment, at least one of both ends of the resin of the present invention may contain a phenol group and/or a thiophenol group. Introduction of an alkali-soluble group to the end can be carried out by imparting the alkali-soluble group to a terminal blocking agent. As the terminal blocking agent, monoamine, acid anhydride, monocarboxylic acid, monoacid chloride compound, monoactive ester compound, or the like can be used.

[0077]

Specific examples of monoamine used as a terminal blocking agent include 5-amino-8-hydroxyquinoline, 4-amino-8-hydroxyquinoline, 1-hydroxy-8-aminonaphthalene, 1-hydroxy-7-aminonaphthalene, 1-hydroxy-6-aminonaphthalene, 1-hydroxy-5-aminonaphthalene, 1-hydroxy-4-aminonaphthalene, 1-hydroxy-3-aminonaphthalene, 1-hydroxy-2-aminonaphthalene, 1-amino-7-hydroxynaphthalene, 2-hydroxy-7-aminonaphthalene, 2-hydroxy-6-aminonaphthalene, 2-hydroxy-5-aminonaphthalene, 2-hydroxy-4-aminonaphthalene, 2-hydroxy-3-aminonaphthalene, 1-amino-2-hydroxynaphthalene, 1-carboxy-8-aminonaphthalene, 1-carboxy-7-aminonaphthalene, 1-carboxy-6-aminonaphthalene, 1-carboxy-5-aminonaphthalene, 1-carboxy-4-aminonaphthalene, 1-carboxy-3-aminonaphthalene, 1-carboxy-2-aminonaphthalene, 1-amino-7-carboxynaphthalene, 2-carboxy-7-aminonaphthalene, 2-carboxy-6-aminonaphthalene, 2-carboxy-5-aminonaphthalene, 2-carboxy-4-aminonaphthalene, 2-carboxy-3-aminonaphthalene, 1-amino-2-carboxynaphthalene, 2-aminonicotinic acid,

4-aminonicotinic acid, 5-aminonicotinic acid,

6-aminonicotinic acid, 4-aminosalicylic acid,

5-aminosalicylic acid, 6-aminosalicylic acid,

3-amino-o-toluic acid, ammelide, 2-aminobenzoic acid,

3-aminobenzoic acid, 4-aminobenzoic acid,

2-aminobenzenesulfonic acid, 3-aminobenzenesulfonic acid,

4-aminobenzenesulfonic acid, 3-amino-4,6-dihydroxypyrimidine,

2-aminophenol, 3-aminophenol, 4-aminophenol,

5-amino-8-mercaptoquinoline, 4-amino-8-mercaptoquinoline,

1-mercapto-8-aminonaphthalene,

1-mercapto-7-aminonaphthalene,

1-mercapto-6-aminonaphthalene,

1-mercapto-5-aminonaphthalene,

1-mercapto-4-aminonaphthalene,

1-mercapto-3-aminonaphthalene,

1-mercapto-2-aminonaphthalene,

1-amino-7-mercaptonaphthalene,

2-mercapto-7-aminonaphthalene,

2-mercapto-6-aminonaphthalene,

2-mercapto-5-aminonaphthalene, 2-

mercapto-4-aminonaphthalene, 2- mercapto-3-aminonaphthalene,

1-amino-2-mercaptonaphthalene,

3-amino-4,6-dimercaptopyrimidine, 2-aminothiophenol,

3-aminothiophenol, and 4-aminothiophenol.

[0078]

Among them, 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, 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-aminobenzenesulfonic acid, 3-aminobenzenesulfonic acid, 4-aminobenzenesulfonic acid, 3-amino-4,6-dihydroxypyrimidine, 2-aminophenol, 3-aminophenol, 4-aminophenol, 2-aminothiophenol, 3-aminothiophenol, 4-aminothiophenol, and the like are preferable. These may be used alone or in combination of two or more.

[0079]

Specific examples of acid anhydride, monocarboxylic acid, monoacid chloride compound, and monoactive ester compound used as a terminal blocking agent include acid anhydrides such as phthalic anhydride, maleic anhydride, nadic acid, cyclohexanedicarboxylic anhydride, and 3-hydroxyphthalic anhydride; monocarboxylic acids such as 2-carboxyphenol, 3-carboxyphenol, 4-carboxyphenol, 2-carboxythiophenol, 3-carboxythiophenol, 4-carboxythiophenol,

1-hydroxy-8-carboxynaphthalene,

1-hydroxy-7-carboxynaphthalene,

1-hydroxy-6-carboxynaphthalene,

1-hydroxy-5-carboxynaphthalene,

1-hydroxy-4-carboxynaphthalene,

1-hydroxy-3-carboxynaphthalene, 1-hydroxy

2-carboxynaphthalene, 1-mercapto-8-carboxynaphthalene,

1-mercapto-7-carboxynaphthalene,

1-mercapto-6-carboxynaphthalene,

1-mercapto-5-carboxynaphthalene,

1-mercapto-4-carboxynaphthalene,

1-mercapto-3-carboxynaphthalene,

1-mercapto-2-carboxynaphthalene, 2-carboxybenzenesulfonic acid, 3-carboxybenzenesulfonic acid, and 4-carboxybenzenesulfonic acid, and monoacid chloride compounds with the carboxyl group of the monocarboxylic acid formed into an acid chloride; monoacid chloride compounds with only a monocarboxyl group of dicarboxylic acids such as terephthalic acid, phthalic acid, maleic acid, cyclohexanedicarboxylic acid, 3-hydroxyphthalic acid, 5-norbornene-2,3-dicarboxylic acid, 1,2-dicarboxynaphthalene, 1,3-dicarboxynaphthalene, 1,4-dicarboxynaphthalene, 1,5-dicarboxynaphthalene, 1,6-dicarboxynaphthalene, 1,7-dicarboxynaphthalene, 1,8-dicarboxynaphthalene, 2,3-dicarboxynaphthalene, 2,6-dicarboxynaphthalene, and

2,7-dicarboxynaphthalene formed into an acid chloride; and active ester compounds obtained by reaction of a monoacid chloride compound with N-hydroxybenzotriazole and N-hydroxy-5-norbornene-2,3-dicarboxyimide.

[0080]

Among them, acid 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-carboxybenzenesulfonic acid and 4-carboxybenzenesulfonic acid, and monoacid chloride compounds with the carboxyl group of the monocarboxylic acid formed into an acid chloride; monoacid chloride compounds with only a monocarboxyl group of 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 formed into an acid chloride; and active ester compounds obtained by reaction of a monoacid

chloride compound with N-hydroxybenzotriazole and N-hydroxy-5-norbornene-2,3-dicarboxyimide are preferable. These may be used alone or in combination of two or more.

[0081]

The content of the terminal sealing agent such as the monoamine, acid anhydride, acid chloride or monocarboxylic acid described above, is preferably within a range of 0.1 mol% to 70 mol%, more preferably from 5 mol% to 50 mol%, of the number of moles of the charged acid component monomer or the charged diamine component monomer. By adjusting the content to such a range, a resin composition that is moderate in viscosity of its solution when applying the resin composition and that has superior film properties can be obtained.

[0082]

The resin may also have a polymerizable functional group at its end. Examples of the polymerizable functional group include an ethylenically unsaturated linking group, an acetylene group, a methylol group, and an alkoxymethyl group. When a reaction is carried out by selectively combining diamine or tetracarboxylic acid dianhydride in the various known synthesis methods described above, a resin having a terminal blocking agent can be obtained by adding the terminal blocking agent at the same time as them, or slightly thereafter.

[0083]

The resin of the present invention is characterized by

low absorbance. The absorbance at a wavelength of 365 nm per 1 μm thickness of a resin film formed of the resin of the present invention is preferably 0.005 or more and 0.3 or less, more preferably 0.008 or more and 0.2 or less, most preferably 0.01 or more and 0.1 or less. If the absorbance is 0.3 or less, when used for a photosensitive resin composition, energy loss can be reduced by suppressing absorption of the resin itself, and if the absorbance is 0.005 or more, poor pattern formation due to optical reflection from a substrate does not occur. In the case of polyimide represented by the general formula (4), for example, the absorbance is set by selecting the structures of R^{12} and R^{13} and adjusting the copolymerization ratio. The resin having such characteristics can be preferably used from the viewpoint of enhancing photosensitive performance, particularly when a photosensitive resin composition is formed, particularly sensitivity.

[0084]

The resin film preferably has a film thickness reduction rate of 10 nm/min or more and 30,000 nm/min or less when immersed in a 2.38% tetramethylammonium hydroxide aqueous solution. The film thickness reduction rate is more preferably 50 nm/min or more and 20000 nm/min or less, most preferably 100 nm/min or more and 15000 nm/min or less. If the film thickness reduction rate is 30000 nm/min or less, developability of the resin increases to such an extent that poor pattern formation

does not occur when the resin is used in a photosensitive resin composition, and if the film thickness reduction rate is 10 nm/min or more, it is possible to impart solubility capable of obtaining a relief pattern by development. In the case of a polyimide precursor represented by the general formula (3), for example, the film thickness reduction rate is set by, for example, selecting the structures of R^9 and R^{10}, adjusting the copolymerization ratio, adjusting the proportion of hydrogen in R^{11}, or changing n_2n_1 and adjusting a molecular weight. The resin having such characteristics can be preferably used from the viewpoint of enhancing photosensitive performance, particularly when a photosensitive resin composition is formed, particularly sensitivity. The term "resin film" used herein refers to a film having a thickness of 3 μm to 10 μm and obtained by applying a γ-butyrolactone solution (resin concentration: 40%) of a resin to a "Pyrex (registered trademark)" glass substrate and baking it on a hotplate (manufactured by Dainippon Screen Mfg. Co., SKW-636) at 120°C for 2 to 4 minutes.
[0085]

An average linear thermal expansion coefficient at 50 to 200°C measured after heat-treating the resin of the present invention at 250°C is preferably -10 to 40 ppm/°C, more preferably 0 to 30 ppm/°C, further preferably 1 to 25 ppm/°C, and most preferably 3 to 20 ppm/°C. If this average linear thermal expansion coefficient is larger or smaller than this

range, there is a possibility that a difference in thermal expansion coefficient from a substrate becomes large, stress caused by the resin applied to the device becomes large, and the yield at the time of device manufacturing and reliability of a product are adversely affected. In the case of polyimide represented by the general formula (4), for example, the average linear thermal expansion coefficient is set by selecting the structures of R^{12} and R^{13} and adjusting the copolymerization ratio. A resin having such characteristics can be preferably used from the viewpoint that warpage of the device can be reduced.

[0086]

More preferably, the resin of the present invention is precipitated in a poor solvent to the resin, such as methanol or water, after completion of polymerization, followed by washing and drying. Reprecipitation makes it possible to remove esterification agents, condensation agents, by-products of acid chloride, low molecular weight components of resin precursors and the like used at the time of polymerization so that it is advantageously possible to significantly improve mechanical properties after heat curing of a resin composition.

[0087]

The resin composition of the present invention may contain a solvent in the resin of the present invention and,

if necessary, additives for functionalization. Specific examples of the solvent preferably used in the resin composition of the present invention include ethers such as ethyleneglycolmonomethylether, ethyleneglycolmonoethylether, propylene glycol monomethyl ether, propyleneglycolmonoethylether, ethyleneglycoldimethylether, ethyleneglycoldiethylether, ethyleneglycoldibutyletherr, diethyleneglycoldiethylether, diethyleneglycoldimethylether and diethyleneglycolmethylethylether; acetates such as ethyleneglycolmonomethyletheracetate, propyleneglycolmonomethyletheracetate, propyl acetate, butyl acetate, isobutyl acetate, 3-methoxybutyl acetate, 3-methyl-3-methoxybutyl acetate, methyl lactate, ethyl lactate, and butyl lactate; ketones such as acetylacetone, methyl propyl ketone, methyl butyl ketone, methyl isobutyl ketone, cyclopentanone, and 2-heptanone; alcohols such as butyl alcohol, isobutyl alcohol, pentanol, 4-methyl-2-pentanol, 3-methyl-2-butanol, 3-methyl-3-methoxybutanol, and diacetone alcohol; aromatic hydrocarbons such as toluene and xylene; N-methyl-2-pyrrolidone, N-cyclohexyl-2-pyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, dimethyl sulfoxide, and γ-butyrolactone. These can be used alone or in admixture thereof.

[0088]

The resin composition of the present invention may

contain an alkali-soluble resin other than the resin of the present invention. Specific examples thereof include acrylic polymers copolymerized with acrylic acid, phenol resins, siloxane resins, polyhydroxystyrene resins, resins obtained by introducing crosslinking groups such as a methylol group, an alkoxymethyl group and an epoxy group into them, and copolymers thereof. Preferred are phenol resins, polyhydroxystyrene resins, resins obtained by introducing crosslinking groups such as methylol groups, alkoxymethyl groups, and epoxy groups into them, and copolymers thereof. Such a resin is a substance that is soluble in an aqueous solution of an alkali, such as tetramethylammonium hydroxide, choline, triethylamine, dimethylaminopyridine, monoethanolamine, diethylaminoethanol, sodium hydroxide, potassium hydroxide, and sodium carbonate. Inclusion of these alkali-soluble resins enables imparting of properties of each alkali-soluble resin while maintaining adhesion of a heat resistance coating film and excellent sensitivity.

[0089]

Preferred phenolic resins include novolak resins and resol resins, which can be obtained by polycondensing various phenols alone or a mixture of a plurality of these phenols with aldehydes such as formalin.

[0090]

Examples of the phenols constituting the novolac resin

and the resol resin include phenol, p-cresol, m-cresol, o-cresol, 2,3-dimethylphenol, 2,4-dimethylphenol, 2,5-dimethylphenol, 2,6-dimethylphenol, 3,4-dimethylphenol, 3,5-dimethylphenol, 2,3,4-trimethylphenol, 2,3,5-trimethylphenol, 3,4,5-trimethylphenol, 2,4,5-trimethylphenol, methylenebisphenol, methylenebis p-cresol, resorcin, catechol, 2-methylresorcin, 4-methylresorcin, o-chlorophenol, m-chlorophenol, p-chlorophenol, 2,3-dichlorophenol, m-methoxyphenol, p-methoxyphenol, p-butoxyphenol, o-ethylphenol, m-ethylphenol, p-ethylphenol, 2,3-diethylphenol, 2,5-diethylphenol, p-isopropylphenol, α-naphthol, and β-naphthol, and these can be used alone or as a mixture of two or more.

[0091]

In addition to formalin, examples of aldehydes include paraformaldehyde, acetaldehyde, benzaldehyde, hydroxybenzaldehyde, and chloroacetaldehyde, which can be used alone or as a mixture of two or more.

[0092]

The phenol resin used in the present invention may have a structure in which one to four hydrogen atoms added to an aromatic ring are partially substituted with an alkyl group having 1 to 20 carbon atoms, a fluoroalkyl group, an alkoxyl group, an ester group, a nitro group, a cyano group, a fluorine

atom, or a chlorine atom.

[0093]

The weight average molecular weight of the phenol resin used in the present invention is within a range of 2,000 to 50,000, preferably a range of 3,000 to 30,000 in terms of polystyrene using gel permeation chromatography (GPC). When the molecular weight is 2,000 or more, it is excellent in pattern shape, resolution, developability and heat resistance, and when the molecular weight is 50,000 or less, sufficient sensitivity can be maintained.

[0094]

Preferable examples of the polyhydroxystyrene resin include polymers or copolymers, obtained by polymerizing by a known method at least one of aromatic vinyl compounds having a phenolic hydroxyl group, such as p-hydroxystyrene, m-hydroxystyrene, o-hydroxystyrene, p-isopropenylphenol, m-isopropenylphenol, and o-isopropenylphenol, and polymers or copolymers obtained by adding and reacting by a known method an alkoxy group to/with a portion of polymers or copolymers obtained by polymerizing by a known method at least one of aromatic vinyl compounds such as styrene, o-methylstyrene, m-methylstyrene, and p-methylstyrene.

[0095]

As the aromatic vinyl compound having a phenolic hydroxyl group, p-hydroxystyrene and/or m-hydroxystyrene are/is

preferably used, and as the aromatic vinyl compound, styrene is preferably used.

[0096]

The polyhydroxystyrene resin used in the present invention may have a structure in which one to four hydrogen atoms added to an aromatic ring are partially substituted with an alkyl group having 1 to 20 carbon atoms, a fluoroalkyl group, an alkoxyl group, an ester group, a nitro group, a cyano group, a fluorine atom, or a chlorine atom.

[0097]

The weight average molecular weight of the polyhydroxystyrene resin used in the present invention is preferably within a range of 3,000 to 60,000, more preferably a range of 3,000 to 25,000 in terms of polystyrene using gel permeation chromatography (GPC). When the molecular weight is 3,000 or more, it is excellent in pattern shape, resolution, developability and heat resistance, and when the molecular weight is 60,000 or less, sufficient sensitivity can be maintained.

[0098]

The content of such a phenolic resin or polyhydroxystyrene resin in the resin composition is from 5 to 50 parts by weight, preferably from 10 to 40 parts by weight, based on 100 parts by weight of the resin of the present invention. If the content is 40 parts by weight or less, the heat resistance

and strength of the heat resistance coating film after heat treatment can be maintained, whereas if the content is 10 parts by weight or more, the pattern formability of the resin film is improved.

[0099]

The resin composition of the present invention may contain a photo acid generator and can impart positive type photosensitivity. Although examples of the photo acid generator include a quinone diazide compound, a sulfonium salt compound, a phosphonium salt compound, a diazonium salt compound, and an iodonium salt compound, the quinone diazide compound is preferable, and an o-quinonediazide compound is particularly preferable. Examples of the quinonediazide compound include a compound in which the sulfonic acid of quinone diazide has been bonded to a polyhydroxy compound via an ester, a compound in which the sulfonic acid of quinone diazide has been sulfonamide-bonded to a polyamino compound, and a compound in which the sulfonic acid of quinone diazide has been ester-bonded and/or sulfonamide-bonded to a polyhydroxypolyamino compound. Although all functional groups of these polyhydroxy compounds and polyamino compounds may not be substituted with quinone diazide, it is preferable that 50 mol% or more of the whole functional groups have been substituted with quinone diazide. When 50 mol% or more is substituted with quinone diazide, solubility of the resin film

in an alkaline developer becomes satisfactory, and it is advantageously possible to obtain a fine pattern with high contrast with an unexposed portion. By using such a quinonediazide compound, it is possible to obtain a resin composition having positive photosensitivity to the i-line (365 nm), h-line (405 nm), and g-line (436 nm) of mercury lamps, which are commonly used ultraviolet rays.

[0100]

Examples of the polyhydroxy compound include, but are not limited to, Bis-Z, BisP-EZ, TekP-4HBPA, TrisP-HAP, TrisP-PA, TrisP-SA, TrisOCR-PA, BisOCHP-Z, BisP-MZ, BisP-PZ, BisP-IPZ, BisOCP-IPZ, BisP-CP, BisRS-2P, BisRS-3P, BisP-OCHP, methylenetris-FR-CR, BisRS-26X, DML-MBPC, DML-MBOC, DML-OCHP, DML-PCHP, DML-PC, DML-PTBP, DML-34X, DML-EP, DML-POP, dimethylol-BisOC-P, DML-PFP, DML-PSBP, DML-MTrisPC, TriML-P, TriML-35XL, TML-BP, TML-HQ, TML-pp-BPF, TML-BPA, TMOM-BP, HML-TPPHBA, and HML-TPHAP (trade names, each produced 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, 46DMOC, 46DMOEP, and TM-BIP-A (trade names, each produced by Asahi Organic Chemicals Industry Co., Ltd.); 2,6-dimethoxymethyl-4-t-butylphenol, 2,6-dimethoxymethyl-p-cresol, 2,6-diacetoxymethyl-p-cresol, naphthol, tetrahydroxybenzophenone, gallic acid methyl ester, bisphenol A, bisphenol E, and methylene bisphenol; and BisP-AP

(trade name, produced by Honshu Chemical Industry Co., Ltd.).

[0101]

Examples of the polyamino compound include, but are not limited to, 1,4-phenylenediamine, 1,3-phenylenediamine, 4,4′-diaminodiphenylether, 4,4′-diaminodiphenylmethane, 4,4′-diaminodiphenylsulfone, and 4,4′-diaminodiphenyl sulfide. Examples of the polyhydroxypolyamino compound include, but are not limited to, 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane, and 3,3′-dihydroxybenzidine.

[0102]

In the present invention, both a 5-naphthoquinonediazidesulfonyl group and a 4-naphthoquinonediazidesulfonyl group are preferably used in quinonediazide. A 4-naphthoquinonediazide sulfonyl ester compound is suitable for i-line exposure because it has an absorption in the i-line region of a mercury lamp. A 5-naphthoquinonediazide sulfonyl ester compound is suitable for g-line exposure because it has an absorption extending to the g-line region of a mercury lamp. In the present invention, it is preferable to choose a 4-naphthoquinonediazide sulfonyl ester compound and a 5-naphthoquinonediazide sulfonyl ester compound depending upon the wavelength of light to be applied. A naphthoquinonediazide sulfonyl ester compound that uses both a 4-naphthoquinone diazide sulfonyl group and a

5-naphthoquinone diazide sulfonyl group in the same molecule can be obtained, and both a 4-naphthoquinonediazide sulfonyl ester compound and a 5-naphthoquinonediazide sulfonyl ester compound can be used together.

[0103]

The molecular weight of a quinonediazide compound is preferably 300 or more, more preferably 350 or more. The molecular weight of the quinonediazide compound is preferably 1500 or less, and more preferably 1200 or less. If the molecular weight is 300 or more, exposure sensitivity becomes high. If the molecular weight is 1500 or less, there is an advantage that the mechanical properties of the heat resistance coating film after heat treatment are improved.

[0104]

The content of the photo acid generator is preferably 1 part by weight or more, more preferably 3 parts by weight or more, based on 100 parts by weight of the resin as the whole resin composition. The content of the photo acid generator is preferably 50 parts by weight or less, more preferably 40 parts by weight or less. In the case of a quinonediazide compound, the content is preferably 1 part by weight or more, more preferably 3 parts by weight or more, based on 100 parts by weight of the resin. The content of the photo acid generator is preferably 50 parts by weight or less, more preferably 40 parts by weight or less. Within this range, there is an advantage

that the mechanical properties of the heat resistance coating film after heat treatment are improved.

[0105]

The quinonediazide compound used in the present invention is synthesized from a specific phenol compound by the following method. For example, there is a method of reacting 5-naphthoquinonediazide sulfonyl chloride and a phenol compound in the presence of triethylamine. As a method of synthesizing a phenol compound, there is a method of reacting an α-(hydroxyphenyl)styrene derivative with a polyhydric phenol compound under an acid catalyst.

[0106]

Since the heat resistance coating film after heat treatment obtained from the resin composition of the present invention is used as a permanent film, it is environmentally undesirable that phosphorus and the like remain, since color tone of the film also needs to be taken into consideration, among the examples of photoacid generators, the sulfonium salt compound, phosphonium salt compound, and diazonium salt compound are preferable, and sulfonium salts are preferably used. Especially preferred are triarylsulfonium salts.

[0107]

In the resin composition of the present invention, in order to impart negative photosensitivity, as R^{11} in the general formula (3), there can be used a group having an ethylenically

saturated double bond such as an ethylmethacrylate group, an ethyl acrylate group, a propylmethacrylate group, a propyl acrylate group, an ethyl methacrylamide group, a propylmethacrylamide group, an ethylacrylamide group, and a propylacrylamide group. In addition, in order to improve the photosensitive performance of the resin composition, it is preferable to include a photopolymerizable compound. Examples of the photopolymerizable compound include, but are not limited to, 2-hydroxyethyl methacrylate, trimethylolpropane trimethacrylate, trimethylolpropane triacrylate, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, propylene glycol dimethacrylate, methylenebismethacrylamide, and methylenebisacrylamide. The photopolymerizable compound is preferably contained in a range of 1 to 30 parts by weight based on 100 parts by weight of the resin. Within this range, a composition which has high sensitivity and in which the mechanical properties of the film after thermal curing is satisfactory is provided. These photopolymerizable compounds can be used alone or in combination of two or more.

[0108]

When negative photosensitivity is imparted to the resin composition of the present invention, a photopolymerization initiator may be contained. Examples of the

photopolymerization initiator suitable for the present invention include, but are not limited to, aromatic amines such as N-phenyldiethanolamine and N-phenylglycine, aromatic ketones such as Michler's ketone, cyclic oxime compounds typified by 3-phenyl-5-isoxazolone, chain oxime compounds typified by 1-phenylpropanedione-2-(o-ethoxycarbonyl)oxime, benzophenone derivatives such as benzophenone, o-benzoyl methyl benzoate, dibenzyl ketone, and fluorenone, and thioxanthone derivatives such as thioxanthone, 2-methylthioxanthone, and 2-isopropylthioxanthone.

[0109]

The content of the photopolymerization initiator is preferably 0.01 parts by weight or more, more preferably 0.1 parts by weight or more, based on 100 parts by weight of the resin. The content of the photopolymerization initiator is preferably 30 parts by weight or less, more preferably 20 parts by weight or less. Within this range, a composition which has high sensitivity and in which the mechanical properties of the film after thermal curing is satisfactory is provided. These photopolymerization initiators can be used alone or in combination of two or more.

[0110]

In order to further improve negative photosensitive characteristics, it is more preferable to contain a photosensitizer. Examples of the photosensitizer suitable for

the present invention include aromatic monoazide such as azidoanthraquinone and azidobenzalacetophenone, aminocoumarins such as 7-diethylaminobenzoyl coumarin and 3,3'-carbonylbis(diethylaminocoumarin), aromatic ketones such as benzanthrone and phenanthrenequinone, and those generally used in photo-curable resins. In addition, those which are used as a charge transfer agent of an electrophotographic photoreceptor can also be preferably used.

[0111]

The content of the photosensitizer is preferably 0.01 parts by weight, more preferably 0.1 parts by weight or more, based on 100 parts by weight of the resin. The content of the photosensitizer is preferably 30 parts by weight or less, more preferably 20 parts by weight or less. Within this range, the sensitivity is high, and the mechanical properties of the heat resistance coating film after heat treatment are improved. These photosensitizers can be used alone or in combination of two or more.

[0112]

The resin composition of the present invention may contain a compound having a phenolic hydroxyl group for the purpose of controlling an alkali developing property of the resin film formed from the resin composition. Examples of the compound with a phenolic hydroxyl group which can be used in the present invention include 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, BisOFP-Z, BisRS-2P, BisPG-26X, BisRS-3P, BisOC-OCHP, BisPC-OCHP, Bis25X-OCHP, Bis26X-OCHP, BisOCHP-OC, Bis236T-OCHP, methylene tris-FR-CR, BisRS-26X, and BisRS-OCHP (trade names, produced by Honshu Chemical Industry Co., Ltd.); and BIR-OC, BIP-PC, BIR-PC, BIR-PTBP, BIR-PCHP, BIP-BIOC-F, 4PC, BIR-BIPC-F, and TEP-BIP-A (trade names, produced by Asahi Organic Chemicals Industry Co., Ltd.).

[0113]

Among them, examples of preferred compounds having a phenolic hydroxyl group include Bis-Z, BisP-EZ, TekP-4HBPA, TrisP-HAP, TrisP-PA, BisOCHP-Z, BisP-MZ, BisP-PZ, BisP-IPZ, BisOCP-IPZ, BisP-CP, BisRS-2P, BisRS-3P, BisP-OCHP, methylene tris-FR-CR, BisRS-26X, BIP-PC, BIR-PC, BIR-PTBP, and BIR-BIPC-F. Among them, particularly preferred compounds having a phenolic hydroxyl group are Bis-Z, TekP-4HBPA, TrisP-HAP, TrisP-PA, BisRS-2P, BisRS-3P, BIR-PC, BIR-PTBP, and BIR-BIPC-F. By adding the compound having a phenolic hydroxy group, the resultant resin composition can easily be dissolved in an alkaline developer before exposure and hardly dissolved in the alkaline developer after exposure, leading to decreased film reduction due to development and easily accomplishing development within a short period of time. The content of such

a compound having a phenolic hydroxyl group is preferably from 1 to 60 parts by weight, more preferably from 3 to 50 parts by weight, based on 100 parts by weight of the resin.

[0114]

The resin composition of the present invention may contain a heat-crosslinker. Examples of the heat-crosslinker include a methylol compound, a methoxymethylol compound, a urea compound, an epoxy compound, and an oxetane compound, but any compound can be preferably used. Specific examples of a heat-crosslinker include: as those having one of such a thermally crosslinkable group, ML-26X, ML-24X, ML-236TMP, 4-methylol 3M6C, ML-MC, and ML-TBC (trade names, produced by Honshu Chemical Industry Co., Ltd.), and P-a type benzoxazine (trade name, produced by Shikoku Chemicals Corp.); as those having two or more of such thermally crosslinkable groups, DM-BI25X-F, 46DMOC, 46DMOIPP, 46DMOEP, and TM-BIP-A (trade names, produced by Asahi Organic Chemicals Industry Co., Ltd.), DML-MBPC, DML-MBOC, DML-OCHP, DML-PC, DML-PCHP, DML-PTBP, DML-34X, DML-EP, DML-POP, DML-OC, dimethylol-Bis-C, dimethylol-BisOC-P, DML-BisOC-Z, DML-BisOCHP-Z, DML-PFP, DML-PSBP, DML-MB25, DML-MTrisPC, DML-Bis25X-34XL, and DML-Bis25X-PCHP, 2,6-dimethoxymethyl-4-t-butylphenol, 2,6-dimethoxymethyl-p-cresol, 2,6-diacetoxymethyl-p-cresol, TriML-P, TriML-35XL, TriML-TrisCR-HAP, TML-BP, TML-HQ, TML-pp-BPF, TML-BPA, TMOM-BP, HML-TPPHBA, HML-TPHAP,

HMOM-TPPHBA, and HMOM-TPHAP (trade names, produced by Honshu Chemical Industry Co., Ltd.), Nikalac (registered trademark) MX-290, Nikalac MX-280, Nikalac MX-270, Nikalac MW-390, and Nikalac MW-100LM (trade names, produced by Sanwa Chemical Co., Ltd.), B-a type benzoxazine and B-m type benzoxazine (trade names, produced by Shikoku Chemicals Corp.), Epolight 40E, Epolight 100E, Epolight 200E, Epolight 400E, Epolight 70P, Epolight 200P, Epolight 400P, Epolight 1500NP, Epolight 80MF, Epolight 4000, and Epolight 3002 (trade names, produced by Kyoeisha Chemical Co., Ltd.), Denacol (registered trademark) EX-212L, Denacol EX-214L, Denacol EX-216L, Denacol EX-850L and Denacol EX-321L (trade names, produced by Nagase ChemteX Corporation), GAN, GOT, NC3000, EPPN502H, and NC3000 (trade names, produced by Nippon Kayaku Co.,Ltd.), jER (registered trademark) 828, jER1002, jER1750, jER1007, jERYX8100-BH30, jER1256, jER4250, and jER4275 (trade names, produced by Mitsubishi Chemical Corporation), EPICLON (registered trademark) EXA-9583, EPICLON HP4032, EPICLON N695, and EPICLON HP7200 (trade names, produced by Dainippon Ink and Chemicals Inc.), TEPIC (registered trademark) S, TEPIC G, and TEPIC P (trade names, produced by Nissan Chemical Industries, Ltd.), ETERNACOLL (registered trademark) EHO, ETERNACOLL OXBP, ETERNACOLL OXTP, and ETERNACOLL OXMA (trade names, produced by Ube Industries, Ltd.), and oxetane-modified phenol novolac.

[0115]

In particular, a methoxymethylol compound is preferably used from the standpoint of standing stability after exposure. When these heat-crosslinkers are contained, a film in which the shrinkage after curing is small and which has high dimensional reproducibility is obtained. When the composition is photosensitive, it is hardly dissolved in an alkali developer before exposure and easily dissolved in the alkali developer after exposure, so that there are advantages that film reduction due to development is small, and development can be accomplished within a short period of time. The content of the heat-crosslinker is preferably 0.5 parts by weight or more, more preferably 3 parts by weight or more, and on the other hand, preferably 50 parts by weight or less, more preferably 40 parts by weight or less, based on 100 parts by weight of the resin. Within this range, there is an advantage that the chemical resistance of the composition is improved.

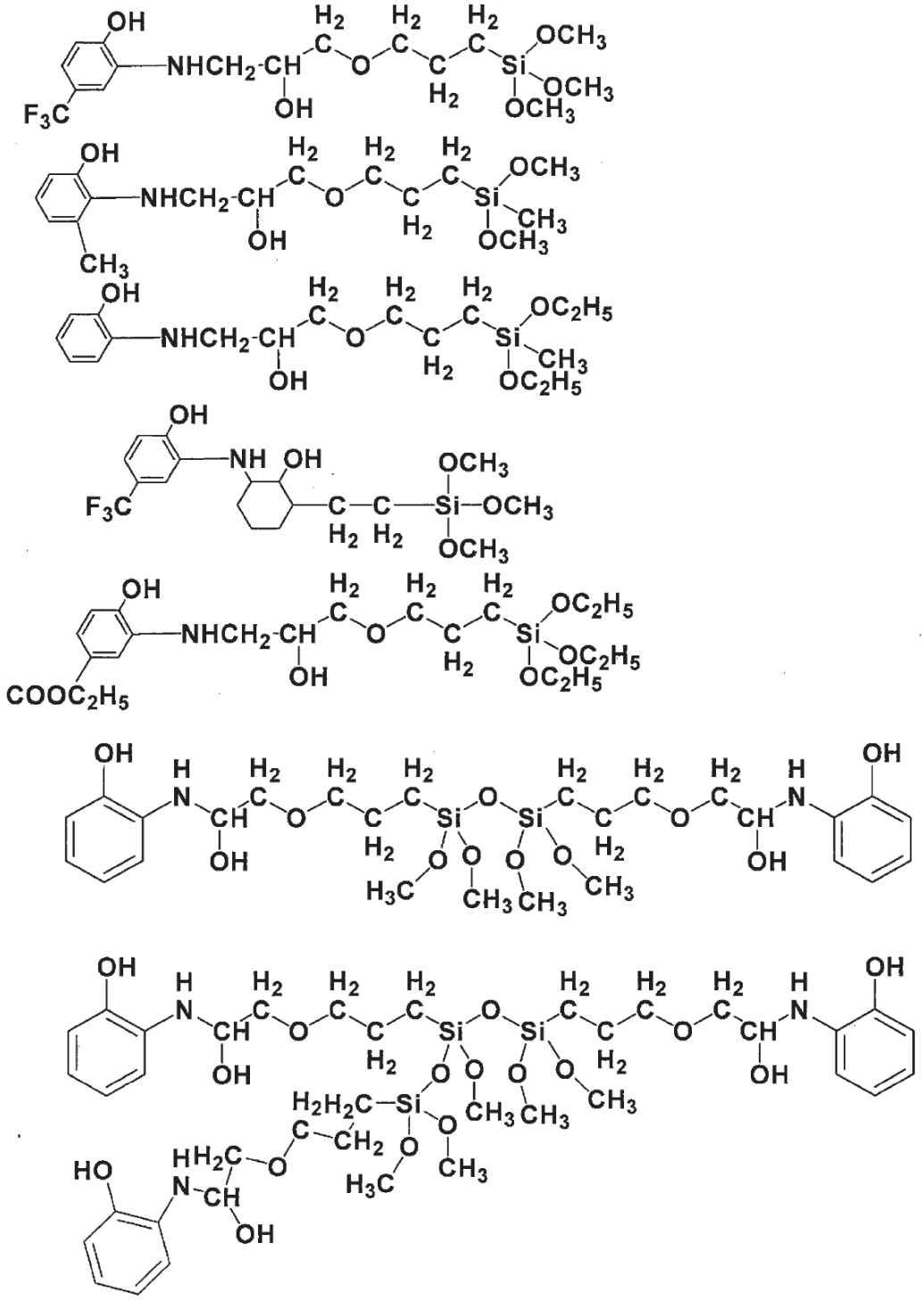
[0116]

In order to further improve adhesion between the heat resistance coating film after heat treatment and a silicon-based substrate, such as silicon, silicon nitride, silicon oxide, and phosphorus silicate glass, an ITO substrate, and various metal substrates or to enhance resistance to oxygen plasma used for cleaning and the like and UV ozone treatment, the resin composition of the present invention may contain adhesion promoters such as a silane coupling agent, a titanium

chelating agent, an aluminum chelating agent, an alkoxysilane-containing aromatic amine compound, and an aromatic amide compound. Preferred specific examples of silane coupling agents include N-phenylaminoethyltrimethoxysilane, N-phenylaminoethyltriethoxysilane, N-phenylaminopropyltrimethoxysilane, N-phenylaminopropyltriethoxysilane, N-phenylaminobutyltrimethoxysilane, N-phenylaminobutyltriethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, vinyltrichlorosilane, vinyltris(β-methoxyethoxy)silane, 3-methacryloxypropyltrimethoxysilane, 3-acrylroxypropyltrimethoxysilane, p-styryltrimethoxysilane, 3-methacryloxypropylmethyldimethoxysilane, and 3-methacryloxypropylmethyldiethoxysilane. Preferred specific examples of alkoxysilane-containing aromatic amine compounds and aromatic amide compounds are provided below. In addition, compounds obtainable by reacting an aromatic amine compound with an alkoxy group-containing silicon compound can also be used, and examples thereof include compounds obtainable by reacting an aromatic amine compound with an alkoxysilane compound having a group that reacts with an amino group, such as an epoxy group and a chloromethyl group.

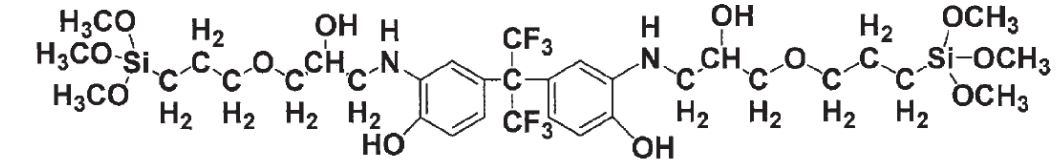
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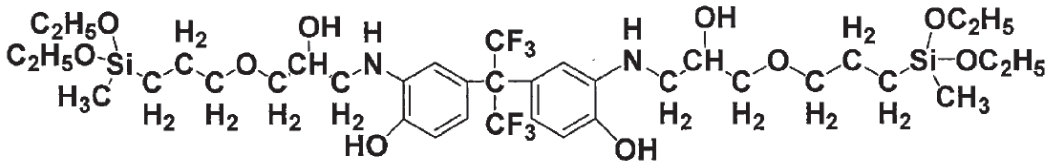
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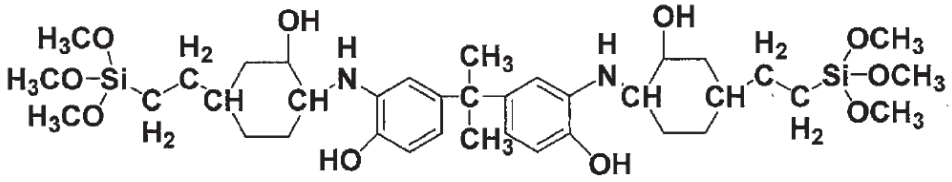


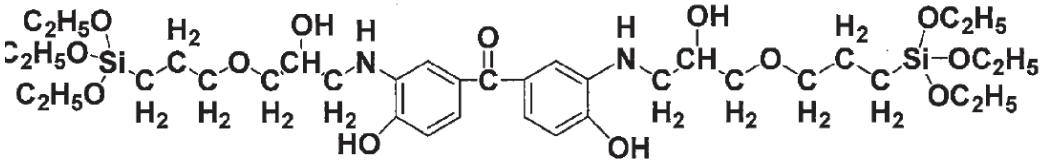
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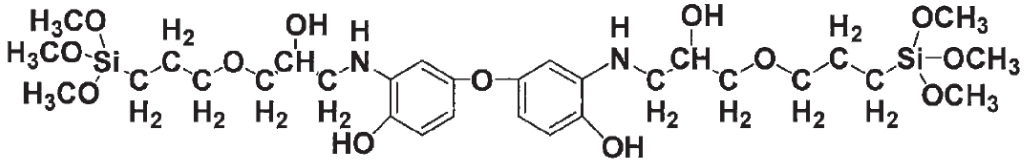
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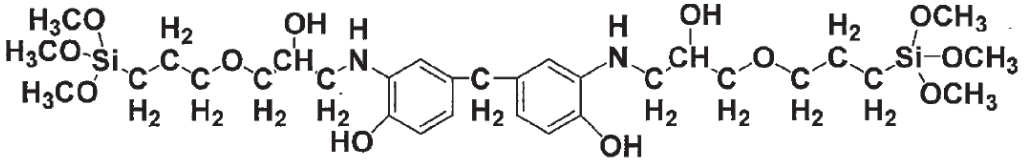


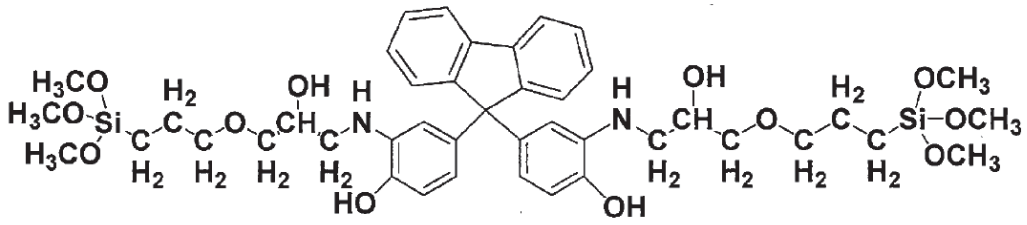


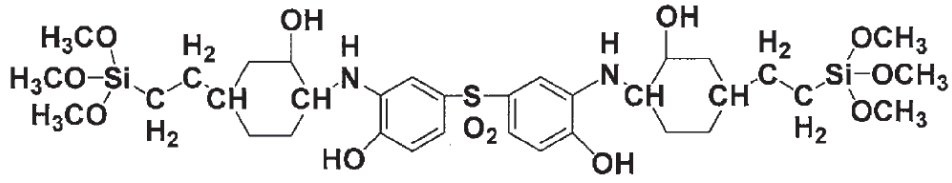






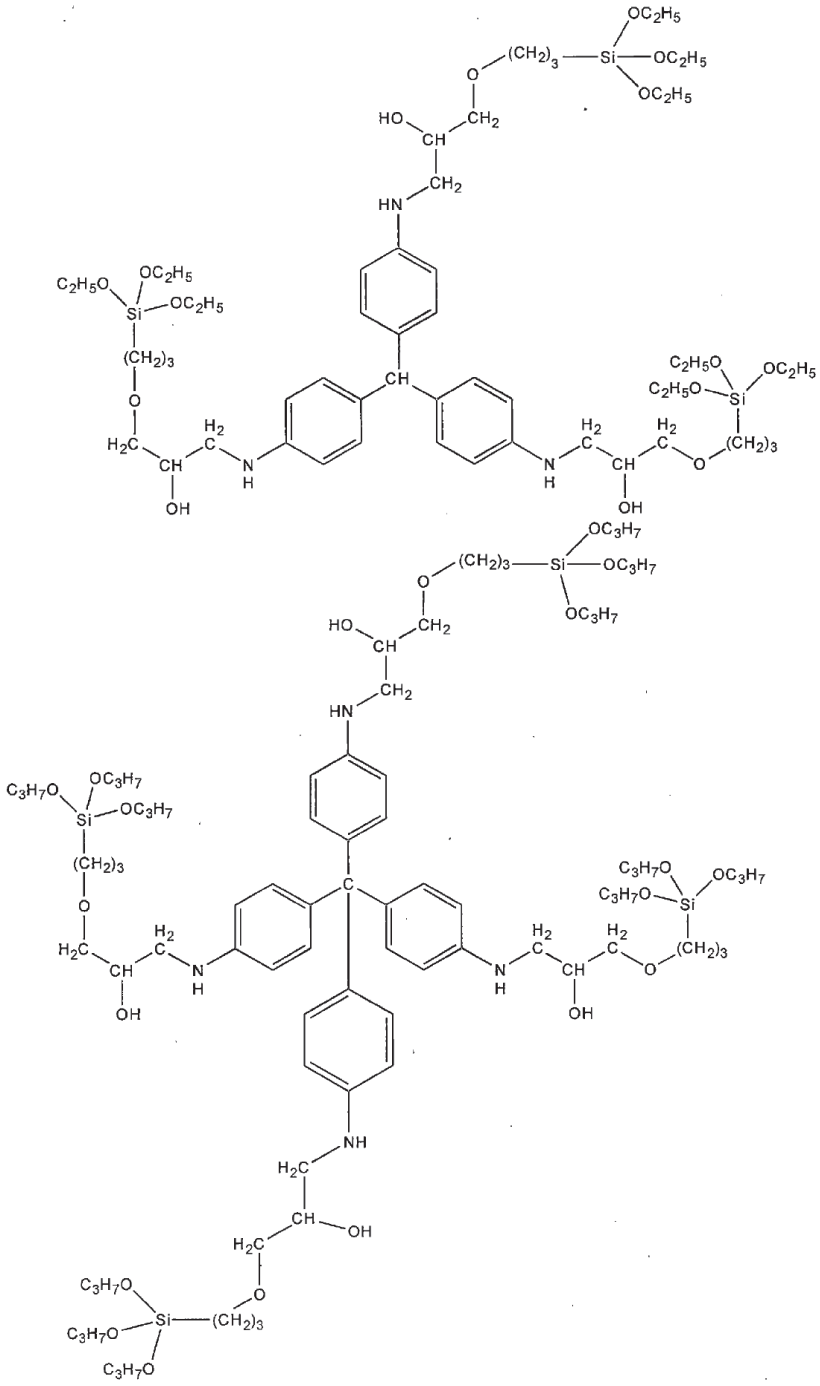






[0119]

[Chemical Formula 19]



[0120]

The content of the adhesion promoter is preferably from 0.01 to 15 parts by weight based on 100 parts by weight of the resin.

[0121]

The adhesion can be further improved by pretreating a surface of a silicon-based material which is a substrate to which the resin composition is applied. As the pretreatment method, the following method is exemplified. A solution obtained by dissolving 0.5 to 20 parts by weight of the above-described adhesion promoter in 100 parts by weight of a solvent such as isopropanol, ethanol, methanol, water, tetrahydrofuran, propyleneglycolmonomethyletheracetate, propylene glycol monomethyl ether, ethyl lactate, and diethyl adipate is used for surface treatment by means of spincoating, dipping, spray coating, vapor treatment, etc. Alternatively, surface treatment may be performed by directly spraying hexamethyldisilazane vapor. Then, if necessary, drying treatment under reduced pressure is carried out, and heating to 50 to 300°C is carried out, so that the reaction between the surface of the silicon-based material and the adhesion promotor is advanced.

[0122]

The resin composition of the present invention may contain a surfactant, and wettability with the substrate can be improved. Examples of the surfactant include

fluorine-based surfactants, such as Fluorad (trade name, produced by Sumitomo 3M Ltd.), Megafac (registered trademark) (trade name, produced by DIC Corporation), and Sulfron (trade name, produced by Asahi Glass Co., Ltd.), organic siloxane surfactants, such as KP341 (trade name, produced by Shin-Etsu Chemical Co., Ltd.), DBE (trade name, produced by Chisso Corporation), GLANOL (trade name, produced by Kyoeisha Chemical Co., Ltd.), and BYK (produced by BYK-Chemie), and acrylic polymer surfactants such as POLYFLOW (trade name, produced by Kyoeisha Chemical Co., Ltd.).

[0123]

The resin composition of the present invention may contain a heat chromogenic compound. The heat chromogenic compound is colored by heat treatment and has an absorbance maximum at 350 nm or more and 700 nm or less, and preferably, the heat chromogenic compound is colored by heat treatment and has an absorbance maximum at 350 nm or more and 500 nm or less. The heat chromogenic compound may be a general thermal dye or pressure sensitive dye, or may be another compound. Examples of such a heat chromogenic compound include those which develop color by changing the chemical structures or state of electric charge by the action of acidic groups exiting in the system during heat treatment, and those which develop color by thermal oxidation reaction or the like with the oxygen in the air. Examples of the skeleton structure of the heat chromogenic

compound include a triarylmethane skeleton, a diarylmethane skeleton, a fluoran skeleton, a bislactone skeleton, a phthalide skeleton, a xanthene skeleton, a rhodamine lactam skeleton, a fluorene skeleton, a phenothiazine skeleton, a phenoxazine skeleton, and a spiropyran skeleton. Specific examples thereof include

4,4′,4″-tris(dimethylamino)triphenylmethane,

4,4′,4″-tris(diethylamino)-2-,2′,2″-trimethyltriphenylmethane, 2,4′,4″-methylidenetrisphenol,

4,4′,4″-methylidenetrisphenol,

4,4′-[(4-hydroxyphenyl)methylene]bis(benzeneamine),

4,4′-[(4-aminophenyl)methylene]bisphenol,

4,4′-[(4-aminophenyl)methylene]bis[3,5-dimethylphenol],

4,4′-[(2-hydroxyphenyl)methylene]bis[2,3,6-trimethylphenol],

4-[bis(4-hydroxyphenyl)methyl]-2-methoxyphenol,

4,4′-[(2-hydroxyphenyl)methylene]bis[2-methylphenol],

4,4′-[(4-hydroxyphenyl)methylene]bis[2-methylphenol],

4-[bis(4-hydroxyphenyl)methyl]-2-ethoxyphenol,

4,4′-[(3-hydroxyphenyl)methylene]bis[2,6-dimethylphenol],

4,4′-[(4-hydroxyphenyl)methylene]bis[2,6-dimethylphenol],

2,2′-[(4-hydroxyphenyl)methylene]bis[3,5-dimethylphenol],

4,4′-[(4-hydroxy-3-methoxyphenyl)methylene]bis[2,6-dimethylphenol],

2,2′-[(2-hydroxyphenyl)methylene]bis[2,3,5-trimethylphenol],

4,4′-[(4-hydroxyphenyl)methylene]bis[2,3,6-trimethylphenol],

4,4′-[(2-hydroxyphenyl)methylene]bis[2-cyclohexyl-5-methylphenol],

4,4′-[(3-hydroxyphenyl)methylene]bis[2-cyclohexyl-5-methylphenol],

4,4′-[(4-hydroxyphenyl)methylene]bis[2-cyclohexyl-5-methylphenol],

4,4′-[(3-methoxy-4-hydroxyphenyl)methylene]bis[2-cyclohexyl-5-methylphenol],

4,4′-[(3,4-dihydroxyphenyl)methylene]bis[2-methylphenol],

4,4′-[(3,4-dihydroxyphenyl)methylene]bis[2,6-dimethylphenol],

4,4′-[(3,4-dihydroxyphenyl)methylene]bis[2,3,6-trimethylphenol],

4-[bis(3-cyclohexyl-4-hydroxy-6-methylphenyl)methyl]-1,2-benzenediol, 4,4′,4″,4‴-(1,2-ethanediylidene)tetrakisphenol,

4,4′,4″,4‴-(1,2-ethanediylidene)tetrakis[2-methylphenol],

4,4′,4″,4‴-(1,2-ethanediylidene)tetrakis[2,6-dimethylphenol], 4,4′,4″,4‴-(1,4-phenylenedimethylidene)tetrakisphenol,

4,4′,4″,4‴-(1,4-phenylenedimethylidene)tetrakis(2,6-dimethylphenol),

4,4′-[(2-hydroxyphenyl)methylene]bis[3-methylphenol],

2,2′-[(3-hydroxyphenyl)methylene]bis[3,5-dimethylphenol],

4,4′-[(2-hydroxy-3-methoxyphenyl)methylene]bis[2,5-dimethylphenol],

4,4′-[(2-hydroxy-3-methoxyphenyl)methylene]bis[2,6-dimethyl

phenol],

2,2′-[(2-hydroxy-3-methoxyphenyl)methylene]bis[3,5-dimethyl

phenol],

2,2′-[(3-hydroxy-4-methoxyphenyl)methylene]bis[3,5-dimethyl

phenol],

4,4′-[(2-hydroxyphenyl)methylene]bis[2-methylethylphenol],

4,4′-[(3-hydroxyphenyl)methylene]bis[2-methylethylphenol],

4,4′-[(4-hydroxyphenyl)methylene]bis[2-methylethylphenol],

2,2′-[(3-hydroxyphenyl)methylene]bis[3,5,6-trimethylphenol],

2,2′-[(4-hydroxyphenyl)methylene]bis[3,5,6-trimethylphenol],

2,2′-[(4-hydroxy-3-ethoxyphenyl)methylene]bis[3,5-dimethylp

henol],

4,4′-[(2-hydroxy-3-methoxyphenyl)methylene]bis[2-(methyleth

yl)phenol],

4,4′-[(3-hydroxy-4-methoxyphenyl)methylene]bis[2-(methyleth

yl)phenol],

4,4′-[(4-hydroxy-3-methoxyphenyl)methylene]bis[2-(methyl

ethyl)phenol],

2,2′-[(2-hydroxy-3-methoxyphenyl)methylene]bis[3,5,6-trimet

hylphenol],

2,2′-[(3-hydroxy-4-methoxyphenyl)methylene]bis[3,5,6-trimet

hylphenol],

2,2′-[(4-hydroxy-3-methoxyphenyl)methylene]bis[3,5,6-trimet

hylphenol],

4,4′-[(4-hydroxy-3-ethoxyphenyl)methylene]bis[2-(methylethy

l)phenol],

2,2′-[(4-hydroxy-3-ethoxyphenyl)methylene]bis[3,5,6-trimeth
ylphenol],

4,4′-[(4-hydroxy-3-ethoxyphenyl)methylene]bis[2,3,6-trimeth
ylphenol],

4,4′-[(4-hydroxy-3-methoxyphenyl)methylene]bis[2-(1,1-dimet
hylethyl)-5-methylphenol],

4,4′[(2-hydroxyphenyl)methylene]bis[2-cyclohexylphenol],

4,4′-[(3-hydroxyphenyl)methylene]bis[2-cyclohexylphenol],

4,4′-[(4-hydroxyphenyl)methylene]bis[2-cyclohexylphenol],

4,4′-[(2-hydroxy-3-methoxyphenyl)methylene]bis[2-cyclohexyl
phenol],

4,4′-[(3-hydroxy-4-methoxyphenyl)methylene]bis[2-cyclohexyl
phenol],

4,4′-[(4-hydroxy-3-ethoxyphenyl)methylene]bis[2-(1,1-dimeth
ylethyl)-6-methylphenol],

4,4′-[(4-hydroxy-3-ethoxyphenyl)methylene]bis[2-cyclohexyl-
5-methylphenol],

4,4′,4″-methylidenetris[2-cyclohexyl-5-methylphenol],

2,2′-[(3,4-dihydroxyphenyl)methylene]bis[3,5-dimethylphenol
],

4,4′-[(3,4-dihydroxyphenyl)methylene]bis[2-(methylethyl)phe
nol],

2,2′-[(3,4-dihydroxyphenyl)methylene]bis[3,5,6-trimethylphe
nol],

4,4′-[(3,4-dihydroxyphenyl)methylene]bis[2-cyclohexylphenol],

3,3′-[(2-hydroxyphenyl)methylene]bis[5-methylbenzene-1,2-diol],

4,4′-[4-[[bis(4-hydroxy-2,5-dimethylphenyl)methyl]phenyl]methylene]bis[1,3-benzenediol],

4,4′-methylenebis[2-[di(4-hydroxy-3-methylphenyl)]methyl]phenol,

4,4′-methylenebis[2-[di(4-hydroxy-2,5-dimethylphenyl)]methyl]phenol,

4,4′-methylenebis[2-[di(4-hydroxy-3,5-dimethylphenyl)]methyl]phenol,

4,4′-methylenebis[2-[di(3-cyclohexyl-4-hydroxy-6-methylphenyl)]methyl]phenol,

4,4′-(3,5-dimethyl-4-hydroxyphenylmethylene)-bis(2,6-dimethylphenol),

3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide,

3,6-bis(dimethylamino)fluorane-γ-(4′-nitro)-aminolactam,

2-(2-chloroanilino)-6-diethylaminofluorane,

2-(2-chloroanilino)-6-dibutylaminofluorane,

2-N,N-dibenzylamino-6-diethylaminofluorane,

6-diethylamino-benzo [a]-fluorane,

2,2′-bis(2-chlorophenyl)-4,4′,5,5′-tetraphenyl-1,2′-bi(imidazole), 1,3-dimethyl-6-diethylaminofluorane,

2-anilino-3-methyl-6-dibutylaminofluorane,

3,7-bis(dimethylamino)-10-benzoylphenothiazine,

3-diethylamino-6-chloro-7-(β-ethoxyethylamino)fluorane,

3-diethylamino-6-methyl-7-anilinofluorane,

3-triethylamino-6-methyl-7-anilinofluorane, and

3-cyclohexylamino-6-methyl-7-anilinofluorane.

[0124]

Among them, a hydroxyl group-containing compound having a triarylmethane skeleton is preferable. Specific examples thereof include 2,4′,4″-methylidenetrisphenol,

4,4′,4″-methylidenetrisphenol,

4,4′-[(4-hydroxyphenyl)methylene]bis(benzeneamine),

4,4′-[(4-aminophenyl)methylene]bisphenol,

4,4′-[(4-aminophenyl)methylene]bis[3,5-dimethylphenol],

4,4′-[(2-hydroxyphenyl)methylene]bis[2,3,6-trimethylphenol],

4-[bis(4-hydroxyphenyl)methyl]-2-methoxyphenol,

4,4′-[(2-hydroxyphenyl)methylene]bis[2-methylphenol],

4,4′-[(4-hydroxyphenyl)methylene]bis[2-methylphenol],

4-[bis(4-hydroxyphenyl)methyl]-2-ethoxyphenol,

4,4′-[(4-hydroxyphenyl)methylene]bis[2,6-dimethylphenol],

2,2′-[(4-hydroxyphenyl)methylene]bis[3,5-dimethylphenol],

4,4′-[(4-hydroxy-3-methoxyphenyl)methylene]bis[2,6-dimethyl

phenol],

2,2′-[(2-hydroxyphenyl)methylene]bis[2,3,5-trimethylphenol],

4,4′-[(4-hydroxyphenyl)methylene]bis[2,3,6-trimethylphenol],

4,4′-[(2-hydroxyphenyl)methylene]bis[2-cyclohexyl-5-methylp

henol],

4,4′-[(4-hydroxyphenyl)methylene]bis[2-cyclohexyl-5-methylp
henol],

4,4′-[(3-methoxy-4-hydroxyphenyl)methylene]bis[2-cyclohexyl
-5-methylphenol],

4,4′-[(3,4-dihydroxyphenyl)methylene]bis[2-methylphenol],

4,4′-[(3,4-dihydroxyphenyl)methylene]bis[2,6-dimethylphenol
],

4,4′-[(3,4-dihydroxyphenyl)methylene]bis[2,3,6-trimethylphe
nol],

4-[bis(3-cyclohexyl-4-hydroxy-6-methylphenyl)methyl]-1,2-be
nzenediol, 4,4′,4″,4′″-(1,2-ethanediylidene)tetrakisphenol,

4,4′,4″,4′″-(1,2-ethanediylidene)tetrakis[2-methylphenol],

4,4′,4″,4′″-(1,2-ethanediylidene)tetrakis[2,6-dimethylpheno
l], 4,4′,4′,4′″-(1,4-phenylenedimethylidene)tetrakisphenol,

4,4′,4″,4′″-(1,4-phenylenedimethylidene)tetrakis(2,6-dimeth
ylphenol),

4,4′-[(2-hydroxyphenyl)methylene]bis[3-methylphenol],

4,4′-[(2-hydroxy-3-methoxyphenyl)methylene]bis[2,5-dimethyl
phenol],

4,4′-[(2-hydroxy-3-methoxyphenyl)methylene]bis[2,6-dimethyl
phenol],

2,2′-[(2-hydroxy-3-methoxyphenyl)methylene]bis[3,5-dimethyl
phenol],

4,4′-[(2-hydroxyphenyl)methylene]bis[2-methylethylphenol],

4,4′-[(4-hydroxyphenyl)methylene]bis[2-methylethylphenol],

2,2′-[(4-hydroxyphenyl)methylene]bis[3,5,6-trimethylphenol],

2,2′-[(4-hydroxy-3-ethoxyphenyl)methylene]bis[3,5-dimethylp

henol],

4,4′-[(2-hydroxy-3-methoxyphenyl)methylene]bis[2-(methyleth

yl)phenol],

4,4′-[(4-hydroxy-3-methoxyphenyl)methylene]bis[2-(methyleth

yl)phenol],

2,2′-[(2-hydroxy-3-methoxyphenyl)methylene]bis[3,5,6-trimet

hylphenol],

2,2′-[(4-hydroxy-3-methoxyphenyl)methylene]bis[3,5,6-trimet

hylphenol],

4,4′-[(4-hydroxy-3-ethoxyphenyl)methylene]bis[2-(methylethy

l)phenol],

2,2′-[(4-hydroxy-3-ethoxyphenyl)methylene]bis[3,5,6-trimeth

ylphenol],

4,4′-[(4-hydroxy-3-ethoxyphenyl)methylene]bis[2,3,6-trimeth

ylphenol],

4,4′-[(4-hydroxy-3-methoxyphenyl)methylene]bis[2-(1,1-dimet

hylethyl)-5-methylphenol],

4,4′-[(2-hydroxyphenyl)methylene]bis[2-cyclohexylphenol],

4,4′-[(4-hydroxyphenyl)methylene]bis[2-cyclohexylphenol],

4,4′-[(2-hydroxy-3-methoxyphenyl)methylene]bis[2-cyclohexyl

phenol],

4,4′-[(4-hydroxy-3-ethoxyphenyl)methylene]bis[2-(1,1-dimeth

ylethyl)-6-methylphenol],

4,4′-[(4-hydroxy-3-ethoxyphenyl)methylene]bis[2-cyclohexyl-5-methylphenol],

4,4′,4″-methylidenetris[2-cyclohexyl-5-methylphenol],

2,2′-[(3,4-dihydroxyphenyl)methylene]bis[3,5-dimethylphenol],

4,4′-[(3,4-dihydroxyphenyl)methylene]bis[2-(methylethyl)phenol],

2,2′-[(3,4-dihydroxyphenyl)methylene]bis[3,5,6-trimethylphenol],

4,4′-[(3,4-dihydroxyphenyl)methylene]bis[2-cyclohexylphenol],

3,3′-[(2-hydroxyphenyl)methylene]bis[5-methylbenzene-1,2-diol],

4,4′-[4-[[bis(4-hydroxy-2,5-dimethylphenyl)methyl]phenyl]methylene]bis[1,3-benzenediol],

4,4′-methylenebis[2-[di(4-hydroxy-3-methylphenyl)]methyl]phenol,

4,4′-methylenebis[2-[di(4-hydroxy-2,5-dimethylphenyl)]methyl]phenol,

4,4′-methylenebis[2-[di(4-hydroxy-3,5-dimethylphenyl)]methyl]phenol,

4,4′-methylenebis[2-[di(3-cyclohexyl-4-hydroxy-6-methylphenyl)]methyl]phenol, and

4,4′-(3,5-dimethyl-4-hydroxyphenylmethylene)-bis(2,6-dimeth

ylphenol). Such a hydroxyl group-containing compound having a triarylmethane skeleton is particularly preferable because of high thermal coloring temperature and high heat resistance. These may be used alone or in combination of two or more. The hydroxyl group-containing compound having a triarylmethane skeleton may be used as a quinonediazide compound by ester-bonding sulfonic acid of naphthoquinonediazide to the compound.

[0125]

The content of the heat chromogenic compound in the resin composition of the present invention is preferably from 5 to 80 parts by weight, more preferably from 10 to 60 parts by weight, based on 100 parts by weight of the resin. When the content is 5 parts by weight or more, the transmittance of the heat resistance coating film in an ultraviolet-visible light region can be lowered. On the other hand, when the content is 80 parts by weight or less, the heat resistance and strength of the heat resistance coating film can be maintained and the water absorption rate can be reduced.

[0126]

The resin composition of the present invention may contain a dye and/or an organic pigment. Examples of the use method include a method of using one type of dye or organic pigment, a method of using a mixture of two or more types of dyes or organic pigments, and a method of using a combination

of one or more types of dyes and one or more types of organic pigments. In the present invention, a dye and/or an organic pigment having an absorption maximum at 436 to 750 nm is preferably selected.

[0127]

The dye used in the present invention is preferably one soluble in an organic solvent that dissolves the resin of the present invention and compatible with the resin. Dyes having high heat resistance and light resistance are preferred. Preferred examples of the dyes include oil-soluble dyes, disperse dyes, reactive dyes, acid dyes, and direct dyes. Examples of the skeleton structure of the dye include anthraquinone type, azo type, phthalocyanine type, methine type, oxazine type, quinoline type, and triarylmethane type, and these dyes may be used alone or as metal-containing complex salt dyes. Specifically, examples of such dyes include, but are not limited to, Sumilan Dyes and Lanyl Dyes (produced by Sumitomo Chemical Industry Co., Ltd.); Orasol Dyes, Oracet Dyes, Filamid Dyes, and Irgasperse Dyes (produced by Ciba Specialty Chemicals Co., Ltd.); Zapon Dyes, Neozapon Dyes, Neptune Dyes, and Acidol Dyes (produced by BASF); Kayaset Dyes and Kayakalan Dyes (produced by Nippon Kayaku Co., Ltd.); Valifast Colors Dyes (produced by Orient Chemical Co., Ltd.); Savinyl Dyes, Sandoplast Dyes, Polysynthren Dyes, and Lanasyn Dyes (Produced by Clariant Japan Co., Ltd.); Aizen Spilon Dyes (produced by

Hodogaya Chemical Co., Ltd.); functional dyes (produced by Yamada Chemical Co., Ltd.); and Plast Color Dyes and Oil Color Dyes (produced by Arimoto Chemical Co., Ltd.). These dyes may be used alone or in combination of two or more.

[0128]

The organic pigment used in the present invention is preferably a pigment having high heat resistance and light resistance. Specific examples of the organic pigment used in the present invention are indicated by color index (CI) numbers. Examples of violet pigments include Pigment Violets 19, 23, 29, 32, 33, 36, 37, and 38. Examples of blue pigment include Pigment Blues 15 (15:3, 15:4, 15:6 etc.), 21, 22, 60, and 64. Examples of green pigment include Pigment Greens 7, 10, 36, and 47. Pigments other than these pigments can also be used.

[0129]

The content of the organic pigment in the resin composition of the present invention is preferably from 1 to 300 parts by weight, more preferably from 10 to 200 parts by weight, based on 100 parts by weight of the resin. If the amount used is 1 part by weight or more, light of a corresponding wavelength can be absorbed. By setting the amount to 300 parts by weight or less, it is possible to absorb the light of the corresponding wavelength while maintaining adhesion strength between the resin film and the substrate and the heat resistance and mechanical properties of the heat resistance coating film

after heat treatment.

[0130]

As the organic pigment used in the present invention, if necessary, there may be used one which is subjected to surface treatment such as rosin treatment, acidic group treatment, and basic group treatment. In addition, the organic pigment can be used together with a dispersant as the case may be. Examples of the dispersant include cationic, anionic, nonionic, amphoteric, silicone, and fluorine surfactants.

[0131]

The resin composition of the present invention may contain inorganic particles, and the resin film and the heat resistance coating film after heat treatment can be made into highly elastic and tough films. Preferred examples of inorganic particles include silicon dioxide, titanium dioxide, and alumina, but are not limited thereto.

[0132]

The resin composition of the present invention can be obtained by putting the above-mentioned resin, if necessary, solvent and other additives in a glass flask or a stainless steel container and mixing the resultant by a method of stirring and dissolving the resultant with a mechanical stirrer or the like, a method of dissolving the resultant with ultrasonic waves, a method of stirring and dissolving the resultant by means of a planetary stirring and defoaming apparatus, or the like.

Conditions of stirring and mixing are not particularly limited. The viscosity of the resultant resin composition is preferably 1 to 10,000 mPa·s. In order to remove foreign bodies, the resin composition may be filtered with a filter having a pore size of 0.01 μm to 5 μm. A filtration filter may be formed of polypropylene (PP), polyethylene (PE), nylon (NY), polytetrafluoroethylene (PTFE) or the like, with polyethylene and nylon being preferred. When the resin composition contains an organic pigment, it is preferable to use a filtration filter having a larger pore size than the particle sizes of the pigment.

[0133]

The resin composition of the present invention can be pattern-formed through a process of coating the resin composition onto a support substrate to form a coating film, a process of drying the coating film to form a resin film, a process of exposing the resin film, a process of developing the exposed resin film, and a process of applying heat treatment to the developed resin film.

[0134]

First, the resin composition is coated onto a support substrate. As the substrate, a silicon wafer, ceramics, gallium arsenide, metal, glass, a metal oxide insulating film, silicon nitride, ITO, IZO, amorphous silicon, microcrystalline silicon, polysilicon, IGZO, or the like are used, but is not limited thereto.

[0135]

Examples of the coating method include spin coating using a spinner, spray coating, roll coating, slit die coating, ink-jet coating, or a combination thereof. Although the thickness of the coating film is different depending on the coating method, the solid content concentration of the resin composition, the viscosity and the like, the resin composition is generally applied so that the film thickness after drying is 0.1 to 150 μm. In particular, when the substrate is a rectangular large-sized substrate, in terms of film thickness uniformity of the coating film, slit die coating or a method in which coating is carried out while rotating the substrate after slit die coating is preferably used.

[0136]

Then, the substrate coated with the resin composition is dried to obtain a resin film. Drying is preferably carried out using an oven, a hot plate, infrared light or the like, in a range of 50°C to 150°C for 1 minute to several hours. If necessary, the substrate can also be dried in two or more stages, such as 2 minutes at 80°C and 2 minutes at 120°C. Although the pressure during drying may be normal pressure, in terms of film thickness uniformity of the resin film after drying, a process of first drying under reduced pressure and then drying at normal pressure is also preferably used.

[0137]

Then, the resin film is irradiated with actinic rays through a mask having a desired pattern. Examples of actinic rays used for exposure include ultraviolet light, visible light, electron beam, and X ray. In the present invention, it is preferable to use the i-line (365 nm), h-line (405 nm), or g-line (436 nm) of a mercury lamp.

[0138]

When photosensitivity is not imparted to the resin composition, it is necessary to further form another photoresist coating film on the resin film. As this photoresist, a general novolak type resist such as OFPR-800 (manufactured by Tokyo Ohka Kogyou Co., Ltd.) is preferably used. The photoresist coating film is formed by a method similar to the formation of the resin composition.

[0139]

When the resolution of the pattern at the time of development is improved or the allowable range of development conditions is increased, a process of carrying out a baking treatment before development may be included. The temperature is preferably in a range of 50°C to 180°C, more preferably in a range of 60°C to 150°C. The time is preferably from 10 seconds to several hours. Within this range, there are advantages that the reaction proceeds favorably and the development time can be shortened. In order to form a pattern of the resin composition from the resin film, development processing is

performed. When the resin composition has a negative photosensitivity, a relief pattern can be obtained by removing an unexposed portion with a developer, and when the resin composition has a positive photosensitivity, the relief pattern can be obtained by removing an exposed portion with the developer.

[0140]

Although a suitable developer can be selected according to the structure of the resin composition, there can be preferably used an aqueous solution of a compound showing alkalinity, such as ammonia, tetramethylammonium, diethanolamine, diethylaminoethanol, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, triethylamine, diethylamine, methylamine, dimethylamine, dimethylaminoethyl acetate, dimethylaminoethanol, dimethylaminoethyl methacrylate, cyclohexylamine, ethylenediamine, and hexamethylenediamine. As the case may be, to the alkaline aqueous solution, any one or more in combination of the following may be added: polar solvents such as N-methyl-2-pyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, γ-butyrolactone, and dimethylacrylamide, alcohols such as methanol, ethanol, and isopropanol, esters such as ethyl lactate and propyleneglycolmonomethyletheracetate, and ketones such as cyclopentanone, cyclohexanone, isobutyl ketone, and methyl

isobutyl ketone.

[0141]

As a developer, there can be preferably used a mixture including a combination of one or more of good solvents for the resin composition of the present invention, such as N-methyl-2-pyrrolidone, N-acetyl-2-pyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, and hexamethylphosphoramide, and poor solvents for the resin composition, such as methanol, ethanol, isopropyl alcohol, water, methyl carbitol, ethyl carbitol, toluene, xylene, ethyl lactate, ethyl pyruvate, propyleneglycolmonomethyletheracetate, methyl-3-methoxypropionate, ethyl-3-ethoxypropionate, 2-heptanone, cyclopentanone, cyclohexanone, and ethyl acetate.

[0142]

Development can be carried out by a method such as coating the above developer onto a coating film surface of the resin composition as it is or spraying the developer onto the coating film surface, dipping in the developer, or applying ultrasonic waves while dipping.

[0143]

Then, it is preferable to wash a relief pattern formed by development with a rinsing solution. When an alkaline aqueous solution is used as the developer, water can be

preferably used as the rinsing solution. At this time, rinse treatment may be carried out with a liquid obtained by adding esters, such as ethanol, isopropyl alcohols, and propyleneglycolmonomethyletheracetate, carbonic acid gas, hydrochloric acid, or acetic acid to water.

[0144]

When rinsing with an organic solvent, there are preferably used solvents having satisfactory miscibility with a developer, such as methanol, ethanol, isopropyl alcohol, ethyl lactate, ethyl pyruvate, propyleneglycolmonomethyletheracetate, methyl-3-methoxypropionate, ethyl-3-ethoxypropionate, 2-heptanone and ethyl acetate.

[0145]

When the photosensitivity is not imparted to the resin composition, it is necessary to remove the photoresist coating film formed on the resin film after development. This removal is often carried out by removal by dry etching or wet etching with a peeling solvent. Examples of the pealing solvent include, but are not limited to, organic solvents such as acetone, butyl acetate, ethyl lactate, propyleneglycolmonomethyletheracetate, methyl 3-methoxypropionate, ethyl-3-ethoxypropionate, 2-heptanone, and ethylacetate and aqueous solutions of sodium hydroxide and potassium hydroxide.

[0146]

When a resin which forms a cyclic structure by heating a polyimide precursor, a polybenzimidazole precursor or the like or by catalysis is used as the resin composition, in order to convert the resin into a heat resistance resin having a cyclic structure, a temperature of 150°C to 500°C is applied to the resin after development to convert the resin into a heat resistance coating film. The heat treatment is preferably performed by raising the temperature stepwise from a selected temperature or raising the temperature continuously in a selected temperature range for 5 minutes to 5 hours. As one example, there are a method of heat treatment at 130°C, 200°C, and 350°C for 30 minutes each, a method of linearly raising the temperature from room temperature to 320°C over 2 hours, and the like. There is a possibility that electric characteristics of an element change due to high temperature heating and repetition thereof, and warpage of the substrate becomes large. Therefore, the heat treatment is preferably carried out at 250°C or less.

[0147]

If the heat treatment is carried out at 250°C or less, polyimide or polyamideimide is preferably used as a resin contained in the resin composition, and a resin having a structure represented by the general formula (4) is more preferably used. From the viewpoint of heat resistance, a

polyimide resin represented by the general formula (4) is most preferable. Since the polyimide resin represented by the general formula (4) already has a cyclic structure, it is not necessary to carry out dehydration and ring closure by raising the heat treatment temperature to a high temperature, so that the biggest advantage is that heat treatment at a low temperature of 250°C or less becomes possible.

[0148]

Residual stress attributable to the resin forming the heat resistance coating film of a substrate with the heat resistance coating film obtained by the above-described manufacturing method is preferably 30 MPa or less. The residual stress is more preferably 25 MPa or less, and most preferably 15 MPa or less. If the residual stress attributable to the resin is large, the yield may deteriorate during a process of manufacturing a device including the substrate with the heat resistance coating film, or the reliability of products may become poor.

[0149]

The heat resistance coating film formed from the resin composition of the present invention can be used for electronic components such as semiconductor devices and multilayer wiring boards. Specifically, the heat resistance coating film is preferably used for applications such as a passivation film of a semiconductor, a surface protective film of a semiconductor

element, an interlayer insulating film, an interlayer insulating film of multilayer wiring for high density mounting, an insulating layer of an organic electroluminescent element, a flattening film of a thin film transistor substrate, and an interlayer insulating film of a thin film transistor, but the application is not limited thereto. The heat resistance coating film can have various structures. When the resin composition contains a conductive filler, the heat resistance coating film can also be used as a wiring material.

[0150]

Next, an application example to a semiconductor device with bumps using the resin composition of the present invention will be described with reference to the drawings. Fig. 1 is an enlarged cross-sectional view of a pad portion of a semiconductor device with bumps according to the present invention. As shown in Fig. 1, a passivation film 3 is formed on an input/output Al pad 2 on a silicon wafer 1, and the passivation film 3 has via holes. Further, a pattern (insulating film) 4 according to the resin composition of the present invention is formed on the passivation film 3. Furthermore, a metal (Cr, Ti, Ni, TiW, etc.) film 5 and a metal (Cu, Au, etc.) wiring 6 are sequentially formed so as to be connected to the Al pad 2, and an insulating film 7 as a second insulating film is formed thereon. In the insulating film 7, a periphery of a solder bump 10 is opened to insulate each pad.

A barrier metal 8 and a solder bump 10 are formed on the insulated pad. When the resin composition of the present invention is introduced, since warpage of the wafer is small, exposure and wafer transfer can be carried out with high accuracy. Since the resin of the present invention is excellent in mechanical properties, stress from a sealing resin can be relaxed during mounting, so that it is possible to provide a highly reliable semiconductor device which prevents damage of a low-k layer.

[0151]

Next, a detailed method for producing a semiconductor device with bumps will be described with reference to Fig. 2. In Fig. 2a, the resin composition of the present invention is coated, and the insulating film 4 is formed through a photolithography process. Then, in Fig. 2b, the metal film 5 is formed by a sputtering method, and in Fig. 2c, the metal wiring 6 is formed by a plating method. Then, in Fig. 2d, the resin composition of the present invention is coated again, and the insulating film 7 as shown in Fig. 2e is formed through a photolithography process. When a multilayer wiring structure including three or more layers is formed, each layer can be formed by repeating the above process.

[0152]

Then, as shown in Figs. 2f and 2g, the barrier metal 8 and the solder bump 10 are formed. Finally, dicing is carried out along the scribe line 9, by which each chip is cut. If stress

attributable to the resin is low in this series of production processes, warpage of the substrate can be reduced, which is extremely preferable because it leads to improvement in yield and reliability of the semiconductor device.

[0153]

Next, an application example to a chip stacked type semiconductor device using the resin composition of the present invention will be described with reference to the drawings. Figs. 3 and 4 are enlarged cross-sectional views of electrode portions of the chip stacked type semiconductor device of the present invention. As shown in Fig. 3, a passivation film 13 is formed on an input/output Al pad 12 on a silicon wafer 11, and the passivation film 13 has via holes. Further, a pattern (insulating film) 14 according to the resin composition of the present invention is formed on the passivation film 13, these chips are stacked in multiple layers via an adhesive film 15 such as a die attach film, and the Al pad is connected to an external terminal via a wire (Cu, Au, etc.) 16. As shown in Fig. 4, a through electrode 22 is formed in a silicon wafer 21, passivation films 24 are formed on input/output pads (Al, Cu, etc.) 23 at both ends of the through electrode 22, and a viahole is formed in the passivation film 24. Moreover, a pattern (insulating film) 25 according to the resin composition of the present invention is formed thereon, and a barrier metal 26 and a solder bump 27 are sequentially formed. These chips are

vertically stacked via an adhesive film 28 such as a die attach film. When the resin composition of the present invention is introduced, since warpage of the wafer is small, exposure and wafer transfer can be carried out with high accuracy. Since the resin of the present invention is excellent in mechanical properties, stress from a sealing resin can be relaxed during mounting, so that it is possible to provide a highly reliable semiconductor device which prevents damage of a low-k layer.

[0154]

Next, a detailed method for producing a chip stacked type semiconductor device will be described with reference to Figs. 5 and 6. In Fig. 5a, the resin composition of the present invention is applied onto a device substrate with a pad, and a pattern (insulating film 14) as shown in Fig. 5b is formed through a photolithography process. Then, if necessary, the substrate is ground and thinned, diced along the scribe line 9 in Fig. 5c, and cut for each chip. In Fig. 5d, the cut and divided chips are stacked via the adhesive films 15 such that the pads are exposed. In FIG.5e, an exposed electrode is connected to the outside via a wire. If stress attributable to the resin is low in this series of production processes, warpage of the substrate can be reduced, which is extremely preferable because it leads to improvement in yield and reliability of the semiconductor device.

[0155]

As shown in Fig. 6a, the resin composition of the present invention is applied onto a through electrode and a device substrate with a pad, and a pattern (insulating film 25) as shown in Fig. 6b is formed through a photolithography process. Then, as shown in Fig. 6c, dicing is carried out along a scribe line 29, by which each chip is cut. Then, as shown in Fig. 6d, a barrier metal 26 and a solder bump 27 are formed. As shown in Fig. 6e, the cut and divided chips are stacked via an adhesive film 28 so that the through electrodes are vertically aligned. If stress attributable to the resin is low in this series of production processes, warpage of the substrate can be reduced, which is extremely preferable because it leads to improvement in yield and reliability of the semiconductor device.

[0156]

The heat resistance coating film obtained from the resin composition of the present invention is suitably used as a flattening film of a display device having a substrate on which a TFT (Thin Film Transistor) is formed, a flattening film, and a display element in this order. Examples of the display device having such a configuration include a liquid crystal display device and an organic EL display device. An active matrix type display device has a TFT and a wiring located at a side portion of the TFT and connected to the TFT on a substrate such as glass or various plastics and has a flattening film thereon to cover concavoconvexes, and a display element is further provided on

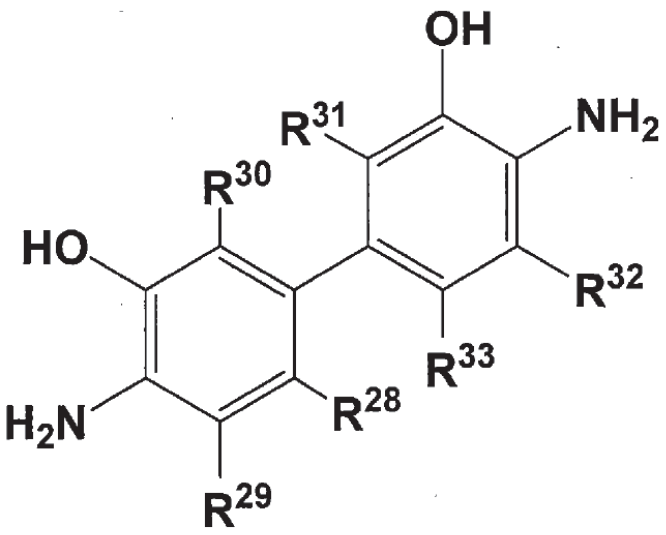
the flattening film. The display element and the wiring are connected via a contact hole formed in the flattening film. Fig. 7 shows a cross-sectional view of a TFT substrate. TFTs 31 of a bottom gate type or a top gate type are provided in rows and columns on a substrate 36, and an insulating film 33 is formed so as to cover the TFTs 31. On the insulating film 33, a wiring 32 connected to the TFT 31 is provided. Further, on the insulating film 33, a flattening film 34 is provided in a state of embedding the wiring 32. In the flattening film 34, a contact hole 37 reaching the wiring 32 is provided. An ITO (transparent electrode) 35 is formed on the flattening film 34 in a state of being connected to the wiring 32 via the contact hole 37. Here, the ITO 35 serves as an electrode of a display element (for example, an organic EL element). This organic EL element may be of a top emission type which emits emitted light from the side opposite to the substrate 36 or a bottom emission type which extracts light from the substrate 36 side, and is preferably of the top emission type. In this manner, an active matrix type organic EL display device in which TFTs 31 for driving the organic EL elements are connected to each organic EL element is obtained.

[0157]

Next, a 5,5'-dihydroxyl-4,4'-diaminobiphenyl derivative represented by the following general formula (10) in the present invention will be explained.

[0158]

[Chemical Formula 20]



(10)

[0159]

In the above general formula (10), R^{28} and R^{33} are the same and each independently one kind selected from the group consisting of a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group. R^{29} and R^{32} are the same, R^{30} and R^{31} are the same, and they are one kind selected from the group consisting of hydrogen, halogen, a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a

halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group. One or more substituents among them may be the same or different and are one or more of halogen, trifluoromethyl, trimethylsilyl, a C_1 to C_6 alkoxyl group, a C_1 to C_6 alkyl group, an arylalkoxyl group, a C_6 to C_{30} aryl group, and a C_4 to C_{30} heterocyclic group.

[0160]

In R^{28} and R^{33} described above, the substituted or unsubstituted C_1 to C_6 alkyl group is preferably a C_1 to C_6 linear alkyl group, a C_1 to C_6 side chain alkyl group or a C_1 to C_6 cycloalkyl group, more preferably methyl, trifluoromethyl, ethyl, trifluoroethyl, n-propyl, isopropyl, n-butyl, sec-butyl, t-butyl, n-pentyl, isopentyl, neopentyl, n-hexyl, cyclohexyl or the like. The substituted or unsubstituted C_1 to C_6 alkoxyl group is preferably a C_1 to C_6 linear alkyl group, a C_1 to C_6 side chain alkyl group or a C_1 to C_6 cycloalkyl group, which is bound by an ether group, more preferably methoxy, trifluoromethoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, t-butoxy, n-pentyloxy, n-hexyloxy or cyclohexyloxy. The halogenated alkyl group is preferably trifluoromethyl, trifluoroethyl, trichloromethyl, trichloroethyl, tribromomethyl, tribromoethyl, triiodomethyl

or the like, more preferably trifluoromethyl or trifluoroethyl. The substituted or unsubstituted amino group is preferably a primary amino group, secondary amino group or tertiary amino group, the amino group can be substituted by one or two groups, and substituents may be the same or different. A C_1 to C_6 alkyl group, a C_6 to C_{30} aryl group or a C_6 to C_{30} heteroaryl group is preferred, and an amino group, methylamino, ethylamino, dimethylamino, phenylamino, benzylamino, pyridinamino or furanylamino is more preferred. The substituted or unsubstituted amide group is preferably an alkylamido group, an arylamido group, an alkoxyamido group or the like. Among them, the substituent may be connected to a carbonyl group or an amino group, and formamide, acetamide, benzamide, t-butoxyamide, benzyloxycarbonylamino, propylacetamide, acetanilide, or the like is more preferred. The substituted or unsubstituted C_6 to C_{30} aryl group is preferably a substituted or unsubstituted aromatic hydrocarbon group such as a phenyl group, a naphthyl group, an anthracenyl group, a phenanthryl group, a pyrenyl group, a biphenyl group, or a terphenyl. The substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group is preferably a furanyl group or a pyridine group, and the ester group is an alkoxylcarbonate ester group, among which the alkoxyl group is not particularly limited, and methoxycarbonate ester, ethoxycarbonate ester, propoxycarbonate ester, butoxycarbonate ester, t-butoxycarbonate ester,

benzyloxycarbonate ester, fluorenylmethoxy carbonate ester and the like are preferred.

[0161]

In R^{29}, R^{30}, R^{31} and R^{32} described above, the halogen is preferably fluoro, chloro or iodo, and the substituted or unsubstituted C_1 to C_6 alkyl group, the substituted or unsubstituted C_1 to C_6 alkoxy group, the halogenated alkyl group, the substituted or unsubstituted amino group, the substituted or unsubstituted amide group, the substituted or unsubstituted C_6 to C_{30} aryl group, the substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, and the ester group are all the same as those described above.

[0162]

In the substituent, the halogen is preferably fluoro, chloro or iodo. The C_1 to C_6 alkoxy group is preferably a C_1 to C_6 linear alkyl group, a C_1 to C_6 side chain alkyl group or a C_1 to C_6 cycloalkyl group, which is bound by an ether group, more preferably methoxy, trifluoromethoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, t-butoxy, n-pentyloxy, n-hexyloxy or cyclohexyloxy. The C_1 to C_6 alkyl group is preferably a C_1 to C_6 linear alkyl group, a C_1 to C_6 side chain alkyl group or a C_1 to C_6 cycloalkyl group, more preferably methyl, trifluoromethyl, ethyl, trifluoroethyl, n-propyl, isopropyl, n-butyl, sec-butyl, t-butyl, n-pentyl, isopentyl, neopentyl, n-hexyl, cyclohexyl or the like. The arylalkoxy group is

preferably benzyloxy, naphthylmethoxy, anthracenylmethoxy, fluorenylmethoxy, 3,5-di t-butylphenyl-1-isopropoxy, phenylethoxy, naphthylethoxy, benzidine-3-methoxy or the like, more preferably benzyloxy or fluorenylmethoxy.

[0163]

The C_6 to C_{30} aryl group is preferably a substitutable aromatic hydrocarbon group such as a phenyl group, a naphthyl group, an anthracenyl group, a phenanthryl group, a pyrenyl group, a biphenyl group, or a terphenyl, and the C_4 to C_{30} heteroaryl group is preferably a pyridine group, a carbazoyl group, an imidazole group, a furanyl group, a thiophene group, an oxazole group, an indolyl group, a benzofuranyl group or a benzothiophene group.

[0164]

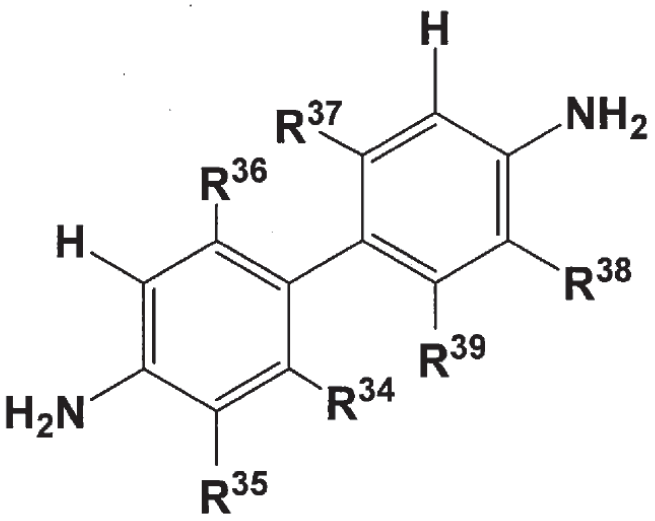
In R^{29}, R^{30}, R^{31} and R^{32} described above, R^{29}, R^{30}, R^{31} and R^{32} are preferably hydrogen.

[0165]

The present invention further describes a process for producing a 5,5'-dihydroxyl-4,4'-diaminobiphenyl derivative. First, a 5,5'-dibromo-4,4'-diaminobiphenyl derivative represented by the general formula (12) is obtained by bromination reaction of a 4,4'-diaminobiphenyl derivative represented by the general formula (11).

[0166]

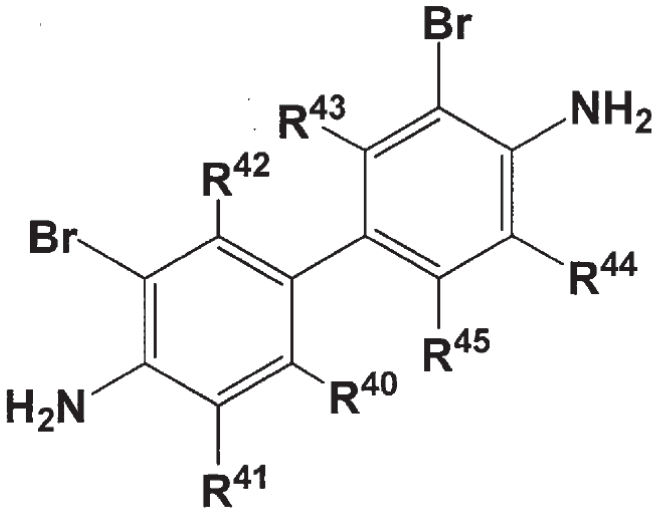
[Chemical Formula 21]



(11)

[0167]

[Chemical Formula 22]



(12)

[0168]

In the above general formula (11), R^{34} and R^{39} are the same and each independently one kind selected from the group consisting of a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl

group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group. R^{35} and R^{38} are the same, R^{36} and R^{37} are the same, and they each independently one kind selected from the group consisting of hydrogen, halogen, a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group.

[0169]

In the above general formula (12), R^{40} and R^{45} are the same and each independently one kind selected from the group consisting of a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group. R^{41} and R^{44} are the same, R^{42} and R^{43} are the same, and they are each independently one kind

selected from the group consisting of hydrogen, halogen, a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group.

[0170]

The substituents may be the same or different and each independently represent one or more of halogen, trifluoromethyl, trimethylsilyl, a C_1 to C_6 alkoxyl group, a C_1 to C_6 alkyl group, an aryl alkoxyl group, a C_6 to C_{30} aryl group, and a C_4 to C_{30} heterocyclic group.

In R^{34} and R^{39}, R^{40} and R^{45} described above, the substituted or unsubstituted C_1 to C_6 alkyl group, the substituted or unsubstituted C_1 to C_6 alkoxy group, the halogenated alkyl group, the substituted or unsubstituted amino group, the substituted or unsubstituted amide group, the substituted or unsubstituted C_6 to C_{30} aryl group, the substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, and the ester group are all the same as those described above.

[0171]

In R^{35}, R^{36}, R^{37}, R^{38}, R^{41}, R^{42}, R^{43} and R^{44} described above, the halogen is preferably fluoro, chloro or iodo. The

substituted or unsubstituted C_1 to C_6 alkyl group, the substituted or unsubstituted C_1 to C_6 alkoxy group, the halogenated alkyl group, the substituted or unsubstituted amino group, the substituted or unsubstituted amide group, the substituted or unsubstituted C_6 to C_{30} aryl group, the substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, and the ester group are all the same as those described above.

[0172]

In the substituent described above, the halogen, the substituted or unsubstituted C_1 to C_6 alkoxy group, the substituted or unsubstituted C_1 to C_6 alkyl group, the arylalkoxy group, the C_6 to C_{30} aryl group, and the C_4 to C_{30} heterocyclic groups are all the same as those described above.

In the above production process, it is preferable that R^{35}, R^{36}, R^{37} and R^{38} are hydrogen, and R^{41}, R^{42}, R^{43} and R^{44} are hydrogen.

[0173]

A reaction solvent used for the above bromination reaction is preferably an aprotic organic solvent, and one or more of the mixed solvents of methyl acetate, ethyl acetate, propyl acetate, butyl acetate, ethylene glycol dimethyl ether, tetrahydrofuran, 1,4-dioxane and the solvent are more preferred.

[0174]

A brominated solvent used for the bromination reaction is preferably liquid bromine or NBS. In the bromination

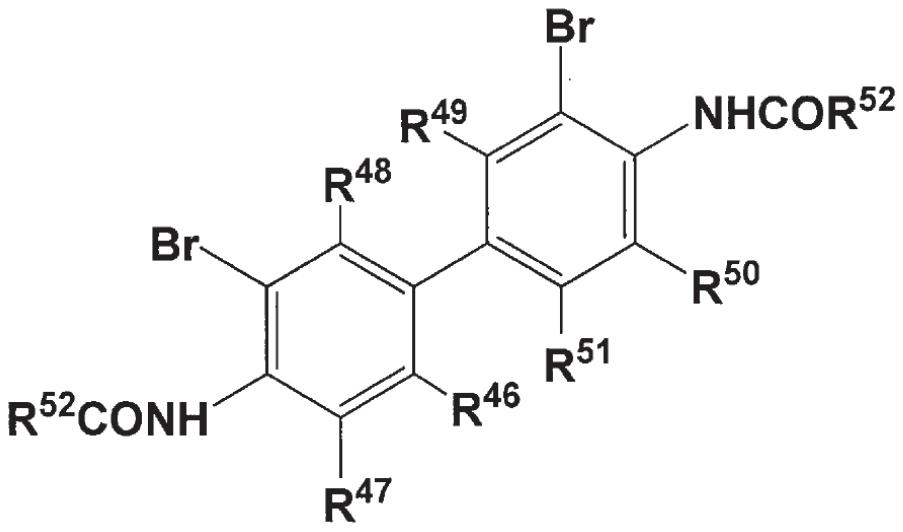
reaction process, the reaction temperature is preferably from −30°C to 60°C, more preferably from −20°C to 60°C. The reaction time is preferably from 1 h to 48 h, and more preferably from 1 h to 12 h from the viewpoints of reaction rate and industrialization cost.

[0175]

In the present invention, an amidation reaction of a 5,5'-dibromo-4,4'-diaminobiphenyl derivative represented by the general formula (12) obtained by the above production process is carried out using acid anhydride or acyl chloride, whereby a 5,5'-dibromo-4,4'-diamidobiphenyl derivative represented by the general formula (13) is further obtained.

[0176]

[Chemical Formula 23]



(13)

[0177]

In the above general formula (13), R^{46} and R^{51} are the same

and each independently one kind selected from the group consisting of a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group. R^{47} and R^{50} are the same, R^{48} and R^{49} are the same, and they are each independently one kind selected from the group consisting of hydrogen, halogen, a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group. Among them, the substituents may be the same or different and each independently represent one or more of halogen, trifluoromethyl, trimethylsilyl, a C_1 to C_6 alkoxyl group, a C_1 to C_6 alkyl group, an aryl alkoxyl group, a C_6 to C_{30} aryl group, and a C_4 to C_{30} heterocyclic group, and R^{52} is one kind selected from the group consisting of a substituted or unsubstituted C_1 to C_6 alkyl group or a substituted or unsubstituted aryl group. The substituent in R^{52} is one or more of a methyl group, a sulfo group, a fluorine

atom, an amino group, and a methoxy group.

[0178]

In R^{46} and R^{51} described above, the substituted or unsubstituted C_1 to C_6 alkyl group, the substituted or unsubstituted C_1 to C_6 alkoxy group, the halogenated alkyl group, the substituted or unsubstituted amino group, the substituted or unsubstituted amide group, the substituted or unsubstituted C_6 to C_{30} aryl group, the substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, and the ester group are all the same as those described above.

[0179]

In R^{47}, R^{48}, R^{49} and R^{50} described above, the halogen is preferably fluoro, chloro or iodo, and the substituted or unsubstituted C_1 to C_6 alkyl group, the substituted or unsubstituted C_1 to C_6 alkoxy group, the halogenated alkyl group, the substituted or unsubstituted amino group, the substituted or unsubstituted amide group, the substituted or unsubstituted C_6 to C_{30} aryl group, the substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, and the ester group are all the same as those described above.

[0180]

In the substituent described above, the halogen, the C_1 to C_6 alkoxy group, the C_1 to C_6 alkyl group, the arylalkoxy group, the C_6 to C_{30} aryl group, and the C_4 to C_{30} heterocyclic groups are all the same as those described above.

[0181]

In R^{52} described above, the substituted or unsubstituted C_1 to C_6 alkyl group is preferably a substituted or unsubstituted C_1 to C_6 linear alkyl group, a C_1 to C_6 side chain alkyl group or a C_1 to C_6 cycloalkyl group, more preferably methyl, trifluoromethyl, ethyl, trifluoroethyl, n-propyl, isopropyl, n-butyl, sec-butyl, t-butyl, n-pentyl, isopentyl, neopentyl, n-hexyl, cyclohexyl or the like. The substituent of R^{52} is more preferably one or more of a methyl group, a sulfo group, a fluorine atom, an amino group and a methoxy group.

[0182]

The substituted or unsubstituted aryl group is preferably a substituted or unsubstituted phenyl group, a substituted or unsubstituted naphthyl group, a substituted or unsubstituted anthracenyl group, a substituted or unsubstituted phenanthryl group, a substituted or unsubstituted pyrenyl group, or a substituted or unsubstituted biphenyl group. A phenyl group, p-methylphenyl, o-methylphenyl, m-methylphenyl, sulfophenyl, p-methoxyphenyl, p-fluorophenyl or the like is preferred, and the substituent of R^{52} is preferably one or more of a methyl group, a sulfo group, a fluorine atom, an amino group and a methoxy group. In R^{47}, R^{48}, R^{49} and R^{50} described above, R^{47}, R^{48}, R^{49} and R^{50} are preferably hydrogen.

[0183]

The acid anhydride has the general formula $(R^{52}CO)_2O$, and

from the viewpoint of industrialization cost, the acid anhydride is preferably acetic anhydride, benzoic anhydride, or trifluoroacetic anhydride. The acyl chloride has the general formula $R^{52}COCl$, wherein R_{25} is the same as described above, and from the viewpoint of industrialization cost, the acyl chloride is preferably acetyl chloride, propionyl chloride, hexanoyl chloride, benzoyl chloride or pivaloyl chloride.

[0184]

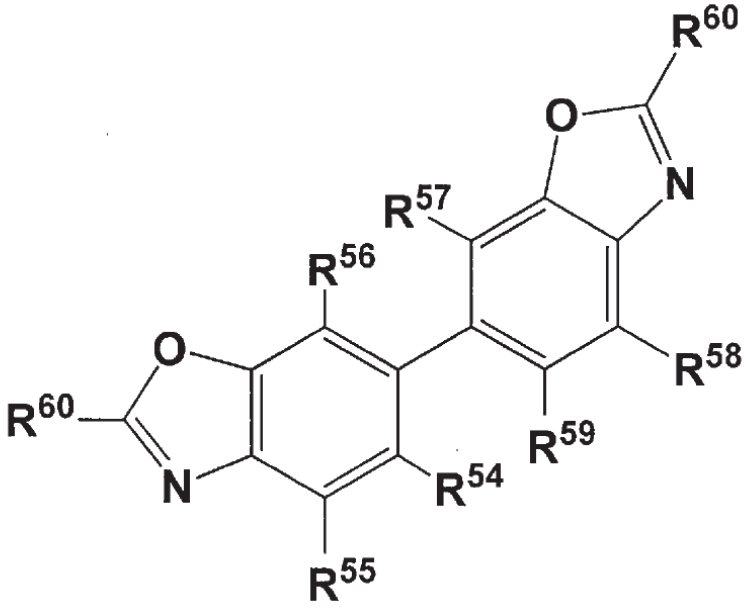
The temperature of the amidation reaction is preferably 0°C to 80°C, more preferably 10°C to 40°C. A solvent of the amide reaction to be used is an aprotic solvent, more preferably tetrahydrofuran or dichloromethane. The reaction time is preferably from 1 h to 48 h, and more preferably from 1 h to 12 h from the viewpoints of reaction rate and industrialization cost.

[0185]

In the present invention, the 5,5'-dibromo-4,4'-diamidobiphenyl derivative represented by the general formula (13) obtained by the above production process is reacted under the action of a catalyst and inorganic alkali, whereby a 6,6'-dibenzoxazole derivative represented by the general formula (14) is further obtained.

[0186]

[Chemical Formula 24]



(14)

[0187]

In the general formula (14), R^{54} and R^{59} are the same and each independently one kind selected from the group consisting of a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group. R^{55} and R^{58} are the same, R^{56} and R^{57} are the same, and they are each independently one kind selected from the group consisting of hydrogen, halogen, a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino

group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group. Among them, the substituents may be the same or different and each independently represent one or more of halogen, trifluoromethyl, trimethylsilyl, a C_1 to C_6 alkoxyl group, a C_1 to C_6 alkyl group, an aryl alkoxyl group, a C_6 to C_{30} aryl group, and a C_4 to C_{30} heterocyclic group, and R^{60} is one kind selected from the group consisting of a substitutable C_1 to C_6 alkyl group and a substitutable aryl group. The substituent in R^{60} is one or more of a methyl group, a sulfo group, a fluorine atom, an amino group, and a methoxy group.

[0188]

In R^{54} and R^{59} described above, the substituted or unsubstituted C_1 to C_6 alkyl group, the substituted or unsubstituted C_1 to C_6 alkoxy group, the halogenated alkyl group, the substituted or unsubstituted amino group, the substituted or unsubstituted amide group, the substituted or unsubstituted C_6 to C_{30} aryl group, the substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, and the ester group are all the same as those described above.

[0189]

In R^{55}, R^{56}, R^{57} and R^{58} described above, the halogen is preferably fluoro, chloro or iodo, and the substituted or unsubstituted C_1 to C_6 alkyl group, the substituted or

unsubstituted C_1 to C_6 alkoxy group, the halogenated alkyl group, the substituted or unsubstituted amino group, the substituted or unsubstituted amide group, the substituted or unsubstituted C_6 to C_{30} aryl group, the substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, and the ester group are all the same as those described above.

[0190]

In the substituent described above, the halogen, the C_1 to C_6 alkoxy group, the C_1 to C_6 alkyl group, the arylalkoxy group, the C_6 to C_{30} aryl group, and the C_4 to C_{30} heterocyclic groups are all the same as those described above.

[0191]

In R^{60} described above, the substituted or unsubstituted C_1 to C_6 alkyl group is preferably a substituted or unsubstituted C_1 to C_6 linear alkyl group, a C_1 to C_6 side chain alkyl group or a C_1 to C_6 cycloalkyl group, more preferably methyl, trifluoromethyl, ethyl, trifluoroethyl, n-propyl, isopropyl, n-butyl, sec-butyl, t-butyl, n-pentyl, isopentyl, neopentyl, n-hexyl, cyclohexyl or the like. The substituent of R^{60} is more preferably one or more of a methyl group, a sulfo group, a fluorine atom, an amino group, and a methoxy group.

[0192]

The substituted or unsubstituted aryl group is preferably a substituted or unsubstituted phenyl group, a substituted or unsubstituted naphthyl group, a substituted or unsubstituted

anthracenyl group, a substituted or unsubstituted phenanthryl group, a substituted or unsubstituted pyrenyl group, or a substituted or unsubstituted biphenyl group. A phenyl group, p-methylphenyl, o-methylphenyl, m-methylphenyl, sulfophenyl, p-methoxyphenyl, p-fluorophenyl or the like is preferred, and the substituent of R^{60} is preferably one or more of a methyl group, a sulfo group, a fluorine atom, an amino group and a methoxy group. In R^{55}, R^{56}, R^{57} and R^{58} described above, R^{55}, R^{56}, R^{57} and R^{58} are preferably hydrogen.

[0193]

The catalyst contains at least a copper catalyst and may or may not contain a ligand, wherein the copper catalyst is preferably copper (I) iodide, copper (I) oxide, copper (I) acetate, or copper (I) cyanide, more preferably copper (I) iodide or copper (I) oxide, among which the ligand is preferably N,N'-dimethylethylenediamine, ethylenediamine, ethylene glycol or 1,10-o-phenanthroline, more preferably N,N'-dimethylethylenediamine, inorganic alkali in a catalytic reaction process is preferably one or more of potassium carbonate or potassium phosphate, and the reaction temperature is preferably 100℃ to 140℃.

[0194]

The solvent used is preferably a high-boiling organic solvent, more preferably toluene or xylene.

In the present invention, a

5,5'-dihydroxyl-4,4'-diaminobiphenyl derivative is further obtained by a ring-opening reaction of a 6,6'-dibenzoxazole derivative, obtained by the above production process, under acidic conditions.

[0195]

As the acidic condition, an inorganic strong acid is preferred, and the inorganic strong acid is preferably hydrochloric acid, sulfuric acid, acetic acid, phosphoric acid, nitric acid or formic acid, more preferably hydrochloric acid or sulfuric acid from the viewpoint of industrialization cost. The solvent used for the ring-opening reaction is a protic solvent, ethanol, methanol, isopropanol or water is preferred, and from the viewpoint of industrialization cost, ethanol or water is more preferred.

[0196]

As described above, the present invention relates to a first 5,5'-dihydroxyl-4,4'-diaminobiphenyl derivative and industrial production process thereof, the production yield of the production process is high, the post-treatment is simple, and the production cost is low. The 5,5'-dihydroxyl-4,4'-diaminobiphenyl derivative produced according to the present invention can be used in the field of electronic materials or drug intermediates such as polyimide resin, thin film, liquid crystal material, semiconductor, flat panel display and the like.

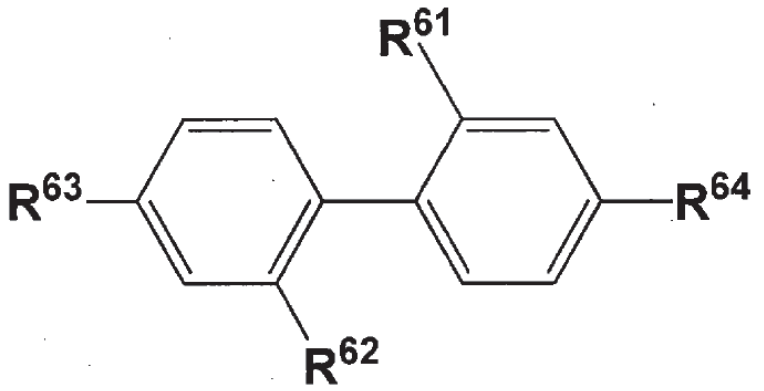
[0197]

Next, a dibromobiphenyl derivative in the present invention will be explained.

With respect to a method for synthesizing the dibromobiphenyl derivative, the above reaction is carried out by using a biphenyl compound having a structure represented by the general formula (15) as a raw material, without using other reactants (catalyst, etc.), and a dibromobiphenyl derivative having a structure represented by the general formula (16) is obtained under the reaction conditions only for an aprotic solvent and a bromination reagent. In this method, the reaction yield is high, the post-treatment is simple, the solvent recovery and use is facilitated, the pollution to the environment is small, and mass production is easily realized.

[0198]

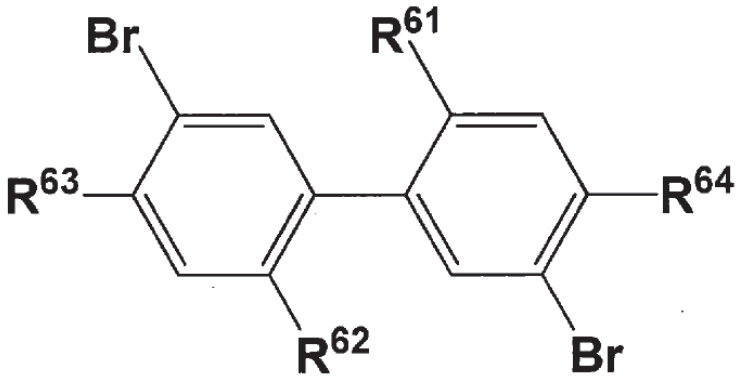
[Chemical Formula 25]



(15)

[0199]

[Chemical Formula 26]



(16)

[0200]

In the general formulae (15) and (16), R^{61} and R^{62} may be the same or different. They are each one kind selected from the group consisting of hydrogen, halogen, a C_1 to C_6 alkyl group, a C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, an ester group and a nitro group. R^3 and R^4 may be the same or different. They are each one kind selected from the group consisting of a C_1 to C_6 alkyl group, a C_1 to C_6 alkoxyl group, a hydroxyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted imide group, a substituted or unsubstituted sulfamine group, a substituted or unsubstituted sulfinamide group, and a substituted or unsubstituted aromatic heterocyclic group. Among them, the substituents may be the same or different and represent one or more of trifluoromethyl,

trimethylsilyl, a C_1 to C_6 alkoxyl group, a C_1 to C_6 alkyl group, an aryl alkoxyl group, a C_6 to C_{30} aryl group, and a heterocyclic group.

[0201]

In R^{61} and R^{62} described above, the halogen is preferably fluoro, chloro or bromo, more preferably fluoro or chloro.

The C_1 to C_6 alkyl group is preferably a C_1 to C_6 linear alkyl group, a C_1 to C_6 side chain alkyl group or a C_1 to C_6 cycloalkyl group, more preferably a C_1 to C_6 saturated aliphatic hydrocarbon group such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, t-butyl, n-pentyl, isopentyl, neopentyl, cyclopentyl, n-hexyl and cyclohexyl. The C_1 to C_6 alkoxyl group is preferably a C_1 to C_6 linear alkoxyl group, a C_1 to C_6 side chain alkoxyl group or a C_1 to C_6 cycloalkoxyl group. More preferred is methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy, t-butoxy, n-pentyloxy, isopentyloxy, neopentyloxy, n-hexyloxy, cyclopentyloxy, cyclohexyloxy or the like.

[0202]

The halogenated alkyl group is preferably trifluoromethyl, trifluoroethyl, chloromethyl, dichloromethyl, trichloromethyl, dichloroethyl, tetrachloroethyl, bromomethyl, bromoethyl or the like, more preferably trifluoromethyl or trifluoroethyl, still more preferably trifluoromethyl. The substituted or unsubstituted amino group is preferably a primary amino group, secondary amino

group or tertiary amino group, the amino group may be substituted by one or two groups, and the substituent in the amino group may be the same or different. The substituent is preferably a linear alkyl group, a side chain alkyl group, a cycloalkyl group, a halogenated alkyl group, an arylalkoxyl group, an aryl group, a heteroaryl group, a heterocyclic group or the like. An amino group, methylamino, ethylamino, propylamino, butylamino, pentylamino, hexylamino, isopropylamino, t-butylamino, cyclopentylamino, cyclohexylamino, dimethylamino, trifluoromethylamino, phenylamino, naphthylamino, anthracene amino, phenanthrylamino, pyrenylamino, benzylamino, pyridinamino, furanylamino, pyronylamino, carbazoylamino, thiopheneamino, quinoline amino or the like is more preferred, and an amino group is still more preferred. The substituted or unsubstituted amide group is preferably an alkylamide group, a halogenated alkylamide group, an arylalkoxyamide group, a heterocyclic group amide group, an arylamide group, an alkoxyamide group, or the like. Among them, the substituent may be connected to a carbonyl group or may be connected to an amino group, and acetamide, propionamide, butyrylamino, pentanamide, hexanamide, trifluoromethylamide, tertiarybutoxideamide, benzamide, naphthamide, bibenzamide, benzyloxyamide, pyridineformamide, furanylformamide, thiopheneformamide, acetopropylamine, or acetanilide is more preferred. Acetamide,

tertiarybutoxideamide, benzyloxyamide or the like is still more preferred. The substituent of the substituted or unsubstituted aryl group is not particularly limited, but an aromatic hydrocarbon group such as a phenyl group, a naphthyl group, an anthracenyl group, a phenanthryl group, a pyrenyl group, a biphenyl group, or a terphenyl is preferred, the ester group is preferably a substituted or unsubstituted alkoxyl carbonic acid ester group, and methoxycarbonate ester, ethoxycarbonate ester, propoxycarbonate ester, butoxycarbonate ester, tertiarybutoxidecarbonate ester, benzyloxycarbonate ester, or fluorenylmethoxycarbonate ester and the like are more preferred.

[0203]

In R^{63} and R^{64} described above, the description of the C_1 to C_6 alkyl group, the C_1 to C_6 alkoxyl group, the substituted or unsubstituted aryl group, the substituted or unsubstituted amino group, the substituted or unsubstituted amide group, and the substituent is as described above.

[0204]

The substituted or unsubstituted imide group is preferably a C_1 to C_6 alkyl imide group, a C_1 to C_6 halogenated alkyl imide group, a C_1 to C_6 alkoxy imide group, a C_6 to C_{30} aryl imide group, an aryl alkoxy imide group, a heterocyclic imide group or the like, more preferably phthalimide, succinimide, ditertiarybutoxidedicarboximide,

dibenzyloxydicarboximide or the like. The substituted or unsubstituted sulfamine group is preferably a C_1 to C_6 alkylsulfamine group, a C_1 to C_6 halogenated alkylsulfamine group, a C_1 to C_6 arylsulfamine group, or a heterocyclic sulfamine group, more preferably methanesulfonamide, trifluoromethylsulfamic, benzenesulfonamide, p-toluenesulfonamide or the like. The substituted or unsubstituted sulfinamide group is preferably a C_1 to C_6 alkylsulfinamide group, a C_1 to C_6 halogenated alkylsulfinamide group, a C_1 to C_6 arylsulfinamide group, a heterocyclic sulfinamide group, or the like, more preferably methylsulfinamide, trifluoromethylsulfinamide, phenylsulfinamide, p-toluenesulfinamide, t-butylsulfinamide or the like. The substituted or unsubstituted aromatic heterocyclic group is preferably a cyclic aromatic group having a hetero atom other than carbon in one or more rings, and may be substituted or unsubstituted. Although not particularly limited to the number of carbon atoms of an aromatic heterocyclic ring, an aromatic heterocyclic group having 2 to 30 carbon atoms is preferred. Preferred is a nitrogen-containing aromatic heterocyclic group such as a pyrrole group, a pyridine group, a pyrimidinyl group, a quinoline group, a pyrazine group, a carbazoyl group, an indolyl group, or a phthalimido group, and more preferred is a phthalimido group.

[0205]

In the substituent, the C_1 to C_6 alkoxyl group is preferably a C_1 to C_6 linear alkoxyl group, a C_1 to C_6 side chain alkoxyl group or a C_1 to C_6 cycloalkoxyl group, more preferably methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy, t-butoxy, n-pentyloxy, isopentyloxy, neopentyloxy, n-hexyloxy, cyclohexyloxy or the like. The C_1 to C_6 alkyl group is preferably a C_1 to C_6 linear alkyl group, a C_1 to C_6 side chain alkyl group or a C_1 to C_6 cycloalkyl group, more preferably a C_1 to C_6 saturated aliphatic hydrocarbon group such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, t-butyl, n-pentyl, isopentyl, neopentyl, cyclopentyl, n-hexyl and cyclohexyl. The arylalkoxyl group is preferably a benzyloxy group, a naphthylmethoxy group, an anthracenylmethoxy group, a fluorenylmethoxy group, a 3,5-di-t-butylphenyl-1-isopropoxy group, a phenylethoxy group, a naphthylethoxy group, benzidine-3-methoxy group or the like, more preferably a benzyloxy group or a fluorenylmethoxy group.

[0206]

The C_6 to C_{30} aryl group is preferably an aromatic hydrocarbon group such as a phenyl group, a naphthyl group, an anthracenyl group, a phenanthryl group, a pyrenyl group, a biphenyl group, or a terphenyl.

[0207]

The heterocyclic group is preferably a pyridine group,

a carbazoyl group, an imidazole group, a furanyl group, a thiophene group, an oxazoyl group, an indolyl group, a benzofuranyl group, a benzothiophene group, a thiazinyl group, a pyrimidine group, a quinolyl group, an isoquinolyl group, a pyrazo group, an imidazole group, a thiazoyl group, a pyranyl group, a bipelazine group, a phenazine group, a phenothiazine group, a pyridazinyl group, a tetrahydrofuran group, a dioxane group, a phthalimide group, a succinimido group or the like, more preferably a phthalimido group or a succinimido group.

[0208]

R^{61} and R^{62} may be the same or different from the viewpoint of difficulty of raw material industrial production and are preferably each one kind selected from the group consisting of halogen, a C_1 to C_6 alkyl group, a C_1 to C_6 alkoxyl group, a halogenated alkane, an ester group and a nitro group. From the viewpoint of raw material cost, the halogenated alkane is preferably one of trifluoromethyl and trifluoroethyl, the C_1 to C_6 alkyl group is more preferably methyl, and the C_1 to C_6 alkoxyl group is more preferably methoxy.

[0209]

From the viewpoints of availability of raw materials and selectivity of bromination reaction, R^{63} and R^{64} may be the same or different, and are preferably each one kind selected from the group consisting of a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a

substituted or unsubstituted imide group, a substituted or unsubstituted sulfamine group, a substituted or unsubstituted sulfinamide group, and a substituted or unsubstituted aromatic heterocyclic group. From the viewpoint of raw material cost, they are more preferably each independently one of an amino group, an acetamide group, a tertiarybutoxideamide group, a benzyloxyamide group, a ditertiarybutoxidedicarboximide group, a dibenzyloxydicarboximide group, and a phthalimide group.

[0210]

Hereinafter, the solvent used in the present invention will be described in detail. The aprotic solvent used in the present invention contains one or more kinds of alkane solvents (such as cyclohexane, normal hexane, and normal pentane), arene solvents (such as benzene, toluene, and xylene), haloalkane solvents (such as dichloromethane, trichloromethane, carbon tetrachloride, dichloroethane, and tetrachloroethane), ester solvents (such as methyl acetate, ethyl acetate, propyl acetate, butyl acetate, and propyleneglycolmethyletheracetate), ether solvents (such as ethyl ether, tetrahydrofuran, and 1,4-dioxane), ketones (such as acetone, butanone, and methylethylketone) and other kinds of aprotic solvents (such as N,N-dimethylformamide, N-methylpyrrolidone, acetonitrile, and dimethylsulfoxide) and is preferably one or more of ester solvents, ether solvents, arene solvents and the above solvents. From the viewpoints of solubility of raw materials and stability

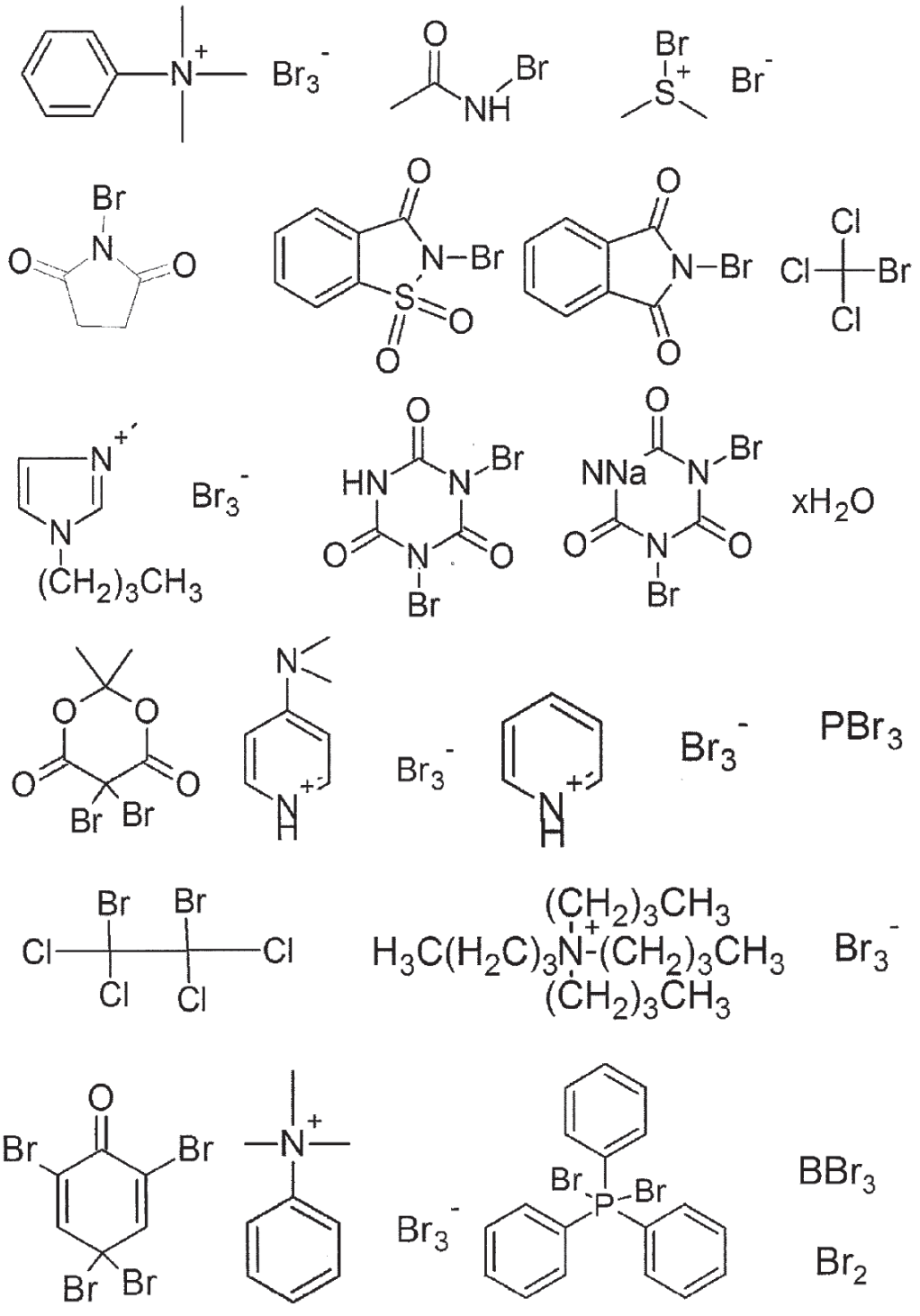
in reactions, ester solvents, ether solvents or mixtures thereof are preferred, and from the comprehensive viewpoint of solubility and price of the solvent, one or more of methylacetate, ethylacetate, propylacetate, butylacetate, propyleneglycolmethyletheracetate, glycoldimethylether, tetrahydrofuran, 1,4-dioxane and the like, and the mixed solvents described above are more preferred.

[0211]

Hereinafter, the bromination solvent used in the present invention will be described in detail. The bromination solvent used in the present invention is selected from one or more of the following reagents.

[0212]

[Chemical Formula 27]



[0213]

From the viewpoints of the price, safety, and operation

convenience of a bromination reagent, NBS or Br_2 is preferred, and Br_2 is more preferred. In the present invention, the molar ratio of a raw material biphenyl compound to a bromination reagent is 1:2 to 1:6, and from the comprehensive viewpoints of the price, yield and difficulty in post-treatment of the raw material, the molar ratio of the raw material biphenyl compound to the bromination reagent is preferably 1:2 to 1:3.

[0214]

The molar concentration of the raw material biphenyl compound in the present invention is preferably from 0.05 mol/L to 5 mol/L, and from the viewpoints of solubility and solvent cost, the molar concentration of the raw material biphenyl compound is more preferably 0.2 mol/L to 2 molL/L.

The reaction temperature in the present invention is preferably from -30°C to 60°C, and more preferably from -20°C to 60°C from the viewpoint of mass production cost. The reaction time in the present invention is preferably from 1 h to 48 h, and more preferably from 1 h to 12 h from the viewpoints of reaction rate and mass production cost.

[0215]

In the post-treatment of the present invention, when an alkali is added to adjust pH, the alkali used is preferably an inorganic alkali, and from the viewpoint of mass production cost, sodium carbonate, potassium carbonate, calcium carbonate, sodium bicarbonate, potassium bicarbonate, sodium hydroxide,

potassium hydroxide, calcium hydroxide, lithium hydroxide or the like is preferred.

[0216]

In the post-treatment of the present invention, when extraction is carried out using an organic solvent, ethyl acetate, butyl acetate, dichloromethane, toluene or the like is preferred from the viewpoints of the cost and solubility of the solvent.

When a crude product of the present invention is purified, from the viewpoints of the cost and solubility of the solvent, the solvent used is preferably one or more solvents such as petroleum ether, ethyl acetate, butyl acetate, toluene, xylene, dichloromethane, 1,2-dichloroethane, acetonitrile, ethanol, methanol, isopropanol, propyleneglycolmethyletheracetate, glycoldimethylether, ethylether, tetrahydrofuran, and 1,4-dioxane.

[Examples]

[0217]

Hereinafter, the present invention will be described with reference to examples and so on in the order of (1) resin, photosensitive resin composition, (2) 5,5'-dihydroxyl-4,4'-diaminobiphenyl derivative, and (3) dibromobiphenyl derivative, but the present invention is not limited by these examples.

<Resin and Photosensitive Resin Composition>

Resins and resin compositions in the examples were evaluated by the following method.

[0218]

1) Method for measuring film thickness

Lambda Ace STM-602 manufactured by Dainippon Screen Mfg. Co., Ltd. was used, and both a resin film and a film after heat curing were measured to have a refractive index of 1.629.

[0219]

2) Method for measuring coefficient of linear thermal expansion

A resin solution was spin-coated on an 8-inch silicon wafer and then baked for 3 minutes on a hot plate (using a coating and developing apparatus Act-8 manufactured by Tokyo Electron Limited) at 120°C to obtain a resin film.

[0220]

The temperature of this resin film was raised to 250°C at an oxygen concentration of 20 ppm or less at 5°C/min using an inert oven CLH-21 CD-S (manufactured by Koyo Thermo Systems Co., Ltd.), heat treatment was carried out at 250°C for 1 hour, and then cooling was carried out to 50°C at 5°C/min. Subsequently, the film was immersed in hydrofluoric acid for 1 to 4 minutes to be peeled from a substrate and then to be air-dried, whereby a film after heat treatment was obtained. A rotational speed at the time of spin coating was adjusted such that thickness of the resin film after heat treatment was 10

μm.

[0221]

The film after the heat treatment was measured in a nitrogen stream using a thermomechanical analyzer (EXSTAR6000 TMA/SS 6000 manufactured by SII Nanotechnology Inc.). A temperature rise method was carried out under the following conditions. In the first stage, a temperature of a sample was raised to 200°C at a rate of temperature rise of 5°C/min to remove adsorbed water from the sample, and in the second stage, the sample was air cooled to room temperature at a rate of temperature fall of 5°C/min. In the third stage, the main measurement was carried out at the temperature rise rate of 5°C/min, and an average value of the coefficient of linear thermal expansion at 50°C to 200°C was obtained.

[0222]

However, only with respect to resins (D1) to (D5) to be described later, while those subjected to heat treatment at 250°C for 1 hour were measured, those subjected to heat treatment at 320°C for 1 hour were measured.

[0223]

3) Method for measuring absorbance

A resin solution was spin-coated on a glass substrate (AN-100, manufactured by Asahi Glass Co., Ltd.) having a thickness of 50 mm × 50 mm × 0.7 mm using a spin coater MS-A 200 manufactured by Mikasa Co., Ltd., and then the coated

substrate was baked for 3 minutes on a hot plate (D-SPIN manufactured by Dainippon Screen Co., Ltd.) at 120°C to obtain a resin film. The rotational speed at the time of spin coating was adjusted such that thickness of the resin film was 10 μm.

[0224]

With respect to the obtained resin film, the absorbance at 365 nm was measured using an ultraviolet-visible spectrophotometer (MultiSpec 1500 manufactured by Shimadzu Corporation). The obtained absorbance was divided by the resin film thickness to obtain the absorbance per 1 μm.

[0225]

4) Method for measuring alkali developing speed

A resin solution was spin-coated on an 8-inch silicon wafer and then baked for 4 minutes on a hot plate (using a coating and developing apparatus Act-8 manufactured by Tokyo Electron Limited) at 120°C to obtain a resin film. The rotational speed at the time of spin coating was adjusted such that thickness of the resin film was 10 μm.

[0226]

The resin film was developed for 60 seconds with a 2.38% by weight tetramethylammonium (TMAH) aqueous solution (ELM-D produced by Mitsubishi Gas Chemical Company, Inc.), and then rinsed with pure water. The film thickness after rinsing was measured, and a reduction in film thickness per minute was calculated.

[0227]

5) Method for measuring residual stress

A resin solution was spin-coated on an 8-inch silicon wafer and then baked for 3 minutes on a hot plate (using a coating and developing apparatus Act-8 manufactured by Tokyo Electron Limited) at 120°C to obtain a resin film.

[0228]

The temperature of this resin film was raised to 250°C at an oxygen concentration of 20 ppm or less at 5°C/min using an inert oven CLH-21 CD-S (manufactured by Koyo Thermo Systems Co., Ltd.), heat treatment was carried out at 250°C for 1 hour, and then cooling was carried out to 50°C at 5°C/min. Subsequently, the film was immersed in hydrofluoric acid for 1 to 4 minutes to be peeled from a substrate and then to be air-dried, whereby a film after heat treatment was obtained. A rotational speed at the time of spin coating was adjusted such that thickness of the resin film after heat treatment was 10 μm.

[0229]

With respect to the film after the heat treatment, residual stress was measured at 23°C and 45% RH under an air atmosphere using a thin film stress measurement device (manufactured by KLA-Tencor Corporation). As a blank, a silicon wafer before coating of the resin solution was used.

[0230]

6) Photosensitivity evaluation method

A resin solution was spin-coated on an 8-inch silicon wafer and then baked for 3 minutes on a hot plate (using a coating and developing apparatus Act-8 manufactured by Tokyo Electron Limited) at 120°C to produce a prebaked film having a thickness of 6 μm. This film was exposed with an exposure energy of 0 to 1000 mJ/cm^2 at a 10 mJ/cm^2 step using an i-line stepper (NIKON NSR i9). After exposure, the film was developed for 90 seconds with a 2.38% by weight tetramethylammonium (TMAH) aqueous solution (ELM-D produced by Mitsubishi Gas Chemical Company, Inc.), and then rinsed with pure water. At this time, the exposure energy (referred to as a minimum exposure energy Eth) at which an exposed portion was completely dissolved and disappeared after the exposure and development was taken as sensitivity. When Eth is 700 mJ/cm^2 or less, it can be judged that sensitivity is high. Eth is more preferably 500 mJ/cm^2 or less.

[0231]

Abbreviations of acid dianhydride and diamine shown in the following examples and comparative examples are as follows.

PMDA: pyromellitic anhydride

ODPA: 3,3', 4,4'-diphenylethertetracarboxylic acid dianhydride

SiDA: 1,1,3,3-tetramethyl-1,3-bis(3-aminopropyl)disiloxane

NMP: N-methyl-2-pyrrolidone

GBL: Gamma-butyrolactone

3-Aph: m-aminophenol

PMDA-H: 1S, 2S, 4R, 5R-cyclohexanetetracarboxylic dianhydride

NA: 5-norbornene-2.3-dicarboxylic anhydride

TFMB: 2,2'-bis(trifluoromethyl)benzidine

HAB: 3,3'-dihydroxybenzidine

BPDA: 3,3', 4,4'-biphenyltetracarboxylic acid dianhydride

KBM-403: 3-glycidoxypropyltrimethoxysilane.

BAHF: 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane

HFHA:

2,2-bis[3-(3-aminobenzamide)-4-hydroxyphenyl]hexafluoroprop

ane

DAE: 4,4'-diaminodiphenylether.

[0232]

Synthesis Example 1 Synthesis of hydroxyl group-containing diamine compound (a)

17.6 g (0.05 mol) of 2,2'-bis(trifluoromethyl)-5,5'-dihydroxybenzidine was dissolved in 100 mL of acetone and 17.4 g (0.3 mol) of propyleneoxide and cooled to -15°C. A solution prepared by dissolving 20.4 g (0.11 mol) of 3-nitrobenzoyl chloride in 100 mL of acetone was dropped thereto. After completion of the dropping, the mixture was allowed to react at -15°C for 4 hours, and then the temperature was returned to room temperature. A precipitated white solid was separated by filtration and vacuum

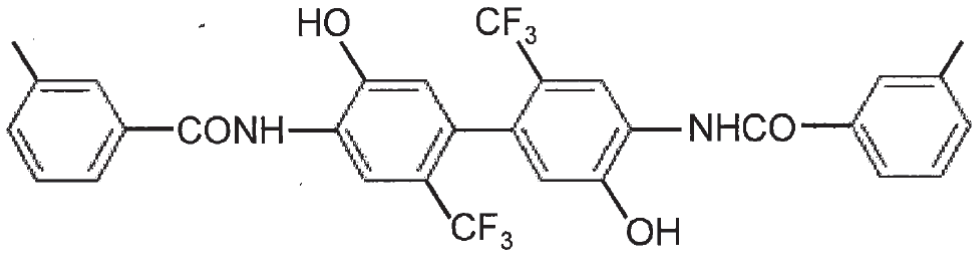
dried at 50°C.

[0233]

30 g of the obtained white solid was placed in a 300 mL stainless steel autoclave and dispersed in 250 mL of methylcellosolve, and 2 g of 5% palladium-carbon was added. Hydrogen was introduced here with a balloon, and a reduction reaction was carried out at room temperature. About 2 hours later, the reaction was terminated on confirmation of the fact that the balloon no longer shrank. After the termination of the reaction, a palladium compound as a catalyst was removed by filtration, followed by concentration with a rotary evaporator, affording a hydroxyl group-containing diamine compound (a) represented by the following formula. An obtained solid was used in the reaction as it was.

[0234]

[Chemical Formula 28]



[0235]

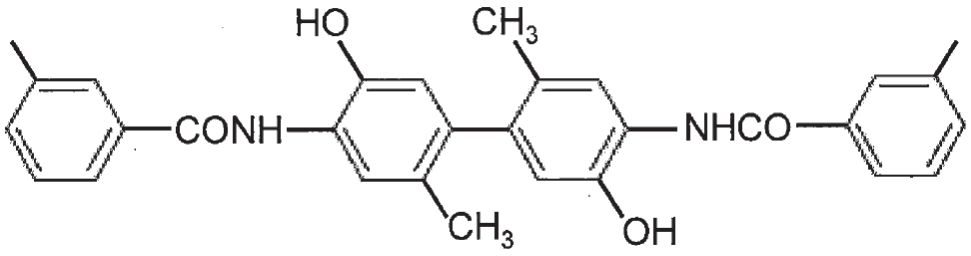
Synthesis Example 2 Synthesis of hydroxyl group-containing diamine compound (b)

A hydroxyl group-containing diamine compound (b)

represented by the following formula was obtained in the same manner as in Synthesis Example 1 except that 17.6 g (0.05 mol) of 2,2'-bis(trifluoromethyl)-5,5'-dihydroxybenzidine was changed to 17.6 g (0.05 mol) of 2,2'-dimethyl-5,5'-dihydroxybenzidine. An obtained solid was used in the reaction as it was.

[0236]

[Chemical Formula 29]



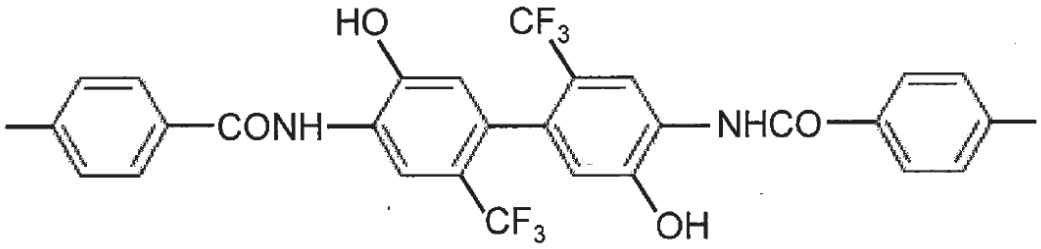
[0237]

Synthesis Example 3 Synthesis of hydroxyl group-containing diamine compound (c)

A hydroxyl group-containing diamine compound (c) represented by the following formula was obtained in the same manner as in Synthesis Example 1 except that 20.4 g (0.11 mol) of 3-nitrobenzoyl chloride was changed to 20.4 g (0.11 mol) of 4-nitrobenzoyl chloride. An obtained solid was used in the reaction as it was.

[0238]

[Chemical Formula 30]



[0239]

Synthesis Example 4 Synthesis of hydroxyl group-containing acid dianhydride (d)

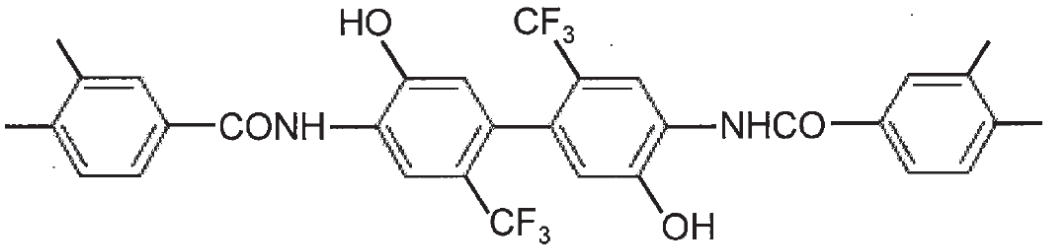
In a dry nitrogen stream, 17.6 g (0.05 mol) of 2,2'-bis(trifluoromethyl)-5,5'-dihydroxybenzidine and 34.2 g (0.3 mol) of allyl glycidyl ether were dissolved in 100 g of ethylacetate and cooled to -15°C. 22.1 g (0.11 mol) of trimellitic anhydride chloride dissolved in 50 g of ethylacetate was dropped thereto so that a temperature of a reaction liquid did not exceed 0°C. After completion of the dropping, the mixture was stirred at 0°C for 4 hours.

[0240]

This solution was concentrated with a rotary evaporator and charged into 1 l of toluene to obtain a hydroxyl group-containing acid dianhydride (d) represented by the following formula. An obtained solid was used in the reaction as it was.

[0241]

[Chemical Formula 31]



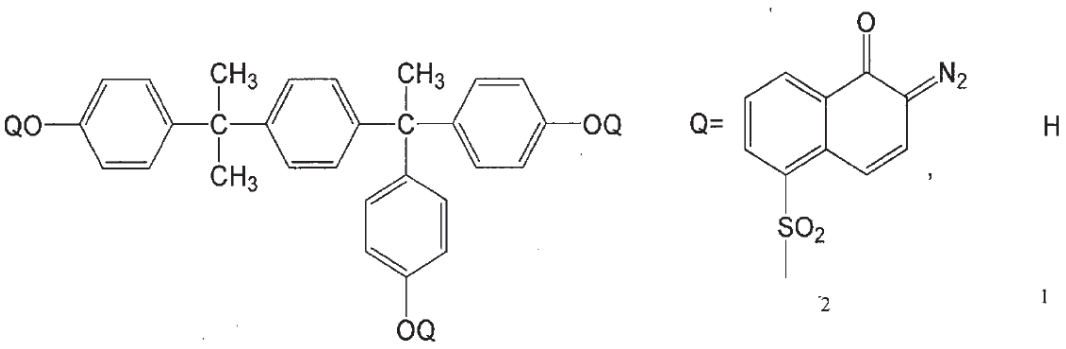
[0242]

Synthesis Example 5 Synthesis of quinonediazide compound (e)

In a dry nitrogen stream, 21.22 g (0.05 mol) of TrisP-PA (trade name, produced by Honshu Chemical Industry Co., Ltd.), 26.86 g (0.10 mol) of 5-naphthoquinonediazidosulfonylchloride, and 13.43 g (0.05 mol) of 4-naphthoquinonediazidosulfonylchloride were dissolved in 50 g of 1,4-dioxane, and the temperature was brought to room temperature. 15.18 g of triethylamine mixed with 50 g of 1,4-dioxane was dropped here so that the temperature of the system did not become 35°C or more. After completion of the dropping, the mixture was stirred at 30°C for 2 hours. A triethylamine salt was filtered, and the filtrate was charged into water. Thereafter, the resulting precipitate was collected by filtration. This precipitate was dried in a vacuum drier to obtain a quinonediazide compound (e) represented by the following formula.

[0243]

[Chemical Formula 32]



[0244]

Synthesis Example 6

In a dry nitrogen stream, 15.8 g (0.045 mol) of 2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine as an amine component and 0.62 g (0.0025 mol) of SiDA were dissolved in 100 g of GBL. 10.91 g (0.05 mol) of PMDA as an acid component was added thereto together with 10 g of GBL and reacted at 60°C for 2 hours, and then 0.545 g (0.005 mol) of 3-Aph as an end-capping agent was added together with 10 g of NMPGBL. The mixture was stirred at 60°C for 2 hours to obtain a resin solution (A1).

[0245]

Synthesis Examples 7 to 31

Resin solutions (A2) to (A26) were obtained in the same manner as in Synthesis Example 6 using a combination of the amine component, the acid component and the end-capping agent shown in Table 1.

[0246]

Synthesis Example 32

In a dry nitrogen stream, 15.8 g (0.045 mol) of 2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine as an amine component and 0.62 g (0.0025 mol) of SiDA were dissolved in 100 g of NMP. 10.91 g (0.05 mol) of PMDA as an acid component was added thereto together with 10 g of NMP and reacted at 40°C for 1 hour, and then 0.545 g (0.005 mol) of 3-Aph as an end-capping agent was added together with 10 g of NMP. The mixture was stirred at 40°C for 2 hours. Then, a solution in which 15.19 g (0.127 mol) of N,N-dimethylformamide dimethylacetal had been diluted with 4 g of NMP was dropped over 10 minutes. After completion of the dropping, the mixture was stirred at 40°C for 2 hours. After the termination of the reaction, 30 g of acetic acid was slowly charged while keeping the solution temperature at 30°C or less. After stirring at 30°C or less for 30 minutes, the solution was charged into 2 L of water, and a precipitate of a polymer powder was collected by filtration. This precipitate was collected by filtration and washed three times with water, and then the polymer powder was dried in a vacuum oven at 50°C for 72 hours to obtain a powder of resin (B1).

[0247]

Synthesis Examples 33 to 57

Resin solutions (B2) to (B26) were obtained in the same manner as in Synthesis Example 32 using a combination of the amine component, the acid component and the end-capping agent

shown in Table 2.

[0248]

Synthesis Example 58

In a dry nitrogen stream, 15.8 g (0.045 mol) of 2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine as an amine component and 0.62 g (0.0025 mol) of SiDA were dissolved in 100 g of NMP. 10.91 g (0.05 mol) of PMDA as an acid component was added thereto together with 10 g of NMP and reacted at 60°C for 1 hour, and then 0.545 g (0.005 mol) of 3-Aph as an end-capping agent was added together with 10 g of NMP. The mixture was stirred at 60°C for 1 hour and further stirred at 200°C for 4 hours. After completion of the stirring, the solution was charged into 2 L of water to obtain a white precipitate. This precipitate was collected by filtration, washed three times with water, and then dried in a vacuum oven at 50°C for 72 hours to obtain a powder of resin (C1).

[0249]

Synthesis Examples 59 to 79

Powders of resins (C2) to (C22) were obtained in the same manner as in Synthesis Example 58 using a combination of the amine component, the acid component and the end-capping agent shown in Table 3.

[0250]

Synthesis Example 80

The procedure was carried out in the same manner as in

Synthesis Example 58 except that 15.8 g (0.045 mol) of 2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine was changed to 9.73 g (0.045 mol) of HAB. However, the polymer was precipitated during cooling the solution after the reaction at 200°C, so that an insoluble resin was produced.

[0251]

Synthesis Example 81

In a dry nitrogen stream, 17.6 g (0.05 mol) of 2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine was dissolved in 50 g of NMP and 26.4 g (0.3 mol) of glycidylmethylether, and the temperature of the solution was cooled to -15°C. A solution prepared by dissolving 8.12 g (0.04 mol) of isophthaloyl dichloride in 25 g of GBL was dropped thereto so that an internal temperature did not exceed 0°C. After completion of the dropping, stirring was continued at -15°C for 6 hours. Then, 3.28 g (0.02 mol) of NA was charged, and the mixture was stirred at room temperature for 4 hours. After completion of the reaction, the solution was charged into 3 L of water containing 10% by weight of methanol to deposit a white precipitate. This precipitate was collected by filtration, washed three times with water, and then dried in a vacuum oven at 50°C for 72 hours to obtain a powder of resin (D1).

[0252]

Synthesis Examples 82 to 84

Powders of resins (D2) to (D4) were obtained in the same manner as in Synthesis Example 81 using a combination of the amine component, the acid component and the end-capping agent shown in Table 4.

[0253]

Synthesis Example 85

In a dry nitrogen stream, 17.6 g (0.05 mol) of 2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine was dissolved in 100 g of NMP. 14.32 g (0.04 mol) of diphenyletherdicarboxylic acid diimidazolide was added thereto together with 10 g of NMP, and the mixture was stirred at 85°C for 4 hours. Then, 3.28 g (0.02 mol) of NA was charged, and the mixture was stirred at 85°C for 2 hours. After the termination of the reaction, 30 g of acetic acid was slowly charged while keeping the solution temperature at 30°C or less. After stirring at 30°C or less for 30 minutes, the solution was charged into 2 L of water, and a precipitate of a polymer powder was collected by filtration. This precipitate was collected by filtration and washed three times with water, and then the polymer powder was dried in a vacuum oven at 50°C for 72 hours to obtain a powder of resin (D5).

[0254]

Examples 1 to 63, Comparative Examples 1 to 16

The resins (A1) to (A26) were maintained in a solution state, the resins (B1) to (B26), the resins (C1) to (C22), and the resins

(D1) to (D5) were dissolved in GBL, and a solution having a concentration of 40% was produced. Table 5-1 and Table 5-2 show results obtained by measuring the coefficient of linear thermal expansion, absorbance, alkali developing speed and residual stress as described above using the obtained solution.

[0255]

Example 64

17.5 g of the resin (B1), 2.3 g of the quinonediazide compound (b) obtained in Synthesis Example 5 and 0.5 g of KBM-403 were added to 45 g of GBL to obtain a photosensitive resin composition. The photosensitivity was evaluated as described above using the obtained photosensitive resin composition. Table 6 show evaluation results.

[0256]

Examples 65 to 106, Comparative Examples 17 to 26

A photosensitive resin composition was obtained in the same manner as in Example 64 for the resins (B2) to (B26), the resins (C1) to (C22) and the resins (D1) to (D5). The photosensitivity was evaluated as described above using the obtained photosensitive resin composition. Table 6 shows evaluation results.

[0257]

[Table 1]

Synthesis example	Resin liquid	Amine component ①	Amine component ②	Acid component ①	Acid component ②	Terminal blocking agent
6	A1	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	PMDA 10.91g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
7	A2	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	PMDA 8.72g (0.04 mol)	PMDA-H 2.24g (0.01 mol)	3-Aph 0.545g (0.005 mol)
8	A3	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
9	A4	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	PMDA 3.27g (0.015 mol)	PMDA-H 7.84g (0.035 mol)	3-Aph 0.545g (0.005 mol)
10	A5	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	PMDA-H 11.2g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
11	A6	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-4,4'-dihydroxy-3,3'-diaminobiphenyl 15.8 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
12	A7	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxy-4,4'-diaminodiphenyl ether 16.56 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
13	A8	SiDA 0.62g (0.0025 mol)	2,2'-dimethyl-3,3'-dihydroxybenzidine 10.98 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
14	A9	SiDA 0.62g (0.0025 mol)	5,5'-dimethyl-3,3'-dihydroxybenzidine 10.98 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
15	A10	SiDA 0.62g (0.0025 mol)	5,5'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
16	A11	SiDA 0.62g (0.0025 mol)	5,5'-dimethyl-3,3'-dihydroxy-4,4'-diaminodiphenyl ether 11.7 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
17	A12	SiDA 0.62g (0.0025 mol)	5,5'-dimethyl-4,4'-dihydroxy-3,3'-diaminobiphenyl 10.98 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
18	A13	SiDA 0.62g (0.0025 mol)	4,4'-dimethyl-5,5'-dihydroxy-3,3'-diaminobiphenyl 10.98 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
19	A14	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	ODPA 15.51g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
20	A15	SiDA 0.62g (0.0025 mol)	diamine (a) 26.55 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
21	A16	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	BPDA 14.71g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
22	A17	SiDA 0.62g (0.0025 mol)	diamine (b) 21.69 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
23	A18	SiDA 0.62g (0.0025 mol)	diamine (c) 26.55 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
24	A19	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	35.0 g of acid dianhydride (d) (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
25	A20	SiDA 0.62g (0.0025 mol)	TFMB 14.4 g (0.045 mol)	35.0 g of acid dianhydride (d)	-	3-Aph 0.545g (0.005 mol)
26	A21	SiDA 0.62g (0.0025 mol)	TFMB 14.4 g (0.045 mol)	PMDA 10.91 g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
27	A22	SiDA 0.62g (0.0025 mol)	HAB 9.72 g (0.045 mol)	PMDA 10.91 g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
28	A23	SiDA 0.62g (0.0025 mol)	BAHF 16.48 g (0.045 mol)	ODPA 15.51g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
29	A24	SiDA 0.62g (0.0025 mol)	HFHA 27.2 g (0.045 mol)	ODPA 15.51g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
30	A25	SiDA 0.62g (0.0025 mol)	DAE 9.01 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
31	A26	SiDA 0.62g (0.0025 mol)	DAE 9.01 g (0.045 mol)	ODPA 15.51g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)

[0258]

[Table 2]

Synthesis example	Resin liquid	Amine component ①	Amine component ②	Acid component ①	Acid component ②	Terminal blocking agent
32	B1	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	PMDA 10.91g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
33	B2	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	PMDA 8.72g (0.04 mol)	PMDA-H 2.24g (0.01 mol)	3-Aph 0.545g (0.005 mol)
34	B3	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
35	B4	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	PMDA 3.27g (0.015 mol)	PMDA-H 7.84g (0.035 mol)	3-Aph 0.545g (0.005 mol)
36	B5	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	PMDA-H 11.2g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
37	B6	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-4,4'-dihydroxy-3,3'-diaminobiphenyl 15.8 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
38	B7	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxy-4,4'-diaminodiphenyl ether 16.56 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
39	B8	SiDA 0.62g (0.0025 mol)	2,2'-dimethyl-3,3'-dihydroxybenzidine 10.98 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
40	B9	SiDA 0.62g (0.0025 mol)	5,5'-dimethyl-3,3'-dihydroxybenzidine 10.98 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
41	B10	SiDA 0.62g (0.0025 mol)	5,5'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
42	B11	SiDA 0.62g (0.0025 mol)	5,5'-dimethyl-3,3'-dihydroxy-4,4'-diaminodiphenyl ether 11.7 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
43	B12	SiDA 0.62g (0.0025 mol)	5,5'-dimethyl-4,4'-dihydroxy-3,3'-diaminobiphenyl 10.98 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
44	B13	SiDA 0.62g (0.0025 mol)	4,4'-dimethyl-5,5'-dihydroxy-3,3'-diaminobiphenyl 10.98 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
45	B14	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	ODPA 15.51g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
46	B15	SiDA 0.62g (0.0025 mol)	diamine (a) 26.55 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
47	B16	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	BPDA 14.71g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
48	B17	SiDA 0.62g (0.0025 mol)	diamine (b) 21.69 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
49	B18	SiDA 0.62g (0.0025 mol)	diamine (c) 26.55 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
50	B19	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	35.0 g of acid dianhydride (d) (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
51	B20	SiDA 0.62g (0.0025 mol)	TFMB 14.4 g (0.045 mol)	35.0 g of acid dianhydride (d) (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
52	B21	SiDA 0.62g (0.0025 mol)	TFMB 14.4 g (0.045 mol)	PMDA 10.91 g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
53	B22	SiDA 0.62g (0.0025 mol)	HAB 9.72 g (0.045 mol)	PMDA 10.91 g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
54	B23	SiDA 0.62g (0.0025 mol)	BAHF 16.48 g (0.045 mol)	ODPA 15.51g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
55	B24	SiDA 0.62g (0.0025 mol)	HFHA 27.2 g (0.045 mol)	ODPA 15.51g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
56	B25	SiDA 0.62g (0.0025 mol)	DAE 9.01 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
57	B26	SiDA 0.62g (0.0025 mol)	DAE 9.01 g (0.045 mol)	ODPA 15.51g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)

[0259]

[Table 3]

Synthesis example	Resin liquid	Amine component ①	Amine component ②	Acid component ①	Acid component ②	Terminal blocking agent
58	C1	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	PMDA 10.91g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
59	C2	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	PMDA 8.72g (0.04 mol)	PMDA-H 2.24g (0.01 mol)	3-Aph 0.545g (0.005 mol)
60	C3	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
61	C4	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	PMDA 3.27g (0.015 mol)	PMDA-H 7.84g (0.035 mol)	3-Aph 0.545g (0.005 mol)
62	C5	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	PMDA-H 11.2g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
63	C6	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-4,4'-dihydroxy-3,3'-diaminobiphenyl 15.8 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
64	C7	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxy-4,4'-diaminodiphenyl ether 16.56 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
65	C8	SiDA 0.62g (0.0025 mol)	2,2'-dimethyl-3,3'-dihydroxybenzidine 10.98 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
66	C9	SiDA 0.62g (0.0025 mol)	5,5'-dimethyl-3,3'-dihydroxybenzidine 10.98 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
67	C10	SiDA 0.62g (0.0025 mol)	5,5'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
68	C11	SiDA 0.62g (0.0025 mol)	5,5'-dimethyl-3,3'-dihydroxy-4,4'-diaminodiphenyl ether 11.7 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
69	C12	SiDA 0.62g (0.0025 mol)	5,5'-dimethyl-4,4'-dihydroxy-3,3'-diaminobiphenyl 10.98 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
70	C13	SiDA 0.62g (0.0025 mol)	4,4'-dimethyl-5,5'-dihydroxy-3,3'-diaminobiphenyl 10.98 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
71	C14	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	ODPA 15.51g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
72	C15	SiDA 0.62g (0.0025 mol)	diamine (a) 26.55 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
73	C16	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	BPDA 14.71g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
74	C17	SiDA 0.62g (0.0025 mol)	diamine (b) 21.69 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
75	C18	SiDA 0.62g (0.0025 mol)	diamine (c) 26.55 g (0.045 mol)	PMDA 5.45g (0.025 mol)	PMDA-H 5.6g (0.025 mol)	3-Aph 0.545g (0.005 mol)
76	C19	SiDA 0.62g (0.0025 mol)	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 15.8 g (0.045 mol)	35.0 g of acid dianhydride (d) (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
77	C20	SiDA 0.62g (0.0025 mol)	TFMB 14.4 g (0.045 mol)	35.0 g of acid dianhydride (d) (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
78	C21	SiDA 0.62g (0.0025 mol)	BAHF 16.48 g (0.045 mol)	ODPA 15.51g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)
79	C22	SiDA 0.62g (0.0025 mol)	TFMB 14.4 g (0.045 mol)	PMDA 10.91 g (0.05 mol)	-	3-Aph 0.545g (0.005 mol)

[0260]

[Table 4]

Synthesis example	Resin liquid	Amine component	Acid component	Terminal blocking agent
81	D1	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 17.6 g (0.05 mol)	isophthaloyl dichloride 8.12 g (0.04 mol)	NA 3.28g (0.02 mol)
82	D2	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 17.6 g (0.05 mol)	terephthalic acid chloride 8.12 g (0.04 mol)	NA 3.28g (0.02 mol)
83	D3	TFMB 16.0 g (0.05 mol)	isophthaloyl dichloride 8.12 g (0.04 mol)	NA 3.28g (0.02 mol)
84	D4	HAB 10.8 g (0.05 mol)	isophthaloyl dichloride 8.12 g (0.04 mol)	NA 3.28g (0.02 mol)
85	D5	2,2'-bis(trifluoromethyl)-3,3'-dihydroxybenzidine 17.6 g (0.05 mol)	diphenyletherdicarboxylic acid diimidazolide 14.32 g (0.04 mol)	NA 3.28g (0.02 mol)

[0261]

[Table 5-1]

	Resin	Linear thermal expansion coefficient (ppm/°C)	Absorbance (/μm)	Alkali developing speed (nm/min)	Residual stress (Mpa)
Example 1	A1	7	0.11	>50000	6
Example 2	A2	10	0.06	>50000	11
Example 3	A3	12	0.03	>50000	16
Example 4	A4	16	0.02	>50000	17
Example 5	A5	22	0.01	>50000	18
Example 6	A6	20	0.02	>50000	22
Example 7	A7	35	0.01	>50000	37
Example 8	A8	12	0.06	>50000	15
Example 9	A9	30	0.06	>50000	31
Example 10	A10	30	0.03	>50000	31
Example 11	A11	35	0.01	>50000	37
Example 12	A12	37	0.04	>50000	39
Example 13	A13	40	0.06	>50000	43
Example 14	A14	27	0.06	>50000	30
Example 15	A15	27	0.04	>50000	30
Example 16	A16	20	0.09	>50000	25
Example 17	A17	27	0.09	>50000	30
Example 18	A18	20	0.06	>50000	18
Example 19	A19	20	0.07	>50000	18
Example 20	A20	20	0.06	>50000	18
Comparative Example 1	A21	13	0.02	>50000	20
Comparative Example 2	A22	6	0.4	>50000	10
Comparative Example 3	A23	45	0.04	>50000	43
Comparative Example 4	A24	45	0.05	>50000	43
Comparative Example 5	A25	40	0.4	>50000	45
Comparative Example 6	A26	40	0.4	>50000	45
Example 21	B1	7	0.13	4000	6
Example 22	B2	10	0.07	14000	11
Example 23	B3	12	0.04	22000	16
Example 24	B4	16	0.02	26000	17
Example 25	B5	22	0.01	32000	18
Example 26	B6	20	0.02	30000	22
Example 27	B7	35	0.01	24000	37
Example 28	B8	12	0.07	24000	15
Example 29	B9	30	0.07	30000	31
Example 30	B10	30	0.04	30000	31
Example 31	B11	35	0.01	32000	37
Example 32	B12	37	0.04	34000	39
Example 33	B13	40	0.07	40000	43
Example 34	B14	28	0.07	200	30
Example 35	B15	27	0.05	10000	30
Example 36	B16	20	0.11	200	25
Example 37	B17	27	0.11	10000	30
Example 38	B18	20	0.07	4000	18
Example 39	B19	20	0.08	8000	18
Example 40	B20	20	0.07	4000	18
Comparative Example 7	B21	13	0.02	1000	20
Comparative Example 8	B22	6	0.45	200	10
Comparative Example 9	B23	45	0.04	8000	43
Comparative Example 10	B24	45	0.06	1000	43
Comparative Example 11	B25	40	0.45	6000	45
Comparative Example 12	B26	40	0.45	4000	45

[0262]

[Table 5-2]

	Resin	Linear thermal expansion coefficient (ppm/°C)	Absorbance (/μm)	Alkali developing speed (nm/min)	Residual stress (Mpa)
Example 41	C1	7	0.18	2000	5
Example 42	C2	10	0.1	7000	9
Example 43	C3	12	0.05	11000	13
Example 44	C4	16	0.03	13000	14
Example 45	C5	22	0.01	16000	15
Example 46	C6	20	0.03	15000	18
Example 47	C7	35	0.02	12000	30
Example 48	C8	12	0.1	12000	12
Example 49	C9	30	0.1	15000	25
Example 50	C10	30	0.05	15000	25
Example 51	C11	35	0.02	16000	30
Example 52	C12	37	0.06	17000	32
Example 53	C13	40	0.1	20000	35
Example 54	C14	27	0.1	100	24
Example 55	C15	27	0.07	5000	24
Example 56	C16	20	0.15	100	20
Example 57	C17	27	0.15	5000	24
Example 58	C18	20	0.1	2000	15
Example 59	C19	20	0.12	4000	15
Example 60	C20	20	0.1	2000	15
Comparative Example 13	C21	45	0.06	4000	35
Comparative Example 14	C22	13	0.03	0	17
Example 61	D1	40 (heat treatment at 250°C) 20 (heat treatment at 320°C)	0.05	22000	48 (heat treatment at 250°C) 40 (heat treatment at 320°C)
Example 62	D2	38 (heat treatment at 250°C) 18 (heat treatment at 320°C)	0.2	17000	48 (heat treatment at 250°C) 40 (heat treatment at 320°C)
Comparative Example 15	D3	50 (heat treatment at 250°C) 25 (heat treatment at 320°C)	0.02	0	55 (heat treatment at 250°C) 45 (heat treatment at 320°C)
Comparative Example 16	D4	45 (heat treatment at 250°C) 20 (heat treatment at 320°C)	0.38	100	48 (heat treatment at 250°C) 40 (heat treatment at 320°C)
Example 63	D5	50 (heat treatment at 250°C) 35 (heat treatment at 320°C)	0.07	9000	53 (heat treatment at 250°C) 45 (heat treatment at 320°C)

[0263]

[Table 6]

	Resin	Sensitivity (mJ/cm2)
Example 64	B1	1050
Example 65	B2	850
Example 66	B3	700
Example 67	B4	650
Example 68	B5	650
Example 69	B6	650
Example 70	B7	650
Example 71	B8	850
Example 72	B9	850
Example 73	B10	700
Example 74	B11	650
Example 75	B12	750
Example 76	B13	850
Example 77	B14	850
Example 78	B15	800
Example 79	B16	1000
Example 80	B17	1000
Example 81	B18	850
Example 82	B19	900
Example 83	B20	850
Comparative Example 17	B21	Not processable
Comparative Example 18	B22	2000
Comparative Example 19	B23	450
Comparative Example 20	B24	500
Comparative Example 21	B25	Not processable
Comparative Example 22	B26	Not processable
Example 84	C1	1000
Example 85	C2	700
Example 86	C3	500
Example 87	C4	400
Example 88	C5	350
Example 89	C6	400
Example 90	C7	350
Example 91	C8	700
Example 92	C9	700
Example 93	C10	500
Example 94	C11	350
Example 95	C12	500
Example 96	C13	650
Example 97	C14	600
Example 98	C15	550
Example 99	C16	800
Example 100	C17	800
Example 101	C18	650
Example 102	C19	700
Example 103	C20	650
Comparative Example 23	C21	500
Comparative Example 24	C22	Not processable
Example 104	D1	500
Example 105	D2	1000
Comparative Example 25	D3	Not processable
Comparative Example 26	D4	2000
Example 106	D5	400

[0264]

<5,5'-dihydroxyl-4,4'-diaminobiphenyl derivative>

The reaction yield corresponds to a molar percentage. Both solvents and catalysts used in the examples are purchased from suppliers of reagents, such as national medicine, Aldrich, TCI and Alfa, and are used directly for reaction without post-treatment. A structure of a reaction product is confirmed by nuclear magnetic resonance spectroscopy, and a nuclear magnetic resonance apparatus used is JEOL (400 MHz). A purity of the reaction product is measured using high performance liquid chromatography, the high performance liquid chromatography used is SHIMADZU Prominence, and a chromatographic column is YMC Pack Ph.

[0265]

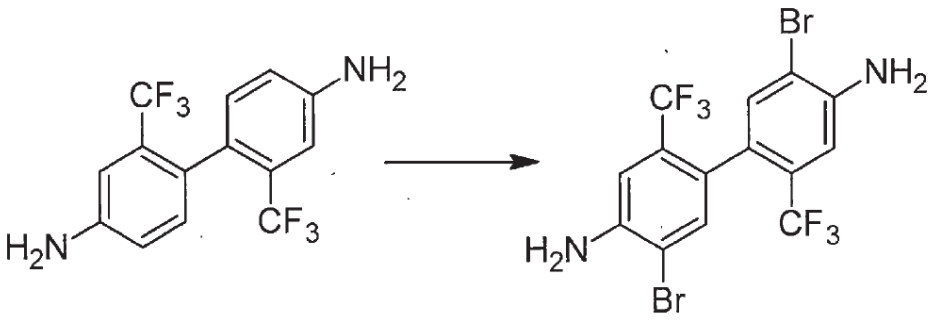
Example 107

2,2'-ditrifluoromethyl-4,4'-diaminobiphenyl (80.0 g, 0.25 mol) and ethylacetate (800 mL) were added to a conical flask, and air in the flask was replaced three times with nitrogen gas. The reaction flask was placed and stirred in an ice bath (-20°C). Then, liquid bromine (26.2 mL, 0.51 mol) was dropped in the reaction flask, and liquid bromine was dropped while controlling the reaction temperature to 20°C or less. The reaction was traced by high performance liquid chromatography, stirring was stopped when the raw material content was less than

3%, saturated sodium carbonate solution was gradually added to the reaction flask, and the pH value was adjusted to neutral. An organic phase was separated, washed with water (500 mL × 2), dried over anhydrous sodium sulfate, and filtered. Then, an organic solvent was removed to obtaine a crude product yellow solid. Subsequently, petroleum ether/ethylacetate (150 ml/5 ml) was added to the crude product, and the mixture was stirred at room temperature for 30 minutes and filtered to obtain 106.5 g of white solid 2,2'-ditrifluoromethyl-5,5'-dibromo-4,4'-diaminobiphenyl (yield 90%, purity 96%).

[0266]

[Chemical Formula 33]



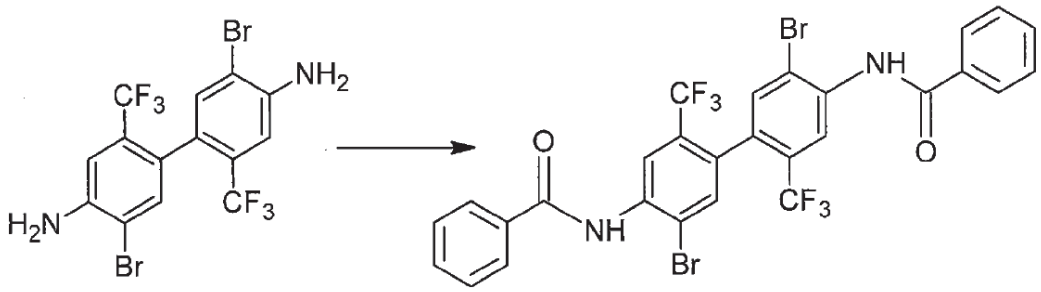
[0267]

2,2'-ditrifluoromethyl-5,5'-dibromo-4,4'-diaminobiphenyl (95.6 g, 0.2 mol) obtained by the above production process and tetrahydrofuran (500 mL) were added to a conical flask, and then benzoyl chloride (56.0 g, 0.4 mol) was added. The reaction flask was placed and stirred in an oil bath kept at a constant

temperature of 40°C and left overnight. The reaction was traced by high performance liquid chromatography, and stirring was stopped when the raw material content was less than 3%. Ethanol and water were added to the reaction solution, and tetrahydrofuran was removed by distillation under reduced pressure to obtain a white floating solution. Subsequently, filtration was carried out, and the filtrated solid was washed with 50 ml of ethanol and then placed and dried in a vacuum oven to obtain 130.2 g of white solid 2,2'-ditrifluoromethyl-5,5'-dibromo-4,4'-dibenzamidebipheny l (yield 94.9%, purity 96%).

[0268]

[Chemical Formula 34]



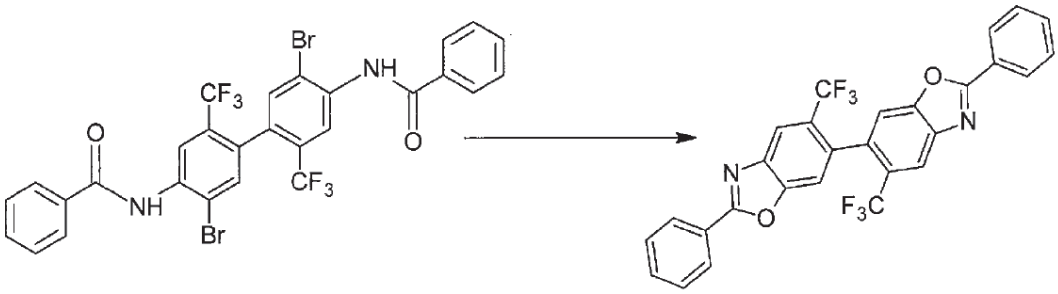
[0269]

2,2'-ditrifluoromethyl-5,5'-dibromo-4,4'-dibenzamideb iphenyl (68.6 g, 0.10 mol) obtained by the above production process, copper iodide (I) (1.91 g, 0.01 mol), N,N'-dimethylethylenediamine (1.76 g, 0.02 mol), potassium phosphate (92.8 g, 0.4 mol) and toluene (600 mL) were added to a conical flask, and the mixture was replaced three times with

nitrogen gas. The reaction was carried out in an oil bath at 100°C and traced by high performance liquid chromatography, and stirring was stopped when the raw material content was less than 3%. The reaction was cooled, 1 L of toluene was added, and the mixture was decolorized with activated charcoal. After filtration, the filtrate was concentrated and then recrystallized to obtain 31.5 g of white solid 2,2'-diphenyl-5,5'-ditrifluoromethyl-[6,6']dibenzoxazole (yield 60%, purity 98%).

[0270]

[Chemical Formula 35]



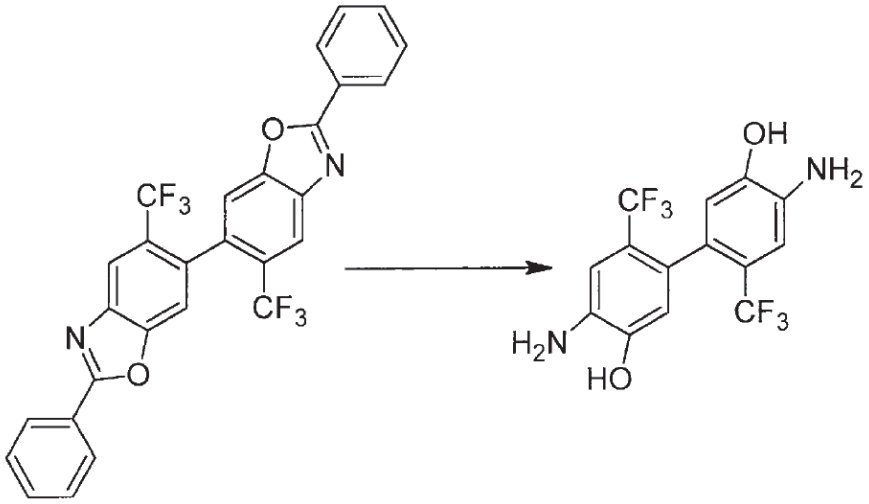
[0271]

2,2'-dimethyl-5,5'-ditrifluoromethyl-[6,6']dibenzoxazole (80.0 g, 0.2 mol) obtained by the preparation process, 36.5% hydrochloric acid (250 ml) and ethanol (1.25 L) were added to a conical flask and stirred in an oil bath kept at a constant temperature of 60°C. The reaction was traced by high performance liquid chromatography, and stirring was stopped when the raw material content was less than 3%. Water was added

to the reaction liquid, ethanol was removed by distillation under reduced pressure, and the pH value was adjusted to be more than 3. Filtration was carried out, and the filtrated solid was washed with 100 ml of ethylacetate and then dried in a vacuum oven to obtain 63.2 g of white solid 2,2'-ditrifluoromethyl-5,5'-dihydroxyl-4,4'-diaminobiphenyl (yield 90%, purity 98%).

[0272]

[Chemical Formula 36]



^{1}H NMR (400MHz, d-DMSO): 9.81 (s, 2 H), 6.90 (s, 2 H), 6.47 (s, 2 H), 4.92(s, 4 H)

Example 108

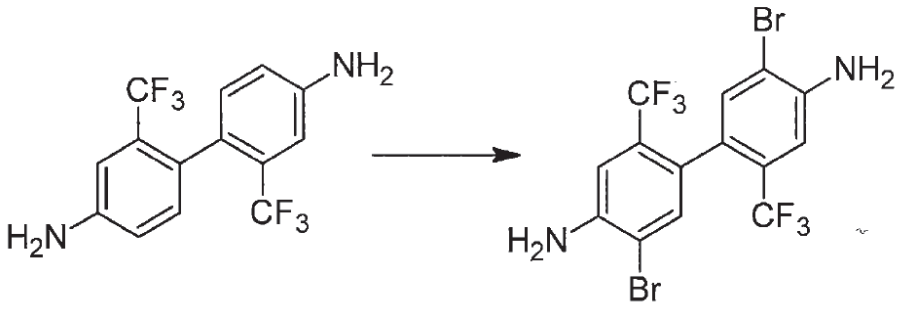
[0273]

2,2'-ditrifluoromethyl-4,4'-diaminobiphenyl (32.0 g, 0.10 mol) and dioxane (300 mL) were added to a conical flask, and the mixture was replaced three times with nitrogen gas. The

reaction flask was placed and stirred in an ice bath. Then, after N-bromosuccinimide (NBS) (35.6 g, 0.20 mol) was added to the reaction flask in several portions, the temperature was raised to 60°C, and stirring was carried out. The reaction was traced by high performance liquid chromatography, and stirring was stopped when the raw material content was less than 3%. A saturated sodium carbonate solution was gradually added to the reaction flask, and the pH value was adjusted to neutral. An organic phase was separated, washed with water (200 mL × 2), dried over anhydrous sodium sulfate, and filtered. Then, an organic solvent was removed to obtain a crude product reddish orange solid. Subsequently, petroleum ether/ethylacetate (60 ml/2 ml) was added to the crude product, and the mixture was stirred at room temperature for 30 minutes and filtered to obtain 37.5 g of white solid 2,2'-ditrifluoromethyl-5,5'-dibromo-4,4'-diaminobiphenyl (yield 78%, purity 95%).

[0274]

[Chemical Formula 37]

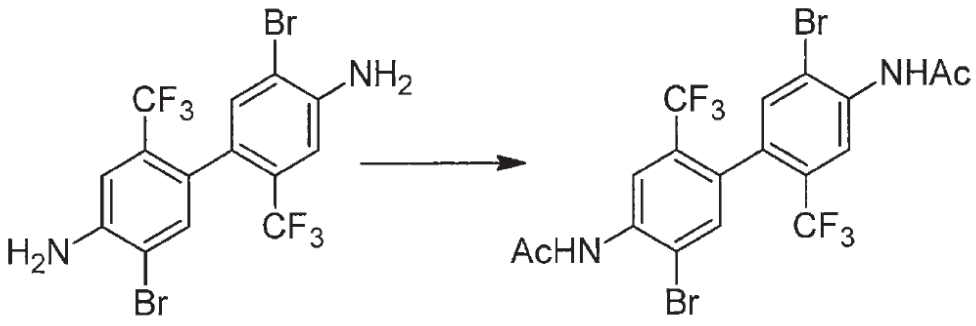


[0275]

2,2'-ditrifluoromethyl-5,5'-dibromo-4,4'-diaminobiphenyl (95.6 g, 0.2 mol) obtained by the above production process and dichloromethane (500 mL) were added to a conical flask, and then acetic anhydride (51.0 g, 0.5 mol) was added. The reaction flask was placed and stirred in an ethanol bath kept at a constant temperature of 10°C and left overnight. The reaction was traced by high performance liquid chromatography, and stirring was stopped when the raw material content was less than 3% to obtain a white floating solution. The reaction solution was filtered, and the filtrated solid was washed twice with 50 ml of dichloromethane, washed twice with 100 ml of water, and placed and dried in a vacuum oven to obtain 106.2 g of white solid 2,2'-ditrifluoromethyl-5,5'-dibromo-4,4'-diformamidebipheny l (yield 94.3%, purity 98%).

[0276]

[Chemical Formula 38]



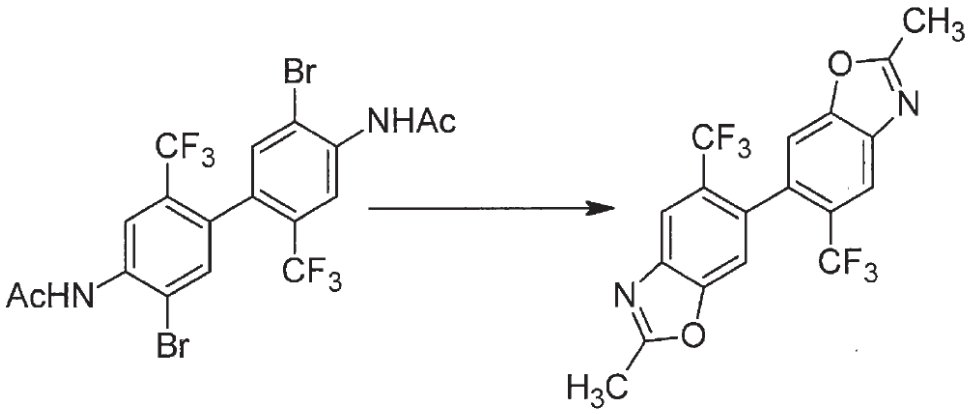
[0277]

2,2'-ditrifluoromethyl-5,5'-dibromo-4,4'-diformamideb

iphenyl (112.4 g, 0.20 mol) obtained by the above production process, copper iodide (I) (3.82 g, 0.02 mol), N,N'-dimethylethylenediamine (3.52 g, 0.04 mol), potassium phosphate (110.4 g, 0.8 mol) and xylene (1200 mL) were added to a conical flask, and the mixture was replaced three times with nitrogen gas. The reaction was carried out in an oil bath at 140°C and traced by high performance liquid chromatography, and stirring was stopped when the raw material content was less than 3%. The reaction was cooled, 1 L of toluene was added, and the mixture was decolorized with activated charcoal and filtered. The filtrate was concentrated and then recrystallized to obtain 48.1 g of white solid 2,2'-dimethyl-5,5'-ditrifluoromethyl-[6,6']dibenzoxazole (yield 60%, purity 97%).

[0278]

[Chemical Formula 39]



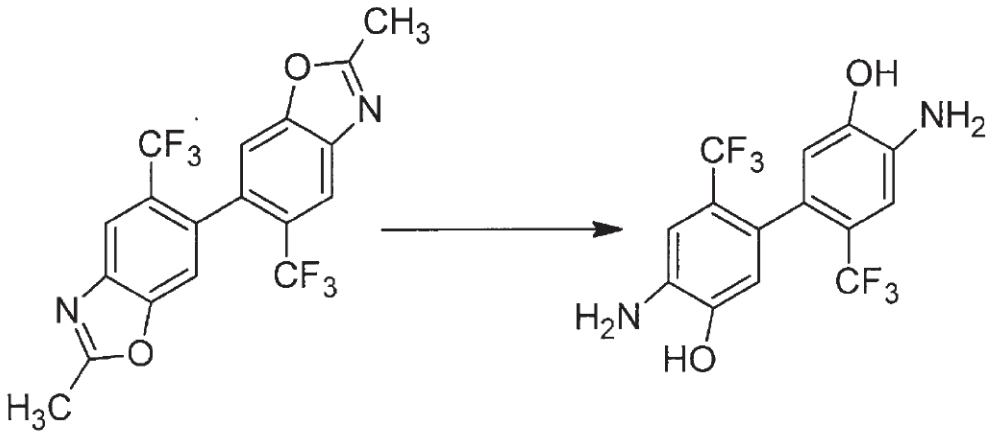
[0279]

2,2'-dimethyl-5,5'-ditrifluoromethyl-[6,6']dibenzoxaz

ole (80.0 g, 0.2 mol) obtained by the production process, 36.5% hydrochloric acid (250 ml) and ethanol (1.25 L) were added to a conical flask and stirred in an oil bath kept at a constant temperature of 60°C. The reaction was traced by high performance liquid chromatography, and stirring was stopped when the raw material content was less than 3%. Water was added to the reaction liquid, ethanol was removed by distillation under reduced pressure, and the pH value was adjusted to be more than 3. Filtration was carried out, and the filtrated solid was washed with 100 ml of ethylacetate and then dried in a vacuum oven to obtain 63.2 g of white solid 2,2'-ditrifluoromethyl-5,5'-dihydroxyl-4,4'-diaminobiphenyl (yield 90%, purity 98%).

[0280]

[Chemical Formula 40]



[0281]

^{1}H NMR (400MHz, d-DMSO): 9.81 (s, 2 H), 6.90 (s, 2 H), 6.47 (s, 2 H), 4.92(s, 4 H).

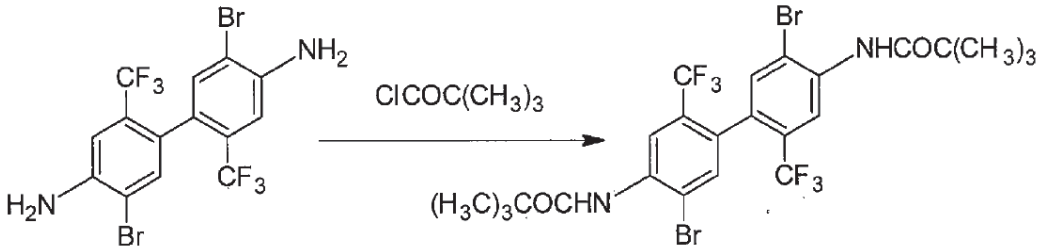
[0282]

Example 109

2,2'-ditrifluoromethyl-5,5'-dibromo-4,4'-diaminobiphenyl (95.6 g, 0.2 mol) obtained by the above production process and dichloromethane (500 mL) were added to a conical flask ,and triethylamine (71.8 ml, 0.514 mol) and pivaloyl chloride (63.0 ml, 0.514 mol) were added. The reaction flask was placed and stirred in an oil bath kept at a constant temperature of 40℃ and left overnight. The reaction was traced by high performance liquid chromatography, and stirring was stopped when the raw material content is less than 3%. A saturated sodium carbonate aqueous solution (200 ml) was added and stirred for 1 hour. An organic layer was washed with water and saturated brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. Washing was carried out with a mixed solvent of petroleum ether (200 ml) and ethylacetate (10 ml), and filtration was carried out. The filtrate was placed and dried in a vacuum oven to obtain 130.2 g of white solid 2,2'-ditrifluoromethyl-5,5'-dibromo-4,4'-dibutylamidebiphenyl (yield 94.9%, purity 97%).

[0283]

[Chemical Formula 41]

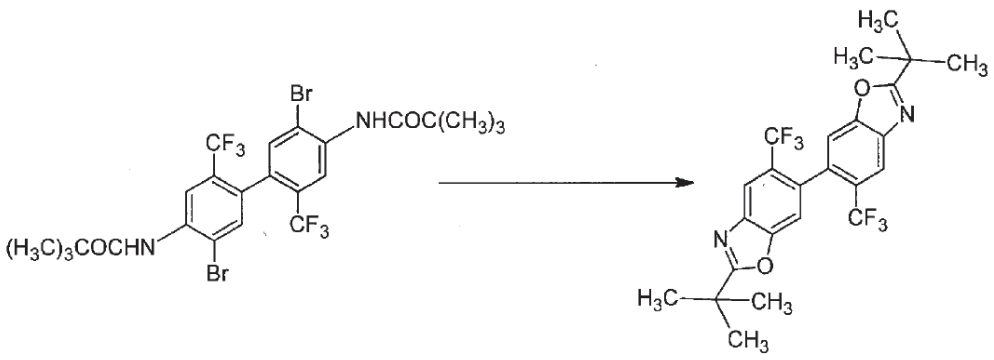


[0284]

2,2'-ditrifluoromethyl-5,5'-dibromo-4,4'-dibutylamide biphenyl (103.5 g, 0.161 mol) obtained by the above production process, copper bromide (I) (2.30 g, 0.161 mol), N,N'-dimethylethylenediamine (2.85 g, 0.0322 mol), potassium phosphate (102.4 g, 0.483 mol), toluene (1000 mL), and dioxane (100 ml) were added to a conical flask, and the mixture was replaced three times with nitrogen gas. The reaction was carried out in an oil bath at 120°C and traced by high performance liquid chromatography, and stirring was stopped when the raw material content was less than 3%. The reaction was cooled, and filtration was carried out. An organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to obtain 49.8 g of white solid 2,2'-di(tert-butyl)-5,5'-ditrifluoromethyl-[6,6']dibenzoxazole (yield 65%, purity 99%).

[0285]

[Chemical Formula 42]

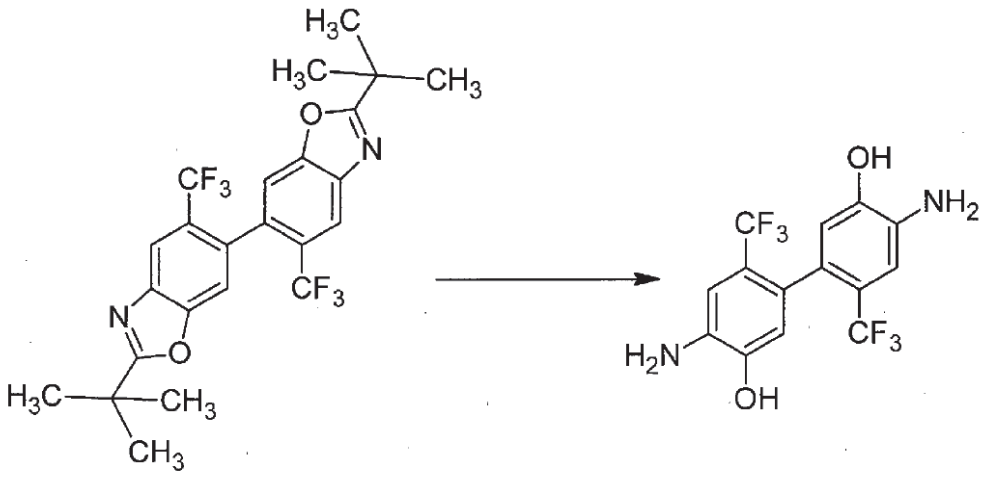


[0286]

2,2'-di(tert-butyl)-5,5'-ditrifluoromethyl-[6,6']dibenzoxazole (48.4 g, 0.1 mol) obtained by the production process, 36.5% hydrochloric acid (250 ml) and ethanol (300 L) were added to a conical flask and stirred in an oil bath kept at a constant temperature of 100°C. The reaction was traced by high performance liquid chromatography, and stirring was stopped when the raw material content was less than 3%. Water was added to the reaction liquid, ethanol was removed by distillation under reduced pressure, and the pH value was adjusted to be more than 3. Filtration was carried out, and the filtrated solid was washed with 100 ml of ethylacetate and then dried in a vacuum oven to obtain 31.6 g of white solid 2,2'-ditrifluoromethyl-5,5'-dihydroxyl-4,4'-diaminobiphenyl (yield 90%, purity 98%).

[0287]

[Chemical Formula 43]



[0288]

^{1}H NMR (400MHz, d-DMSO): 9.81 (s, 2 H), 6.90 (s, 2 H), 6.47 (s, 2 H), 4.92(s, 4 H).

<Dibromobiphenyl Derivative>

Reaction process measurement: Measurement is carried out by high performance liquid chromatography, the model number is SHIMADZU LC-20AD, and chromatography column is YMC-Pack Ph (250 × 4.6 mml.D).

Purity: Measurement is carried out by high performance liquid chromatography, the model number is SHIMADZU LC-20AD, and chromatography column is YMC-Pack Ph (250 × 4.6 mml.D).

Structure identification: nuclear magnetic resonance apparatus, JEOL (400 MHz), solvent is deuterated chloroform or dimethylsulfoxide-d6.

Yield: molar yield, it can be calculated after weighing.

[0289]

Materials and Reagents Used in Comparative Examples and

Examples:

2,2'-ditrifluoromethyl-4,4'-diaminobiphenyl: purchased from J & K Chemical;

Liquid bromine: purchased from the national medicine group;

N-bromosuccinimide: purchased from the national medicine group;

Solvent: purchased from the national medicine group.

[0290]

In the present invention, a raw material biphenyl compound having a structure represented by the general formula (13) is dissolved in an aprotic solvent, a bromination reagent is added to a reaction flask under the condition of -30°C to 60°C, and stirring is continuously carried out until almost no raw material remains. An alkaline aqueous solution is added to the reaction flask until it is neutral, and an organic phase is separated, washed with water, dried, and dissolved to obtain a crude product. The crude product is purified to obtain a dibromobiphenyl derivative as a final product. The yield of the reaction is a molar percentage.

[0291]

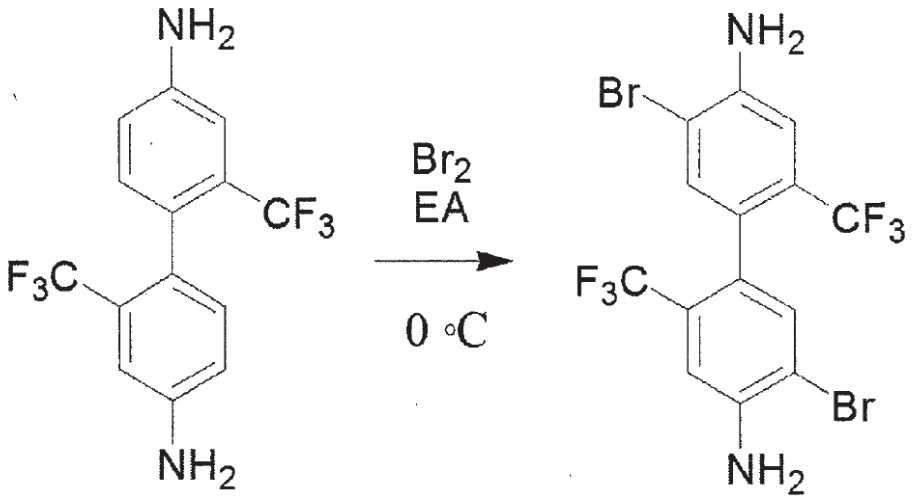
Example 110

2,2'-ditrifluoromethyl-4,4'-diaminobiphenyl (80.0 g, 0.25 mol) and ethylacetate (800 mL) were added to a conical flask, and the mixture was replaced three times with nitrogen gas. The reaction flask was placed and stirred in an ice bath. Then,

liquid bromine (26.2 mL, 0.51 mol) was dropped in the reaction flask and then successively stirred. The reaction was measured by high performance liquid chromatography, and stirring was stopped when the raw material content was less than 3%. A saturated sodium carbonate solution was gradually added to the reaction flask, and the pH value was adjusted to neutral. An organic phase was separated, washed with water (500 mL each time, washed twice), dried over anhydrous sodium sulfate, and filtered. Then, an organic solvent was removed to obtain a crude product yellow solid. Subsequently, petroleum ether/ethylacetate (150 ml/5 ml) was added to the crude product, and the mixture was stirred at room temperature for 30 minutes and filtered to obtain 106.5 g of white solid 2,2'-ditrifluoromethyl-4,4'-diamino-5,5'-dibromobiphenyl (yield 90%, purity 96%).

[0292]

[Chemical Formula 44]



[0293]

^{1}H NMR (400MHz, DMSO-d_6) δ 5.88 (s, 4 H), 7.15 (s, 2 H), 7.26 (s, 2 H)

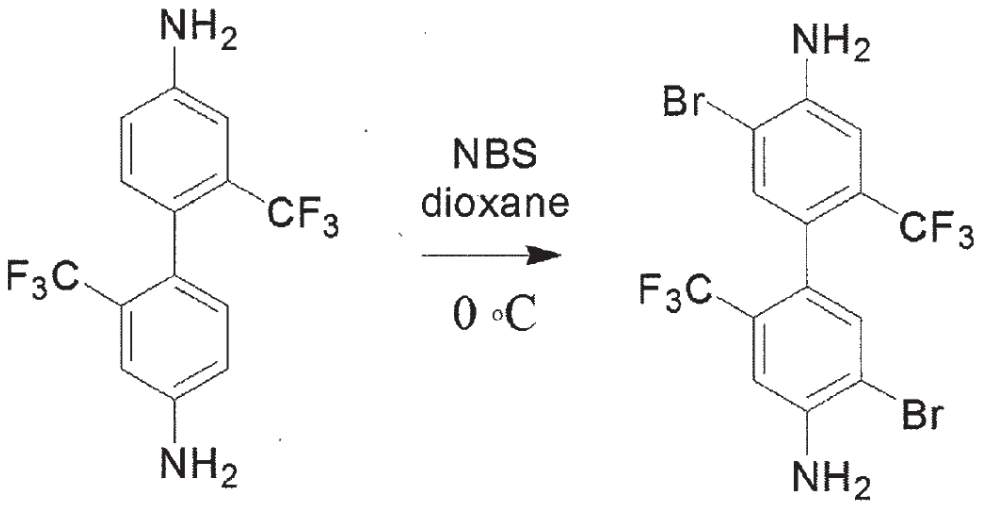
Example 111

2,2'-ditrifluoromethyl-4,4'-diaminobiphenyl (32.0 g, 0.10 mol) and 1,4-dioxane (300 mL) were added to a conical flask, and the mixture was replaced three times with nitrogen gas. The reaction flask was placed and stirred in an ice bath. Then, N-bromosuccinimide (NBS) (35.6 g, 0.20 mol) was added to the reaction flask in several portions and then successively stirred. The reaction was traced by high performance liquid chromatography, and stirring was stopped when the raw material content was 3% or less. A sodium hydroxide solution was gradually added to the reaction flask, and the pH value was adjusted to neutral. Then, an organic phase was separated by adding ethylacetate (300 mL), washed with saturated brine (200

mL each time, washed twice), washed with water (200 mL), dried over anhydrous sodium sulfate, and filtered. Then, an organic solvent was removed to obtain a crude product reddish orange solid. Subsequently, petroleum ether/ethylacetate (60 ml/2 ml) was added to the crude product, and the mixture was stirred at room temperature for 30 minutes and filtered to obtain 33.5 g of white solid 2,2'-ditrifluoromethyl-4,4'-diamine-5,5'-dibromobiphenyl (yield 70%, purity 95%).

[0294]

[Chemical Formula 45]



[0295]

^{1}H NMR (400MHz, DMSO-d_6) δ 5.88 (s, 4 H), 7.15 (s, 2 H), 7.26 (s, 2 H)

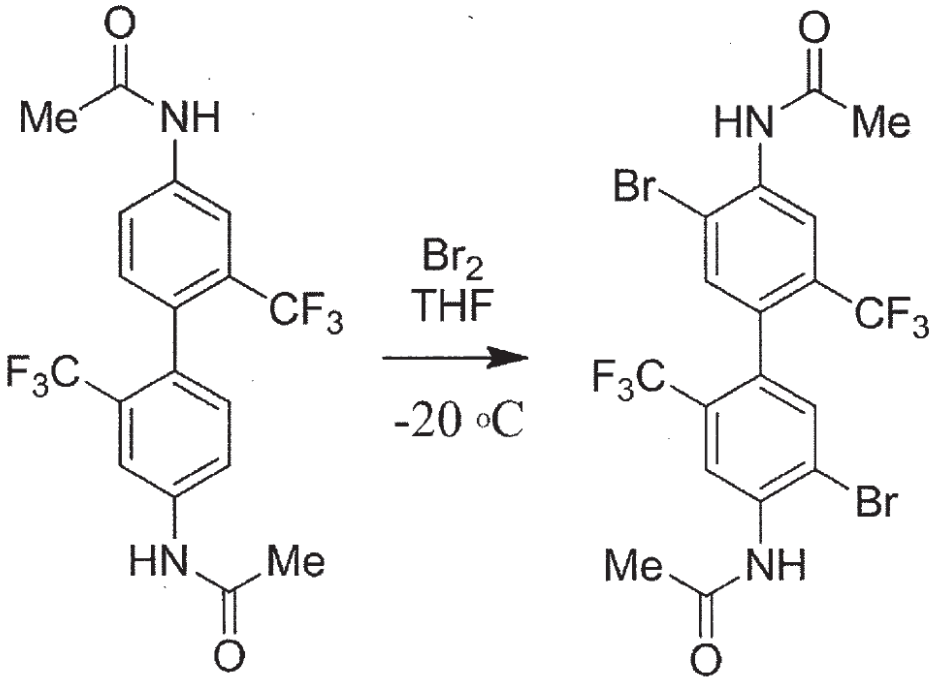
Example 112

2,2'-ditrifluoromethyl-4,4'-diacetamidobiphenyl

(101.0 g, 0.25 mol) and tetrahydrofuran (500 mL) were added to a conical flask, and the mixture was replaced three times with nitrogen gas. The reaction flask was placed and stirred in a low temperature reaction tank at -20°C. Then, liquid bromine (26.2 mL, 0.51 mol) was dropped in the reaction flask and then successively stirred. The reaction was traced by high performance liquid chromatography, and stirring was stopped when the raw material content was 3% or less. A saturated sodium carbonate solution was gradually added to the reaction flask, and the pH value was adjusted to neutral. Then, an organic phase was separated by adding ethylacetate (500 mL), washed with saturated brine (500 mL each time, washed twice), washed with water (200 mL), dried over anhydrous sodium sulfate, and filtered. Then, an organic solvent was removed to obtain a crude product yellow solid. Subsequently, petroleum ether/ethylacetate (150 ml/5 ml) was added to the crude product, and the mixture was stirred at room temperature for 30 minutes and filtered to obtain 119.6 g of white solid 2,2'-ditrifluoromethyl-4,4'-diacetamide-5,5'-dibromobipheny l (yield 85%, purity 96%).

[0296]

[Chemical Formula 46]



[0297]

^{1}H NMR (400MHz, DMSO-d_6) δ 2.16 (s, 6 H), 7.80 (s, 2 H), 8.19 (s, 2 H), 9.76 (s, 2 H)

Example 113

2,2'-ditrifluoromethyl-4,4'-di(phthalimide)biphenyl (145.0 g, 0.25 mol) and propyleneglycolmethyletheracetate (500 mL) were added to a conical flask, and the mixture was replaced three times with nitrogen gas and stirred at room temperature. Then, liquid bromine (26.2 mL, 0.51 mol) was dropped in the reaction flask and then successively stirred. The reaction was traced by high performance liquid chromatography, and stirring was stopped when the raw material content was 3% or less. A saturated sodium carbonate solution was gradually added to the reaction flask, and the pH value was adjusted to neutral. Then,

an organic phase was separated, washed with water (300 mL each time, washed twice), dried over anhydrous sodium sulfate, and filtered. Then, an organic solvent was removed to obtain a crude product yellow solid. Subsequently, petroleum ether/ethylacetate (150 ml/5 ml) was added to the crude product, and the mixture was stirred at room temperature for 30 minutes and filtered to obtain 166.0 g of white solid 2,2'-ditrifluoromethyl-4,4'-di(phthalimide)-5,5'-dibromobiphenyl (yield 90%, purity 95%).

[0298]

[Chemical Formula 47]



[0299]

^{1}H NMR (400MHz, DMSO-d_6) δ 7.98-7.99 (m, 4 H), 8.06-8.07 (m, 4 H), 8.24 (s, 2 H), 8.30 (s, 2 H)

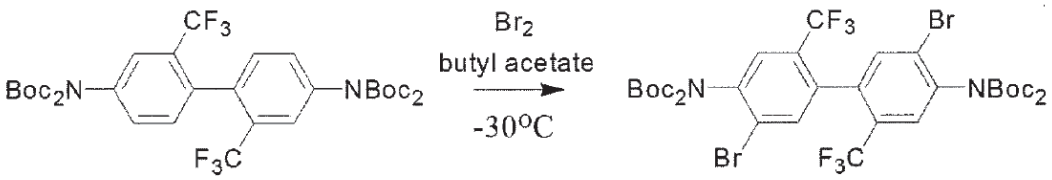
Example 114

2,2'-ditrifluoromethyl-4,4'-di(ditertiarybutoxidedicarboximide)biphenyl (180.0 g, 0.25 mol) and butylacetate (500 mL) were added to a conical flask, and the mixture was replaced three times with nitrogen gas and placed and stirred in a low temperature reaction groove at -30°C. Then, liquid bromine (26.2 mL, 0.51 mol) was dropped in the reaction flask and then

successively stirred. The reaction was traced by high performance liquid chromatography, and stirring was stopped when the raw material content was 3% or less. A saturated sodium carbonate solution was gradually added to the reaction flask, and the pH value was adjusted to neutral. Then, an organic phase was separated, washed with water (500 mL each time, washed twice), dried over anhydrous sodium sulfate, and filtered. Then, an organic solvent was removed to obtain a crude product yellow solid. Subsequently, petroleum ether/ethylacetate (150 ml/5 ml) was added to the crude product, and the mixture was stirred at room temperature for 30 minutes and filtered to obtain 177.6 g of white solid 2,2'-ditrifluoromethyl-4,4'-di(ditertiarybutoxidedicarboximide)-5,5'-dibromobiphenyl (yield 81%, purity 95%).

[0300]

[Chemical Formula 48]



[0301]

^{1}H NMR (400MHz, DMSO-d_6) δ 1.31-1.41 (m, 18 H), 7.88 (s, 1 H), 8.05 (s, 1 H)

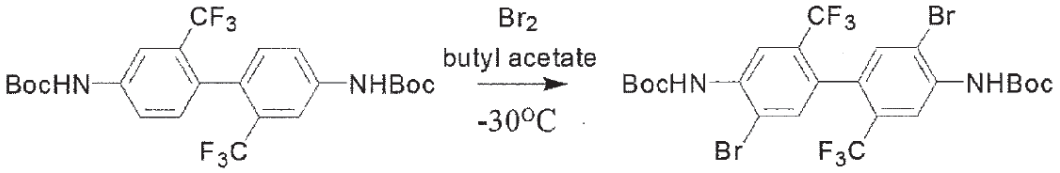
Example 115

2,2'-ditrifluoromethyl-4,4'-di(ditertiarybutoxidecarb

amide)biphenyl (130.0 g, 0.25 mol) and butylacetate (500 mL) were added to a conical flask, and the mixture was replaced three times with nitrogen gas and placed and stirred in a low temperature reaction tank at -30°C. Then, liquid bromine (26.2 mL, 0.51 mol) was dropped in the reaction flask and then successively stirred. The reaction was traced by high performance liquid chromatography, and stirring was stopped when the raw material content was 3% or less. A saturated sodium carbonate solution was gradually added to the reaction flask, and the pH value was adjusted to neutral. Then, an organic phase was separated, washed with water (500 mL each time, washed twice), dried over anhydrous sodium sulfate, and filtered. Then, an organic solvent was removed to obtain a crude product yellow solid. Subsequently, petroleum ether/ethylacetate (150 ml/5 ml) was added to the crude product, and the mixture was stirred at room temperature for 30 minutes and filtered to obtain 141.1 g of white solid 2,2'-ditrifluoromethyl-4,4'-di(ditertiarybutoxidecarbamide)-5,5'-dibromobiphenyl (yield 83%, purity 95%).

[0302]

[Chemical Formula 49]



[0303]

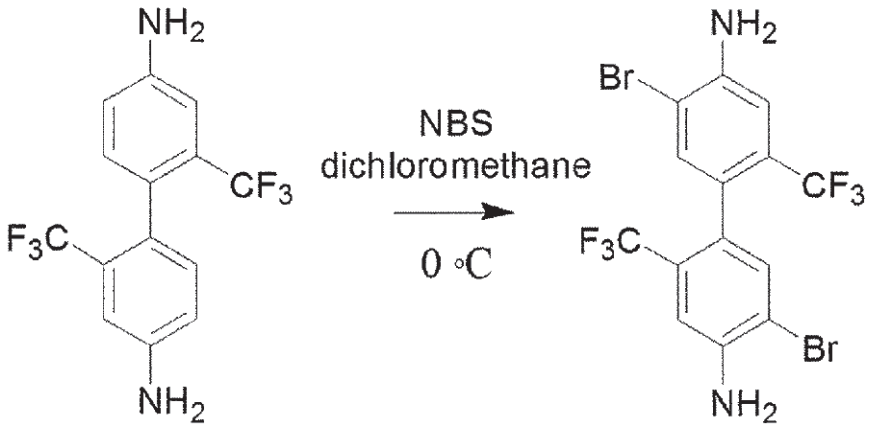
^{1}H NMR (400MHz, DMSO-d_6) δ 1.49 (s, 18 H), 7.73 (s, 1 H), 8.04 (s, 1 H), 8.92 (s, 1 H)

Example 116

2,2'-ditrifluoromethyl-4,4'-diaminobiphenyl (32.0 g, 0.10 mol) and dichloromethane (300 mL) were added to a conical flask, and the mixture was replaced three times with nitrogen gas. The reaction flask was placed and stirred in an ice bath. Then, N-bromosuccinimide (NBS) (35.6 g, 0.20 mol) was added to the reaction flask in several portions and then successively stirred. While the reaction was traced by high performance liquid chromatography, N-bromosuccinimide (17.8 g, 0.10 mmol) was supplied and added, and stirring was stopped when the raw material content was 3% or less. A sodium hydroxide solution was gradually added to the reaction flask, and the pH value was adjusted to neutral. Then, an organic phase was separated, washed with water (200 mL each time, washed twice), dried over anhydrous sodium sulfate, and filtered. Then, an organic solvent was removed to obtain a crude product reddish orange solid. Subsequently, petroleum ether/ethylacetate (60 ml/2 ml) was added to the crude product, and the mixture was stirred at room temperature for 30 minutes and filtered to obtain 23.8 g of white solid 2,2'-ditrifluoromethyl-4,4'-diamino-5,5'-dibromobiphenyl (yield 50%, purity 95%).

[0304]

[Chemical Formula 50]



[0305]

^{1}H NMR (400MHz, DMSO-d_6) δ 5.88 (s, 4 H), 7.15 (s, 2 H), 7.26 (s, 2 H)

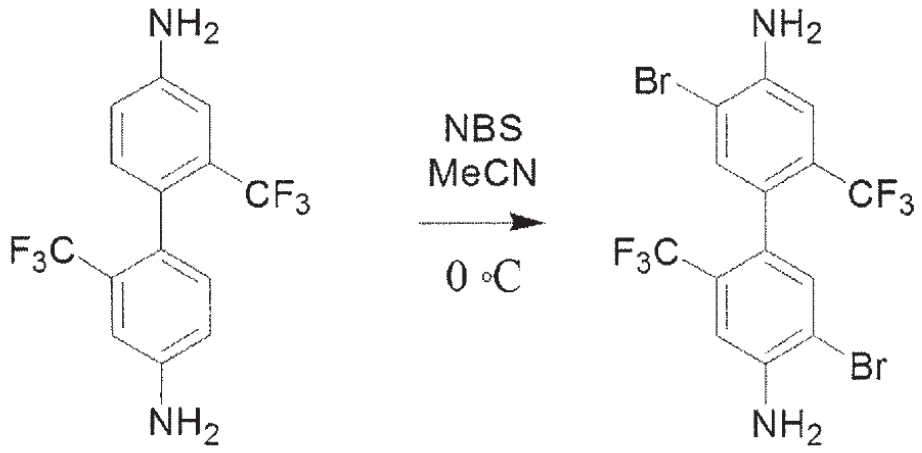
Example 117

2,2'-ditrifluoromethyl-4,4'-diaminobiphenyl (32.0 g, 0.10 mol) and acetonitrile (300 mL) were added to a conical flask, and the mixture was replaced three times with nitrogen gas. The reaction flask was placed and stirred in an ice bath. Then, N-bromosuccinimide (NBS) (35.6 g, 0.20 mol) was added to the reaction flask in several portions and then successively stirred. While the reaction was traced by high performance liquid chromatography, NBS (8.9 g, 0.05 mol) was supplied and added, and stirring was stopped when the raw material content was 3% or less. A sodium hydroxide solution was gradually added to the reaction flask, and the pH value was adjusted to neutral. Then, an organic phase was separated by adding ethylacetate (300

mL), washed with saturated brine (200 mL each time, washed twice), washed with water (200 mL), dried over anhydrous sodium sulfate, and filtered. Then, an organic solvent was removed to obtain a crude product reddish orange solid. Subsequently, petroleum ether/ethylacetate (60 ml/2 ml) was added to the crude product, and the mixture was stirred at room temperature for 30 minutes and filtered to obtain 15.7 g of pale yellow solid 2,2'-ditrifluoromethyl-4,4'-diamino-5,5'-dibromobiphenyl (yield 33%, purity 95%).

[0306]

[Chemical Formula 51]



[0307]

^{1}H NMR (400MHz, DMSO-d_6) δ 5.88 (s, 4 H), 7.15 (s, 2 H), 7.26 (s, 2 H)

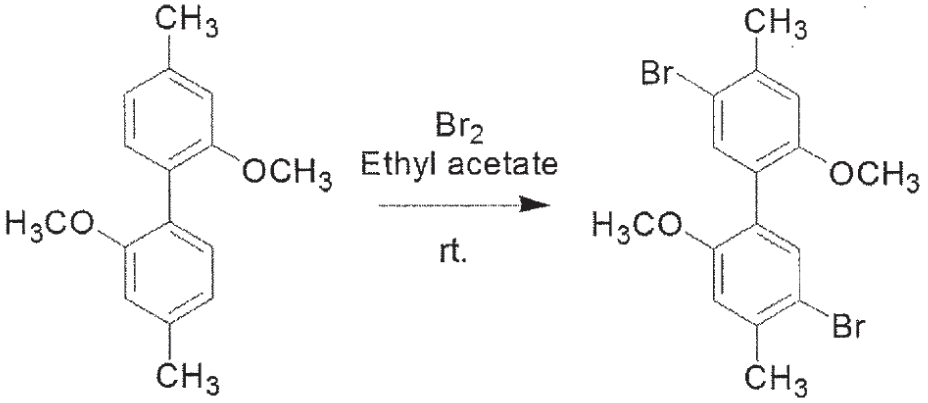
Example 118

2,2'-dimethoxy-4,4'-dimethylbiphenyl (60.5 g, 0.25 mol) and ethylacetate (500 mL) were added to a conical flask, and

the mixture was replaced three times with nitrogen gas. The reaction flask was stirred at room temperature. Then, liquid bromine (26.2 mL, 0.51 mol) was dropped in the reaction flask and then successively stirred. The reaction was traced by high performance liquid chromatography, and stirring was stopped when the raw material content was 3% or less. A saturated sodium carbonate solution was gradually added to the reaction flask, and the pH value was adjusted to neutral. Then, an organic phase was separated, washed with water (500 mL each time, washed twice), dried over anhydrous sodium sulfate, and filtered. Then, an organic solvent was removed to obtain a crude product yellow solid. Subsequently, petroleum ether/ethylacetate (150 ml/5 ml) was added to the crude product, and the mixture was stirred at room temperature for 30 minutes and filtered to obtain 94.3 g of white solid 2,2'-dimethoxy-4,4'-dimethyl-5,5'-dibromobiphenyl (yield 94%, purity 95%).

[0308]

[Chemical Formula 52]



[0309]

^{1}H NMR (400MHz, $CDCl_3$) δ 2.39 (s, 6 H), 3.80 (s, 6 H), 6.79 (s, 2 H), 7.39 (s, 2 H)

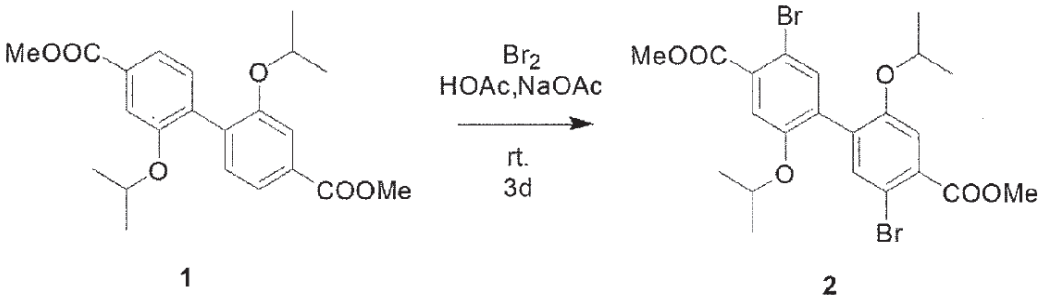
Comparative Example 27

Acetic acid (50 mL), sodium acetate (1.3 g) and a raw material 1 (1.46 g, 3.78 mmol) were added to a conical flask, and the mixture was replaced three times with nitrogen gas and stirred at room temperature. Then, a mixed solution of liquid bromine Br_2 (0.4 mL, 7.76 mmol) and acetic acid (5 mL) was dropped in the reaction flask and then successively reacted at room temperature for 48 h. The reaction was traced by thin layer chromatography (TLC) (developing solvent: petroleum ether/ethyl acetate, 10 mL/1 mL), liquid bromine (0.4 mL) and acetic acid (5 mL) were supplied and added, followed by stirring for 24 h. Saturated sodium sulfite (5 mL) was added to the reaction solution and extracted with dichloromethane (70 mL each time, extracted five times). Organic phases were combined, washed with water, dried over anhydrous magnesium sulfate, and

filtered. Then, an organic solvent was removed to obtain an oily substance. The oily substance was recrystallized using dichloromethane to obtain 1.64 g (yield 80%) of a product 2.

[0310]

[Chemical Formula 53]



1 2

[0311]

^{1}H NMR (400MHz, acetone-d_6) δ 1.24 (d, J = 6.0 Hz, 12 H), 3.96 (s, 6 H), 4.65 (sept, J = 6.1 Hz, 2 H), 7.48 (s, 2 H), 7.58 (s, 2 H).

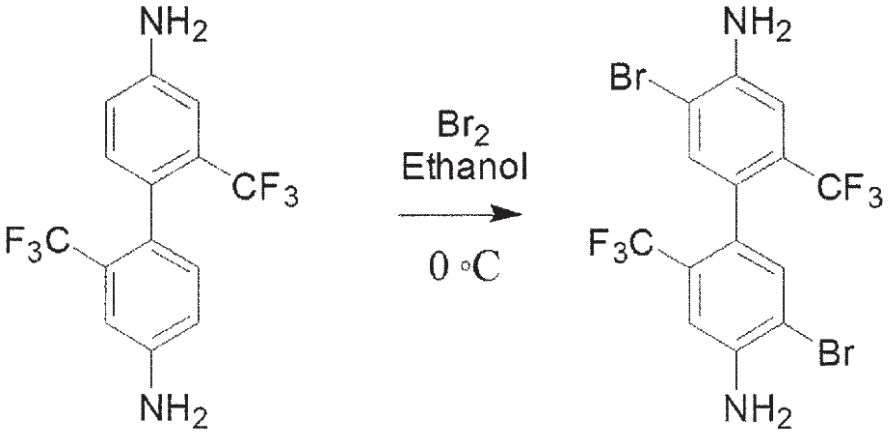
Comparative Example 28

100 ml of ethanol and 20.0 g (62.5 mmol) of 2,2'-ditrifluoromethylbenzidine were added to a conical flask, and the mixture was replaced three times with nitrogen gas. The reaction flask was placed and stirred in an ice bath. Then, 21.0 g (131.2 mmol) of bromine was dropped in the reaction flask and then stirred at room temperature for 1 h. Then, toluene was added, and an organic phase was washed three times with water, then washed twice each with a saturated sodium bicarbonate solution and water, dried, and filtered. Then, after an organic

solvent was removed, recrystallization was carried out with normal hexane/toluene to obtain 11.5 g (yield 38.5%) of 2,2'-ditrifluoromethyl-4,4'-diamino-5,5'-dibromobiphenyl.

[0312]

[Chemical Formula 54]



[0313]

^{1}H NMR (500MHz, $CDCl_3$) δ4.33 (s, 4 H), 7.05 (s, 2 H), 7.32 (s, 2 H).

DESCRIPTION OF REFERENCE SIGNS

[0314]

1: Silicon wafer

2: Al pad

3: Passivation film

4: Insulating film

5: Metal (Cr, Ti, Ni, TiW, etc.) film

6: Metal (Al, Cu, Au, etc.) wiring

7: Insulating film

8: Barrier metal

9: Scribe line

10: Solder bump

11: Silicon wafer

12: Al pad

13: Passivation film

14: Insulating film

15: Adhesive film

16: Wire (Cu, Au, etc.)

21: Silicon wafer

22: Through electrode (Cu etc.)

23: Pad (Al, Cu, etc.)

24: Passivation film

25: Insulating film

26: Barrier metal

27: Solder bump

28: Adhesive film

29: Scribe line

31: TFT

32: Wiring

33: Insulating film

34: Flattening film

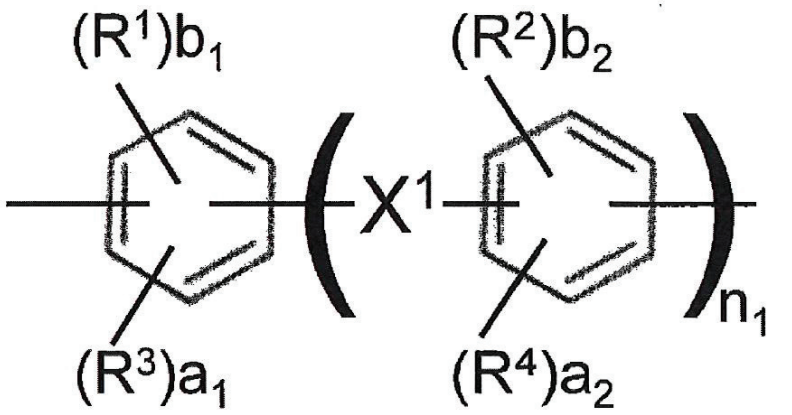
35: ITO

36: Substrate

37: Contact hole

CLAIMS

1. A resin comprising at least one structure selected from structures represented by the following general formulae (1) and (2), wherein the resin comprises at least one selected from polyimide, polyamideimide, polyimide precursor, and a copolymer thereof, and wherein the resin comprises at least one selectd from structures represented by the following general formulae (3) or (4) or a copolymer thereof:

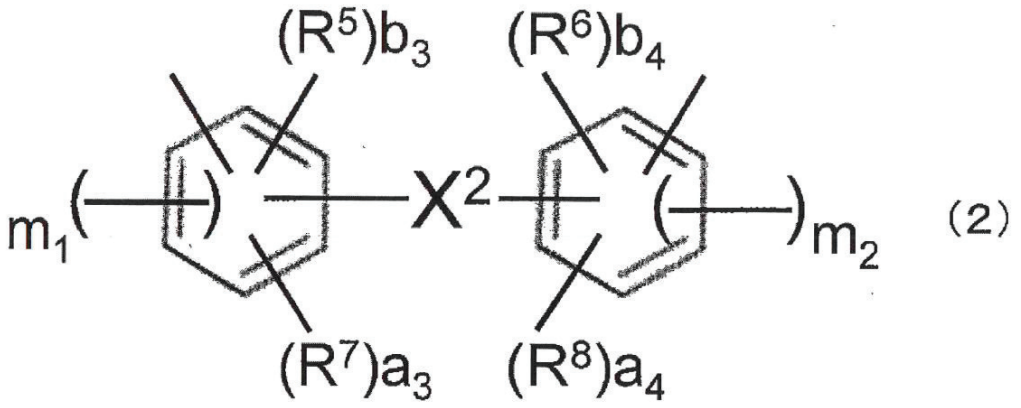


(1)

wherein the general formula (1) is a divalent organic group, and R^1 and R^2 each independently represent a halogen atom or a monovalent organic group having 1 to 3 carbon atoms and are bonded to positions 2 and 2′; R^3 and R^4 each represent an organic group selected from a hydroxyl group, and a carboxyl group; X^1 is a single bond

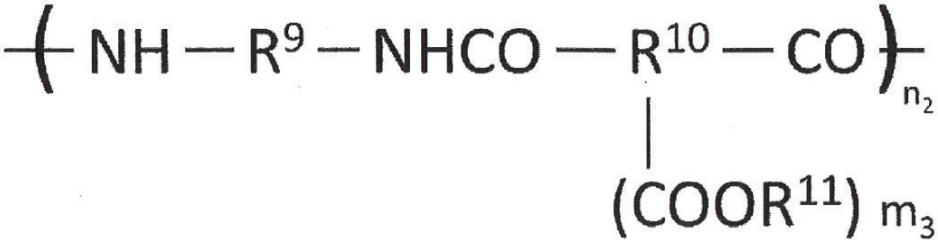
; n_1 is 0 or 1; when $n_1 = 0$, a_1 is an integer of 1 to 3, b_1 is an integer of 1 to 3, and $a_1 + b_1$ is an integer of 2 to 4; when $n_1 = 1$, a_1 is an integer of 1 to 4, b_1 is an integer of 0 to 3, a_2 is an integer of 0 to 4, b_2 is an integer of 0 to 4, $a_1 + b_1$ is an integer of 1 to 4, $a_2 + b_2$ is an integer

of 0 to 4, and at least one of b_1 and b_2 is an integer of 1 or more;



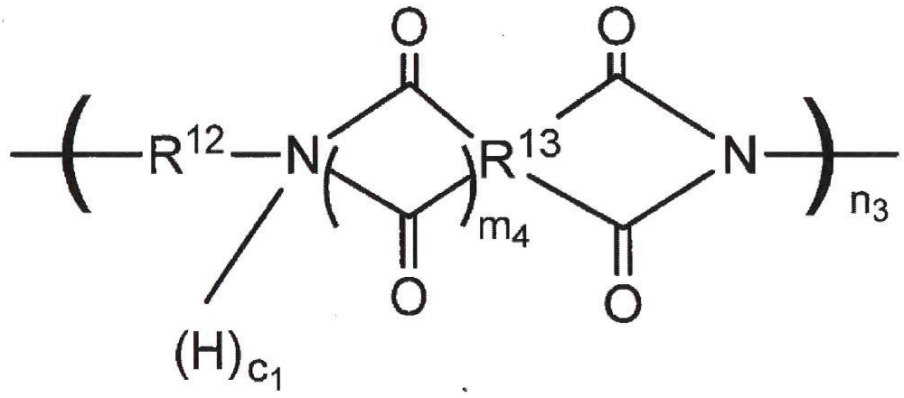
(2)

wherein the general formula (2) is a trivalent or tetravalent organic group, and R^5 and R^6 each independently represent a halogen atom or a monovalent organic group having 1 to 3 carbon atoms; R^7 and R^8 each represent an organic group selected from a hydroxyl group, a carboxyl group and a sulfonic acid group; X^2 is a single bond, O, S, NH, SO_2, CO or a divalent organic group having 1 to 3 carbon atoms or a divalent crosslinked structure formed by linking two or more of these; a_3, a_4, b_3 and b_4 are integers of 0 to 3, $a_3 + b_3$ is an integer of 0 to 3, $a_4 + b_4$ is an integer of 0 to 3, at least one of a_3 and a_4 is an integer of 1 or more, and at least one of b_3 and b_4 is an integer of 1 or more; m_1 and m_2 are integers of 0 or 1, and $m_1 + m_2$ is an integer of 1 or 2;



(3)

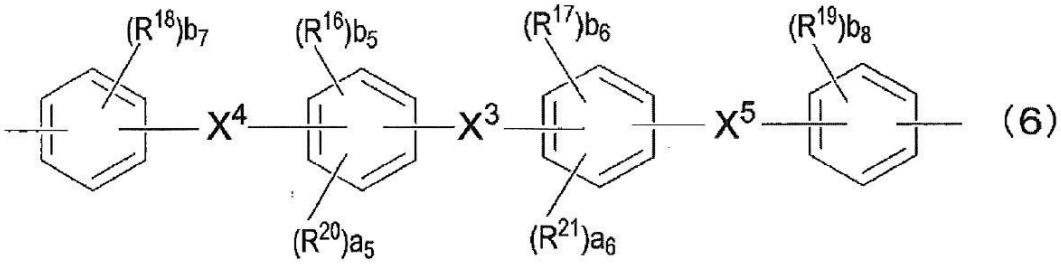
wherein R^9 represents a divalent organic group having 2 to 50 carbon atoms; R^{10} represents a trivalent or tetravalent organic group having 2 to 50 carbon atoms; R^9 represents a structure selected from the general formula (1) or (6), and/or R^{10} represents a structure selected from the general formula (2) or (7); R^{11} represents hydrogen or an organic group having 1 to 10 carbon atoms; m_3 is an integer of 1 or 2; and n_2 represents a range of 10 to 100,000;



(4)

wherein R^{12} represents a divalent organic group having 2 to 50 carbon atoms; R^{13} represents a trivalent or tetravalent organic group having 2 to 50 carbon atoms; R^{12} represents a structure selected from the general formula (1) or (6), and/or R^{13} represents a structure selected from the general formula (2)

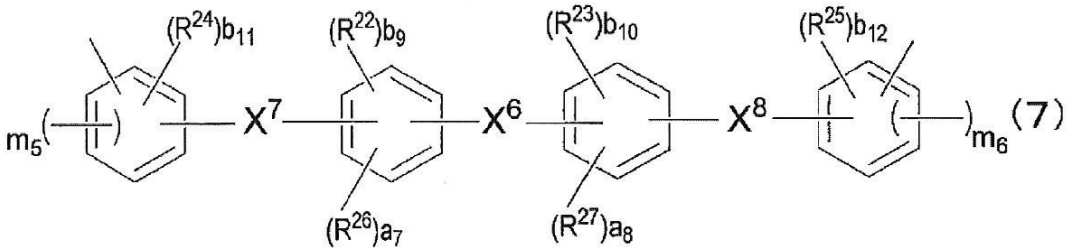
or (7); m_4 is an integer of 0 or 1, c_1 is an integer of 0 or 1, $c_1 = 1$ when $m_4 = 0$, and $c_1 = 0$ when $m_4 = 1$; and n_3 represents a range of 10 to 100,000;



(6)

wherein the general formula (6) is a divalent organic group, and R^{16} to R^{19} each independently represent a halogen atom or a monovalent organic group having 1 to 3 carbon atoms; R^{20} and R^{21} each represent an organic group selected from a hydroxyl group, a carboxyl group, and a sulfonic acid group; X^3 is a single bond, O, S, NH, SO_2, CO or a divalent organic group having 1 to 3 carbon atoms or a divalent crosslinked structure formed by linking two or more of these; X^4 and X^5 each represent a structure selected from an amide bond and an azomethine bond; a_5 is an integer of 1 to 4, b_5 is an integer of 0 to 3, a_6 is

an integer of 0 to 4, b_6 is an integer of 0 to 4, b_7 and b_8 are integers of 0 to 4, $a_5 + b_5$ is an integer of 1 to 4, $a_6 + b_6$ is an integer of 0 to 4, and at least one of b_5 and b_6 is an integer of 1 or more;



wherein the general formula (7) is a trivalent or tetravalent organic group, and R^{22} to R^{25} each independently represent a halogen atom or a monovalent organic group having 1 to 3 carbon atoms; R^{26} and R^{27} each represent an organic group selected from a hydroxyl group, a carboxyl group, and a sulfonic acid group; X^6 is a single bond, O, S, NH, SO_2, CO or a divalent organic group having 1 to 3 carbon atoms or a divalent crosslinked structure formed by linking two or more of these; X^7 and X^8 each represent a structure selected from an amide bond and an azomethine bond; a_7 is an integer of 1 to 4, b_9 is an integer of 0 to 3, a_8 is an integer of 0 to 4, b_{10} is an integer of 0 to 4, b_{11} and b_{12} are integers of 0 to 3, $a_7 + b_9$ is an integer of 1 to 4, $a_8 + b_{10}$ is an integer of 0 to 4, and at least one of b_9 and b_{10} is an integer of 1 or more; m_5 and m_6 are integers of 0 or 1, and $m_5 + m_6$ is an integer of 1 or 2.

2. The resin according to claim 1, wherein the resin is a resin that forms a resin film having an absorbance at a wavelength of 365 nm per 1 μm thickness of 0.005 or more and 0.3 or less.

3. The resin according to claim 1 or 2, wherein an average linear thermal expansion coefficient of the resin at 50 to 200°C measured after heat treatment of the resin at 250°C is -10 to 40 ppm/°C.

4. The resin according to any one of claims 1 to 3, wherein the resin forms a resin film which has a film thickness reduction rate of 10 nm/min or more and 30000 nm/min or less when immersed in a 2.38% tetramethylammonium hydroxide aqueous solution.

5. A resin composition comprising the resin according to any one of claims 1 to 4.

6. The resin composition according to claim 5, comprising a photo acid generator or a photopolymerization initiator.

7. A process for producing a heat resistance coating film, comprising: coating the resin composition according to claim 5 or 6 onto a support substrate to form a coating film; drying the coating film to form a resin film; exposing the resin film; developing the exposed resin film; and applying heat treatment to the developed resin film.

8. A process for producing a heat resistance coating film, comprising: coating the resin composition according to claim 5 or 6 onto a support substrate using a slit nozzle to form a coating film; drying the coating film under reduced pressure to form a resin film; exposing the resin film; developing the exposed resin film; and applying heat treatment to the developed

resin film.

9. The process for producing a heat resistance coating film according to claim 7 or 8, wherein the step of applying heat treatment to the resin film is performed at 250°C or less.

10. The process for producing a heat resistance coating film according to any one of claims 7 to 9, wherein residual stress of a resin forming a heat resistance coating film of a substrate with the heat resistance coating film obtained by the process for producing the heat resistance coating film is 30 MPa or less.

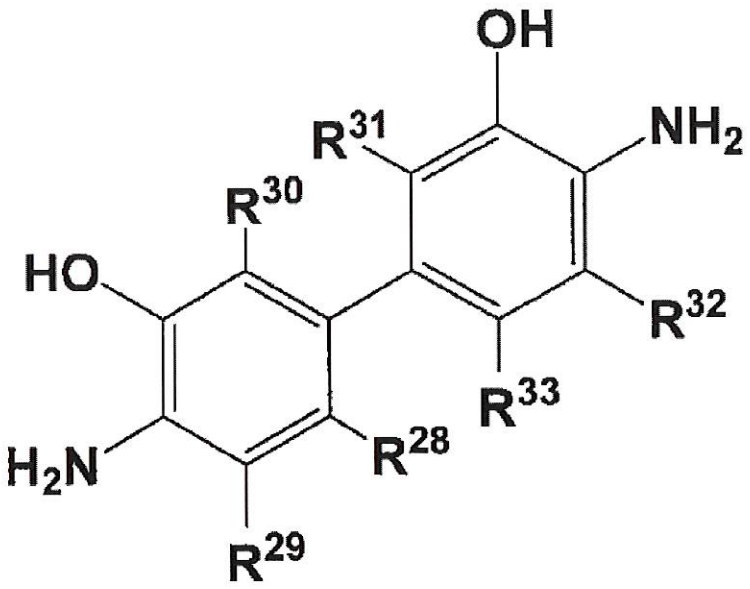
11. An electronic component mounted in such a state that one or a plurality of structures comprising a substrate and a coating film provided on one or both surfaces of the substrate are stacked, the coating film is a heat resistance coating film obtained by the production process according to any one of claims 7 to 10.

12. An electronic component comprising a substrate, a rewiring structure comprising a coating film layer and a wiring layer alternately formed on the substrate, or a multilayer wiring structure, wherein the coating film layer is a heat resistance coating film obtained by the production process according to any one of claims 7 to 10.

13. A display device comprising a first electrode provided on a substrate, an insulating layer provided on the first electrode such that the first electrode is partially exposed, and a second electrode provided facing the first electrode, wherein the insulating layer is a heat resistance coating film obtained by the production process according to any one of claims 7 to 10.

14. A display element comprising a flattening film provided to cover concavoconvexes on a substrate comprising a thin film transistor (TFT) and a display element provided on the flattening film, wherein the flattening film is a heat resistance coating film obtained by the production process according to any one of claims 7 to 10.

15. A 5,5'-dihydroxyl-4,4'-diaminobiphenyl derivative represented by the following general formula (8):



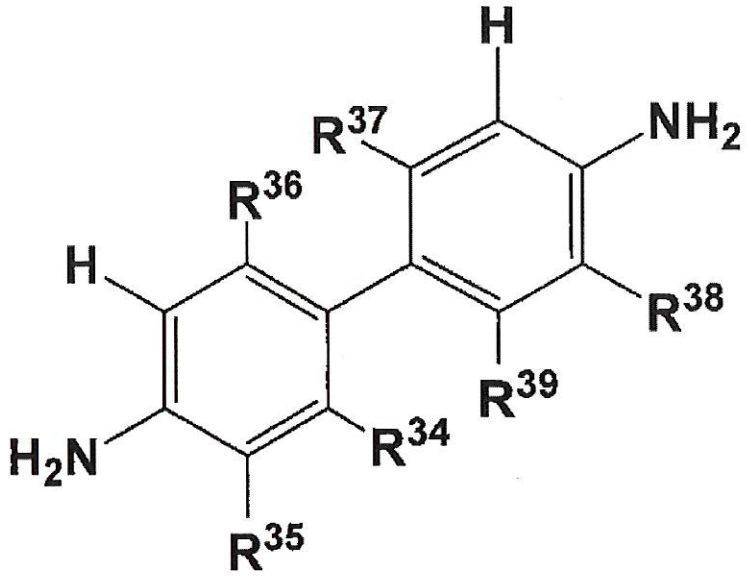
(8)

wherein R^{28} and R^{33} are the same and independently one kind selected from the group consisting of a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group; R^{29} and R^{32} are the same, R^{30} and R^{31} are the same, and they are each one kind selected from the group consisting of hydrogen, halogen, a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6

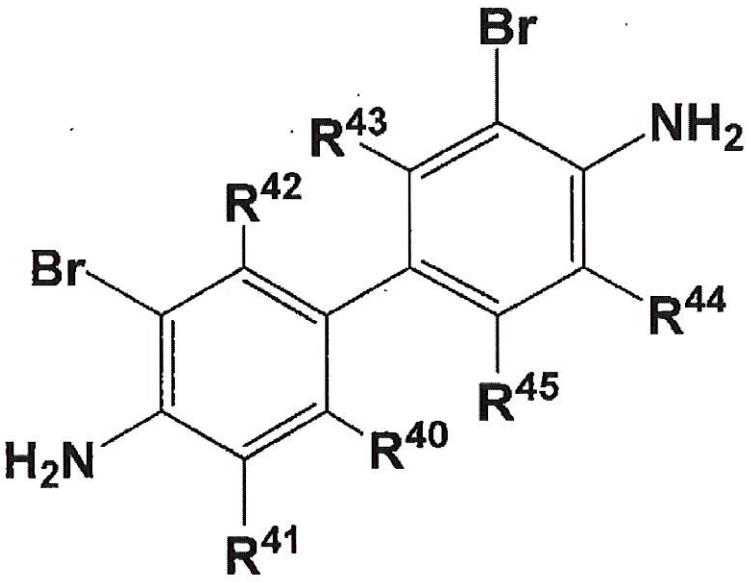
to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group; wherein among them, the substituents may be the same or different and represent one or more of halogen, trifluoromethyl, trimethylsilyl, a C_1 to C_6 alkoxyl group, a C_1 to C_6 alkyl group, an aryl alkoxyl group, a C_6 to C_{30} aryl group, and a C_4 to C_{30} heterocyclic group.

16. The 5,5'-dihydroxyl-4,4'-diaminobiphenyl derivative according to claim 15, wherein R^{29}, R^{30}, R^{31} and R^{32} are each hydrogen.

17. A process for producing a 5,5'-dihydroxy-4,4'-diaminobiphenyl derivative, comprising a production process for obtaining a 5,5'-dibromo-4,4'-diaminobiphenyl derivative of the general formula (10) by bromination reaction of 4,4'-diaminobiphenyl of the general formula (9):



(9)



(10)

wherein R^{34} and R^{39} are the same and each independently one kind selected from the group consisting of a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a

substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group; R^{35} and R^{38} are the same, R^{36} and R^{37} are the same, and they are each independently one kind selected from the group consisting of hydrogen, halogen, a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group; R^{40} and R^{45} are the same and each independently one kind selected from the group consisting of a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group; R^{41} and R^{44} are the same, R^{42} and R^{43} are the same, and they are each independently one kind selected from the group consisting of hydrogen, halogen, a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino

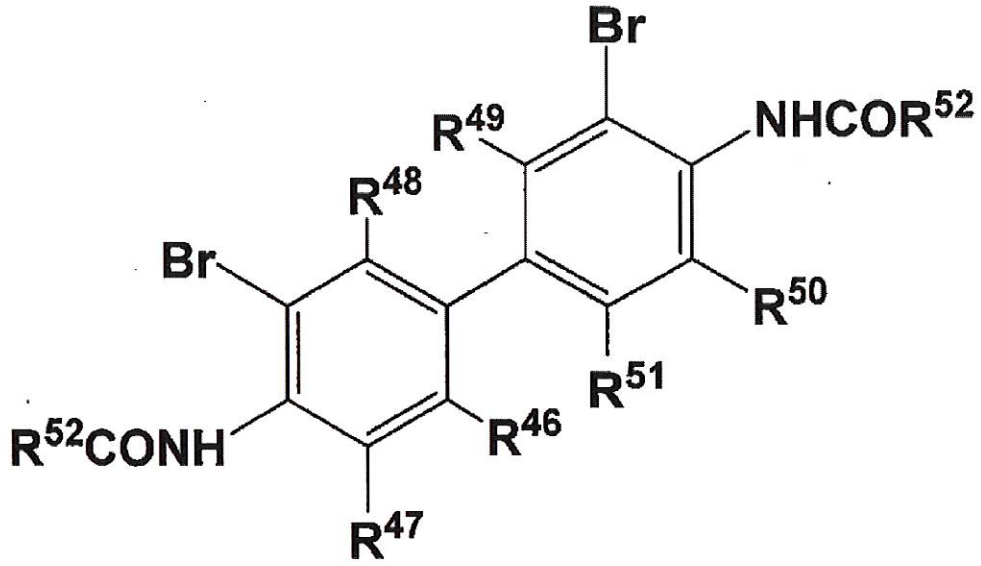
group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group; wherein the substituents may be the same or different and each independently represent one or more of halogen, trifluoromethyl, trimethylsilyl, a C_1 to C_6 alkoxyl group, a C_1 to C_6 alkyl group, an aryl alkoxyl group, a C_6 to C_{30} aryl group, and a C_4 to C_{30} heterocyclic group.

18. The process for producing a 5,5'-dihydroxy-4,4'-diaminobiphenyl derivative according to claim 17, wherein R^{35}, R^{36}, R^{37} and R^{38} are hydrogen, and R^{41}, R^{42}, R^{43}, and R^{44} are hydrogen.

19. The process for producing a 5,5'-dihydroxy-4,4'-diaminobiphenyl derivative according to claim 17, wherein the reaction temperature in the bromination reaction is from -30°C to 60°C, in the bromination reaction, one or more mixed solvents of methyl acetate, ethyl acetate, propyl acetate, butyl acetate, ethylene glycol dimethyl ether, tetrahydrofuran, 1,4-dioxane, and the solvent are reaction solvents, and a brominating reagent used in the bromination reaction is liquid bromine or N-bromosuccinimide.

20. A process for producing a

5,5'-dihydroxy-4,4'-diaminobiphenyl derivative, comprising a production process for obtaining a 5,5'-dibromo-4,4'-diamidebiphenyl derivative of the general formula (11) by amidation reaction of a 5,5'-dibromo-4,4'-diaminobiphenyl derivative using acid anhydride or acyl chloride:



(11)

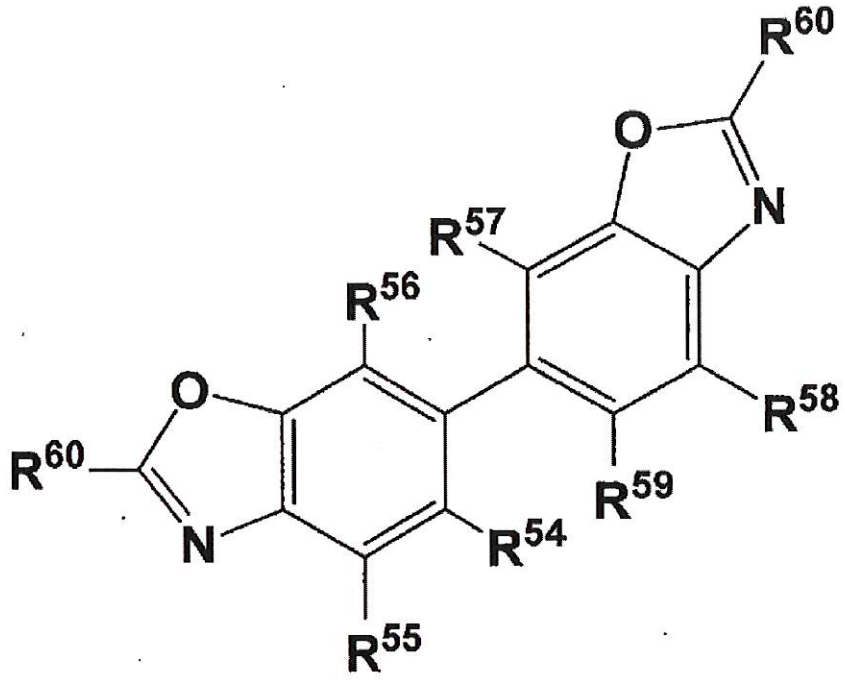
wherein R^{46} and R^{51} are the same and each independently one kind selected from the group consisting of a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group; R^{47} and R^{50} are the same, R^{48} and R^{49} are the same, and they are each

independently one kind selected from the group consisting of hydrogen, halogen, a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group; wherein among them, the substituents may be the same or different and each independently represent one or more of halogen, trifluoromethyl, trimethylsilyl, a C_1 to C_6 alkoxyl group, a C_1 to C_6 alkyl group, an aryl alkoxyl group, a C_6 to C_{30} aryl group, and a C_4 to C_{30} heterocyclic group, and R^{52} is one kind selected from the group consisting of a substituted or unsubstituted C_1 to C_6 alkyl group or a substituted or unsubstituted aryl group; and the substituent in R^{52} is one or more of a methyl group, a sulfo group, a fluorine atom, an amino group, and a methoxy group.

21. The process for producing a 5,5'-dihydroxy-4,4'-diaminobiphenyl derivative according to claim 20, wherein R^{47}, R^{48}, R^{49} and R^{50} in the general formula (11) are hydrogen.

22. A process for producing a 5,5'-dihydroxy-4,4'-diaminobiphenyl derivative, comprising a

production process for obtaining a 6,6'-dibenzoxazole derivative represented by the general formula (12) by reaction of a 5,5'-dibromo-4,4'-diamidobiphenyl derivative under the action of a catalyst and inorganic alkali:



(12)

wherein R^{54} and R^{59} are the same and each independently one kind selected from the group consisting of a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group; R^{55} and R^{58} are the same, R^{56} and R^{57} are the same, and they are each

independently one kind selected from the group consisting of hydrogen, halogen, a substituted or unsubstituted C_1 to C_6 alkyl group, a substituted or unsubstituted C_1 to C_6 alkoxyl group, a hydroxyl group, a halogenated alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted C_6 to C_{30} aryl group, a substituted or unsubstituted C_4 to C_{30} heterocyclic aryl group, an ester group and a nitro group; wherein one or more substituents among them may be the same or different and are each independently represent one or more of halogen, trifluoromethyl, trimethylsilyl, a C_1 to C_6 alkoxyl group, a C_1 to C_6 alkyl group, an arylalkoxyl group, a C_6 to C_{30} aryl group, and a C_4 to C_{30} heterocyclic group; R^{60} is one kind selected from the group consisting of a substitutable C_1 to C_6 alkyl group and a substitutable aryl group; and wherein the substituent in R^{60} is one or more of a methyl group, a sulfo group, a fluorine atom, an amino group, and a methoxy group.

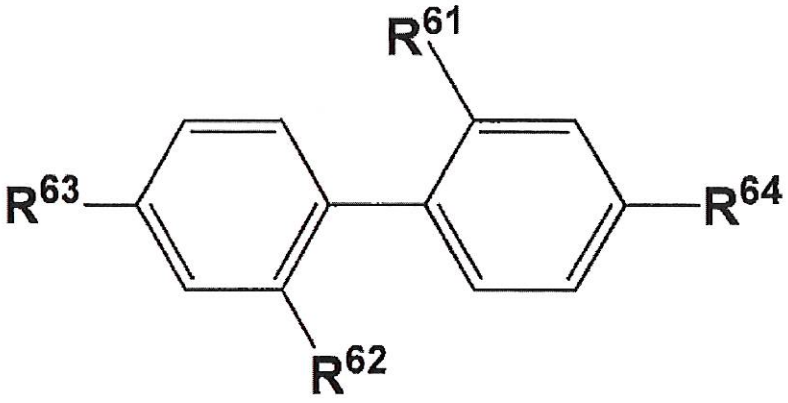
23. The process for producing a 5,5'-dihydroxyl-4,4'-diaminobiphenyl derivative according to claim 22, wherein R^{55}, R^{56}, R^{57} and R^{58} in the general formula (12) are hydrogen.

24. The process for producing a 5,5'-dihydroxyl-4,4'-diaminobiphenyl derivative according to

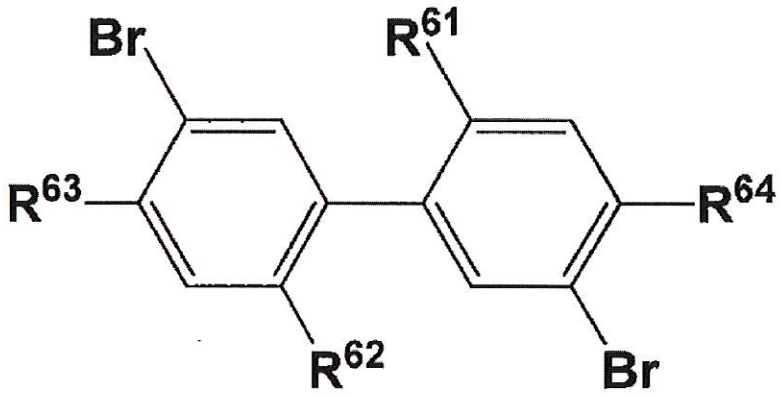
claim 22, wherein the catalyst contains at least a copper catalyst, and inorganic alkali to be used is one or more of potassium carbonate or potassium phosphate, the reaction temperature is 100°C to 140°C, and a reaction solvent is a high-boiling solvent.

25. A process for producing a 5,5'-dihydroxy-4,4'-diaminobiphenyl derivative characterized by obtaining a 6,6'-dibenzoxazole derivative by ring-opening reaction under an inorganic strong acid.

26. A process for producing a 5,5'-dibromobiphenyl derivative characterized by obtaining a 5,5'-dibromobiphenyl derivative having a structure represented by the general formula (14) under the action of an aprotic solvent and a bromination reagent, using a biphenyl compound having a structure represented by the general formula (13) as a raw material:



(13)



(14)

wherein R^{61} and R^{62} may be the same or different and are each one kind selected from the group consisting of halogen, a C_1 to C_6 alkyl group, a halogenated alkyl group, an ester group and a nitro group; R^{63} and R^{64} may be the same or different and are each one kind selected from the group consisting of a C_1 to C_6 alkyl group, a C_1 to C_6 alkoxyl group, a hydroxyl group, a substituted or unsubstituted aryl group, a substituted or

unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted imide group, a substituted or unsubstituted sulfamine group, a substituted or unsubstituted sulfinamide group, and a substituted or unsubstituted aromatic heterocyclic group; and wherein among them, the substituents may be the same or different and represent one or more of trifluoromethyl, trimethylsilyl, a C_1 to C_6 alkoxyl group, a C_1 to C_6 alkyl group, an aryl alkoxyl group, a C_6 to C_{30} aryl group, and a heterocyclic group.

27. The process for producing a 5,5'-dibromobiphenyl derivative according to claim 26, wherein the aprotic solvent is selected from one or more mixed solvents of ester solvents, ether solvents, arene solvents and the solvents.

28. The process for producing a 5,5'-dibromobiphenyl derivative according to claim 27, wherein the aprotic solvent is selected from one or more mixed solvents of methyl acetate, ethyl acetate, propyl acetate, butyl acetate, propyleneglycolmonomethyletheracetate, ethyleneglycoldimethylether, tetrahydrofuran, 1,4-dioxane, and the solvents.

29. The process for producing a 5,5'-dibromobiphenyl derivative according to any one of claims 26 to 28, wherein the halogenated alkyl group is one kind selected from trifluoromethyl and trifluoroethyl.

30. The process for producing a 5,5'-dibromobiphenyl derivative according to any one of claims 26 to 28, wherein the C_1 to C_6 alkyl group is a methyl group.

31. The process for producing a 5,5'-dibromobiphenyl derivative according to claim 26, wherein in the general formulae (13) and (14), R^{63} and R^{64} may be the same or different, and are each one kind selected from the group consisting of a substituted or unsubstituted amino group, a substituted or unsubstituted amide group, a substituted or unsubstituted imide group, a substituted or unsubstituted sulfamine group, a

substituted or unsubstituted sulfinamide group, and a substituted or unsubstituted aromatic heterocyclic group.

32. The process for producing a 5,5'-dibromobiphenyl derivative according to claim 26, wherein in the general formulae (13) and (14), R^{63} and R^{64} may be the same or different, and are each one kind selected from the group consisting of an amino group, an acetamide group, a tertiarybutoxideamide group, a benzyloxyamide group, a ditertiarybutoxidedicarboximide group, a dibenzyloxydicarboximide group, and a phthalimide group.