

DESCRIPTION

Title of Invention: PHOTSENSITIVE ELEMENT, METHOD FOR FORMING RESIST PATTERN, AND METHOD FOR MANUFACTURING PRINTED WIRING BOARD

5 **Technical Field**

[0001] The present disclosure relates to a photosensitive element, a method for forming a resist pattern, and a method for producing a printed wiring board.

10 **Background Art**

[0002] In the field of production of printed wiring boards, photosensitive elements including a layer formed using a photosensitive resin composition (hereinafter, also referred to as "photosensitive layer") on a support film have been widely used as resist materials used for an etching treatment, a plating treatment, or the like.

15 [0003] A printed wiring board is produced using a photosensitive element, for example, by the following procedure. That is, first, a photosensitive layer of a photosensitive element is laminated on a substrate for circuit formation such as a copper-clad laminate plate. Next, the photosensitive layer is exposed through a mask film or the like
20 to form a photo-cured area. At this time, a support film is released before exposure or after exposure. Thereafter, an area other than the photo-cured area of the photosensitive layer is removed with a developing solution to form a resist pattern. Next, the substrate is subjected to an etching treatment or a plating treatment using the resist pattern as a resist
25 to form a conductor pattern, and finally, the photo-cured area (resist pattern) of the photosensitive layer is released (removed).

[0004] As the support film used in the photosensitive element, a support film having a specific haze value, a support film having a specific lubricant particle size, and the like have been known (see, for example, Patent Literatures 1 and 2).

5 **Citation List**

Patent Literature

[0005] Patent Literature 1: JP 2001-13681 A

 Patent Literature 2: JP 2014-74764 A

Summary of Invention

10 **Technical Problem**

[0006] With an increase in resolution of circuit formation in recent years, miniaturization of a conductor pattern is required, and miniaturization of a resist pattern for forming a conductor pattern is also required. However, the lubricant contained in the support film may scatter light during exposure, which may cause roughness (rattling) of the contour of the resist pattern. In particular, a lubricant having a large particle size has a large range in which the light is scattered, and the contour of the resist pattern is likely to become coarse.

15 [0007] An object of the present disclosure is to provide a photosensitive element excellent in formability of a fine resist pattern, a method for forming a resist pattern using this photosensitive element, and a method for producing a printed wiring board.

Solution to Problem

20 [0008] One aspect of the present disclosure relates to a photosensitive element, a method for forming a resist pattern, and a method for producing a printed wiring board described below.

- [0009] [1] A photosensitive element including: a support film containing a lubricant; and a photosensitive layer formed on a first surface of the support film, in which a number of lubricants having a particle size of 0.8 μm or more contained in a second surface on a side opposite to the first surface of the support film is 80 or less per 0.0225 mm^2 .
- [2] The photosensitive element described in [1], in which a total number of lubricants contained in the second surface is 2000 or less per 0.0225 mm^2 .
- [3] The photosensitive element described in [1] or [2], in which a value obtained by dividing the number of lubricants having a particle size of 0.8 μm or more contained in the second surface by the total number of lubricants contained in the second surface is 0.20 or less.
- [4] The photosensitive element described in any of [1] to [3], in which a number of lubricants having a particle size of 0.8 μm or more contained in the first surface is 200 or less per 0.0225 mm^2 .
- [5] The photosensitive element described in any of [1] to [4], in which an average particle size of the lubricants contained in the first surface and the second surface is 0.3 μm or more and 1.0 μm or less.
- [6] The photosensitive element described in any of [1] to [5], in which the support film is a biaxially oriented polyester film.
- [7] The photosensitive element described in any of [1] to [6], in which the support film does not contain a lubricant having a particle size of more than 3.0 μm .
- [8] A method for forming a resist pattern, the method including: a lamination step of laminating the photosensitive element described in any of [1] to [7] on a substrate in order of the photosensitive layer and the

support film; an exposure step of irradiating a predetermined part of the photosensitive layer with an active light ray through the support film to form a photo-cured area; and a development step of removing an area other than the photo-cured area in the photosensitive layer.

- 5 [9] A method for producing a printed wiring board, the method including a step of subjecting a substrate having a resist pattern formed by the method for forming a resist pattern described in [8] to an etching treatment or a plating treatment to form a conductor pattern.

Advantageous Effects of Invention

- 10 [0010] According to the present disclosure, it is possible to provide a photosensitive element excellent in formability of a fine resist pattern, a method for forming a resist pattern using this photosensitive element, and a method for producing a printed wiring board.

Brief Description of Drawings

- 15 [0011] [FIG. 1] FIG. 1 is a schematic cross-sectional view illustrating an embodiment of a photosensitive element.

Description of Embodiments

- [0012] Hereinafter, embodiments for carrying out the present disclosure will be specifically described. However, the present disclosure is not
20 limited to the following embodiments.

- [0013] In the present specification, a numerical range that has been indicated by use of "to" indicates the range that includes the numerical values which are described before and after "to", as the minimum value and the maximum value, respectively. The numerical range "A or more" means A and a range of more than A. The numerical range "A or less" means A and a range of less than A. In the numerical ranges that are
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described stepwise in the present specification, the upper limit value or the lower limit value of the numerical range of a certain stage can be arbitrarily combined with the upper limit value or the lower limit value of the numerical range of another stage. In a numerical range described in the present specification, the upper limit value or the lower limit value of the numerical range may be substituted by a value shown in Examples.

[0014] In the present specification, "A or B" may include either one of A and B, and may also include both of A and B. Materials listed as examples in the present specification can be used singly or in combinations of two or more kinds, unless otherwise specified. When a plurality of substances corresponding to each component exist in the composition, the content of each component in the composition means the total amount of the plurality of substances that exist in the composition, unless otherwise specified. The terms "layer" and "film" include a structure having a shape which is formed on a part, in addition to a structure having a shape which is formed on the whole surface, when the layer has been observed as a plan view. The term "step" includes not only an independent step but also a step by which an intended action of the step is achieved, even though the step cannot be clearly distinguished from other steps.

[0015] In the present specification, the term "(meth)acrylate" means at least one of acrylate and methacrylate corresponding thereto. The same applies to other analogous expressions such as "(meth)acrylic acid". "EO" stands for ethylene oxide, and an "EO-modified" compound means a compound having an oxyethylene group. "PO" stands for propylene oxide, and a "PO-modified" compound means a compound having an

oxypropylene group. The term "solid content" refers to a non-volatile content contained in a photosensitive resin composition excluding volatile substances such as water or a solvent, refers to a component remaining without volatile in drying of the resin composition, and also includes a component present in a liquid, syrupy, and waxy state at room temperature near 25°C.

[0016] [Photosensitive element]

A photosensitive element of the present embodiment includes: a support film containing a lubricant; and a photosensitive layer formed on a first surface of the support film, in which a number of lubricants having a particle size of 0.8 μm or more contained in a second surface on a side opposite to the first surface of the support film is 80 or less per 0.0225 mm^2 .

[0017] FIG. 1 is a schematic cross-sectional view illustrating an embodiment of a photosensitive element. A photosensitive element 1 of the present embodiment includes a support film 10 and a photosensitive layer 20 as illustrated in FIG. 1. The photosensitive layer 20 is provided on a first surface 10a of the support film 10. The support film 10 has a second surface 10b on a side opposite to the first surface 10a.

[0018] In the support film 10, a lubricant is added for improving slidability, and a lubricant is contained on both sides of the support film. By reducing a lubricant having a particle size of 0.8 μm or more among lubricants contained in the second surface 10b of the support film not in contact with the photosensitive layer, the roughness of the contour of the resist pattern can be reduced.

[0019] The lubricant is not particularly limited as long as it is a

component that does not inhibit the light transparency of the support film and is used in the production of a polyester film, and may be an inorganic lubricant or an organic lubricant. Examples of the inorganic lubricant include inorganic particles containing, as an inorganic component, silica, calcium carbonate, alumina, aluminum silicate, mica, clay, talc, wollastonite, kaolin, zinc oxide, barium sulfate, calcium phosphate, calcium, magnesium, barium, zinc, manganese, or the like. Examples of the organic lubricant include crosslinked polymers such as polystyrene, polymethyl methacrylate, polyimide, polyolefin, modified polyolefin, and a silicone resin.

[0020] The number of lubricants having a particle size of 0.8 μm or more contained in the second surface 10b in the support film may be 75 or less, 70 or less, 65 or less, or 60 or less per 0.0225 mm^2 , from the viewpoint of further reducing the roughness of the contour of the resist pattern.

The number of lubricants of the present embodiment is an average value per unit area of 0.0225 mm^2 (0.150 $\text{mm} \times 0.150 \text{ mm}$) of the support film. Note that, the lubricant having a particle size of 0.8 μm or more also includes an aggregate of a lubricant having a particle size of 0.8 μm or less.

[0021] The support film of the present embodiment may contain a lubricant having a particle size of less than 0.8 μm . The total number of lubricants (the number of lubricants having a particle size of 0.8 μm or more and the number of lubricants having a particle size of less than 0.8 μm) contained in the second surface 10b may be 2500 or less, 2200 or less, 2000 or less, or 1800 or less, and may be 10 to 1800, 20 to 1600, 30 to 1400, or 40 to 1200, per 0.0225 mm^2 , from the viewpoint of further

enhancing the slidability of the support film.

[0022] From the viewpoint of further enhancing the slidability of the support film, a value obtained by dividing the number of lubricants having a particle size of 0.8 μm or more contained in the second surface 10b by the total number of lubricants contained in the second surface 10b may be 0.20 or less, 0.18 or less, 0.16 or less, 0.14 or less, or 0.12 or less.

[0023] The number of lubricants having a particle size of 0.8 μm or more contained in the second surface 10b may be smaller than the number of lubricants having a particle size of 0.8 μm or more contained in the first surface 10a. The number of lubricants having a particle size of 0.8 μm or more contained in the first surface 10a may be 400 or less, 300 or less, 200 or less, or 180 or less, and may be 10 to 400, 15 to 300, 20 to 200, or 25 to 180, per 0.0225 mm^2 , from the viewpoint of suppressing resist defects.

[0024] The total number of lubricants contained in the first surface 10a may be 100 to 1600, 150 to 1500, 155 to 1400, or 160 to 1200, per 0.0225 mm^2 , from the viewpoint of further enhancing the slidability of the support film.

[0025] It is preferable that the support film of the present embodiment does not contain a lubricant having a particle size of more than 3.0 μm from the viewpoint of suppressing resist defects. The upper limit value of the size of the lubricant having a particle size of 0.8 μm or more contained in the first surface 10a and the second surface 10b may be 3.0 μm or less, 2.5 μm or less, 2.0 μm or less, or 1.5 μm or less. The lower limit value of the size of the lubricant of 0.8 μm or more contained in the first surface 10a and the second surface 10b may be 0.8 μm or more, 0.9

μm or more, 1.0 μm or more, or 1.1 μm or more, from the viewpoint of improving handling property.

[0026] The average particle size of the lubricants contained in the first surface 10a and the second surface 10b may be 0.2 μm or more, 0.3 μm or more, or 0.4 μm or more from the viewpoint of improving handling property, and may be 1.0 μm or less, 0.8 μm or less, or 0.6 μm or less from the viewpoint of suppressing resist defects.

[0027] The size and number of lubricants contained in the support film can be measured using a confocal microscope. As the confocal microscope, a hybrid laser microscope OPTELICS HYBRID (manufactured by Lasertec Corporation, trade name) and the like can be used. The observation with the confocal microscope is a measurement method in which reflected light from an object to be observed is detected by a light receiving portion. In a case where the object to be observed is brought to a focus (comes into focus), reflected light is strongly obtained, and an intensity of light is strongly observed (light is observed in white in many cases). In a case where the object to be observed is not brought to a focus (misses the point), an intensity of light is weakly observed (light is observed in black in many cases).

[0028] The numerical aperture (Na) of an objective lens used in observation may be 0.8 from the viewpoint of easily performing observation in an efficient manner with high accuracy. In a case where the numerical aperture is 0.8, as compared to a case where the numerical aperture is more than 0.8, since it is easy to suppress that the lens and the object to be observed are in contact with each other to cause contamination of the microscope and an excessive increase in

magnification is suppressed, a decrease in detection level caused by a decrease in quantity of light of a field of view is easy to be suppressed. Furthermore, in a case where the numerical aperture (Na) is 0.8, as compared to a case where the numerical aperture is less than 0.8, since a decrease in resolution is suppressed so that the size detection of the object to be observed is less likely to be influenced by errors, measurement is easily performed with high accuracy.

[0029] In the observation with the confocal microscope, the measurement magnification may be 50 times, and the digital zooming in software may be 2 times. In a case where the measurement magnification is 50 times, as compared to a case where the measurement magnification is more than 50 times, a decrease in quantity of light of a field of view is suppressed so that a decrease in detection level is easy to be suppressed, and as compared to a case where the measurement magnification is less than 50 times, the sizes of defects are easy to be accurately measured. In a case where the digital zooming is 2 times, as compared to a case where the digital zooming is the actual size (without setting), a decrease in quantity of light of a field of view is suppressed so that a decrease in detection level is easy to be suppressed.

[0030] Examples of constituent materials for the support film include polyesters such as polyethylene terephthalate (PET), polybutylene terephthalate (PBT), and polyethylene-2,6-naphthalate (PEN); and polyolefins such as polypropylene and polyethylene. The support film may have a polyester film and may have a PET film from the viewpoint of easily suppressing occurrence of defects of a resist. The support film is a light transmissive film and may be a transparent resin film.

[0031] As the support film, a multilayer film having a lubricant layer can be used. The support film may have a polyester film and a lubricant layer disposed on at least one surface of the polyester film. The lubricant layer can be formed using a known method such as a roll coater, a flow coater, a spray coater, a curtain flow coater, a dip coater, or a slit die coater. As the support film, it is preferable to use a biaxially oriented polyester film with a two- or three-layer structure, and more preferable to use a biaxially oriented PET film with a three-layer structure.

[0032] The haze value of the support film may be 0.01% or more, 0.05% or more, 0.1% or more, 0.3% or more, 0.5% or more, or 0.7% or more, from the viewpoint of easily improving handleability when the photosensitive element is laminated on the substrate, handleability when the photosensitive layer is formed on the support film, and the like. The haze value of the support film may be 3.0% or less, 1.5% or less, 0.8% or less, or 0.7% or less, from the viewpoint of easily obtaining favorable sensitivity and resolution. From these viewpoints, the haze value of the support film may be 0.01 to 3.0%, 0.01 to 1.5%, 0.01 to 0.8%, or 0.01 to 0.7%. The "haze value" means the degree of haze. The haze value of the support film can be measured using a commercially available haze meter (turbidimeter; for example, trade name "NDH-5000" manufactured by NIPPON DENSHOKU INDUSTRIES CO., LTD.) according to the method defined in JIS K 7105.

[0033] The light transmission (for example, light transmission in the whole range of wavelengths of 380 to 780 nm) of the support film may be in the following range. The light transmission of the support film may be 80% or more, 85% or more, 87% or more, 88% or more, or 89%

or more. The light transmission of the support film may be 95% or less, 93% or less, 90% or less, or 89% or less. From these viewpoints, the light transmission of the support film may be 80 to 95%. The light transmission of the support film can be measured using a commercially available haze meter (for example, trade name "NDH-5000" manufactured by NIPPON DENSHOKU INDUSTRIES CO., LTD.).

[0034] The thickness of the support film or the thickness of the polyester film may be in the following range. The thickness may be 5 μm or more, 10 μm or more, 11 μm or more, 12 μm or more, 15 μm or more, or 16 μm or more, from the viewpoint that the support film is less likely to be torn when the support film is peeled off from the photosensitive element. The thickness may be 200 μm or less, 100 μm or less, 50 μm or less, 40 μm or less, 30 μm or less, 20 μm or less, or 18 μm or less, from the viewpoint of easily securing a focus latitude at the time of exposure. From these viewpoints, the thickness may be 5 to 200 μm , 11 to 100 μm , 12 to 50 μm , or 15 to 40 μm .

[0035] The photosensitive layer 20 is a layer formed from a photosensitive resin composition. The photosensitive resin composition used for forming the photosensitive layer 20 may contain (A) a binder polymer (a component (A)), (B) a photopolymerizable compound (a component (B)), and (C) a photopolymerization initiator (a component (C)).

[0036] Examples of constituent materials for the binder polymer that is the component (A) include an acrylic resin, a styrene resin, an epoxy resin, an amide resin, an amide-epoxy resin, an alkyd resin, and a phenolic resin. The component (A) may contain an acrylic resin from

the viewpoint of easily obtaining favorable alkali developability. As the component (A), a binder polymer that is used in a conventional photosensitive resin composition can be used.

5 [0037] The component (A) can be produced, for example, by radical polymerization of a polymerizable monomer. Examples of the polymerizable monomer include styrene or a styrene derivative, acrylamides such as diacetone acrylamide, acrylonitriles, vinyl alcohol ethers such as vinyl-n-butyl ether, alkyl (meth)acrylate ester, benzyl (meth)acrylate ester, hydroxyalkyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate ester, dimethylaminoethyl (meth)acrylate ester, diethylaminoethyl (meth)acrylate ester, glycidyl (meth)acrylate ester, 10 2,2,2-trifluoroethyl (meth)acrylate, 2,2,3,3-tetrafluoropropyl (meth)acrylate, (meth)acrylic acid, α -bromoacrylic acid, α -chloracrylic acid, β -furyl (meth)acrylic acid, β -styryl (meth)acrylic acid, maleic acid, maleic anhydride, maleic acid monoesters such as monomethyl malate, 15 monoethyl malate, and monoisopropyl malate, fumaric acid, cinnamic acid, α -cyanocinnamic acid, itaconic acid, crotonic acid, and propiolic acid. The polymerizable monomer can be used singly or in combination of two or more kinds thereof.

20 [0038] The component (A) may have a carboxy group from the viewpoint of alkali developability. The component (A) having a carboxy group can be produced, for example, by radical polymerization of a polymerizable monomer having a carboxy group with another polymerizable monomer. The polymerizable monomer having a 25 carboxy group may be (meth)acrylic acid, or may be methacrylic acid.

[0039] From the viewpoint of improving alkali developability and alkali

resistance in a well-balanced manner, the content of the structural unit based on the polymerizable monomer having a carboxy group may be 10 to 50% by mass, 15 to 40% by mass, or 20 to 35% by mass, on the basis of the total amount of the component (A). When the content of the carboxy group is 10% by mass or more, there is a tendency that the alkali developability is improved, and when the content of the carboxy group is 50% by mass or less, there is a tendency that the alkali resistance is excellent.

[0040] From the viewpoint of adhesiveness and release property, the component (A) may have a structural unit based on styrene or a styrene derivative. The styrene derivative is a polymerizable compound in which the hydrogen atom at the α -position or of the aromatic ring of styrene such as vinyl toluene or α -methylstyrene has been substituted. The content of the structural unit based on the styrene or the styrene derivative in the component (A) may be 10 to 60% by mass, 15 to 50% by mass, 35 to 50% by mass, or 40 to 50% by mass. When the content thereof is 10% by mass or more, there is a tendency that adhesiveness is improved, and when the content thereof is 60% by mass or less, there are tendencies that an increase in size of the released pieces can be suppressed during the development, and thus an increase in time required for releasing can be suppressed.

[0041] The component (A) may have a structural unit based on benzyl (meth)acrylate ester from the viewpoint of improving resolution. The content of the structural unit derived from the benzyl (meth)acrylate ester in the component (A) may be 10 to 40% by mass, 15 to 35% by mass, or 20 to 30% by mass.

[0042] The component (A) may have a structural unit based on alkyl (meth)acrylate ester from the viewpoint of improving plasticity. Examples of the alkyl (meth)acrylate ester include methyl (meth)acrylate ester, ethyl (meth)acrylate ester, propyl (meth)acrylate ester, butyl (meth)acrylate ester, pentyl (meth)acrylate ester, hexyl (meth)acrylate ester, heptyl (meth)acrylate ester, octyl (meth)acrylate ester, 2-ethylhexyl (meth)acrylate ester, nonyl (meth)acrylate ester, decyl (meth)acrylate ester, undecyl (meth)acrylate ester, and dodecyl (meth)acrylate ester.

[0043] The component (A) may have a structural unit based on hydroxyalkyl (meth)acrylate from the viewpoint of further improving resolution and adhesiveness. The hydroxyalkyl (meth)acrylate may be, for example, hydroxymethyl (meth)acrylate, hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate, hydroxypentyl (meth)acrylate, hydroxyhexyl (meth)acrylate, and the like. Furthermore, in a case where the number of carbon atoms of the alkyl moiety in the hydroxyalkyl (meth)acrylate unit is 3 or more, the component (A) may have a branched structure.

[0044] The weight average molecular weight (M_w) of the component (A) may be 10000 or more, 15000 or more, 20000 or more, or 25000 or more from the viewpoint that the adhesiveness of the resist pattern is excellent, and may be 100000 or less, 80000 or less, 70000 or less, or 60000 or less from the viewpoint that development can be suitably performed. The degree of dispersion (M_w/M_n) of the component (A) may be, for example, 1.0 or more, 1.5 or more, or 1.8 or more, and may be 3.0 or less, 2.5 or less, or 2.0 or less from the viewpoint of further improving adhesiveness and resolution.

[0045] The weight average molecular weight (Mw) and the degree of dispersion (Mw/Mn) in the present specification can be obtained by measurement by gel permeation chromatography (GPC) and conversion using a calibration curve of standard polystyrene.

5 [0046] The acid value of the component (A) may be 60 mgKOH/g or more, 80 mgKOH/g or more, 90 mgKOH/g or more, or 100 mgKOH/g or more from the viewpoint that development can be suitably performed, and may be 250 mgKOH/g or less, 230 mgKOH/g or less, 210 mgKOH/g or less, or 200 mgKOH/g or less from the viewpoint of improving the
10 adhesiveness (developing solution resistance) of the resist pattern. The acid value of the component (A) can be adjusted by the content of the structural unit constituting the component (A) (for example, a structural unit derived from a (meth)acrylic acid).

[0047] The component (A) can be used singly or in combination of two
15 or more kinds thereof. Examples of the component (A) in the case of being used in combination of two or more kinds thereof include two or more kinds of binder polymers each including a different polymerizable monomer, two or more kinds of binder polymers each having a different Mw, and two or more kinds of binder polymers each having a different
20 degree of dispersion.

[0048] The content of the component (A) may be 30 to 80 parts by mass, 40 to 75 parts by mass, 50 to 70 parts by mass, or 50 to 60 parts by mass, with respect to 100 parts by mass of the total amount of the component (A) and a component (B) described below. When the content of the
25 component (A) is within this range, the strength of the photo-cured area of the photosensitive layer becomes more favorable.

[0049] As the photopolymerizable compound that is the component (B), a compound having at least one ethylenically unsaturated bond in the molecule can be used. The component (B) can be used singly or in combination of two or more kinds thereof.

5 [0050] The ethylenically unsaturated bond of the component (B) is not particularly limited as long as photopolymerization is possible. Examples of the ethylenically unsaturated bond include α,β -unsaturated carbonyl groups such as a (meth)acryloyl group. Examples of the photopolymerizable compound having an α,β -unsaturated carbonyl
10 group include α,β -unsaturated carboxylic acid esters of polyhydric alcohols, bisphenol-type (meth)acrylates, α,β -unsaturated carboxylic acid adducts of glycidyl group-containing compounds, (meth)acrylates having a urethane bond, nonylphenoxypolyethylene oxyacrylate, (meth)acrylates having a phthalic acid skeleton, and alkyl (meth)acrylate
15 esters.

[0051] Examples of the α,β -unsaturated carboxylic acid esters of polyhydric alcohols include polyethylene glycol di(meth)acrylate in which the number of ethylene groups is 2 to 14, polypropylene glycol di(meth)acrylate in which the number of propylene groups is 2 to 14,
20 polyethylene-polypropylene glycol di(meth)acrylate in which the number of ethylene groups is 2 to 14 and the number of propylene groups is 2 to 14, trimethylol propane di(meth)acrylate, trimethylol propane tri(meth)acrylate, EO-modified trimethylol propane tri(meth)acrylate, PO-modified trimethylol propane tri(meth)acrylate, EO,PO-modified
25 trimethylol propane tri(meth)acrylate, tetramethylolmethane tri(meth)acrylate, tetramethylolmethane tetra(meth)acrylate, and a

(meth)acrylate compound having a skeleton derived from dipentaerythritol or pentaerythritol. The term "EO-modified" means having a block structure of an ethylene oxide (EO) group, and the term "PO-modified" means having a block structure of a propylene oxide (PO) group.

[0052] From the viewpoint of improving the flexibility of the resist pattern, the component (B) may contain polyalkylene glycol di(meth)acrylate. The polyalkylene glycol di(meth)acrylate may have at least one of the EO group and the PO group, and may have both the EO group and the PO group. In the polyalkylene glycol di(meth)acrylate having both the EO group and the PO group, the EO group and the PO group may be present as continuous blocks or present randomly. Furthermore, the PO group may be either an oxy-n-propylene group or an oxyisopropylene group. Note that, in a (poly)oxyisopropylene group, the secondary carbon of the propylene group may be bonded to an oxygen atom, and the primary carbon may be bonded to an oxygen atom.

[0053] Examples of commercially available products of polyalkylene glycol di(meth)acrylate include FA-023M (manufactured by Resonac Corporation), FA-024M (manufactured by Resonac Corporation), and NK ESTETR HEMA-9P (manufactured by SHIN-NAKAMURA CHEMICAL Co., Ltd.).

[0054] From the viewpoint of improving the flexibility of the resist pattern, the component (B) may contain a (meth)acrylate having a urethane bond. Examples of the (meth)acrylate having a urethane bond include addition reaction products of (meth)acrylic monomers with an

OH group at the β -position and diisocyanate (such as isophorone diisocyanate, 2,6-toluene diisocyanate, 2,4-toluene diisocyanate, or 1,6-hexamethylene diisocyanate), tris((meth)acryloxytetraethylene glycol isocyanate) hexamethylene isocyanurate, EO-modified urethane di(meth)acrylate, and EO,PO-modified urethane di(meth)acrylate.

[0055] Examples of commercially available products of the EO-modified urethane di(meth)acrylate include "UA-11" and "UA-21EB" (manufactured by SHIN-NAKAMURA CHEMICAL Co., Ltd.). Examples of commercially available products of the EO,PO-modified urethane di(meth)acrylate include "UA-13" (manufactured by SHIN-NAKAMURA CHEMICAL Co., Ltd.).

[0056] From the viewpoint of easily forming a thick resist pattern and improving resolution and adhesiveness in a well-balanced manner, the component (B) may contain a (meth)acrylate compound having a skeleton derived from dipentaerythritol or pentaerythritol. The (meth)acrylate compound having a skeleton derived from dipentaerythritol or pentaerythritol preferably has four or more (meth)acryloyl groups and may be dipentaerythritol penta(meth)acrylate or dipentaerythritol hexa(meth)acrylate.

[0057] As the component (B), a polyfunctional (meth)acrylate compound obtained by reacting an α,β -unsaturated carboxylic acid with a polyhydric alcohol may be contained. The polyfunctional (meth)acrylate compound may have at least one of the EO group and the PO group, and may have both the EO group and the PO group. As such a compound, dipentaerythritol (meth)acrylate having an EO group, and the like can be used. Examples of commercially available products of

the dipentaerythritol (meth)acrylate having an EO group include DPEA-12 (manufactured by Nippon Kayaku Co., Ltd.).

[0058] From the viewpoint of improving resolution and release property after curing, the component (B) may contain bisphenol-type (meth)acrylates, and may contain a bisphenol A-type (meth)acrylate among the bisphenol-type (meth)acrylates. Examples of the bisphenol A-type (meth)acrylate include 2,2-bis(4-((meth)acryloxypolyethoxy)phenyl)propane, 2,2-bis(4-((meth)acryloxypolypropoxy)phenyl)propane, 2,2-bis(4-((meth)acryloxypolybutoxy)phenyl)propane, and 2,2-bis(4-((meth)acryloxypolyethoxypolypropoxy)phenyl)propane.

[0059] Examples of commercially available products of 2,2-bis(4-((meth)acryloxydiethoxy)phenyl)propane include BPE-200 (manufactured by SHIN-NAKAMURA CHEMICAL Co., Ltd.), and examples of commercially available products of 2,2-bis(4-(methacryloxypentaethoxy)phenyl)propane include BPE-500 (manufactured by SHIN-NAKAMURA CHEMICAL Co., Ltd.) and FA-321M (manufactured by Resonac Corporation).

[0060] Examples of the nonylphenoxy polyethylene oxyacrylate include nonylphenoxytetraethylene oxyacrylate, nonylphenoxyhexaethylene oxyacrylate, nonylphenoxyheptaethylene oxyacrylate, nonylphenoxyoctaethylene oxyacrylate, nonylphenoxy nonaethylene oxyacrylate, nonylphenoxydecaethylene oxyacrylate, and nonylphenoxyundecaethylene oxyacrylate.

[0061] Examples of the (meth)acrylates having a phthalic acid skeleton

include γ -chloro- β -hydroxypropyl- β' -(meth)acryloyloxyethyl-o-phthalate, β -hydroxyethyl- β' -(meth)acryloyloxyethyl-o-phthalate, and β -hydroxypropyl- β' -(meth)acryloyloxyethyl-o-phthalate. The γ -chloro- β -hydroxypropyl- β' -methacryloyloxyethyl-o-phthalate is commercially available as FA-MECH (manufactured by Resonac Corporation).

[0062] The photopolymerization initiator that is the component (C) is not particularly limited as long as it can polymerize the component (B), and can be appropriately selected from photopolymerization initiators generally used. The component (C) can be used singly or in combination of two or more kinds thereof.

[0063] Examples of the component (C) include an imidazole compound, an aromatic ketone (excluding a compound corresponding to the benzophenone compound), a quinone compound, a benzoin compound, an acridine compound, an N-phenylglycine compound, and a benzyl derivative.

[0064] Examples of the imidazole compound include 2-(o-chlorophenyl)-4,5-diphenylbiimidazole, 2,2',5-tris-(o-chlorophenyl)-4-(3,4-dimethoxyphenyl)-4',5'-diphenylbiimidazole, 2,4-bis-(o-chlorophenyl)-5-(3,4-dimethoxyphenyl)-diphenylbiimidazole, 2,4,5-tris-(o-chlorophenyl)-diphenylbiimidazole, 2-(o-chlorophenyl)-bis-4,5-(3,4-dimethoxyphenyl)-biimidazole, 2,2'-bis-(2-fluorophenyl)-4,4',5,5'-tetrakis-(3-methoxyphenyl)-biimidazole, 2,2'-bis-(2,3-difluoromethylphenyl)-4,4',5,5'-tetrakis-(3-methoxyphenyl)-biimidazole, 2,2'-bis-(2,4-difluorophenyl)-4,4',5,5'-tetrakis-(3-methoxyphenyl)-biimidazole, and 2,2'-bis-(2,5-difluorophenyl)-4,4',5,5'-tetrakis-(3-methoxyphenyl)-biimidazole.

[0065] Examples of the acridine compound include 9-phenylacridine, 9-(p-methylphenyl)acridine, 9-(m-methylphenyl)acridine, 9-(p-chlorophenyl)acridine, 9-(m-chlorophenyl)acridine, 9-aminoacridine, 9-dimethylaminoacridine, 9-diethylaminoacridine, 9-pentylaminoacridine, 5 bis(9-acridinyl)alkanes such as 1,2-bis(9-acridinyl)ethane, 1,4-bis(9-acridinyl)butane, 1,6-bis(9-acridinyl)hexane, 1,8-bis(9-acridinyl)octane, 1,10-bis(9-acridinyl)decane, 1,12-bis(9-acridinyl)dodecane, 1,14-bis(9-acridinyl)tetradecane, 1,16-bis(9-acridinyl)hexadecane, 1,18-bis(9-acridinyl)octadecane, and 1,20-bis(9-acridinyl)eicosane, 1,3-bis(9-acridinyl)-2-oxapropane, 1,3-bis(9-acridinyl)-2-thiapropane, and 1,5-bis(9-acridinyl)-3-thiapentane. 10

[0066] Examples of the N-phenylglycine compound include N-phenylglycine, N-methyl-N-phenylglycine, and N-ethyl-N-phenylglycine. Examples of the aromatic ketone include 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1 and 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propanone-1. Examples of the quinone compound include alkylanthraquinone. Examples of the benzoin compound include benzoin, alkyl benzoin, and a benzoin ether compound (such as benzoin alkyl ether). Examples of the benzyl 15 derivative include benzyl dimethylketol. 20

[0067] The content of the component (C) may be 0.1 to 10 parts by mass, 1 to 5 parts by mass, or 2 to 4.5 parts by mass, with respect to 100 parts by mass of the total amount of the component (A) and the component (B). When the content of the component (C) is 0.1 parts by mass or more, 25 there is a tendency that photosensitivity, resolution, and adhesiveness are improved, and when the content of the component (C) is 10 parts by mass

or less, there is a tendency that the resist pattern formability is more excellent.

[0068] The photosensitive resin composition of the present embodiment may further contain a photosensitizer as a component (D). By containing the component (D), the absorption wavelength of active light rays used for exposure can be effectively utilized. The component (D) can be used singly or in combination of two or more kinds thereof.

[0069] Examples of the component (D) include a pyrazoline compound, a benzophenone compound, an anthracene compound, a coumarin compound, a xanthone compound, a thioxanthone compound, an oxazole compound, a benzoxazole compound, a thiazole compound, a benzothiazole compound, a triazole compound, a stilbene compound, a triazine compound, a thiophene compound, a naphthalimide compound, a triarylamine compound, and an aminoacridine compound. The sensitizer may contain at least one selected from the group consisting of a pyrazoline compound, a benzophenone compound, an anthracene compound, and a coumarin compound, from the viewpoint of easily suppressing occurrence of defects of a resist, the viewpoint of easily shortening the minimum developing time, and the viewpoint of easily obtaining favorable sensitivity, resolution, and adhesiveness.

[0070] Examples of the pyrazoline compound include 1-(4-methoxyphenyl)-3-styryl-5-phenyl-pyrazoline, 1-phenyl-3-(4-methoxystyryl)-5-(4-methoxyphenyl)-pyrazoline, 1,5-bis-(4-methoxyphenyl)-3-(4-methoxystyryl)-pyrazoline, 1-(4-isopropylphenyl)-3-styryl-5-phenyl-pyrazoline, 1-phenyl-3-(4-isopropylstyryl)-5-(4-isopropylphenyl)-pyrazoline, 1,5-bis-(4-

isopropylphenyl)-3-(4-isopropylstyryl)-pyrazoline, 1-(4-methoxyphenyl)-3-(4-tert-butyl-styryl)-5-(4-tert-butyl-phenyl)-pyrazoline, 1-(4-tert-butyl-phenyl)-3-(4-methoxystyryl)-5-(4-methoxyphenyl)-pyrazoline, 1-(4-isopropyl-phenyl)-3-(4-tert-butyl-styryl)-5-(4-tert-butyl-phenyl)-pyrazoline, 1-(4-tert-butyl-phenyl)-3-(4-isopropyl-styryl)-5-(4-isopropyl-phenyl)-pyrazoline, 1-(4-methoxyphenyl)-3-(4-isopropylstyryl)-5-(4-isopropylphenyl)-pyrazoline, 1-(4-isopropyl-phenyl)-3-(4-methoxystyryl)-5-(4-methoxyphenyl)-pyrazoline, 1-phenyl-3-(3,5-dimethoxystyryl)-5-(3,5-dimethoxyphenyl)-pyrazoline, 1-phenyl-3-(3,4-dimethoxystyryl)-5-(3,4-dimethoxyphenyl)-pyrazoline, 1-phenyl-3-(2,6-dimethoxystyryl)-5-(2,6-dimethoxyphenyl)-pyrazoline, 1-phenyl-3-(2,5-dimethoxystyryl)-5-(2,5-dimethoxyphenyl)-pyrazoline, 1-phenyl-3-(2,3-dimethoxystyryl)-5-(2,3-dimethoxyphenyl)-pyrazoline, 1-phenyl-3-(2,4-dimethoxystyryl)-5-(2,4-dimethoxyphenyl)-pyrazoline, 1-(4-methoxyphenyl)-3-(3,5-dimethoxystyryl)-5-(3,5-dimethoxyphenyl)-pyrazoline, 1-(4-methoxyphenyl)-3-(3,4-dimethoxystyryl)-5-(3,4-dimethoxyphenyl)-pyrazoline, 1-(4-methoxyphenyl)-3-(2,6-dimethoxystyryl)-5-(2,6-dimethoxyphenyl)-pyrazoline, 1-(4-methoxyphenyl)-3-(2,5-dimethoxystyryl)-5-(2,5-dimethoxyphenyl)-pyrazoline, 1-(4-methoxyphenyl)-3-(2,3-dimethoxystyryl)-5-(2,3-dimethoxyphenyl)-pyrazoline, 1-(4-methoxyphenyl)-3-(2,4-dimethoxystyryl)-5-(2,4-dimethoxyphenyl)-pyrazoline, 1-(4-tert-butyl-phenyl)-3-(3,5-dimethoxystyryl)-5-(3,5-dimethoxyphenyl)-pyrazoline, 1-(4-tert-butyl-phenyl)-3-(3,4-dimethoxystyryl)-5-(3,4-dimethoxyphenyl)-pyrazoline, 1-(4-tert-butyl-phenyl)-3-(2,6-dimethoxystyryl)-5-(2,6-

dimethoxyphenyl)-pyrazoline, 1-(4-tert-butyl-phenyl)-3-(2,5-dimethoxystyryl)-5-(2,5-dimethoxyphenyl)-pyrazoline, 1-(4-tert-butyl-phenyl)-3-(2,3-dimethoxystyryl)-5-(2,3-dimethoxyphenyl)-pyrazoline, 1-(4-tert-butyl-phenyl)-3-(2,4-dimethoxystyryl)-5-(2,4-dimethoxyphenyl)-pyrazoline, 1-(4-isopropyl-phenyl)-3-(3,5-dimethoxystyryl)-5-(3,5-dimethoxyphenyl)-pyrazoline, 1-(4-isopropyl-phenyl)-3-(3,4-dimethoxystyryl)-5-(3,4-dimethoxyphenyl)-pyrazoline, 1-(4-isopropyl-phenyl)-3-(2,6-dimethoxystyryl)-5-(2,6-dimethoxyphenyl)-pyrazoline, 1-(4-isopropyl-phenyl)-3-(2,5-dimethoxystyryl)-5-(2,5-dimethoxyphenyl)-pyrazoline, 1-(4-isopropyl-phenyl)-3-(2,3-dimethoxystyryl)-5-(2,3-dimethoxyphenyl)-pyrazoline, and 1-(4-isopropyl-phenyl)-3-(2,4-dimethoxystyryl)-5-(2,4-dimethoxyphenyl)-pyrazoline. The sensitizer may contain 1-phenyl-3-(4-methoxystyryl)-5-(4-methoxyphenyl)-pyrazoline from the viewpoint of easily obtaining favorable resolution and adhesiveness.

[0071] Examples of the benzophenone compound include benzophenone; N,N,N',N'-tetraalkyl-4,4'-diaminobenzophenone such as N,N,N',N'-tetramethyl-4,4'-diaminobenzophenone (also known as: Michler's ketone) and N,N,N',N'-tetraethyl-4,4'-diaminobenzophenone; and dialkylaminobenzophenone such as 4-methoxy-4'-dimethylaminobenzophenone. The sensitizer may contain N,N,N',N'-tetraalkyl-4,4'-diaminobenzophenone from the viewpoint of easily obtaining favorable resolution and adhesiveness.

[0072] Examples of the anthracene compound include 9,10-dimethoxyanthracene, 9,10-diethoxyanthracene, 9,10-dipropoxyanthracene, 9,10-dibutoxyanthracene, and 9,10-

dipentoxanthracene. The sensitizer may contain 9,10-dialkoxyanthracene from the viewpoint of easily obtaining favorable sensitivity.

[0073] Examples of the coumarin compound include 7-amino-4-methylcoumarin, 7-dimethylamino-4-methylcoumarin, 7-diethylamino-4-methylcoumarin, 7-methylamino-4-methylcoumarin, 7-ethylamino-4-methylcoumarin, 7-aminocyclopenta[c]coumarin, 7-dimethylaminocyclopenta[c]coumarin, 7-diethylaminocyclopenta[c]coumarin, 4,6-dimethyl-7-dimethylaminocoumarin, 4,6-dimethyl-7-ethylaminocoumarin, 4,6-dimethyl-7-diethylaminocoumarin, 4,6-diethyl-7-dimethylaminocoumarin, 4,6-diethyl-7-ethylaminocoumarin, 4,6-diethyl-7-diethylaminocoumarin, 3-benzoyl-7-diethylaminocoumarin, 3,3'-carbonylbis(7-diethylaminocoumarin), and 2,3,6,7-tetrahydro-9-methyl-1H,5H,11H-[1]benzopyrano [6,7,8-ij]quinolizin-11-one. The sensitizer may contain 2,3,6,7-tetrahydro-9-methyl-1H,5H,11H-[1]benzopyrano[6,7,8-ij]quinolizin-11-one from the viewpoint of easily obtaining favorable sensitivity.

[0074] From the viewpoint of improving photosensitivity and resolution, the content of the component (D) may be 0.01 to 5 parts by mass, 0.01 to 1 parts by mass, or 0.01 to 0.2 parts by mass, with respect to 100 parts by mass of the total amount of the component (A) and the component (B).

[0075] The photosensitive resin composition of the present embodiment may further contain, as necessary, additives such as a dye, a photochromic agent, a thermal development inhibitor, a plasticizer, a pigment, a filler, an antifoaming agent, a flame retardant, a tackifier, a leveling agent, a

release promoter, an antioxidant, an aroma, an imaging agent, a thermal crosslinking agent, and a polymerization inhibitor. These additives can be used singly or in combination of two or more kinds thereof.

5 [0076] Examples of the dye include Malachite Green, Victoria Pure Blue, Brilliant Green, and Methyl Violet. Examples of the photochromic agent include tribromophenylsulfone, leuco crystal violet, diphenylamine, benzylamine, triphenylamine, diethylaniline, and o-chloroaniline. Examples of the plasticizer include p-toluenesulfonamide.

10 [0077] The photosensitive resin composition can be prepared as a solution having a solid content of about 30 to 60% by mass, as necessary, by dissolving the photosensitive resin composition in a solvent such as methanol, ethanol, acetone, methyl ethyl ketone, methyl cellosolve, ethyl cellosolve, toluene, N,N-dimethylformamide, or propylene glycol monomethyl ether, or a mixed solvent of such solvents.

15 [0078] The thickness of the photosensitive layer 20 may be 1 to 200 μm , 5 to 100 μm , 10 to 50 μm , or 10 to 30 μm .

20 [0079] The photosensitive element of the present embodiment may include a protective film (not illustrated) on a side (the second surface 10b side) of the photosensitive layer 20 opposite to the support film 10. As the protective film, it is preferable to use a film such that the adhesive force between the photosensitive layer 20 and the support film 10 is smaller than the adhesive force between the photosensitive layer 20 and the protective film. As the protective film, polyolefin films such as
25 polyethylene and polypropylene can be used. The protective film may be a polyethylene film.

[0080] The thickness of the protective film may be 5 to 100 μm , 5 to 70 μm , 10 to 60 μm , 10 to 50 μm , 15 to 40 μm , or 15 to 30 μm .

[0081] The photosensitive element of the present embodiment may include an intermediate layer (not illustrated) between the support film and the photosensitive layer. The adhesive force between the support film and the intermediate layer may be smaller than the adhesive force between the intermediate layer and the photosensitive layer. The intermediate layer may have water solubility, and may have dissolubility with respect to a developing solution. The intermediate layer is a layer formed using a resin composition for forming an intermediate layer described below.

[0082] The resin composition for forming an intermediate layer may contain a water-soluble resin. By containing a water-soluble resin, there is a tendency that the dissolubility of an intermediate layer to be formed is improved. Furthermore, since it becomes easy to maintain the layer isolation between the intermediate layer to be formed and the photosensitive layer for a long period of time, there is a tendency that stability is improved. Examples of the water-soluble resin include polyvinyl alcohol and polyvinylpyrrolidone. From the viewpoint that an oxygen transmission coefficient is low and deactivation of radicals occurring due to active light rays used for exposure can be further suppressed, the resin composition for forming an intermediate layer may contain polyvinyl alcohol. The polyvinyl alcohol can be obtained, for example, by saponification of polyvinyl acetate obtained by polymerization of vinyl acetate. The saponification degree of the polyvinyl alcohol used in the present embodiment may be 50 mol% or

more, 70 mol% or more, or 80 mol% or more. By using polyvinyl alcohol having a saponification degree of 50 mol% or more, there are tendencies that the gas barrier properties of the intermediate layer can be further improved, and the resolution of a resist pattern to be formed can be further improved. Note that, the "saponification degree" in the present specification refers to a value measured according to JIS K 6726 (1994) (Testing methods for polyvinyl alcohol) defined in Japanese Industrial Standards. The upper limit value of the saponification degree may be 100 mol%.

[0083] The average polymerization degree of polyvinyl alcohol may be 300 to 3500, 300 to 2500, or 300 to 1000. Furthermore, the average polymerization degree of polyvinylpyrrolidone may be 10000 to 100000 or 10000 to 50000. As for the above-described polyvinyl alcohol, two or more kinds of polyvinyl alcohols having different saponification degrees, different viscosities, different polymerization degrees, different modification types, and the like may be used in combination.

[0084] The resin composition for forming an intermediate layer may contain a resin having dissolubility with respect to a developing solution. As the resin having dissolubility with respect to a developing solution, for example, the component (A) used in the photosensitive resin composition may be contained, and the component (B) may be contained. By containing the resin having dissolubility with respect to a developing solution, there are tendencies that the adhesiveness between the intermediate layer to be formed and the photosensitive layer is improved and the photosensitive layer is easily formed on the intermediate layer to be formed.

[0085] In order to improve the handleability of the resin composition or adjust the viscosity and storage stability, the resin composition for forming an intermediate layer can contain at least one kind of solvents as necessary. Examples of the solvent include water and an organic solvent. Examples of the organic solvent include methanol, acetone, toluene, and a mixed solvent of these. From the viewpoint of improving drying efficiency at the time of forming the intermediate layer, methanol may be contained. Furthermore, in a case where the resin composition for forming an intermediate layer contains a water-soluble resin, water, and methanol, the content of the methanol may be 1 to 100 parts by mass, 10 to 80 parts by mass, or 20 to 60 parts by mass, with respect to 100 parts by mass of water, from the viewpoint of dissolubility with respect to the water-soluble resin. The content of the water-soluble resin may be 1 to 50 parts by mass, 5 to 40 parts by mass, or 10 to 30 parts by mass, with respect to 100 parts by mass of water.

[0086] The resin composition for forming an intermediate layer may be blended with known additives such as a surfactant, a plasticizer, and a leveling agent. Examples of the leveling agent include a silicone-based leveling agent. Examples of commercially available products of the silicone-based leveling agent include POLYFLOW KL-401 (manufactured by Kyoeisha Chemical Co., Ltd.). In the case of containing a leveling agent, the content of the leveling agent may be 0.01 to 2.0 parts by mass, 0.03 to 1.5 parts by mass, or 0.05 to 1.0 parts by mass, with respect to 100 parts by mass of the resin composition for forming an intermediate layer, from the viewpoint of ease of formation of an intermediate layer.

[0087] From the viewpoint of improving releasability with the support film, a silicone-based surfactant or a fluorine-based surfactant can be contained as the surfactant. These surfactants can be used singly or in combination of two or more kinds thereof. In the case of containing a surfactant, the content of the surfactant may be 0.01 to 1.0 parts by mass, 0.05 to 0.5 parts by mass, or 0.1 to 0.3 parts by mass, with respect to 100 parts by mass of the resin composition for forming an intermediate layer, from the viewpoint of ease of formation of an intermediate layer.

[0088] For example, from the viewpoint of improving ease of formation of an intermediate layer, a polyhydric alcohol compound can be contained as the plasticizer. Examples of the plasticizer include glycerins such as glycerin, diglycerin, and triglycerin; (poly)alkylene glycols such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, and polypropylene glycol; and trimethylol propane. These plasticizers can be used singly or in combination of two or more kinds thereof.

[0089] The thickness of the intermediate layer is not particularly limited, and may be 12 μm or less, 10 μm or less, or 8 μm or less, from the viewpoint of developability. Furthermore, the thickness of the intermediate layer may be 1.0 μm or more, 1.5 μm or more, or 2.0 μm or more, from the viewpoint of ease of formation of the intermediate layer and resolution.

[0090] [Method for forming resist pattern]

A method for forming a resist pattern of the present embodiment includes a lamination step of laminating the photosensitive layer 20 of the photosensitive element 1 on a substrate in order of the photosensitive

layer and the support film, an exposure step of irradiating a predetermined part of the photosensitive layer 20 with an active light ray through the support film 10 to form a photo-cured area, and a development step of removing an area other than the photo-cured area in the photosensitive layer 20.

[0091] In the lamination step, for example, the photosensitive layer and the support film of the photosensitive element are laminated on the substrate in this order. In the lamination step, as a method of laminating the photosensitive layer 20 on the substrate, for example, in a case where the protective film exists on the photosensitive layer 20, a method of laminating the photosensitive layer on the substrate by pressure-bonding the substrate at a pressure of about 0.1 to 1 MPa while heating the photosensitive layer 20 to about 70 to 130°C after removing the protective film is exemplified. In the lamination step, lamination can also be performed under reduced pressure. Note that, a surface of the substrate on which the photosensitive layer 20 is laminated is usually a metal surface, but is not particularly limited. Furthermore, in order to further improve laminating properties, the substrate may be subjected to a preheating treatment.

[0092] Next, in the exposure step, for example, a predetermined part of the photosensitive layer 20 is irradiated with an active light ray through the support film 10 to form a photo-cured area on the photosensitive layer 20. Examples of the exposure method include a method of emitting active light rays imagewise through a negative or positive mask pattern, referred to as artwork (mask exposure method), a method of emitting active light rays imagewise by a projection exposure method, and a

method of emitting active light rays imagewise by a direct writing exposure method such as an LDI (Laser Direct Imaging) exposure method or a DLP (Digital Light Processing) exposure method.

5 [0093] Known light sources can be used as a light source for the active light ray, and for example, a carbon arc lamp, a mercury vapor arc lamp, a high-pressure mercury lamp, a xenon lamp, a gas laser such as an argon laser, a solid-state laser such as a YAG laser, and a semiconductor laser, which efficiently emit ultraviolet rays or visible light, are used.

10 [0094] From the viewpoint of improving adhesiveness, post exposure bake (PEB) may be performed after the exposure and before the development. The temperature in the case of performing PEB may be 50 to 100°C. As a heating machine, a hot plate, a box-type dryer, a heating roll, and the like may be used.

15 [0095] In the development step, at least a part of the photosensitive layer other than the photo-cured area is removed from the substrate, so that a resist pattern is formed on the substrate.

20 [0096] In the development step, after the support film 10 is released and removed from the photosensitive layer 20, an area other than the photo-cured area in the photosensitive layer is removed. In the development step, a resist pattern can be produced, for example, by removing and developing an unexposed area (non-photo-cured area) of the photosensitive layer 20 with wet development using a developing solution such as an alkaline aqueous solution, an aqueous developing solution, or an organic solvent, dry development, or the like.

25 [0097] Examples of the alkaline aqueous solution include a 0.1 to 5% by mass sodium carbonate solution, a 0.1 to 5% by mass potassium

carbonate solution, and a 0.1 to 5% by mass sodium hydroxide solution. The pH of the alkaline aqueous solution is preferably in a range of 9 to 11. The temperature of the alkaline aqueous solution is adjusted according to the developability of the photosensitive layer 20.

5 Furthermore, the alkaline aqueous solution may contain a surfactant, an antifoaming agent, an organic solvent, and the like. Examples of the development method include a dip method, a spray method, brushing, and scrubbing.

[0098] As a treatment after the development step, heating at about 60 to 250°C or exposure at about 0.2 to 10 J/cm² may be performed as necessary to further cure the resist pattern.

[0099] [Method for producing printed wiring board]

A method for producing a printed wiring board of the present embodiment includes a step of subjecting a substrate having a resist pattern formed by the above-described method for forming a resist pattern to an etching treatment or a plating treatment to form a conductor pattern. Herein, the etching or plating of the substrate can be performed by etching or plating the surface of the substrate by a known method using the resist pattern as a mask.

20 [0100] Examples of an etching solution used in etching include a cupric chloride solution, a ferric chloride solution, and an alkali etching solution. Examples of the plating include copper plating, solder plating, nickel plating, and gold plating.

[0101] After etching or plating is performed, the resist pattern can be released, for example, with an aqueous solution of stronger alkalinity than the alkaline aqueous solution used for the development. As this strong

alkaline aqueous solution, for example, a 1 to 10% by mass sodium hydroxide aqueous solution and a 1 to 10% by mass potassium hydroxide aqueous solution are used. Furthermore, examples of the releasing method include a dip method and a spray method. Note that, a printed wiring board on which the resist pattern has been formed may be a multilayer printed wiring board, and may have small through-holes.

[0102] In the case of subjecting a substrate including an insulation layer and a conductor layer formed on the insulation layer to plating, it is necessary to remove an area of the conductor layer other than the resist pattern. Examples of this removing method include a method of releasing the resist pattern and then lightly etching; and a method of performing solder plating or the like after the plating and then releasing the resist pattern to leave a solder mask on the wiring sections, and then performing treatment using an etching solution capable of etching only the conductor layer on the sections where the solder mask is not formed.

Examples

[0103] Hereinafter, the contents of the present disclosure will be described in more detail with reference to Examples and Comparative Example; however, the present invention is not limited to Examples.

[0104] [Photosensitive resin composition]

Respective components were mixed at blending amounts (parts by mass) shown in Table 1 to prepare a photosensitive resin composition. The details of respective components shown in Table 1 are as follows.

[0105] (Binder polymer)

A-1: Ethylene glycol monomethyl ether/toluene solution (solid content: 40% by mass) of copolymer of methacrylic acid/styrene/benzyl

methacrylate/2-hydroxyethyl methacrylate (mass ratio: 27/50/20/3, Mw: 35000, acid value: 176 mgKOH/g)

[0106] The Mw of the binder polymer was calculated by measurement by gel permeation chromatography (GPC) under the following conditions and conversion using a calibration curve of standard polystyrene.

Pump: L-2130 type (manufactured by Hitachi High-Tech Co., Ltd.)

Detector: L-2490 type RI (manufactured by Hitachi High-Tech Co., Ltd.)

Column oven: L-2350 (manufactured by Hitachi High-Tech Co., Ltd.)

Column: Gelpack GL-R440 + Gelpack GL-R450 + Gelpack GL-R400M

(three in total) (manufactured by Resonac Corporation)

Column size: 10.7 mm I.D × 300 mm

Eluent: Tetrahydrofuran

Sample concentration: 10 mg/2 mL

Injection amount: 200 µL

Flow rate: 2.05 mL/min

Measurement temperature: 25°C

[0107] The acid value of the binder polymer was measured by the following procedure. First, the binder polymer was weighed in an Erlenmeyer flask. Next, the binder polymer was dissolved by addition of a mixed solvent (mass ratio: toluene/methanol = 70/30), and then a phenolphthalein solution was added as an indicator thereto. Then, the acid value was obtained by performing a titration using a 0.1 mol/L (N/10) potassium hydroxide solution (alcohol solution).

[0108] (Photopolymerizable compound)

FA-321M: EO-modified bisphenol A dimethacrylate (manufactured by Resonac Corporation, the number of EO groups: 10 (average value))

- FA-024M: Polyalkylene glycol dimethacrylate (manufactured by Resonac Corporation, the number of EO groups: 12 (average value), the number of PO groups: 4 (average value))
- 5 BP-2EM: 2,2-Bis(4-(methacryloxydiethoxy)phenyl)propane
(manufactured by Kyoeisha Chemical Co., Ltd.)
(Photopolymerization initiator)
- B-CIM: 2,2'-Bis(2-chlorophenyl)-4,4',5,5'-tetraphenyl biimidazole
(manufactured by Hodogaya Chemical Co., Ltd.)
(Sensitizer)
- 10 PZ-501D: 1-Phenyl-3-(4-methoxystyryl)-5-(4-methoxyphenyl)-pyrazoline (manufactured by NIPPON CHEMICAL WORKS CO., LTD.)
(Polymerization inhibitor)
- TBC: 4-tert-Butylcatechol (manufactured by DIC Corporation)
- 15 LA-7RD: 4-Hydroxy-2,2,6,6-tetramethylpiperidine-N-oxyl
(manufactured by ADEKA CORPORATION)
(Dye)
- MKG: Malachite green (manufactured by OSAKA ORGANIC CHEMICAL INDUSTRY LTD.)
- 20 (Color developer)
- LCV: Leuco crystal violet (manufactured by Yamada Chemical Co., Ltd.)

[0109] [Table 1]

Photosensitive resin composition		P1
Binder polymer	A-1	123
Photopolymerizable compound	FA-321M	34
	FA-024M	2
	BP-2EM	6
Photopolymerization initiator	B-CIM	5.5
Sensitizer	PZ-501D	0.027
Polymerization inhibitor	TBC	0.04
	LA-7RD	0.01
Dye	MKG	0.05
Color developer	LCV	0.3
Solvent	Methanol	6
	Toluene	16
	Acetone	10

[0110] [Support film]

Biaxially oriented PET films (thickness: 16 μm) S1 to S12 were prepared as the support film of the photosensitive element. The number of lubricants contained in a 0.0225 mm² (0.150 mm $\times$ 0.150 mm) area in the first surface and the second surface of the support film was measured using a confocal microscope (manufactured by Lasertec Corporation, trade name "Hybrid laser microscope OPTELICS HYBRID"). An image was acquired at a lens numerical aperture (Na) of 0.8, a magnification of 50 times, and a digital zooming of 2 times and under the conditions of Table 2 below, and the size and number of lubricants were calculated from pixels in the image. The results of S1 to S7 are shown in Table 3, and the results of S8 to S12 are shown in Table 4. Note that, in S1 to S12, a lubricant having a particle size of 2.0 μm or less was contained.

[0111] [Table 2]

Name	Item	Setting
Objective lens	TU Apo50x	ON
Nomarski prism	MBH 63200	ON
Surface observation mode	Differential interference mode	ON
Autofocus	Setting of Ref position	Checked
Image acquisition condition setting	Confocal	ON
	CCD mode	Green
	Scanning rate/image size	Standard/1024 × 1024
	HDR	OFF
	Zoom	200%
	Brightness	700 (adjustment item)
	Exposure time	4
Surface shape	UP position	3
	LOW position	-3
	Scanning time	10 sec
	Scanning resolution	0.17
	Algorithm	MaxPeak
Image processing	Target image	Luminance
	Spline (highpass)	X: 140 Y: 140 μm
	Brightness	2
	Contrast	2
Shape property	Creation method for two images	Binarization of brightness image
	Threshold setting	Auto
	Automatic threshold algorithm	Histogram peak method
	Effective region	Up
	Display format	Gradation value
	Histogram peak setting	Up
		30

[0112] [Photosensitive element]

5 A solution of the photosensitive resin composition was applied uniformly on the first layer of the support film using a comma coater. Subsequently, the solution was dried for 2 minutes with a hot air convection drier at 100°C to form a photosensitive layer having a thickness of 15 μm. Next, a PE film (manufactured by TAMAPOLY CO., LTD., trade name "NF-15A", thickness: 28 μm) as the protective

film was laminated on the photosensitive layer to produce a photosensitive element.

[0113] [Evaluation]

(Production of laminate)

5 After sputtering titanium of 10 nm on a PET film (manufactured by TOYOBO CO., LTD., trade name "COSMOSHINE A4160", thickness: 125 μm), a substrate a sputtered with copper of 100 nm was prepared. This substrate a was heated to 80°C, and then the photosensitive element was laminated such that the photosensitive layer was in contact with the copper layer while peeling off the protective film of the above-described photosensitive element. As such, a laminate including the substrate a, the photosensitive layer, and the support film in the lamination direction in this order was obtained. The lamination was performed using a heat roll set at 110°C at a pressure-bonding pressure of 0.4 MPa and at a roll speed of 1.5 m/min.

[0114] (Formation of resist pattern)

20 The photosensitive layer of the above-described laminate was exposed with an irradiation energy dose for 11 steps remaining after development of a 41-step tablet, using a high-resolution projection-type exposure apparatus (manufactured by Ushio Inc., trade name "UX-2240") having a phototool with a 41-step tablet, a glass chromium-type phototool having a wiring pattern with a line width/space width of 20/20 to 1.0/1.0 (unit: μm) as a negative for evaluation of adhesiveness, and a high-pressure mercury lamp. Next, the support film was peeled off, and a 1% by mass sodium carbonate aqueous solution was spray-developed at 30°C to remove the unexposed area, thereby forming a resist pattern with a line

width/space width of 5.0/5.0 (unit: μm).

[0115] A $73\ \mu\text{m} \times 55\ \mu\text{m}$ area of the substrate on which the resist pattern had been formed was captured using NEXIV VMZ-R4540 (manufactured by NIKON CORPORATION, trade name). In the scanning measurement of NEXIV VMZ-R4540, the contour of the formed resist pattern was specified, and the coordinates of the contour of the resist pattern were measured for six lines of the resist pattern. In the measurement of the coordinates, the measurement of the coordinates of 260 points in which the length of $52\ \mu\text{m}$ was scribed at $0.2\ \mu\text{m}$ was performed for each of the contour on one side of the line and the contour of the other side. Furthermore, these measurements were performed for three places of each of the six lines. Thereby, a total of 9360 coordinates were measured. Based on the measured 9360 coordinates, the variation (3σ) of the contour of the resist pattern was calculated. 3σ of the contour is also called LER (Line Edge Roughness). As the numerical value is smaller, a finer resist pattern is formed.

[0116] [Table 3]

Example		1	2	3	4	5	6	7
Support film		S1	S2	S3	S4	S5	S6	S7
First surface	Number of lubricants of $0.8\ \mu\text{m}$ or more	378	14	64	27	47	101	160
	Total number of lubricants	662	161	558	300	1138	683	883
	Average particle size (μm) of lubricant	0.96	0.49	0.52	0.52	0.47	0.56	0.62
Second surface	Number of lubricants of $0.8\ \mu\text{m}$ or more	40	4	63	47	27	5	1
	Total number of lubricants	775	1585	1135	1138	300	42	100
	Average particle size (μm) of lubricant	0.47	0.37	0.47	0.47	0.52	0.46	0.58
3σ of contour		116	77	106	112	84	66	39

[0117] [Table 4]

Comparative Example		1	2	3	4	5
Support film		S8	S9	S10	S11	S12
First surface	Number of lubricants of 0.8 μm or more	273	40	16	5	1
	Total number of lubricants	355	775	1036	42	12
	Average particle size (μm) of lubricant	1.03	0.47	0.54	0.46	0.58
Second surface	Number of lubricants of 0.8 μm or more	273	378	160	101	160
	Total number of lubricants	355	662	1038	683	883
	Average particle size (μm) of lubricant	1.03	0.96	0.44	0.56	0.62
3 σ of contour		270	162	155	138	144

Reference Signs List

[0118] 1: photosensitive element, 10: support film, 10a: first surface, 10b: second surface, 20: photosensitive layer.

CLAIMS

[Claim 1] A photosensitive element comprising: a support film containing a lubricant; and a photosensitive layer formed on a first surface of the support film,

5 wherein a number of lubricants having a particle size of 0.8 μm or more contained in a second surface on a side opposite to the first surface of the support film is 80 or less per 0.0225 mm^2 .

[Claim 2] The photosensitive element according to claim 1, wherein
10 a total number of lubricants contained in the second surface is 2000 or less per 0.0225 mm^2 .

[Claim 3] The photosensitive element according to claim 1, wherein a value obtained by dividing the number of lubricants having a particle size of 0.8 μm or more contained in the second surface by the total number of lubricants contained in the second surface is 0.20 or less.

15 [Claim 4] The photosensitive element according to claim 1, wherein a number of lubricants having a particle size of 0.8 μm or more contained in the first surface is 200 or less per 0.0225 mm^2 .

[Claim 5] The photosensitive element according to claim 1, wherein
20 an average particle size of the lubricants contained in the first surface and the second surface is 0.3 μm or more and 1.0 μm or less.

[Claim 6] The photosensitive element according to claim 1, wherein the support film is a biaxially oriented polyester film.

[Claim 7] The photosensitive element according to claim 1, wherein
25 the support film does not contain a lubricant having a particle size of more than 3.0 μm .

[Claim 8] A method for forming a resist pattern, the method

comprising:

a lamination step of laminating the photosensitive element according to any one of claims 1 to 7 on a substrate in order of the photosensitive layer and the support film;

5 an exposure step of irradiating a predetermined part of the photosensitive layer with an active light ray through the support film to form a photo-cured area; and

a development step of removing an area other than the photo-cured area in the photosensitive layer.

10 [Claim 9] A method for producing a printed wiring board, the method comprising a step of subjecting a substrate having a resist pattern formed by the method for forming a resist pattern according to claim 8 to an etching treatment or a plating treatment to form a conductor pattern.