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(54) LITHOGRAPHIC PRINTING PLATE PRECURSOR, METHOD OF PREPARING A LITHOGRAPHIC PRINTING PLATE, AND LITHOGRAPHIC PRINTING METHOD

(57) Provided are a lithographic printing plate precursor having excellent crystal precipitation suppressiveness, and a method of preparing a lithographic printing plate and a lithographic printing method in which the lithographic printing plate precursor is used.

A lithographic printing plate precursor including a support and an image-recording layer on the support, in which the image-recording layer contains a non-onium-based polymerization initiator, a borate compound, an infrared absorber, and a compound A which is an onium salt with a cation having a shape index equal to or less than 2 times a shape index of a cationic moiety of the infrared absorber.

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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present disclosure relates to a lithographic printing plate precursor, a method of preparing a lithographic printing plate, and a lithographic printing method.

2. Description of the Related Art

[0002] In general, a lithographic printing plate is composed of lipophilic image areas that receive ink during a printing process and hydrophilic non-image areas that receive a dampening water. Lithographic printing is a printing method that utilizes the property that water and oil-based ink repel each other to cause differences in ink attachment behavior on a surface of the lithographic printing plate by using lipophilic image areas on the lithographic printing plate as an ink-receiving area and using hydrophilic non-image areas on the lithographic printing plate as dampening water-receiving areas (non-ink-receiving areas), thereby depositing the ink only to the image areas, and then transferring the ink to a printing material, such as paper.

[0003] In the related art, in order to prepare this lithographic printing plate, a lithographic printing plate precursor (PS plate) has been widely used which is obtained by providing a lipophilic photosensitive resin layer (image-recording layer) on a hydrophilic support. Usually, a lithographic printing plate is obtained by a plate making method of exposing a lithographic printing plate precursor through an original picture such as a lith film, then keeping a portion of an image-recording layer that will be an image area while removing other unnecessary portions of the image-recording layer by dissolving such portions in an alkaline developer or an organic solvent, and forming a non-image area by exposing a surface of the hydrophilic support.

[0004] In response to the intensifying interest in the global environment, an environmental issue of waste liquid generated by wet treatments such as a development treatment has gathered more attention.

[0005] Regarding the environmental issue described above, an attempt is made to simplify development or plate making or to remove treatments. As one of simple preparation methods, a method called "on-press development" is being carried out. That is, the on-press development is a method of exposing a lithographic printing plate precursor, then immediately mounting the precursor on a printer without performing development of the related art, and removing an unnecessary portion of the image-recording layer at an initial stage of the ordinary printing step.

[0006] In the present disclosure, a lithographic printing plate precursor that can be used for such on-press development is called "on-press development type lithographic printing plate precursor".

[0007] Examples of the lithographic printing plate precursors in the related art include those described in WO2021/259637A.

[0008] WO2021/259637A describes a lithographic printing plate precursor including a support, a photopolymerizable layer, and protective layer, in which the photopolymerizable layer contains a polymerizable compound, a first infrared absorber having a specific structure, and a photopolymerization initiator, and the protective layer contains a second infrared absorber which includes a thermally decomposable group transformed into a group that is a stronger electron donor upon exposure to heat and/or infrared radiation, and which is capable of forming a print-out image upon exposure to heat and/or infrared radiation.

SUMMARY OF THE INVENTION

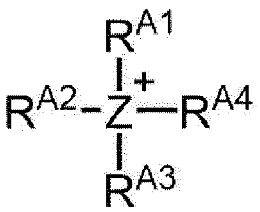
[0009] An object of an embodiment of the present disclosure is to provide a lithographic printing plate precursor having excellent crystal precipitation suppressiveness.

[0010] An object of another embodiment of the present disclosure is to provide a method of preparing a lithographic printing plate and a lithographic printing method in which the lithographic printing plate precursor is used.

[0011] Means for solving the above issues include the following aspects.

<1> A lithographic printing plate precursor including a support and an image-recording layer on the support, in which the image-recording layer contains a non-onium-based polymerization initiator, a borate compound, an infrared absorber, and a compound A which is an onium salt with a cation having a shape index equal to or less than 2 times a shape index of a cationic moiety of the infrared absorber.

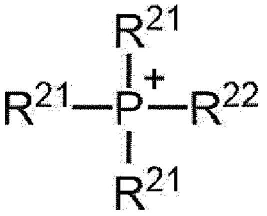
<2> The lithographic printing plate precursor described in <1>, in which the cation in the compound A is a cation represented by Formula (A).



$$R^{A2}-\overset{\overset{\displaystyle R^{A1}}{|}}{\underset{\underset{\displaystyle R^{A3}}{|}}{Z^{+}}}-R^{A4} \qquad (A)$$

[0012] In Formula (A), Z represents P or N, and R^{A1} to R^{A4} each independently represent a hydrogen atom, an alkyl group, or an aryl group.

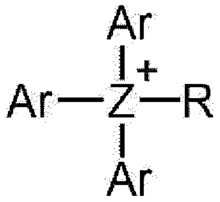
[0013] <3> The lithographic printing plate precursor described in <1>, in which the cation in the compound A is a cation represented by Formula (2).



$$R^{21}-\overset{\overset{\displaystyle R^{21}}{|}}{\underset{\underset{\displaystyle R^{21}}{|}}{P^{+}}}-R^{22} \qquad (2)$$

[0014] In Formula (2), R^{21}'s each independently represent an alkyl group and R^{22} represents a hydrogen atom or an alkyl group.

[0015] <4> The lithographic printing plate precursor described in <1>, in which the cation in the compound A is a cation represented by Formula (1).



$$Ar-\overset{\overset{\displaystyle Ar}{|}}{\underset{\underset{\displaystyle Ar}{|}}{Z^{+}}}-R \qquad (1)$$

[0016] In Formula (1), Z represents P or N, R represents an alkyl group, and Ar's each independently represent an aryl group.

[0017] <5> The lithographic printing plate precursor described in any one of <1> to <4>, in which the cation in the compound A has a polymerizable group.

[0018] <6> The lithographic printing plate precursor described in any one of <1> to <4>, in which clogP of the cation in the compound A is 0 or more and 10 or less.

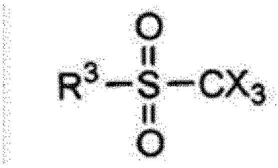
[0019] <7> The lithographic printing plate precursor described in any one of <1> to <4>, in which an anion in the compound A is a conjugate base of an organic acid.

[0020] <8> The lithographic printing plate precursor described in any one of <1> to <4>, in which an anion in the compound A is at least one anion selected from the group consisting of $R^1SO_3^-$, $R^1SO_2^-$, $R^1R^2PO_2^-$, $R^1PO_3^{2-}$, $R^1CO_2^-$, R^1O^-, R^1S^-, $(R^1SO_2)_2N^-$, and $R^1R^2R^3R^4B^-$.

[0021] R^1 to R^4 each independently represent a hydrogen atom, an alkyl group, or an aryl group.

[0022] <9> The lithographic printing plate precursor described in any one of <1> to <4>, in which a molar content of the cation in the compound A is 0.2 times to 4 times a molar content of an anion in the borate compound.

[0023] <10> The lithographic printing plate precursor according to any one of <1> to <4>, in which the non-onium-based polymerization initiator includes a compound represented by Formula (II).



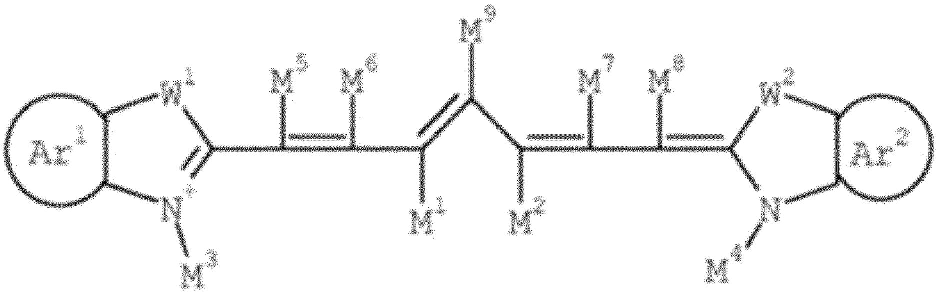
$$R^3-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-CX_3 \qquad (II)$$

[0024] In Formula (II), X's each independently represent a halogen atom, and R^3 represents an aryl group.

[0025] <11> The lithographic printing plate precursor described in any one of <1> to <4>, further including a protective layer on the image-recording layer.

[0026] <12> The lithographic printing plate precursor according to <11>, in which the protective layer contains a second infrared absorber which includes a thermally decomposable group transformed into a group that is a stronger electron donor upon exposure to heat and/or infrared radiation, and which is capable of forming a print-out image upon exposure to heat and/or infrared radiation.

[0027] <13> The lithographic printing plate precursor according to <12>, in which the second infrared absorber is a compound represented by Formula (VI).



(VI)

[0028] In Formula (VI), Ar^1 and Ar^2 each independently represent an optionally substituted aromatic hydrocarbon group or an aromatic hydrocarbon group having an optionally substituted benzene ring, W^1 and W^2 each independently represent a sulfur atom, an oxygen atom, or NR*, where R* represents an optionally substituted alkyl group, NH, or $-CM^{10}M^{11}$ group, where M^{10} and M^{11} each independently represent an optionally substituted aliphatic hydrocarbon group or an optionally substituted aryl group or heteroaryl group, M^1 and M^2 each independently represent a hydrogen atom, an optionally substituted aliphatic hydrocarbon group, or a group of atoms required to form an optionally substituted cyclic structure of M^1 and M^2, M^3 and M^4 each independently represent an optionally substituted aliphatic hydrocarbon group, M^5 to M^8 each independently represent a hydrogen atom, a halogen atom, or an optionally substituted aliphatic hydrocarbon group, and M^9 is a group which is converted into a group that is an electron donor stronger than M^9 by a chemical reaction induced by exposure to infrared or heat, and which increases an integrated light absorption of the compound represented by Formula (VI) in a wavelength range of 350 nm to 700 nm by the conversion, M^9 having optionally one or a plurality of counter ions in order to obtain an electrically neutral compound.

[0029] <14> A method of preparing a lithographic printing plate, including a step of exposing the lithographic printing plate precursor according to any one of <1> to <4> in a shape of an image, and
a step of supplying at least one material selected from the group consisting of a printing ink and dampening water on a printer to remove the image-recording layer in a non-image area.

[0030] <15> A lithographic printing method including a step of exposing the lithographic printing plate precursor according to any one of <1> to <4> in a shape of an image,

a step of supplying at least one material selected from the group consisting of a printing ink and dampening water to remove the image-recording layer in a non-image area on a printer and to prepare a lithographic printing plate, and
a step of performing printing by using the obtained lithographic printing plate.

[0031] According to an embodiment of the present disclosure, it is possible to provide a lithographic printing plate precursor having excellent crystal precipitation suppressiveness.

[0032] According to another embodiment of the present disclosure, it is possible to provide a method of preparing a lithographic printing plate and a lithographic printing method in which the lithographic printing plate precursor is used.

BRIEF DESCRIPTION OF THE DRAWINGS

[0033]

Fig. 1 is a graph showing an example of an alternating waveform current waveform diagram used for an electrochemical roughening treatment in a manufacturing method of an aluminum support having an anodic oxide film.
Fig. 2 is a lateral view showing an example of a radial cell in an electrochemical roughening treatment using alternating

current in the manufacturing method of an aluminum support having an anodic oxide film.

Fig. 3 is a lateral view conceptually showing a brush graining step used in a mechanical roughening treatment in the manufacturing method of an aluminum support having an anodic oxide film.

Fig. 4 is a schematic view of an anodization treatment device used for an anodization treatment in the manufacturing method of an aluminum support having an anodic oxide film.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0034] Hereinafter, the contents of the present disclosure will be described in detail. The description of configuration requirements below is made based on representative embodiments of the present disclosure in some cases, but the present disclosure is not limited to such embodiments.

[0035] In the present specification, a numerical range expressed using "to" includes numerical values listed before and after "to" as the lower limit and the upper limit.

[0036] In addition, in the present specification, in a case where there is no description regarding whether a group (atomic group) is substituted or unsubstituted, such a group includes both a group having no substituent and a group having a substituent. For example, "alkyl group" includes not only an alkyl group having no substituent (unsubstituted alkyl group) but also an alkyl group having a substituent (substituted alkyl group).

[0037] In the present specification, "(meth)acryl" is a term used to explain a concept including both the acryl and methacryl, and "(meth)acryloyl" is a term used to explain a concept including both the acryloyl and methacryloyl.

[0038] In addition, the term "step" in the present specification means not only an independent step but also a step that cannot be clearly differentiated from other steps as long as the intended goal of the step is achieved.

[0039] In the present disclosure, "% by mass" has the same definition as "% by weight", and "part by mass" has the same definition as "part by weight".

[0040] Unless otherwise specified, each of the values of physical properties is measured at 25°C.

[0041] In the present disclosure, unless otherwise specified, as each component contained in a composition or each constitutional unit contained in a polymer, one component or one constitutional unit may be used alone, or two or more components or two or more constitutional units may be used in combination.

[0042] Furthermore, in the present disclosure, in a case where there is a plurality of substances corresponding to each component in a composition, or in a case where there is a plurality of constitutional units corresponding to each constitutional unit in a polymer, unless otherwise specified, the amount of each component in the composition or the amount of each constitutional unit in the polymer means the total amount of the plurality of corresponding substances present in the composition or the total amount of the plurality of corresponding constitutional units present in the polymer.

[0043] Furthermore, in the present disclosure, a combination of two or more preferred aspects is a more preferred aspect.

[0044] In addition, in the present disclosure, unless otherwise specified, each of the weight-average molecular weight (Mw) and number-average molecular weight (Mn) is a molecular weight that is detected using a gel permeation chromatography (GPC) analysis device using TSKgel GMHxL, TSKgel G4000HxL, and TSKgel G2000HxL (trade names, manufactured by Tosoh Corporation) as columns, tetrahydrofuran (THF) as a solvent, and a differential refractometer, and expressed in terms of polystyrene as a standard substance.

[0045] In the present disclosure, the term "lithographic printing plate precursor" refers not only to a lithographic printing plate precursor but also to a key plate precursor. In addition, the term "lithographic printing plate" refers not only to a lithographic printing plate prepared by performing operations such as exposure and development as necessary on a lithographic printing plate precursor but also to a key plate. The key plate precursor is not necessarily subjected to the operations such as exposure and development. The key plate refers to a lithographic printing plate precursor to be mounted on a plate cylinder that is not used, in a case where monochromatic or dichromatic printing is carried out on a part of paper during, for example, color newspaper printing.

[0046] In the present disclosure, "excellent in printing durability" means the large number of sheets can be printed using the lithographic printing plate.

[0047] Hereinafter, the present disclosure will be described in detail.

(Lithographic printing plate precursor)

[0048] The lithographic printing plate precursor according to the present disclosure includes a support and an image-recording layer on the support, in which the image-recording layer contains a non-onium-based polymerization initiator, a borate compound, an infrared absorber, and a compound A which is an onium salt consisting of a cation having a shape index equal to or less than 2 times a shape index of a cationic moiety of the infrared absorber.

[0049] In addition, the lithographic printing plate precursor according to the present disclosure is suitably used as an on-press development type lithographic printing plate precursor.

[0050] As a result of studies, the inventors of the present invention have found that in a lithographic printing plate precursor in which the image-recording layer contains the borate compound and the infrared absorber, precipitation of the crystal formed from the borate compound and the infrared absorber may be observed.

[0051] In the lithographic printing plate precursor according to the present disclosure, the image-recording layer contains a non-onium-based polymerization initiator, a borate compound, an infrared absorber, and a compound A which is an onium salt consisting of a cation having a shape index equal to or less than 2 times a shape index of a cationic moiety of the infrared absorber. Presumably, the compound A can weaken the interaction between the borate compound and the infrared absorber, which are used together in the image-recording layer, and as a result, can inhibit the precipitation of the crystal formed from the borate compound and the infrared absorber. Therefore, the lithographic printing plate precursor according to the present disclosure has excellent crystal precipitation suppressiveness.

[0052] Hereinafter, each of the configuration requirements in the lithographic printing plate precursor according to the present disclosure will be specifically described.

<Image-recording layer>

[0053] The image-recording layer contains a non-onium-based polymerization initiator, a borate compound, an infrared absorber, and a compound A which is an onium salt consisting of a cation having a shape index equal to or less than 2 times a shape index of a cationic moiety of the infrared absorber.

[0054] The image-recording layer is preferably a negative tone image-recording layer and more preferably a water-soluble or water-dispersible negative tone image-recording layer.

[0055] In the lithographic printing plate precursor according to the present disclosure, from the viewpoint of on-press developability, a non-exposed portion of the image-recording layer is preferably removable by at least any of dampening water or printing ink.

[0056] Hereinafter, each of the components to be contained in the image-recording layer will be specifically described.

[Compound A]

[0057] The image-recording layer contains the compound A. The compound A is an onium salt consisting of a cation having a shape index equal to or less than 2 times a shape index of the cationic moiety of the infrared absorber.

[0058] In the present disclosure, the infrared absorber may be a salt of a cation and an anion or may be a compound having a betaine structure, and both of the salt and compound are collectively called "cationic moiety".

[0059] In addition, the compound A is an onium salt consisting of an onium cation having a shape index equal to or less than 2 times a shape index of the cationic moiety of the infrared absorber, and an anion. That is, in a case where a shape index of the cationic moiety of the infrared absorber represents "S_I" and a shape index of the cation of the compound A represents "S_A", the infrared absorber and the compound A according to the present disclosure satisfy the relationship in which the ratio (S_A/S_I) is less than 2.

[0060] Furthermore, the compound A is preferably a compound having no polymerization initiation ability.

[0061] In the present disclosure, a shape index is a molecular shape index which is calculated by the following method.

[0062] The shape index is calculated using DataWarrior (an open source program provided by openmolecules.org) Ver. 5.5.0.

[0063] Specifically, in a two-dimensional molecular graph structure consisting of atoms other than hydrogen atoms in a molecule, two atoms having the longest topological distance are determined.

[0064] The length of the shortest chain connecting the two atoms is larger than the length of the shortest chain connecting any other atomic pairs.

[0065] A shape index is a value obtained by dividing the number of atoms included in the shortest chain connecting the two atoms by the total number of atoms included in the molecule.

[0066] Therefore, the shape index of a compound that has a perfectly linear shape is 1.0, and the larger the number of rings or branches in a molecule is, the lower the shape index is.

[0067] The value of the ratio (S_A/S_I) may be less than 2.0, and is preferably 1.8 or less, and from the viewpoint of printing durability, more preferably 1.5 or less, and even more preferably 1.0 or less.

[0068] Examples of the shape index of the cation of the compound A include 0.90 or less, and from the viewpoint of crystal precipitation suppressiveness, the shape index thereof is preferably less than 0.75, more preferably 0.70 or less, even more preferably 0.60 or less, and particularly preferably equal to or less than the shape index of the cationic moiety of the infrared absorber.

[0069] Examples of the lower limit of the shape index of the cation of the compound A include 0.20 or more, and from the viewpoint close to the shape index of the borate compound, the lower limit thereof is preferably 0.3 or more.

[0070] That is, the shape index of the cation of the compound A is preferably 0.20 to 0.90, more preferably 0.20 to 0.70, and even more preferably 0.30 to 0.70, from the viewpoint of satisfying the value of the above-described ratio (S_A/S_I)

and from the viewpoint close to the shape index of the borate compound.

[0071] From the viewpoints of printing durability and on-press developability, clogP of the cation in the compound A is preferably -10 or more and 20 or less, more preferably -5 or more and 15 or less, even more preferably 0 or more and 10 or less, and particularly preferably 2 or more and 8 or less.

[0072] In the present disclosure, clogP is calculated by the following method.

[0073] By using DataWarrior (an open source program provided by openmolecules.org) Ver. 5.5.0, clogP is calculated which is the logarithm of its partition coefficient between n-octanol and water log(Coctanol/Cwater).

[0074] The compound A is not particularly limited as long as it is an onium salt consisting of a cation having a shape index equal to or less than a shape index of the cationic moiety of the infrared absorber, but from the viewpoint of crystal precipitation suppressiveness, the compound A is preferably an ammonium salt compound, a phosphonium salt compound, a sulfonium salt compound, or a sulfoxonium salt compound, more preferably an ammonium salt compound, a phosphonium salt compound, or a sulfonium salt compound, even more preferably an ammonium salt compound or a phosphonium salt compound, and particularly preferably a phosphonium salt compound.

[0075] From the viewpoint of crystal precipitation suppressiveness, the phosphonium salt compound is preferably a quaternary phosphonium salt compound and more preferably a monoalkyl triaryl phosphonium salt compound.

[0076] From the viewpoint of crystal precipitation suppressiveness, the ammonium salt compound is preferably a quaternary ammonium salt compound and more preferably a monoalkyl triaryl ammonium salt compound.

[0077] From the viewpoint of crystal precipitation suppressiveness, the sulfonium salt compound is preferably a tertiary sulfonium salt compound and more preferably a monoalkyl diaryl sulfonium salt compound.

[0078] From the viewpoint of crystal precipitation suppressiveness, the sulfoxonium salt compound is preferably a trialkyl sulfoxonium salt compound.

[0079] In addition, it is preferable that the central element of the cation of the compound A and the central element of the cationic moiety of the infrared absorber be different elements.

[0080] The anion that the compound A has may be a monovalent anion or a polyvalent anion having a valency of two or more, but from the viewpoint of crystal precipitation suppressiveness, is preferably a monovalent anion.

[0081] The anion that the compound A has is not particularly limited, but from the viewpoint of crystal precipitation suppressiveness, is preferably at least one anion selected from the group consisting of a halide ion, a tetrafluoroborate anion, a hexafluorophosphate anion, a benzene sulfonate anion, a 1-naphthalene sulfonate anion, a 2-naphthalene sulfonate anion, a benzoate anion, a phenyl phosphate anion, a phenol anion, a thiophenol anion, a tetraphenyl borate anion, and a tosylate anion, more preferably at least one anion selected from the group consisting of a bromide ion, an iodide ion, a tetrafluoroborate anion, and a tosylate anion, even more preferably a bromide ion or a tetrafluoroborate ion, and particularly preferably a bromide ion.

[0082] From the viewpoints of crystal precipitation suppressiveness and temporal stability of the compound, the anion that the compound A has is preferably at least one anion selected from the group consisting of a bromide ion, an iodide ion, a tetrafluoroborate anion, a benzene sulfonate anion, a 1-naphthalene sulfonate anion, a 2-naphthalene sulfonate anion, a benzoate anion, a phenyl phosphate anion, and a tosylate anion, more preferably at least one anion selected from the group consisting of a benzene sulfonate anion, a 1-naphthalene sulfonate anion, a 2-naphthalene sulfonate anion, and a tosylate anion, and particularly preferably at least one anion selected from the group consisting of a 1-naphthalene sulfonate anion and tosylate anion.

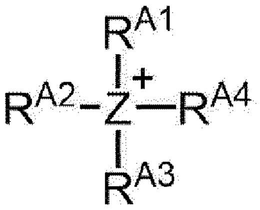
[0083] In addition, from the viewpoint of crystal precipitation suppressiveness and temporal stability of the compound, the anion that the compound A has is preferably a conjugate base of an organic acid, more preferably a conjugate base of an organic carboxylic acid or an organic sulfonic acid, even more preferably a conjugate base of an organic sulfonic acid, and particularly preferably a conjugate base of an aromatic sulfonic acid.

[0084] Furthermore, from the viewpoints of crystal precipitation suppressiveness and temporal stability of the compound, the anion that the compound A has is preferably at least one anion selected from the group consisting of $R^1SO_3^-$, $R^1SO_2^-$, $R^1R^2PO_2^-$, $R^1PO_3^{2-}$, $R^1CO_2^-$, R^1O^-, R^1S^-, $(R^1SO_2)_2N^-$, and $R^1R^2R^3R^4B^-$, more preferably at least one anion selected from the group consisting of $R^1SO_3^-$, $R^1SO_2^-$, $R^1R^2PO_2^-$, $R^1PO_3^{2-}$, and $R^1CO_2^-$, and particularly preferably $R^1SO_3^-$.

[0085] R^1 to R^4 each independently represent a hydrogen atom, an alkyl group, or an aryl group.

[0086] From the viewpoint of crystal precipitation suppressiveness, the anion that the compound A has is preferably an anion having a conjugate acid with a pKa of 4 or less and more preferably an anion having a conjugate acid with a pKa of 0 or less.

[0087] From the viewpoint of crystal precipitation suppressiveness, the cation in the compound A is preferably a cation represented by Formula (A).



$$R^{A2}-\overset{R^{A1}}{\underset{R^{A3}}{\overset{|+}{\underset{|}{Z}}}}-R^{A4} \qquad (A)$$

[0088] In Formula (A), Z represents P or N, and R^{A1} to R^{A4} each independently represent a hydrogen atom, an alkyl group, or an aryl group.

[0089] From the viewpoint of crystal precipitation suppressiveness, Z in Formula (A) is preferably P.

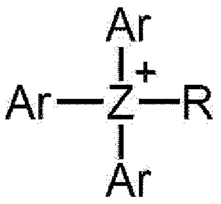
[0090] From the viewpoint of crystal precipitation suppressiveness, the alkyl group represented by R^{A1} to R^{A4} in Formula (A) is preferably an alkyl group having 1 to 16 carbon atoms, more preferably an alkyl group having 1 to 12 carbon atoms, and particularly preferably an alkyl group having 1 to 8 carbon atoms. The alkyl group may be a linear or branched alkyl group or may be an alkyl group having a ring structure.

[0091] The alkyl group may have a substituent. Examples of the substituent include a halogen atom, an aryl group, an alkenyl group, an alkoxy group, an aryloxy group, a vinyl ether group, an acyl group, an acyloxy group, an alkoxycarbonyl group, an aryloxycarbonyl group, a vinyloxycarbonyl group, a (meth)acryloxy group, a (meth)acrylamide group, and the like. The substituents may be further substituted with the substituents.

[0092] From the viewpoint of crystal precipitation suppressiveness, the aryl groups represented by R^{A1} to R^{A4} in Formula (A) preferably each independently represent a phenyl group or a 2,4,6-trimethylphenyl group and more preferably each independently represent a phenyl group.

[0093] The aryl group may have a substituent. Examples of the substituent include a halogen atom, an alkyl group, an aryl group, an alkenyl group, an alkoxy group, an aryloxy group, an acyl group, an acyloxy group, an alkoxycarbonyl group, an aryloxycarbonyl group, a vinyloxycarbonyl group, a (meth)acryloxy group, a (meth)acrylamide group, and the like. The substituents may be further substituted with the substituents.

[0094] In addition, from the viewpoint of crystal precipitation suppressiveness, the cation in the compound A is more preferably a cation represented by Formula (1).



$$Ar-\overset{Ar}{\underset{Ar}{\overset{|+}{\underset{|}{Z}}}}-R \qquad (1)$$

[0095] In Formula (1), Z represents P or N, R represents an alkyl group, and Ar's each independently represent an aryl group.

[0096] From the viewpoint of crystal precipitation suppressiveness, Z in Formula (1) is preferably P.

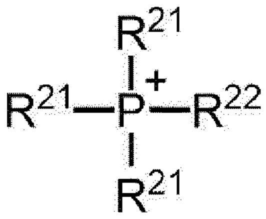
[0097] From the viewpoint of crystal precipitation suppressiveness, R in Formula (1) is preferably an alkyl group having 1 to 16 carbon atoms, more preferably an alkyl group having 1 to 12 carbon atoms, and particularly preferably an alkyl group having 1 to 8 carbon atoms. The alkyl group may be a linear or branched alkyl group or may be an alkyl group having a ring structure.

[0098] The alkyl group may have a substituent. Examples of the substituent include a halogen atom, an aryl group, an alkenyl group, an alkoxy group, an aryloxy group, a vinyl ether group, an acyl group, an acyloxy group, an alkoxycarbonyl group, an aryloxycarbonyl group, a vinyloxycarbonyl group, a (meth)acryloxy group, a (meth)acrylamide group, and the like. The substituents may be further substituted with the substituents.

[0099] From the viewpoint of crystal precipitation suppressiveness, Ar in Formula (1) each independently are preferably a phenyl group or a 2,4,6-trimethylphenyl group and more preferably a phenyl group.

[0100] The aryl group may have a substituent. Examples of the substituent include a halogen atom, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an acyl group, an acyloxy group, and the like.

[0101] From the viewpoints of crystal precipitation suppressiveness and solubility in a coating solvent, the cation in the compound A is more preferably a cation represented by Formula (2).



$$R^{21}-\underset{\displaystyle R^{21}}{\overset{\displaystyle R^{21}}{\overset{+}{P}}}-R^{22} \qquad (2)$$

[0102] In Formula (2), R^{21}'s each independently represent an alkyl group and R^{22} represents a hydrogen atom or an alkyl group.

[0103] From the viewpoints of crystal precipitation suppressiveness and solubility in a coating solvent, R^{21} in Formula (2) is preferably an alkyl group having 1 to 16 carbon atoms, more preferably a branched alkyl group having 3 to 12 carbon atoms, even more preferably a branched alkyl group having 3 to 8 carbon atoms, and particularly preferably a t-butyl group.

[0104] From the viewpoints of crystal precipitation suppressiveness and solubility in a coating solvent, three R^{21}'s in Formula (2) are preferably the same groups.

[0105] From the viewpoints of crystal precipitation suppressiveness and solubility in a coating solvent, R^{22} in Formula (2) is preferably a hydrogen atom or an alkyl group having 1 to 16 carbon atoms, more preferably a hydrogen atom or an alkyl group having 1 to 8 carbon atoms, even more preferably a hydrogen atom, a methyl group, or an ethyl group, and particularly preferably a hydrogen atom.

[0106] The alkyl group represented by R^{21} and R^{22} may have a substituent. Examples of the substituent include a halogen atom, an aryl group, an alkenyl group, an alkoxy group, an aryloxy group, a vinyl ether group, an acyl group, an acyloxy group, an alkoxycarbonyl group, an aryloxycarbonyl group, a vinyloxycarbonyl group, a (meth)acryloxy group, a (meth)acrylamide group, and the like. The substituents may be further substituted with the substituents.

[0107] From the viewpoints of crystal precipitation suppressiveness, curing property, and solubility in a coating solvent, it is preferable that the cation in the compound A have a polymerizable group.

[0108] The polymerizable group is preferably an ethylenically unsaturated group, and preferred examples thereof include a (meth)acryloxy group, a (meth)acrylamide group, an allyl group, a styryl group, a vinyl ether group, a vinyl ester group, and the like.

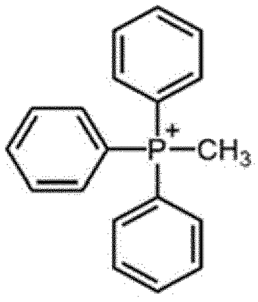
[0109] Among these, from the viewpoints of crystal precipitation suppressiveness, curing property, and solubility in a coating solvent, at least one group selected from the group consisting of a (meth)acryloxy group and a (meth)acrylamide group is preferable, and a (meth)acryloxy group is more preferable.

[0110] Preferred examples of the cation having a polymerizable group include a cation obtained by adding a polymerizable compound which will be described later (preferably a (meth)acrylic compound, and more preferably a (meth)acrylate compound) to a compound having a direct bond between a phosphorus atom or a nitrogen atom and a hydrogen atom by the Michael addition reaction.

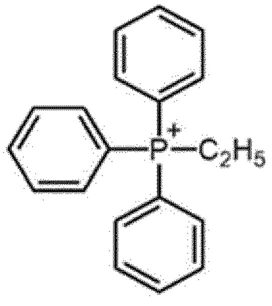
[0111] Furthermore, the polymerizable compound is preferably a polyfunctional (meth)acrylic compound and more preferably a polyfunctional (meth)acrylate compound.

[0112] Specifically, suitable examples of the cation forming the compound A include the following cations. It goes without saying that the cation is not limited thereto.

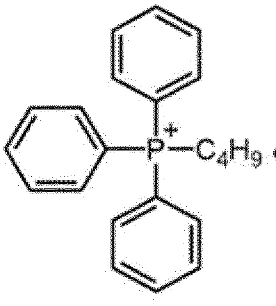
[0113] In addition, specifically, suitable examples of the compound A include an onium salt of any one of D1 to D24 and D29 to D31 described below and one anion selected from the group consisting of a halide ion, a tetrafluoroborate anion, a hexafluorophosphate anion, a benzene sulfonate anion, a 1-naphthalene sulfonate anion, 2-naphthalene sulfonate anion, a benzoate anion, a phenyl phosphate anion, a phenol anion, a thiophenol anion, a tetraphenylborate anion, and a tosylate anion.



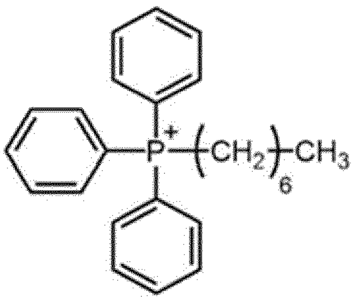
D1



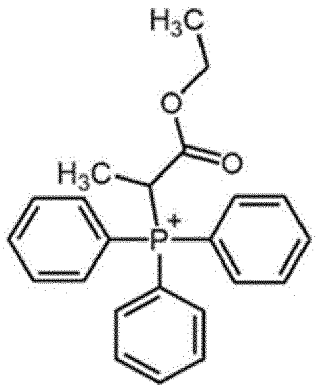
D2



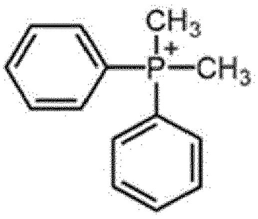
D3



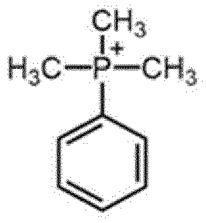
D4



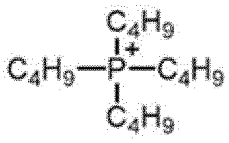
D5



D6

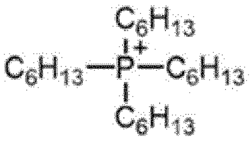


D7



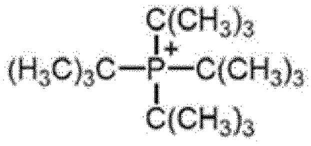
$$C_4H_9-\overset{C_4H_9}{\underset{C_4H_9}{P^+}}-C_4H_9$$

D8



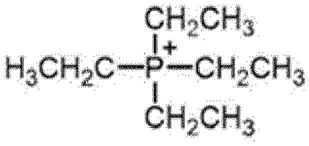
$$C_6H_{13}-\overset{C_6H_{13}}{\underset{C_6H_{13}}{P^+}}-C_6H_{13}$$

D9



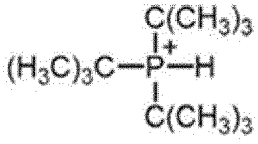
$$(H_3C)_3C-\overset{C(CH_3)_3}{\underset{C(CH_3)_3}{P^+}}-C(CH_3)_3$$

D10



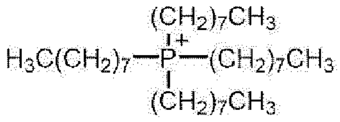
$$H_3CH_2C-\overset{CH_2CH_3}{\underset{CH_2CH_3}{P^+}}-CH_2CH_3$$

D11



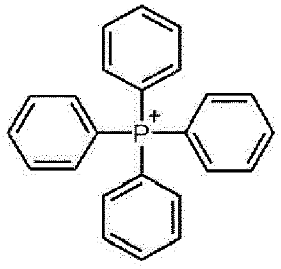
$$(H_3C)_3C-\overset{C(CH_3)_3}{\underset{C(CH_3)_3}{P^+}}-H$$

D12

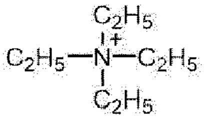


$$H_3C(CH_2)_7-\overset{(CH_2)_7CH_3}{\underset{(CH_2)_7CH_3}{P^+}}-(CH_2)_7CH_3$$

D13

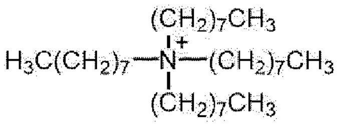


D14



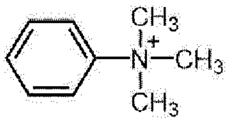
$$C_2H_5-\overset{C_2H_5}{\underset{C_2H_5}{N^+}}-C_2H_5$$

D15

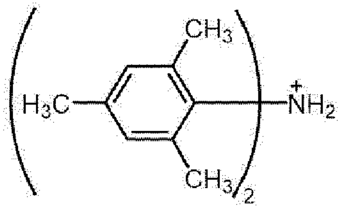


$$H_3C(CH_2)_7-\overset{(CH_2)_7CH_3}{\underset{(CH_2)_7CH_3}{N^+}}-(CH_2)_7CH_3$$

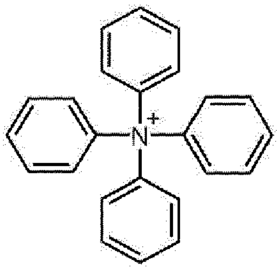
D16



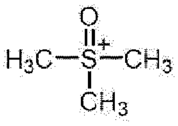
D17



D18

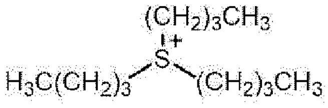


D19

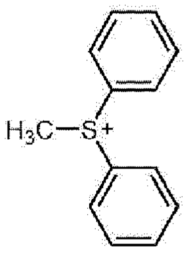


$$H_3C-\overset{O}{\underset{CH_3}{S^+}}-CH_3$$

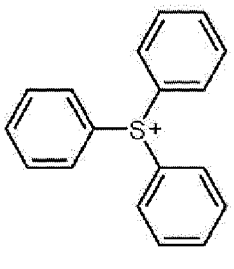
D20



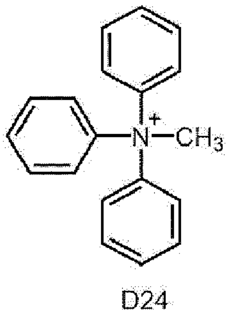
D21



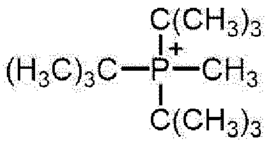
D22



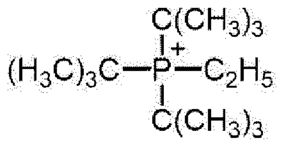
D23



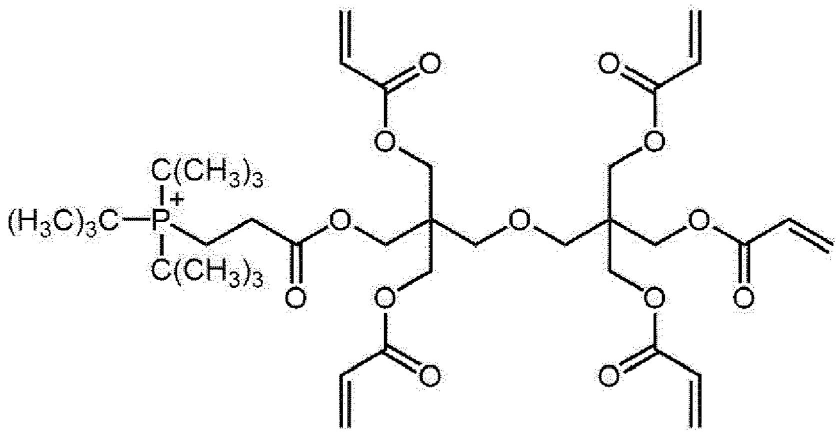
D24



D29



D30



D31

[0114] Only one compound A may be added to the image-recording layer, or two or more compounds A may be used in combination.

[0115] From the viewpoint of crystal precipitation suppressiveness, the content of the compound A with respect to the total mass of the image-recording layer is preferably 0.01% by mass to 30% by mass, more preferably 0.05% by mass to 25% by mass, and even more preferably 0.1% by mass to 20% by mass.

[0116] From the viewpoint of crystal precipitation suppressiveness, the content of the compound A per unit area of the image-recording layer is preferably 0.001 g/m^2 to 3 g/m^2, more preferably 0.005 g/m^2 to 1 g/m^2, even more preferably 0.01 g/m^2 to 0.1 g/m^2, and particularly preferably 0.01 g/m^2 to 0.05 g/m^2.

[0117] In the image-recording layer, from the viewpoints of crystal precipitation suppressiveness and printing durability, the molar content of the cation of the compound A is preferably 0.1 times to 5 times the molar content of the anion in the borate compound, more preferably 0.2 times to 4 times the molar content of the anion in the borate compound, and particularly preferably 0.5 times to 3 times the molar content of the anion in the borate compound.

[Non-onium-based polymerization initiator]

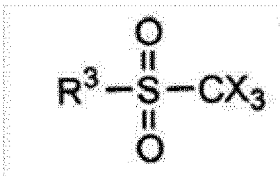
[0118] The image-recording layer contains a non-onium-based polymerization initiator.

[0119] The non-onium-based polymerization initiator means a polymerization initiator other than the onium-based polymerization initiator. Specifically, the non-onium-based polymerization initiator is a compound other than the onium salt compound, which accepts one electron by intermolecular electron migration in a case where electrons of an infrared absorber are excited by exposure to infrared, and generates a polymerization initiation species such as radicals.

[0120] As the non-onium-based polymerization initiator, a known non-onium-based polymerization initiator used for an image-recording layer of a lithographic printing plate precursor can be suitably used.

[0121] From the viewpoints of sensitivity, printing durability, on-press developability, and receptivity, the non-onium-based polymerization initiator preferably includes an electron-donating polymerization initiator.

[0122] From the viewpoints of developability and printing durability, the non-onium-based polymerization initiator preferably includes a compound represented by Formula (II) as an electron-donating polymerization initiator.



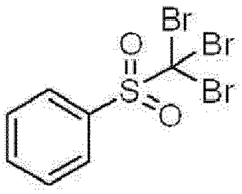
$$R^3-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-CX_3 \quad (II)$$

[0123] In Formula (II), X's each independently represent a halogen atom, and R^3 represents an aryl group.

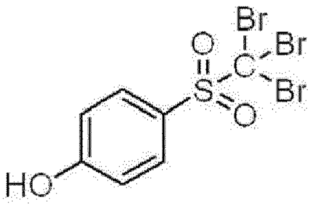
[0124] Specific examples of X in Formula (II) include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom. Among these, X is preferably a chlorine atom or a bromine atom because these have excellent sensitivity, and is particularly preferably a bromine atom.

[0125] In addition, in Formula (II), specific examples of R^3 include a phenyl group and a naphthyl group. Examples of the substituent of the aryl group represented by R^3 include a halogen atom, a hydroxy group, an amide group, an amino group, a cyano group, an alkyl group, and an alkoxy group. Among these, the substituent is preferably a hydroxy group. R^3 is preferably a phenyl group substituted with a hydroxy group.

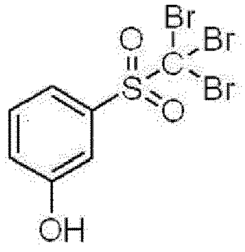
[0126] As a specific example of the electron-accepting polymerization initiator represented by Formula (II), those described in WO2020/262692A can be suitably used.



(IS-1)



(IS-2)



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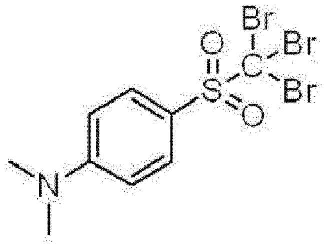

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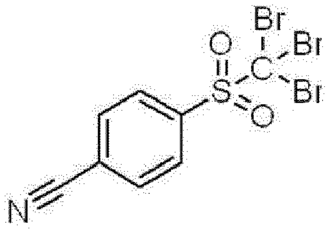

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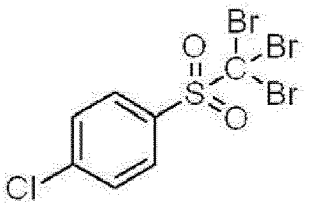

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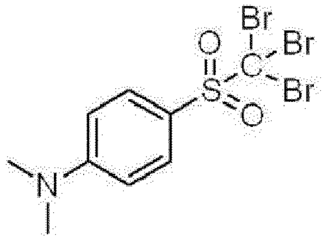

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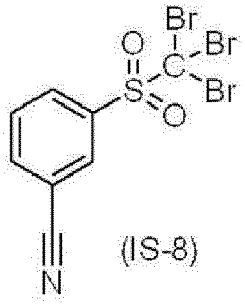

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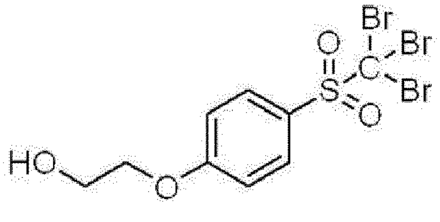

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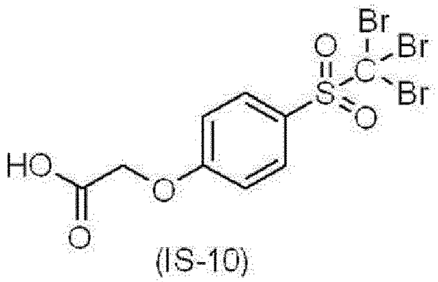

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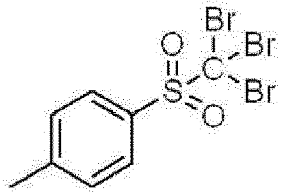

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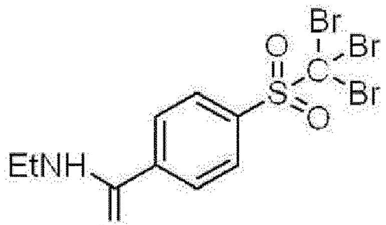

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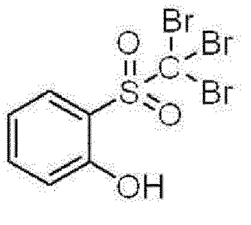

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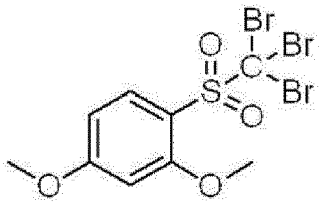


(IS-14)

[0127] From the viewpoint of improving sensitivity, the lowest unoccupied molecular orbital (LUMO) of the electron-accepting polymerization initiator as the non-onium-based polymerization initiator is preferably -3.00 eV or less and more preferably -3.02 eV or less.

[0128] The lower limit of LUMO is preferably -3.80 eV or more and more preferably -3.60 eV or more.

[0129] In the present disclosure, the energy of molecular orbital (MO) such as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is calculated by the following methods.

[0130] First, free counter ions in the compound as a calculation object are excluded from the calculation object. For example, for a cationic infrared absorber, counter anions are excluded from the calculation object, and for an anionic borate compound, counter cations are excluded from the calculation object. "Free" mentioned herein means that the compound as an object and the counter ions thereof are not covalently linked to each other.

[0131] The structural optimization is carried out by DFT (B3LYP/6-31G(d)) using quantum chemical calculation software Gaussian 16.

[0132] The MO energy is calculated by DFT (B3LYP/6-31+G(d,p)/PCM (solvent = methanol)) with the optimum structure obtained by the structural optimization, using quantum chemical calculation software Gaussian 16. For an iodine-containing compound, the MO energy is calculated under the condition of DFT (B3LYP/DGDZVP/PCM (solvent = methanol)).

[0133] The optimum structure mentioned herein means a structure in which the total energy obtained by DFT calculation is the most stable. The most stable structure is found by repeating the structural optimization as necessary.

[0134] By the following formula, the MO energy Ebare (unit: hartree) obtained by the above-described MO energy calculation is converted into Escaled (unit: eV) used as the values of HOMO and LUMO in the present disclosure.

$$\text{[Calculation formula for HOMO] Escaled} = 0.823168 \text{ x } 27.2114 \text{ x Ebare} - 1.07634$$

$$\text{[Calculation formula for LUMO] Escaled} = 0.820139 \times 27.2114 \times \text{Ebare} - 1.086039$$

[0135] 27.2114 is simply a coefficient for converting hartree into eV, and 0.823168 and -1.07634 used for calculating HOMO and 0.820139 and -1.086039 used for calculating LUMO are adjustment coefficients. These are determined such that the calculated values of HOMO and LUMO of the compound as a calculation object match the measured values.

[0136] One non-onium-based polymerization initiator may be used alone, or two or more non-onium-based polymerization initiators may be used in combination.

[0137] The content of the non-onium-based polymerization initiator with respect to the total mass of the image-recording layer is preferably 0.1% by mass to 50% by mass, more preferably 0.5% by mass to 30% by mass, and particularly preferably 0.8% by mass to 20% by mass.

[Borate compound]

[0138] The image-recording layer contains a borate compound.

[0139] The borate compound is preferably a tetraaryl borate compound or a monoalkyltriaryl borate compound, from the viewpoint of compound stability, more preferably a tetraaryl borate compound, and particularly preferably a tetraphenyl borate compound.

[0140] The counter cation that the borate compound has is not particularly limited, but is preferably an alkali metal ion or a tetraalkyl ammonium ion and more preferably a sodium ion, a potassium ion, or a tetrabutylammonium ion.

[0141] In addition, the counter cation that the borate compound has may be the cationic moiety of the infrared absorber.

[0142] Specifically, preferred examples of the borate compound include sodium tetraphenyl borate.

[0143] From the viewpoints of chemical resistance and printing durability, the highest occupied molecular orbital (HOMO) of the borate compound is preferably -6.00 eV or more, more preferably -5.95 eV or more, even more preferably

-5.93 eV or more, and particularly preferably more than -5.90 eV

[0144] The upper limit of HOMO is preferably -5.00 eV or less and more preferably -5.40 eV or less.

[0145] Specifically, preferred examples of the borate compound suitably include the electron-donating polymerization initiators described in WO2020/262692A.

[0146] In the image-recording layer, HOMO of the infrared absorber - HOMO of the borate compound preferably is 0.70 eV or less.

[0147] Only one borate compound may be added to the image-recording layer, or two or more borate compounds may be used in combination.

[0148] The content of the borate compound with respect to the total mass of the image-recording layer is preferably 0.01% by mass to 30% by mass, more preferably 0.05% by mass to 25% by mass, and even more preferably 0.1% by mass to 20% by mass.

[Infrared absorber]

[0149] The image-recording layer contains an infrared absorber.

[0150] The infrared absorber is not particularly limited as long as it is an infrared absorber having a cationic moiety in the molecule, and examples thereof include a pigment and a dye.

[0151] The shape index of the cationic moiety of the infrared absorber is, for example, preferably 0.2 to 0.8 and more preferably 0.3 to 0.6.

[0152] As the dye that is used as the infrared absorber, it is possible to use the dyes which has the cationic moiety in the molecule, of commercially available dyes and known dyes described in publications, for example, "Dye Handbooks" (edited by the Society of Synthetic Organic Chemistry, Japan, 1970). Specific examples thereof include dyes such as an azo dye, a metal complex azo dye, a pyrazolone azo dye, a naphthoquinone dye, an anthraquinone dye, a phthalocyanine dye, a carbonium dye, a quinoneimine dye, a methine dye, a cyanine dye, a squarylium colorant, a pyrylium salt, and a metal thiolate complex.

[0153] Among the infrared absorbers, a cyanine dye having a cationic moiety and an anionic moiety in the molecule is particularly preferable.

[0154] Specific examples of the cyanine dye include the compounds described in paragraphs "0017" to "0019" of JP2001-133969A and the compounds described in paragraphs "0016" to "0021" of JP2002-023360A and paragraphs "0012" to "0037" of JP2002-040638A. As the cyanine dye, for example, the compounds described in paragraphs "0034" to "0041" of JP2002-278057A and paragraphs "0080" to "0086" of JP2008-195018A are preferable, and the compounds described in paragraphs "0035" to "0043" of JP2007-90850A and the compounds described in paragraphs "0105" to "0113" of JP2012-206495A are particularly preferable.

[0155] Furthermore, the compounds described in paragraphs "0008" and "0009" of JP1993-5005A (JP-H05-5005A) and paragraphs "0022" to "0025" of JP2001-222101A can also be preferably used.

[0156] As pigments, the compounds described in paragraphs "0072" to " 0076" of JP2008-195018A are preferable.

[0157] In addition, as the infrared absorber, as long as it has a cationic moiety in the molecule, for example, an infrared absorber that decomposes by exposure to infrared (decomposition-type infrared absorber) can also be used.

[0158] Presumably, in a case where a decomposition-type infrared absorber is used as the infrared absorber, the infrared absorber or a decomposition product thereof may promote polymerization, and the decomposition product of the infrared absorber and the polymerizable compound may interact with each other, which may result in excellent printing durability.

[0159] The decomposition-type infrared absorber is preferably an infrared absorber that performs a function of forming color by absorbing infrared and decomposing by exposure to infrared.

[0160] Hereinafter, a color-forming compound formed as a result of infrared absorption and decomposition of the decomposition-type infrared absorber by exposure to infrared will be also called "color forming substance of the decomposition-type infrared absorber".

[0161] In addition, it is preferable that the decomposition-type infrared absorber have a function of absorbing infrared by exposure to infrared and converting the absorbed infrared into heat.

[0162] The decomposition-type infrared absorber may be an infrared absorber that decomposes by absorbing at least a part of light in the infrared wavelength region (wavelength of 750 nm to 1 mm). The decomposition-type infrared absorber is preferably an infrared absorber having a maximal absorption wavelength in a wavelength region of 750 nm to 1,400 nm, and more preferably an infrared absorber having a maximal absorption wavelength in a wavelength region of 760 nm to 900 nm.

[0163] More specifically, the decomposition-type infrared absorber is preferably a compound that decomposes upon the exposure to infrared and generates a compound having maximal absorption wavelength in a wavelength region of 500 nm to 600 nm.

[0164] The decomposition-type infrared absorber is preferably an infrared absorber that decomposes by either or both of heat and electron migration resulting from exposure to infrared, and more preferably an infrared absorber that decomposes by electron migration resulting from exposure to infrared. "Decomposes by electron migration" mentioned herein means that electrons excited to the lowest unoccupied molecular orbital (LUMO) from the highest occupied molecular orbital (HOMO) of the decomposition-type infrared absorber by exposure to infrared move to electron accepting groups (groups having potential close to LUMO) in a molecule by means of intramolecular electron migration and thus result in decomposition.

[0165] As the infrared absorber and the infrared absorber that decomposes by exposure to infrared, those described in WO2020/262692A can also be suitably used.

[0166] As the infrared absorber that decomposes by exposure to infrared, those described in JP2008-544322A or WO2016/027886A can also be suitably used.

[0167] In addition, as the cyanine dye which is a decomposition-type infrared absorber, the infrared absorbing compounds described in WO2019/219560A can be suitably used.

[0168] From the viewpoints of printing durability and halftone dot reproducibility, the highest occupied molecular orbital (HOMO) of the infrared absorber used in the present disclosure is preferably -5.00 eV or less and more preferably -5.30 eV or less.

[0169] From the viewpoints of printing durability and halftone dot reproducibility, the lower limit of HOMO of the infrared absorber is preferably -5.90 eV or more, more preferably -5.75 eV or more, and even more preferably -5.60 eV or more.

[0170] Only one infrared absorber may be used, or two or more infrared absorbers may be used in combination. In addition, as the infrared absorber, a pigment and a dye may be used in combination.

[0171] The total content of the infrared absorber in the image-recording layer with respect to the total mass of the image-recording layer is preferably 0.1% by mass to 10.0% by mass and more preferably 0.5% by mass to 5.0% by mass.

[0172] One of the preferred aspects in the present disclosure is an aspect including a compound in which an infrared absorber (preferably a cyanine dye) and a borate compound form a salt. Specific examples of the compound in which the infrared absorber and the borate compound form a salt include a salt of a cationic moiety of an infrared absorber (preferably a cyanine dye) and a borate anion (for example, a tetraphenyl borate anion).

[0173] In a case where a compound containing a cationic moiety of the infrared absorber and a borate anion is used (that is, a case where the compound forming the salt is used), the image-recording layer contains both the infrared absorber and the borate compound.

[0174] In addition, the compound in which the infrared absorber and the borate compound form a salt may be used in combination with another infrared absorber or in combination with another borate compound.

[Relationship among infrared absorber, borate compound, and non-onium-based polymerization initiator]

[0175] In the image-recording layer of the present disclosure, HOMO of the borate compound is preferably -6.0 eV or more, and LUMO of the non-onium-based polymerization initiator is preferably -3.0 eV or less.

[0176] More preferred aspects of HOMO of the borate compound and LUMO of the non-onium-based polymerization initiator are as described above.

[0177] Presumably, in the image-recording layer of the present disclosure, energy transfer may occur among the borate compound, the infrared absorber, and the non-onium-based polymerization initiator.

[0178] Accordingly, it is considered that in a case where HOMO of the borate compound is -6.0 eV or more and LUMO of the non-onium-based polymerization initiator is -3.0 eV or less, radicals may be more efficiently generated, which may facilitate further improvement of chemical resistance and printing durability.

[0179] From the viewpoints of printing durability and chemical resistance, HOMO of the infrared absorber - HOMO of the borate compound is preferably 1.0 eV or less, more preferably 0.70 eV or less, and particularly preferably 0.60 eV or less. From the same viewpoints as above, HOMO of the infrared absorber - HOMO of the borate compound is preferably -0.200 eV or more and more preferably -0.100 eV or more. The negative sign means that HOMO of the borate compound is higher than HOMO of the infrared absorber.

[0180] From the viewpoints of printing durability and chemical resistance, LUMO of the non-onium-based polymerization initiator - LUMO of the infrared absorber is preferably 1.00 eV or less, and more preferably 0.700 eV or less. From the same viewpoints as above, LUMO of the non-onium-based polymerization initiator - LUMO of the infrared absorber is preferably -0.200 eV or more, and more preferably -0.100 eV or more.

[0181] From the same viewpoints as above, LUMO of the non-onium-based polymerization initiator - LUMO of the infrared absorber is preferably 1.00 eV to -0.200 eV, more preferably 0.700 eV to -0.100 eV The negative sign means that LUMO of the infrared absorber is higher than LUMO of the non-onium-based polymerization initiator.

[Acid color forming agent]

[0182] From the viewpoint of visibility, the image-recording layer may contain an acid color forming agent.

[0183] "Acid color forming agent" used in the present disclosure means a compound having a property of forming color by being heated in a state of accepting an electron-accepting compound (for example, a proton of an acid or the like) and thus changing the color of the image-recording layer. The acid color forming agent is particularly preferably a colorless compound which has a partial skeleton such as lactone, lactam, sultone, spiropyran, an ester, or an amide and allows such a partial skeleton to rapidly open the ring or to be cleaved when coming into contact with an electron-accepting compound.

[0184] From the viewpoint of UV printing durability, the hydrogen abstraction enthalpy of all hydrogen atoms present in a molecule of the acid color forming agent is preferably -6.5 kcal/mol or more, more preferably -4.0 kcal/mol or more, even more preferably -2.0 kcal/mol or more, and particularly preferably -2.0 kcal/mol to 50 kcal/mol.

[0185] The higher the hydrogen abstraction enthalpy is, the further the hydrogen atoms are inhibited from being abstracted from the acid color forming agent by a polymerization initiation species such as radicals, and the further the polymerization reaction is prolonged. Therefore, excellent curing property is obtained, and printing durability, particularly, UV printing durability is further improved.

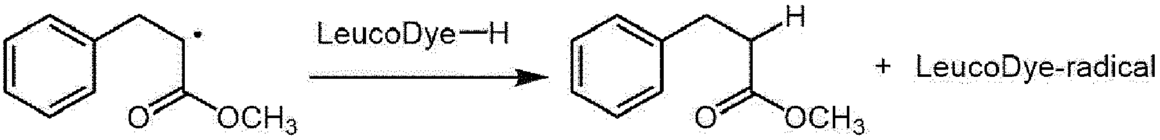
[0186] In the present disclosure, the hydrogen abstraction enthalpy of all hydrogen atoms present in a molecule of the acid color forming agent is calculated by the following method.

[0187] Regarding a reaction with propagating radicals caused by hydrogen abstraction, the enthalpy of each of the reactant and product is calculated using Gaussian 16 as a calculation program at a calculation level of density functional theory (B3LYP/6-31+G**). The solvent effect (solvent: methanol) is examined by the SCRF method. By finding the difference in the enthalpy between the reactant and the product, a reaction enthalpy is calculated.

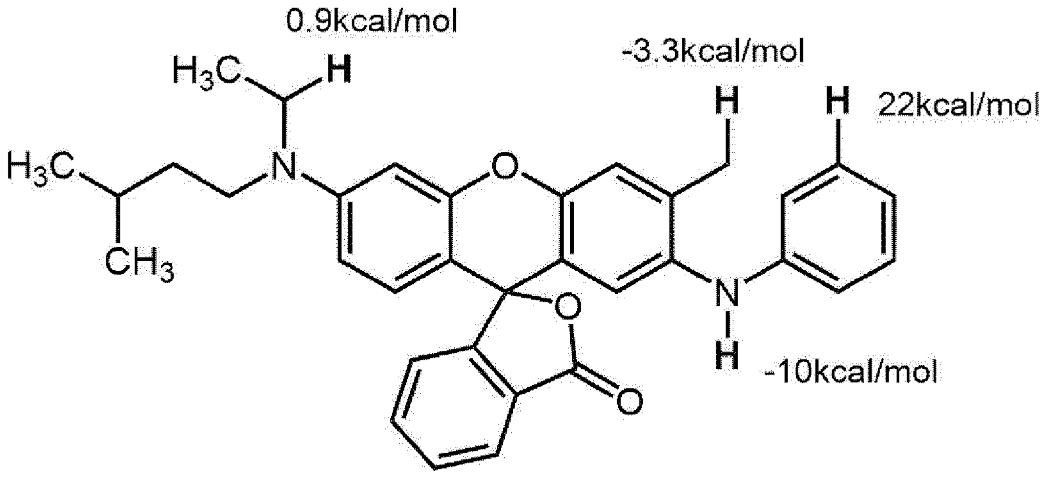
[0188] More specifically, the hydrogen abstraction enthalpy is calculated as follows. In the following chemical reaction formula, for each of the propagating radical, LeucoDye-H, the hydrogenated propagating radical, and LeucoDye-radical, modeling is carried out using Gaussian pre/post software GaussView6. The calculation condition is specified to #p opt b3lyp/6-31+g(d,p) scrf = (solvent =methanol), and is set to charge of 0 and multiplicity of 2 in a case of being a radical, or charge of 0 and multiplicity of 1 in a case of being a non-radical.

[0189] #p is specified for detailed logging output, and may not be specified.

[0190] From the energy (unit: hartree) of the structure optimized by performing calculation, the enthalpy of formation of the reactant (sum of the energy of the propagating radical and LeucoDye-H) and the enthalpy of formation of the product (sum of the energy of the hydrogenated propagating radical and LeucoDye-radical) are calculated. The enthalpy of formation of the reactant is subtracted from the enthalpy of formation of the product, and the result is adopted as the hydrogen abstraction enthalpy. The unit is converted as 1 hartree = 627.51 kcal/mol.



[0191] For example, the hydrogen abstraction enthalpy for each hydrogen atom of the following compound is as follows.



[0192] From the viewpoint of UV printing durability, it is preferable that the acid color forming agent do not have a structure in which a hydrogen atom is directly bonded to a nitrogen atom.

[0193] The structure in which a hydrogen atom is directly bonded to a nitrogen atom (N-H structure) is a structure in which a hydrogen abstraction reaction readily occurs by a radical or the like. In a case where the acid color forming agent is a compound that does not have such a structure, the hydrogen atom abstraction from the acid color forming agent is inhibited, and the polymerization reaction is prolonged. Therefore, excellent curing property is obtained, and printing durability, particularly, UV printing durability is further improved.

[0194] Particularly, from the viewpoint of color formability, the acid color forming agent used in the present disclosure is preferably at least one compound selected from the group consisting of a spiropyran compound, a spirooxazine compound, a spirolactone compound, and a spirolactam compound.

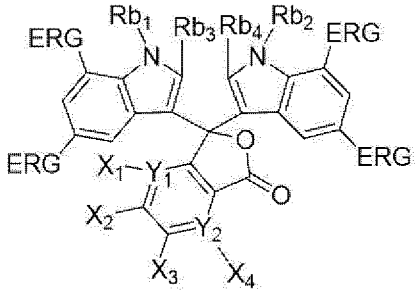
[0195] From the viewpoint of visibility, the color tone of the acid color forming agent after color forming (that is, the color tone of the color forming substance generated from the acid color forming agent) is preferably green, blue, or black.

[0196] From the viewpoints of color formability and visibility, the acid color forming agent preferably includes a leuco dye, and is more preferably a leuco dye.

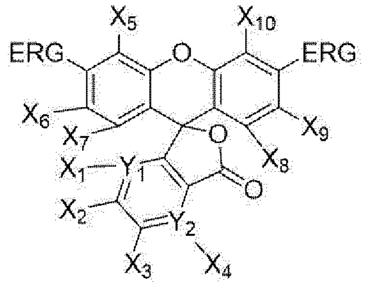
[0197] The leuco dye is not particularly limited as long as it has a leuco structure. The leuco dye preferably has a spiro structure, and more preferably has a spirolactone ring structure.

[0198] From the viewpoints of color formability and visibility of exposed portions, the leuco dye is preferably a leuco dye having a phthalide structure or a fluoran structure.

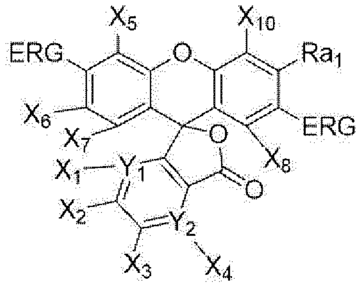
[0199] Furthermore, from the viewpoints of color formability and visibility of exposed portions, the leuco dye having a phthalide structure or a fluoran structure is preferably a compound represented by any of Formula (Le-1) to Formula (Le-3), and more preferably a compound represented by Formula (Le-2).



(Le - 1)



(Le - 2)



(Le - 3)

[0200] In Formula (Le-1) to Formula (Le-3), ERG's each independently represent an electron-donating group, X_1 to X_4 each independently represent a hydrogen atom, a halogen atom, or dialkylanilino group, X_5 to X_{10} each independently represent a hydrogen atom, a halogen atom, or a monovalent organic group, Y_1 and Y_2 each independently represent C or N, X_1 does not exist in a case where Y_1 is N, X_4 does not exist in a case where Y_2 is N, Ra_1 represents a hydrogen atom, an alkyl group, or an alkoxy group, and Rb_1 to Rb_4 each independently represent a hydrogen atom, an alkyl group, an aryl group, or a heteroaryl group.

[0201] From the viewpoint of color formability and visibility of exposed portions, the electron-donating group represented by ERG in Formula (Le-1) to Formula (Le-3) is preferably an amino group, an alkylamino group, an arylamino group, a heteroarylamino group, a dialkylamino group, a monoalkyl monoarylamino group, a monoalkyl monoheteroarylamino group, a diarylamino group, a diheteroarylamino group, a monoaryl monoheteroarylamino group, an alkoxy group, an aryloxy group, a heteroaryloxy group, or an alkyl group, more preferably an amino group, an alkylamino group, an arylamino group, a heteroarylamino group, a dialkylamino group, a monoalkyl monoarylamino group, a monoalkyl monoheteroarylamino group, a diarylamino group, a diheteroarylamino group, a monoaryl monoheteroarylamino group, an alkoxy group, or an aryloxy group, even more preferably a monoalkyl monoarylamino group, a diarylamino group, a diheteroarylamino group, or a monoaryl monoheteroarylamino group, and particularly preferably a monoalkyl monoarylamino group.

[0202] From the viewpoints of color formability and visibility of exposed portions, the electron-donating group represented by ERG is preferably a disubstituted amino group having an aryl group that has a substituent on at least one ortho position or a heteroaryl group that has a substituent on at least one ortho position, more preferably a disubstituted amino group having a phenyl group having a substituent on at least one ortho position and an electron-donating group at a para position, even more preferably an amino group having a phenyl group having a substituent on at least one ortho position and an electron-donating group at a para position, and an aryl group or a heteroaryl group, and particularly preferably an amino group having a phenyl group having a substituent on at least one ortho position and an electron-donating group at a para position, and an aryl group having an electron-donating group or a heteroaryl group having an electron-donating group.

[0203] In the present disclosure, in a case where a bonding position of an aryl group or a heteroaryl group with other structures is defined as position 1, the ortho position in the aryl group or heteroaryl group other than a phenyl group is called a bonding position (for example, position 2 or the like) adjacent to the position 1.

[0204] Furthermore, from the viewpoints of color formability and visibility of exposed portions, the electron-donating group that the aryl group or heteroaryl group has is preferably an amino group, an alkylamino group, an arylamino group, a heteroarylamino group, a dialkylamino group, a monoalkyl monoarylamino group, a monoalkyl monoheteroarylamino group, a diarylamino group, a diheteroarylamino group, a monoaryl monoheteroarylamino group, an alkoxy group, an aryloxy group, a heteroaryloxy group, or an alkyl group, more preferably an alkoxy group, an aryloxy group, a heteroaryloxy group, or an alkyl group, and particularly preferably an alkoxy group.

[0205] From the viewpoints of color formability and visibility of exposed portions, X_1 to X_4 in Formula (Le-1) to Formula (Le-3) each independently are preferably a hydrogen atom or a chlorine atom, and more preferably each independently represent a hydrogen atom.

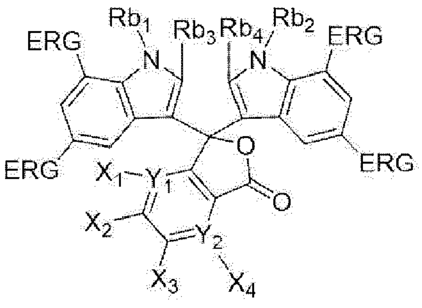
[0206] From the viewpoints of color formability and visibility of exposed portions, X_5 to X_{10} in Formula (Le-2) or Formula (Le-3) each independently are preferably a hydrogen atom, a halogen atom, an alkyl group, an aryl group, an amino group, an alkylamino group, an arylamino group, a heteroarylamino group, a dialkylamino group, a monoalkyl monoarylamino group, a monoalkyl monoheteroarylamino group, a diarylamino group, a diheteroarylamino group, a monoaryl monoheteroarylamino group, a hydroxy group, an alkoxy group, an aryloxy group, a heteroaryloxy group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a heteroaryloxycarbonyl group, or a cyano group, more preferably a hydrogen atom, a halogen atom, an alkyl group, an aryl group, an alkoxy group, or an aryloxy group, even more preferably a hydrogen atom, a halogen atom, an alkyl group, or an aryl group, and particularly preferably a hydrogen atom.

[0207] From the viewpoints of color formability and visibility of exposed portions, it is preferable that at least one of Y_1 or Y_2 in Formula (Le-1) to Formula (Le-3) be C, and it is more preferable that both of Y_1 and Y_2 be C.

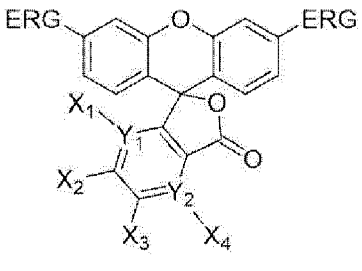
[0208] From the viewpoints of color formability and visibility of exposed portions, Ra_1 in Formula (Le-1) to Formula (Le-3) is preferably an alkyl group or an alkoxy group, more preferably an alkoxy group, and particularly preferably a methoxy group.

[0209] From the viewpoints of color formability and visibility of exposed portions, Rb_1 to Rb_4 in Formula (Le-1) to Formula (Le-3) each independently are preferably a hydrogen atom or an alkyl group, more preferably an alkyl group, and particularly preferably a methyl group.

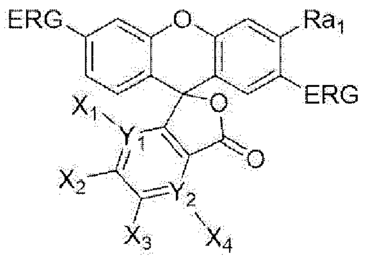
[0210] In addition, from the viewpoints of color formability and visibility of exposed portions, the leuco dye having a phthalide structure or a fluoran structure is more preferably a compound represented by any of Formula (Le-4) to Formula (Le-6), and even more preferably a compound represented by Formula (Le-5).



(Le - 4)



(Le - 5)

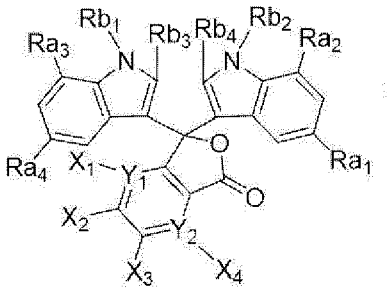


(Le - 6)

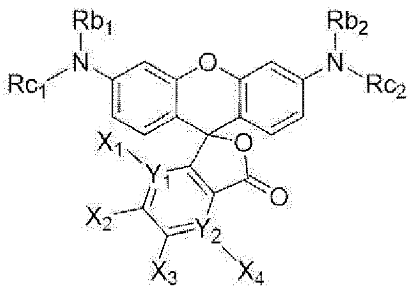
[0211] In Formula (Le-4) to Formula (Le-6), ERG's each independently represent an electron-donating group, X_1 to X_4 each independently represent a hydrogen atom, a halogen atom, or a dialkylanilino group, Y_1 and Y_2 each independently represent C or N, X_1 does not exist in a case where Y_1 is N, X_4 does not exist in a case where Y_2 is N, Ra_1 represents a hydrogen atom, an alkyl group, or an alkoxy group, and Rb_1 to Rb_4 each independently represent a hydrogen atom, an alkyl group, an aryl group, or a heteroaryl group.

[0212] ERG, X_1 to X_4, Y_1, Y_2, Ra_1, and Rb_1 to Rb_4 in Formula (Le-4) to Formula (Le-6) have the same definitions as ERG, X_1 to X_4, Y_1, Y_2, Ra_1, and Rb_1 to Rb_4 in Formula (Le-1) to Formula (Le-3) respectively, and preferred aspects thereof are also the same.

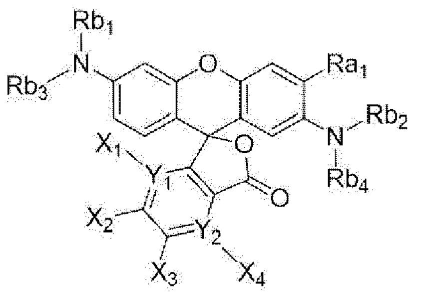
[0213] Furthermore, from the viewpoints of color formability and visibility of exposed portions, the leuco dye having a phthalide structure or a fluoran structure is even more preferably a compound represented by any of Formula (Le-7) to Formula (Le-9), and particularly preferably a compound represented by Formula (Le-8).



(Le - 7)



(Le - 8)



(Le - 9)

[0214] In Formula (Le-7) to Formula (Le-9), X_1 to X_4 each independently represent a hydrogen atom, a halogen atom, or a dialkylanilino group, Y_1 and Y_2 each independently represent C or N, X_1 does not exist in a case where Y_1 is N, X_4 does not exist in a case where Y_2 is N, Ra_1 to Ra_4 each independently represent a hydrogen atom, an alkyl group, or an alkoxy group, Rb_1 to Rb_4 each independently represent a hydrogen atom, an alkyl group, an aryl group, or a heteroaryl group, and Rc_1 and Rc_2 each independently represent an aryl group or a heteroaryl group.

[0215] X_1 to X_4, Y_1, and Y_2 in Formula (Le-7) to Formula (Le-9) have the same definition as X_1 to X_4, Y_1, and Y_2 in Formula (Le-1) to Formula (Le-3) respectively, and preferred aspects thereof are also the same.

[0216] From the viewpoints of color formability and visibility of exposed portions, Ra_1 to Ra_4 in Formula (Le-7) or Formula (Le-9) each independently are preferably an alkyl group or an alkoxy group, more preferably an alkoxy group, and particularly preferably represent a methoxy group.

[0217] From the viewpoints of color formability and visibility of exposed portions, Rb_1 to Rb_4 in Formula (Le-7) to Formula (Le-9) each independently are preferably a hydrogen atom, an alkyl group, or an aryl group substituted with an alkoxy group, more preferably an alkyl group, and particularly preferably a methyl group.

[0218] From the viewpoints of color formability and visibility of exposed portions, Rc_1 and R_{c2} in Formula (Le-8) each independently are preferably a phenyl group or an alkylphenyl group, and more preferably a phenyl group.

[0219] From the viewpoints of color formability and visibility of exposed portions, Rc_1 and R_{c2} in Formula (Le-8) each independently are preferably an aryl group having a substituent on at least one ortho position or a heteroaryl group having a substituent on at least one ortho position, more preferably an aryl group having a substituent on at least one ortho position, even more preferably a phenyl group having a substituent on at least one ortho position, and particularly preferably a phenyl group having a substituent on at least one ortho position and having an electron-donating group at the para position. Examples of the substituent in Rc_1 and Rc_2 include substituents that will be described later.

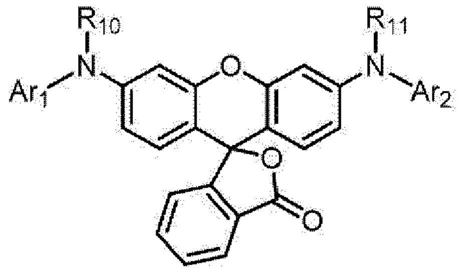
[0220] In Formula (Le-8), from the viewpoints of color formability and visibility of exposed portions, it is preferable that X_1 to X_4 are a hydrogen atom, and Y_1 and Y_2 are C.

[0221] Furthermore, from the viewpoints of color formability and visibility of exposed portions, in Formula (Le-8), Rb_1 and Rb_2 each independently are preferably an alkyl group or an aryl group substituted with an alkoxy group.

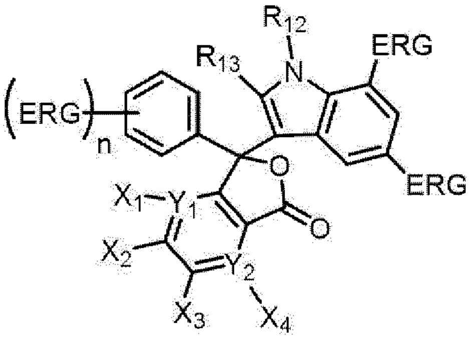
[0222] Moreover, from the viewpoints of color formability and visibility of exposed portions, in Formula (Le-8), Rb_1 and Rb_2 each independently are preferably an aryl group or a heteroaryl group, more preferably an aryl group, even more preferably an aryl group having an electron-donating group, and particularly preferably a phenyl group having an electron-donating group at the para position.

[0223] From the viewpoints of color formability and visibility of exposed portions, the electron-donating group in Rb_1, Rb_2, Rc_1, and Rc_2 is preferably an amino group, an alkylamino group, an arylamino group, a heteroarylamino group, a dialkylamino group, a monoalkyl monoarylamino group, a monoalkyl monoheteroarylamino group, a diarylamino group, a diheteroarylamino group, a monoaryl monoheteroarylamino group, an alkoxy group, an aryloxy group, a heteroaryloxy group, or an alkyl group, more preferably an alkoxy group, an aryloxy group, a heteroaryloxy group, or an alkyl group, and particularly preferably an alkoxy group.

[0224] From the viewpoints of color formability and visibility of exposed portions, the acid color forming agent preferably includes a compound represented by Formula (3a) or Formula (3b), and more preferably includes a compound represented by Formula (3a).



(3a)



(3b)

[0225] In Formula (3a), Ar_1 and Ar_2 each independently represent an aryl group or a heteroaryl group, and R_{10} and R_{11} each independently represent a hydrogen atom, an alkyl group, an aryl group, or a heteroaryl group.

[0226] In Formula (3b), ERG's each independently represent an electron-donating group, n represents an integer of 1 to 5, X_1 to X_4 each independently represent a hydrogen atom, a halogen atom, or a monovalent organic group, Y_1 and Y_2 each independently represent C or N, X_1 does not exist in a case where Y_1 is N, X_4 does not exist in a case where Y_2 is N, and R_{12} and R_{13} each independently represent a hydrogen atom, an alkyl group, an aryl group, or a heteroaryl group.

[0227] R_{10} and R_{11} in Formula (3a) have the same definition as Rb_1 and Rb_2 in Formula (Le-7) to Formula (Le-9) respectively, and preferred aspects thereof are also the same.

[0228] Ar_1 and Ar_2 in Formula (3a) have the same definition as Rc_1 and R_{c2} in Formula (Le-7) to Formula (Le-9) respectively, and preferred aspects thereof are also the same.

[0229] ERG, X_1 to X_4, Y_1, and Y_2 in Formula (3b) have the same definition as ERG, X_1 to X_4, Y_1, and Y_2 in Formula (Le-1) to Formula (Le-3) respectively, and preferred aspects thereof are also the same.

[0230] R_{12} and R_{13} in Formula (3b) have the same definition as Rb_2 and Rb_4 in Formula (Le-1) respectively, and preferred aspects thereof are also the same.

[0231] n in Formula (3b) is preferably an integer of 1 to 3, and more preferably 1 or 2.

[0232] The alkyl group in Formula (Le-1) to Formula (Le-9), Formula (3a), or Formula (3b) may be linear or branched, or may have a ring structure.

[0233] The number of carbon atoms in the alkyl group in Formula (Le-1) to Formula (Le-9), Formula (3a), or Formula (3b) is preferably 1 to 20, more preferably 1 to 8, even more preferably 1 to 4, and particularly preferably 1 or 2.

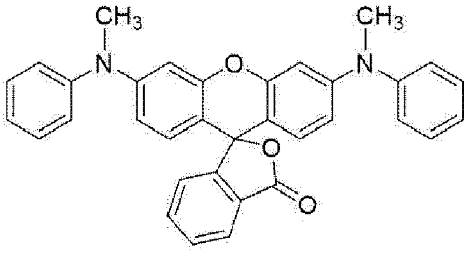
[0234] The number of carbon atoms in the aryl group in Formula (Le-1) to Formula (Le-9), Formula (3a), or Formula (3b) is preferably 6 to 20, more preferably 6 to 10, and particularly preferably 6 to 8.

[0235] Specific examples of the aryl group in Formula (Le-1) to Formula (Le-9), Formula (3a), or Formula (3b) include a phenyl group, a naphthyl group, an anthracenyl group, a phenanthrenyl group, and the like, which may have a substituent.

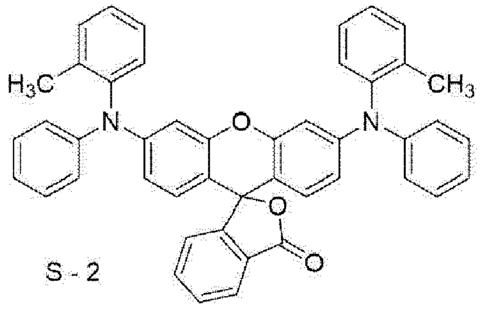
[0236] Specific examples of the heteroaryl group in Formula (Le-1) to Formula (Le-9), Formula (3a), or Formula (3b) include a furyl group, a pyridyl group, a pyrimidyl group, a pyrazole group, a thiophenyl group, and the like, which may have a substituent.

[0237] Each of the groups in Formula (Le-1) to Formula (Le-9), Formula (3a), or Formula (3b), such as a monovalent organic group, an alkyl group, an aryl group, a heteroaryl group, a dialkylanilino group, an alkylamino group, and an alkoxy group, may have a substituent. Examples of the substituent include an alkyl group, an aryl group, a heteroaryl group, a halogen atom, an amino group, an alkylamino group, an arylamino group, a heteroarylamino group, a dialkylamino group, a monoalkyl monoarylamino group, a monoalkyl monoheteroarylamino group, a diarylamino group, a diheteroarylamino group, a monoaryl monoheteroarylamino group, a hydroxy group, an alkoxy group, an aryloxy group, a heteroaryloxy group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a heteroaryloxycarbonyl group, a cyano group, and the like. In addition, these substituents may be further substituted with these substituents.

[0238] Examples of the acid color forming agent to be suitably used include the following compounds. Me represents a methyl group, Et represents an ethyl group, Oct represents an octyl group, and Ph represents a phenyl group.



S - 1



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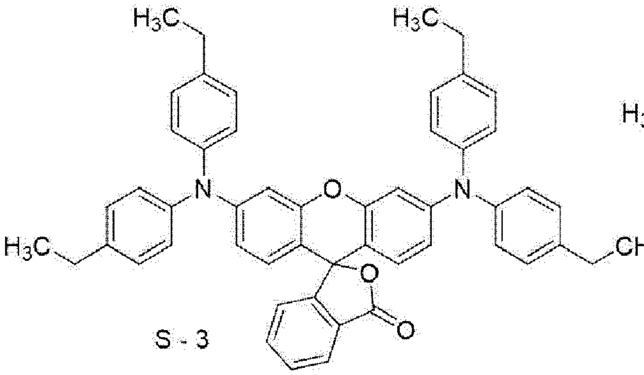

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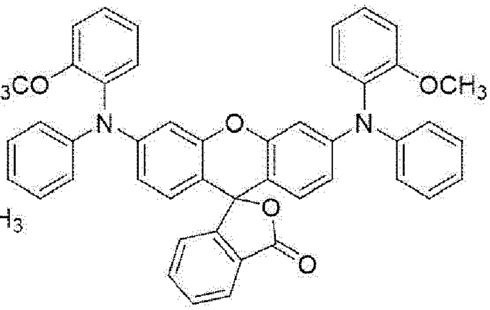

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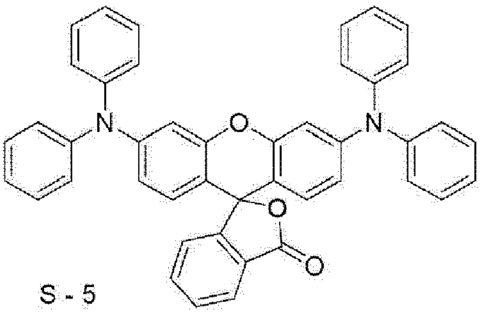

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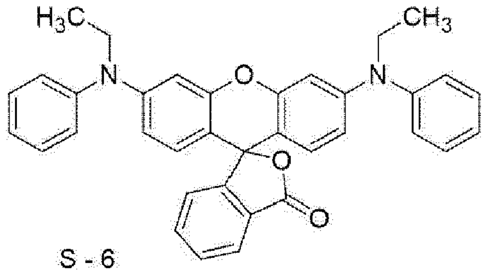

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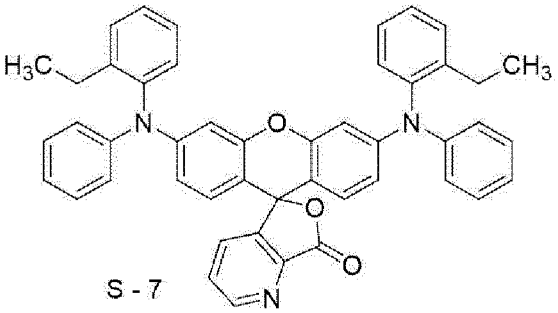

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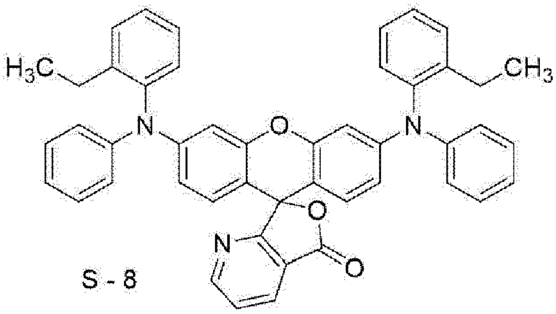

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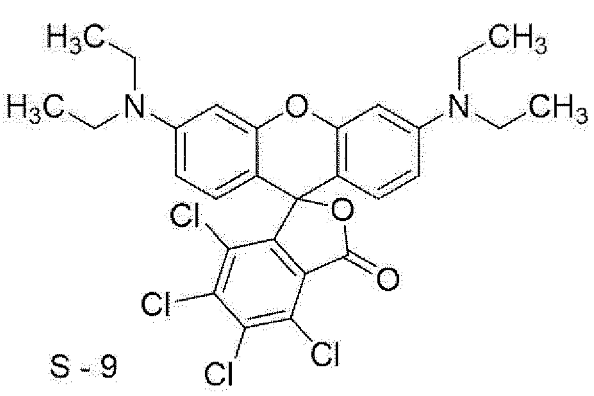

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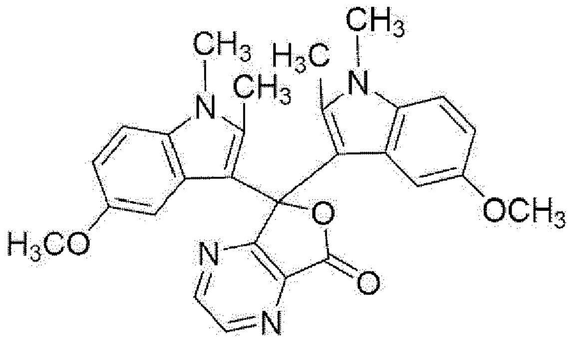

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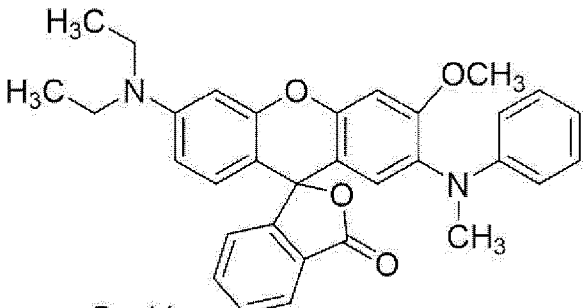

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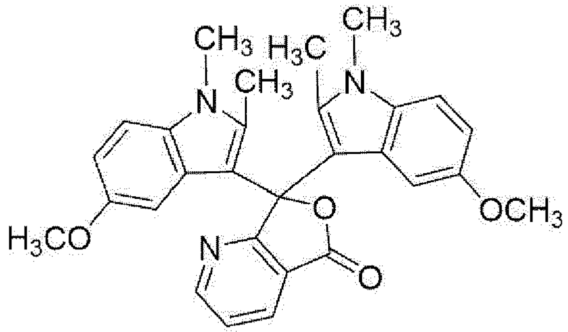

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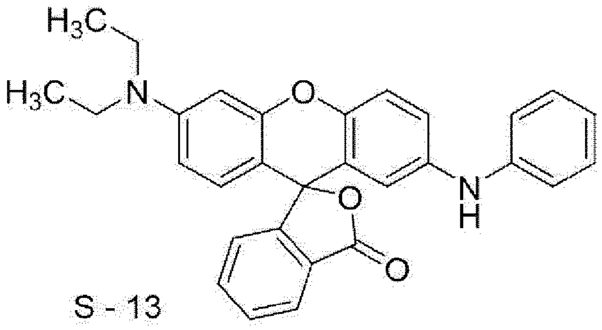

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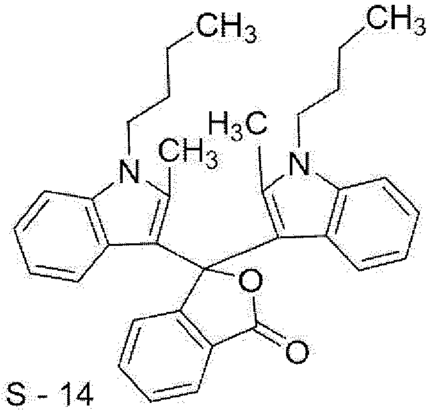

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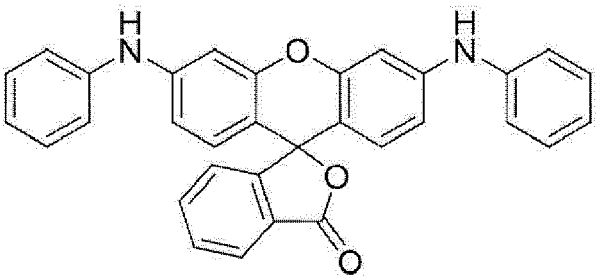

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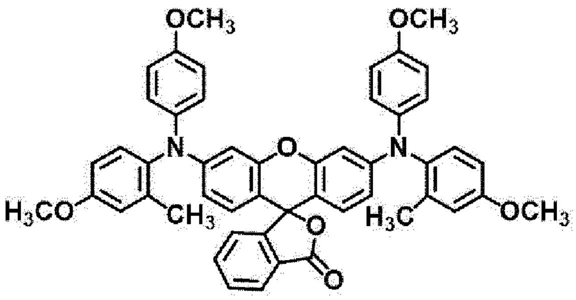

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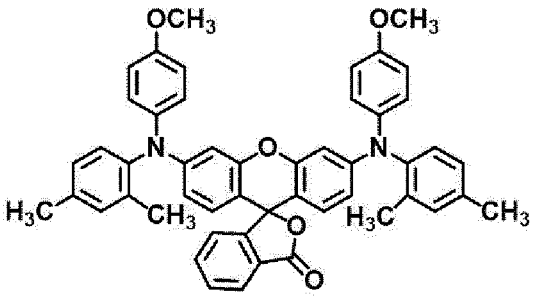

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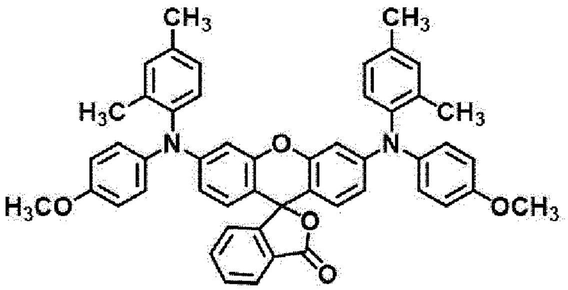

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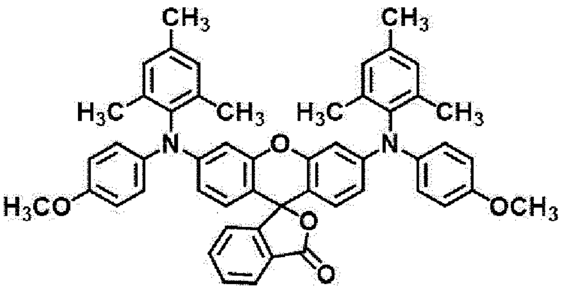

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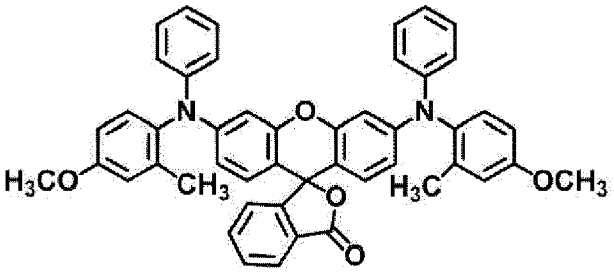

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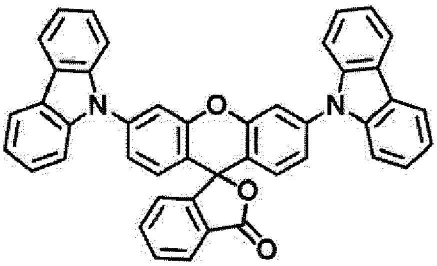

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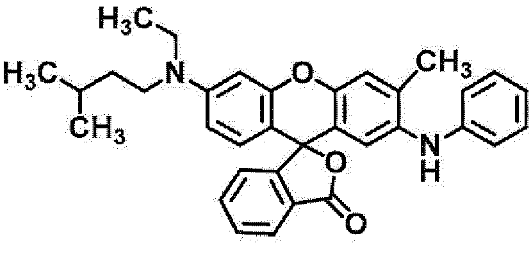

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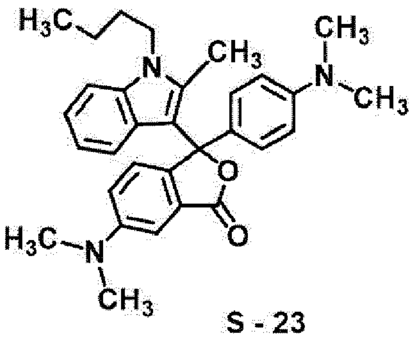

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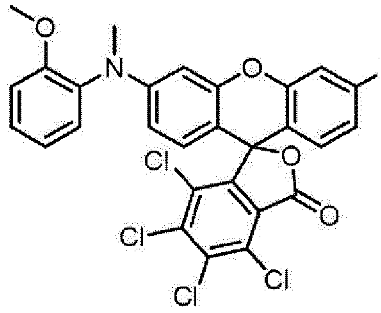

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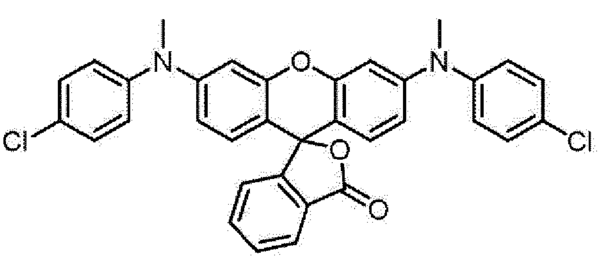

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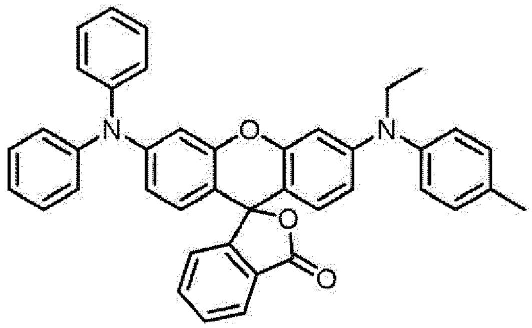

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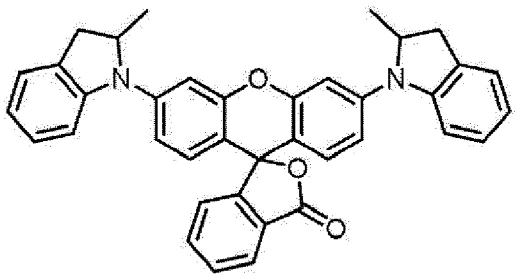

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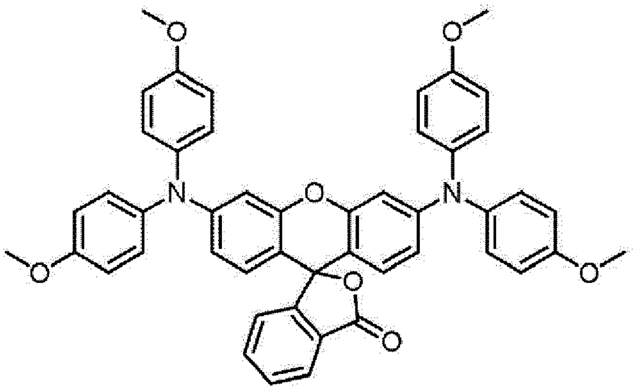

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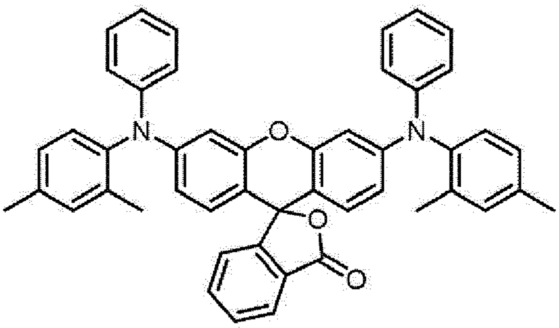

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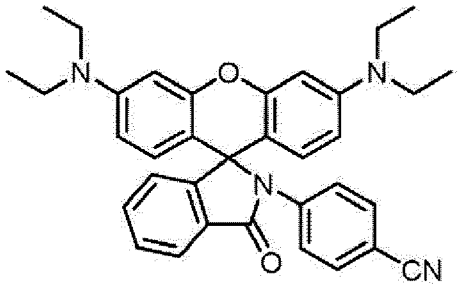

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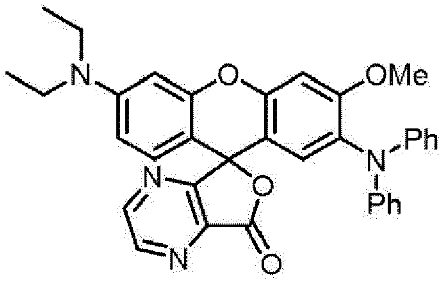

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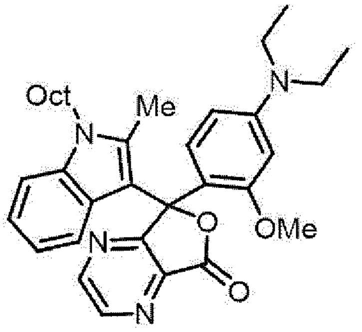

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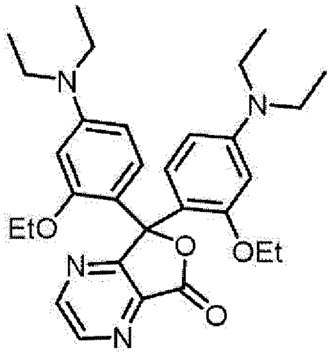

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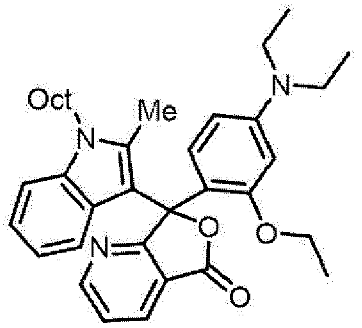

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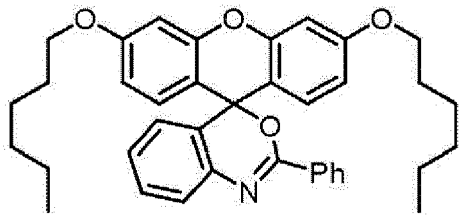


S - 35

[0239] As the acid color forming agent, a commercially available product can be used, and examples thereof include ETAC, RED500, RED520, CVL, S-205, BLACK305, BLACK400, BLACK100, BLACK500, H-7001, GREEN300, NIRBLACK78, BLUE220, H-3035, BLUE203, ATP, H-1046, and H-2114 (all manufactured by Fukui Yamada Chemical Co., Ltd.), ORANGE-DCF, Vermilion-DCF, PINK-DCF, RED-DCF, BLMB, CVL, GREEN-DCF, and TH-107 (all manufactured by HODOGAYA CHEMICAL CO.,LTD.), ODB, ODB-2, ODB-4, ODB-250, ODB-BlackXV, Blue-63, Blue-502, GN-169, GN-2, Green-118, Red-40, and Red-8 (all manufactured by Yamamoto Chemicals Inc.), and Crystal Violet Lactone (manufactured by Tokyo Chemical Industry Co., Ltd.), and the like. Among these commercially available products, ETAC, S-205, BLACK305, BLACK400, BLACK100, BLACK500, H-7001, GREEN300, NIRBLACK78, H-3035, ATP, H-1046, H-2114, GREEN-DCF, Blue-63, GN-169, and crystal violet lactone are preferable because these form a film having excellent visible light absorbance.

[0240] From the viewpoint of visibility, a molar absorption coefficient ε of a color forming substance generated from the acid color forming agent is preferably 35,000 or more, more preferably 35,000 or more and 200,000 or less, and particularly preferably 50,000 or more and 150,000 or less.

[0241] In the present disclosure, the molar absorption coefficient ε of the color forming substance generated from the acid color forming agent is measured by the following method.

[0242] 0.04 mmol of the acid color forming agent to be measured is accurately weighed and put in a 100 mL volumetric flask.

[0243] About 90 mL of acetic acid is added thereto. After it is visually confirmed that the measurement sample has completely dissolved, acetic acid is added thereto such that the volume increases up to 100 mL, thereby preparing a dye solution A.

[0244] About 80 mL of acetic acid is added to another 100 mL volumetric flask, then 5 mL of deionized water and 5 mL of the dye solution A are added thereto by using a 5 mL transfer pipette, and the solution is gently shaken to mix.

[0245] After it is visually confirmed that the solution has no precipitate of the acid color forming agent, acetic acid is added thereto such that the volume increases up to 100 mL, thereby preparing a dye solution B. In the dye solution B, the concentration of the acid color forming agent is 0.02 mmol/L.

[0246] A measurement cell (quartz glass, optical path width: 10 mm) is filled with the dye solution B, and the solution is measured using an ultraviolet-visible spectrophotometer (UV-1800, manufactured by Shimadzu Corporation.).

[0247] As a blank, a solution of water:acetic acid = 5:95 is used.

[0248] From the obtained spectrum, the maximal absorption wavelength in the visible light region (380 nm to 750 nm) is read. From the absorbance at the wavelength, the molar absorption coefficient ε is calculated.

[0249] From the viewpoint of visibility, a ring-opening rate of the acid color forming agent calculated by the following equation is preferably 15% or more and 100% or less, more preferably 40% or more and 99% or less, even more preferably 60% or more and 99% or less, particularly preferably 75% or more and 99% or less, and most preferably 85% or more and 99% or less.

$$\text{Ring-opening rate} = \text{a molar absorption coefficient in a case where 1 molar equivalent of an acid is added to the acid color forming agent/a molar absorption coefficient } \varepsilon \text{ of a color forming substance generated from the acid color forming agent} \times 100.$$

[0250] From the viewpoint of visibility, in the visible light region (380 nm to 750 nm), the maximum absorption wavelength λmax of the color forming substance generated from the acid color forming agent is preferably 500 nm to 650 nm, more preferably 520 nm to 600 nm, even more preferably 530 nm to 580 nm, and particularly preferably 540 nm to 570 nm.

[0251] In the present disclosure, the ring-opening rate and λmax are measured by the following methods.

-Preparation of dye solution C-

[0252] 0.1 mmol of the acid color forming agent is accurately weighed and put in a 50 mL volumetric flask.

[0253] About 40 mL of acetonitrile is added thereto. After it is visually confirmed that the measurement sample has completely dissolved, acetonitrile is added thereto such that the volume increases up to 50 mL, thereby preparing a dye solution C.

-Preparation of acid solution D-

[0254] 0.2 mmol of 10-camphorsulfonic acid (CSA) is added to a 100 mL volumetric flask, and about 80 mL of acetonitrile is added thereto. After it is confirmed that CSA has completely dissolved, acetonitrile is added thereto such that the volume increases up to 100 mL, thereby preparing an acid solution D.

-Preparation of measurement solution E-

[0255] 5 mL of deionized water is added to a 100 mL volumetric flask by using a transfer pipette, and 80 mL of acetonitrile is added thereto. 1 mL of the dye solution C and 1 mL of the acid solution D are added thereto, and acetonitrile is added thereto such that the volume increases up to 100 mL, thereby preparing a measurement solution E.

[0256] In the measurement solution E, the concentration of the acid color forming agent including the generated color forming substance is 0.02 mmol/L.

[0257] A measurement cell (quartz glass, optical path width: 10 mm) is filled with the measurement solution E, and the solution is measured using an ultraviolet-visible spectrophotometer (UV-1800, manufactured by Shimadzu Corporation.).

[0258] As a blank, a solution of water: acetonitrile = 5:95 is used.

[0259] From the obtained spectrum, the maximal absorption wavelength λmax in the visible light region (380 nm to

750 nm) is read. From the absorbance at the wavelength, the molar absorption coefficient ε is calculated.

[0260] The ring-opening rate is calculated according to the equation described above.

[0261] From the viewpoint of visibility, in the acid color forming agent, it is preferable that a molar absorption coefficient ε of the color forming substance generated from the acid color forming agent is 35,000 or more, a ring-opening rate of the acid color forming agent is 40 mol% to 99 mol%, and a maximum absorption wavelength of the color forming substance generated from the acid color forming agent is 500 nm to 650 nm in a wavelength range of 380 nm to 750 nm.

[0262] Each of these acid color forming agents may be used alone. Alternatively, two or more components can be used in combination.

[0263] The content of the acid color forming agent with respect to the total mass of the image-recording layer is preferably 0.5% by mass to 10% by mass and more preferably 1% by mass to 5% by mass.

[Polymerizable compound]

[0264] It is preferable that the image-recording layer contain a polymerizable compound.

[0265] In the present disclosure, the polymerizable compound refers to a compound having a polymerizable group.

[0266] The polymerizable group is not particularly limited, may be a known polymerizable group, and is preferably an ethylenically unsaturated group. The polymerizable group may be a radically polymerizable group or a cationically polymerizable group, and is preferably a radically polymerizable group.

[0267] Examples of the radically polymerizable group include a (meth)acryloyl group, an allyl group, a vinylphenyl group, a vinyl group, and the like. From the viewpoint of reactivity, a (meth)acryloyl group is preferable.

[0268] The molecular weight of the polymerizable compound (weight-average molecular weight in a case where the polymerizable compound has molecular weight distribution) is preferably 50 or more and less than 2,500.

[0269] The polymerizable compound used in the present disclosure may be, for example, a radically polymerizable compound or a cationically polymerizable compound, and is preferably an addition polymerizable compound having at least one ethylenically unsaturated bond (ethylenically unsaturated compound).

[0270] The ethylenically unsaturated compound is preferably a compound having at least one terminal ethylenically unsaturated bond, and more preferably a compound having two or more terminal ethylenically unsaturated bonds. The chemical form of the polymerizable compound is, for example, a monomer, a prepolymer which is in other words a dimer, a trimer, or an oligomer, a mixture of these, or the like.

[0271] Particularly, from the viewpoint of printing durability, the polymerizable compound preferably includes a polymerizable compound having functionalities of 3 or more, more preferably includes a polymerizable compound having functionalities of 7 or more, and even more preferably includes a polymerizable compound having functionalities of 10 or more. Particularly, from the viewpoint of printing durability of the lithographic printing plate to be obtained, the polymerizable compound preferably includes an ethylenically unsaturated compound having functionalities of 3 or more (preferably having functionalities of 7 or more and more preferably having functionalities of 10 or more), and more preferably includes a (meth)acrylate compound having functionalities of 3 or more (preferably having functionalities of 7 or more and more preferably having functionalities of 10 or more).

[0272] From the viewpoints of on-press developability and contamination suppressiveness, the polymerizable compound preferably includes a polymerizable compound having functionalities of 2 or less, more preferably includes a difunctional polymerizable compound, and particularly preferably includes a difunctional (meth)acrylate compound.

[0273] From the viewpoints of printing durability, on-press developability, and contamination suppressiveness, the content of the polymerizable compound having functionalities of 2 or less (preferably a difunctional polymerizable compound) with respect to the total mass of polymerizable compounds in the image-recording layer is preferably 5% by mass to 100% by mass, more preferably 10% by mass to 100% by mass, and even more preferably 15% by mass to 100% by mass.

-Oligomer-

[0274] As the polymerizable compound contained in the image-recording layer, a polymerizable compound which is an oligomer (hereinafter, also simply called "oligomer") is preferable.

[0275] In the present disclosure, an oligomer represents a polymerizable compound which has a molecular weight (weight-average molecular weight in a case where the compound has molecular weight distribution) of 600 or more and 40,000 or less and contains at least one polymerizable group.

[0276] From the viewpoints of excellent chemical resistance and excellent printing durability, the molecular weight of the oligomer is preferably 1,000 or more and 25,000 or less.

[0277] In addition, from the viewpoint of improving printing durability, the number of polymerizable groups in one molecule of the oligomer is preferably 2 or more, more preferably 3 or more, even more preferably 6 or more, and particularly preferably 10 or more.

[0278] The upper limit of the number of polymerizable groups in the oligomer is not particularly limited, but the number of polymerizable groups is preferably 20 or less.

[0279] From the viewpoints of printing durability and on-press developability, an oligomer having 7 or more polymerizable groups and a molecular weight of 1,000 or more and 40,000 or less is preferable, and an oligomer having 7 or more and 20 or less polymerizable groups and a molecular weight of 1,000 or more and 25,000 or less is more preferable.

[0280] The image-recording layer may contain a polymer component which may be generated in the process of manufacturing the oligomer.

[0281] From the viewpoints of printing durability, visibility, and on-press developability, the oligomer preferably has at least one selected from the group consisting of a compound having a urethane bond, a compound having an ester bond, and a compound having an epoxy residue, and more preferably has a compound having a urethane bond.

[0282] In the present disclosure, an epoxy residue refers to a structure formed of an epoxy group and for example, means a structure similar to a structure obtained by the reaction between an acid group (carboxylic acid group or the like) and an epoxy group.

[0283] As the compound having a urethane bond, those described in WO2020/262692A can be suitably used.

[0284] As the compound having a urethane bond, a compound may also be used which is prepared by obtaining polyurethane by a reaction between a polyisocyanate compound and a polyol compound and introducing a polymerizable group into the obtained polyurethane by a polymer reaction.

[0285] For example, the compound having a urethane bond may be obtained by reacting a polyol compound having an acid group with a polyisocyanate compound to obtain a polyurethane oligomer and reacting the obtained polyurethane oligomer with a compound having an epoxy group and a polymerizable group.

[0286] The number of polymerizable groups in the compound having an ester bond, which is an example of oligomer, is preferably 3 or more, and more preferably 6 or more.

[0287] As the compound having an epoxy residue, which is an example of oligomer, a compound containing a hydroxy group is preferable.

[0288] The number of polymerizable groups in the compound having an epoxy residue is preferably 2 to 6, and more preferably 2 or 3.

[0289] The compound having an epoxy residue can be obtained, for example, by reacting a compound having an epoxy group with an acrylic acid.

[0290] As the oligomer, commercially available products may also be used. Examples thereof include UA-510H, UA-306H, UA-306I, and UA-306T (all manufactured by KYOEISHA CHEMICAL Co., Ltd.), UV-1700B, UV-6300B, and UV7620EA (all manufactured by The Nippon Synthetic Chemical Industry Co., Ltd.), U-15HA (manufactured by SHIN-NAKAMURA CHEMICAL Co., Ltd.), EBECRYL450, EBECRYL657, EBECRYL885, EBECRYL800, EBECRYL3416, and EBECRYL860 (all manufactured by DAICEL-ALLNEX LTD.), and the like. However, the oligomer is not limited to these.

[0291] From the viewpoints of improving chemical resistance and printing durability and further suppressing the residues of on-press development, the content of the oligomer with respect to the total mass of polymerizable compounds in the image-recording layer is preferably 30% by mass to 100% by mass, more preferably 50% by mass to 100% by mass, and even more preferably 80% by mass to 100% by mass.

-Low-molecular-weight polymerizable compound-

[0292] The polymerizable compound may further include a polymerizable compound other than the oligomer described above.

[0293] From the viewpoint of chemical resistance, the polymerizable compound other than the oligomer is preferably a low-molecular-weight polymerizable compound. The low-molecular-weight polymerizable compound may take a chemical form such as a monomer, a dimer, a trimer, or a mixture of these.

[0294] From the viewpoint of chemical resistance, the low-molecular-weight polymerizable compound is preferably at least one polymerizable compound selected from the group consisting of a polymerizable compound having three or more ethylenically unsaturated groups and a polymerizable compound having an isocyanuric ring structure.

[0295] In the present disclosure, a low-molecular-weight polymerizable compound refers to a polymerizable compound having a molecular weight (weight-average molecular weight in a case where the compound has molecular weight distribution) of 50 or more and less than 800.

[0296] From the viewpoints of excellent chemical resistance, excellent printing durability, and excellently suppressing the residues of on-press development, the molecular weight of the low-molecular-weight polymerizable compound is preferably 100 or more and less than 800, more preferably 300 or more and less than 800, and even more preferably 400 or more and less than 800.

[0297] In a case where the polymerizable compound includes a low-molecular-weight polymerizable compound as the polymerizable compound other than the oligomer, from the viewpoints of chemical resistance and printing durability and suppressing the residues of on-press development, the ratio (oligomer/low-molecular-weight polymerizable compound) of the oligomer to the low-molecular-weight polymerizable compound (total amount in a case where the polymerizable compound includes two or more low-molecular-weight polymerizable compounds) based on mass is preferably 10/1 to 1/10, more preferably 10/1 to 3/7, and even more preferably 10/1 to 7/3.

[0298] As the low-molecular-weight polymerizable compound, the polymerizable compounds described in paragraphs "0082" to "0086" of WO2019/013268A can also be suitably used.

[0299] The details of how to use the polymerizable compound, such as the structure of the compound, whether the compound is used alone or used in combination with other compounds, and the amount of the compound to be added, can be optionally set.

[0300] Particularly, from the viewpoint of printing durability, the image-recording layer preferably contains two or more polymerizable compounds.

[0301] The content of the polymerizable compound (total content of polymerizable compounds in a case where the image-recording layer contains two or more polymerizable compounds) with respect to the total mass of the image-recording layer is preferably 5% by mass to 75% by mass, more preferably 10% by mass to 70% by mass, and even more preferably 15% by mass to 60% by mass.

[Particles]

[0302] From the viewpoint of printing durability, the image-recording layer preferably contains particles.

[0303] The particles may be organic particles or inorganic particles. From the viewpoint of printing durability, the image-recording layer preferably contains organic particles, and more preferably contains polymer particles.

[0304] As inorganic particles, known inorganic particles can be used, and metal oxide particles such as silica particles and titania particles can be suitably used.

[0305] The polymer particles are preferably selected from the group consisting of thermoplastic resin particles, thermal reactive resin particles, polymer particles having a polymerizable group, microcapsules encapsulating a hydrophobic compound, and a microgel (crosslinked polymer particles). Among these, polymer particles having a polymerizable group or a microgel are preferable. In a particularly preferred embodiment, the polymer particles have at least one ethylenically unsaturated group. The presence of such polymer particles brings about effects of improving the printing durability of an exposed portion and improving the on-press developability of a non-exposed portion.

[0306] From the viewpoints of printing durability and on-press developability, the polymer particles are preferably thermoplastic resin particles.

[0307] The thermoplastic resin particles are preferably the thermoplastic polymer particles described in Research Disclosure No. 33303 published in January 1992, JP1997-123387A (JP-H09-123387A), JP1997-131850A (JP-H09-131850A), JP1997-171249A (JP-H09-171249A), JP1997-171250A (JP-H09-171250A), EP931647B, and the like.

[0308] Specific examples of polymers constituting the thermoplastic resin particles include homopolymers or copolymers of monomers of ethylene, styrene, vinyl chloride, methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, vinylidene chloride, acrylonitrile, vinylcarbazole, acrylate or methacrylate having a polyalkylene structure, and the like and mixtures of these. Preferred examples thereof can include polystyrene, copolymers having styrene and acrylonitrile, or polymethyl methacrylate. The average particle diameter of the thermoplastic resin particle is preferably 0.01 μm to 3.0 μm.

[0309] Examples of the thermal reactive resin particles include polymer particles having a thermal reactive group. The thermal reactive polymer particles form a hydrophobilized region through crosslinking by a thermal reaction and the accompanying change in functional groups.

[0310] The thermal reactive group in the polymer particles having a thermal reactive group may be a functional group that causes any reaction as long as chemical bonds are formed, and is preferably a polymerizable group. Preferred examples thereof include an ethylenically unsaturated group that causes a radical polymerization reaction (for example, an acryloyl group, a methacryloyl group, a vinyl group, an allyl groups, and the like), a cationically polymerizable group (for example, a vinyl group, a vinyloxy group, an epoxy group, an oxetanyl group, and the like), an isocyanato group or a blocked isocyanato group that causes an addition reaction, an epoxy group, a vinyloxy group, an active hydrogen atom-containing functional group that is a reaction partner thereof (for example, an amino group, a hydroxy group, a carboxy group, and the like), a carboxy group that causes a condensation reaction, a hydroxy group or an amino group that is a reaction partner of the carboxy group, an acid anhydride that causes a ring-opening addition reaction, an amino group or a hydroxy group which is a reaction partner of the acid anhydride, and the like.

[0311] Examples of the microcapsules include microcapsules encapsulating at least some of the constituent components of the image-recording layer as described in JP2001-277740A and JP2001-277742A. The constituent components of the image-recording layer can also be contained in the exterior of the microcapsules. In a preferred aspect, the image-recording layer containing microcapsules is constituted such that hydrophobic constituent components are encapsulated in the microcapsules and hydrophilic constituent components are contained in the exterior of the microcapsules.

[0312] The microgel (crosslinked polymer particles) can contain some of the constituent components of the image-recording layer, in at least one of the surface or the interior of the microgel. From the viewpoints of sensitivity of the lithographic printing plate precursor to be obtained and printing durability of the lithographic printing plate to be obtained, a reactive microgel having a radically polymerizable group on the surface thereof is particularly preferable.

[0313] In order to encapsulate the constituent components of the image-recording layer in microcapsules or microgel, known methods can be used.

[0314] From the viewpoints of printing durability, antifouling property, and storage stability of the lithographic printing plate to be obtained, the polymer particles are preferably polymer particle which are obtained by a reaction of a polyvalent isocyanate compound that is an adduct of a polyhydric phenol compound having two or more hydroxy groups in a molecule and isophorone diisocyanate with a compound having active hydrogen.

[0315] The polyhydric phenol compound is preferably a compound having a plurality of benzene rings having a phenolic hydroxy group.

[0316] The compound having active hydrogen is preferably a polyol compound or a polyamine compound, more preferably a polyol compound, and even more preferably at least one compound selected from the group consisting of propylene glycol, glycerin, and trimethylolpropane.

[0317] Preferred examples of the resin particles obtained by the reaction of a polyvalent isocyanate compound that is an adduct of a polyhydric phenol compound having two or more hydroxy groups in a molecule and isophorone diisocyanate, with a compound having active hydrogen include the polymer particles described in paragraphs "0032" to "0095" of JP2012-206495A.

[0318] Furthermore, from the viewpoints of printing durability and solvent resistance of the lithographic printing plate to be obtained, the polymer particles preferably include polymer particles containing a polymer having both i: a constitutional unit having a pendant cyano group directly bonded to the hydrophobic main chain and ii: a constitutional unit having a pendant group including a hydrophilic poly(alkylene oxide) segment.

[0319] Preferred examples of the hydrophobic main chain include an acrylic resin chain.

[0320] Preferred examples of the pendant cyano group include $-[CH_2CH(C{\equiv}N)]-$ or $-[CH_2C(CH_3)(C{\equiv}N)]-$.

[0321] In addition, the constitutional unit having the pendant cyano group can be easily derived from an ethylenically unsaturated monomer, for example, acrylonitrile or methacrylonitrile, or a combination of these.

[0322] Furthermore, as an alkylene oxide in the hydrophilic polyalkylene oxide segment, ethylene oxide or a propylene oxide is preferable, and ethylene oxide is more preferable.

[0323] The number of repeating alkylene oxide structures in the hydrophilic polyalkylene oxide segment is preferably 10 to 100, more preferably 25 to 75, and even more preferably 40 to 50.

[0324] Preferred examples of the resin particles including both i: the constitutional unit having the pendant cyano group directly bonded to the hydrophobic main chain and ii: the constitutional unit having the pendant group including the hydrophilic polyalkylene oxide segment include the particles described in paragraphs "0039" to "0068" of JP2008-503365A.

[0325] From the viewpoints of printing durability and on-press developability, the polymer particles preferably have a hydrophilic group.

[0326] The hydrophilic group is not particularly limited as long as it has a hydrophilic structure, and examples thereof include an acid group such as a carboxy group, a hydroxy group, an amino group, a cyano group, a polyalkylene oxide structure, and the like.

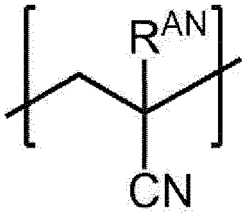
[0327] Among these, from the viewpoints of on-press developability and printing durability, a polyalkylene oxide structure is preferable, and a polyethylene oxide structure, a polypropylene oxide structure, or a polyethylene/propylene oxide structure is more preferable.

[0328] In addition, from the viewpoints of on-press developability and suppressing the residues of development during on-press development, the polyalkylene oxide structure preferably has a polypropylene oxide structure, and more preferably has a polyethylene oxide structure and a polypropylene oxide structure.

[0329] From the viewpoints of printing durability, receptivity, and on-press developability, the hydrophilic group preferably has a constitutional unit having a cyano group, or a group represented by Formula Z, more preferably has a constitutional unit represented by Formula (AN) or a group represented by Formula Z, and particularly preferably has a group represented by Formula Z.

$$*\text{-Q-W-Y} \qquad \text{Formula Z}$$

[0330] In Formula Z, Q represents a divalent linking group, W represents a divalent group having a hydrophilic structure or a divalent group having a hydrophobic structure, and Y represents a monovalent group having a hydrophilic structure or a monovalent group having a hydrophobic structure, either W or Y has a hydrophilic structure, and * represents a bonding site with another structure.



(AN)

[0331] In Formula (AN), R^{AN} represents a hydrogen atom or a methyl group.

[0332] From the viewpoint of printing durability, the polymer contained in the polymer particles preferably has a constitutional unit formed of a compound having a cyano group.

[0333] Generally, it is preferable that a cyano group is introduced as a constitutional unit having a cyano group into a resin by using a compound (monomer) having a cyano group. Examples of the compound having a cyano group include acrylonitrile compounds and suitable examples thereof include (meth)acrylonitrile.

[0334] The constitutional unit having a cyano group is preferably a constitutional unit formed of an acrylonitrile compound, and more preferably a constitutional unit formed of (meth)acrylonitrile, that is, a constitutional unit represented by Formula (AN).

[0335] In a case where the polymer includes a polymer having a constitutional unit having a cyano group, from the viewpoint of printing durability, the content of the constitutional unit having a cyano group which is preferably a constitutional unit represented by Formula (AN) in the polymer having the constitutional unit having a cyano group with respect to the total mass of the polymer having the constitutional unit having a cyano group is preferably 5% by mass to 90% by mass, more preferably 20% by mass to 80% by mass, and particularly preferably 30% by mass to 60% by mass.

[0336] In addition, from the viewpoints of printing durability, receptivity, and on-press developability, the polymer particles preferably include polymer particles having a group represented by Formula Z.

[0337] Q in Formula Z is preferably a divalent linking group having 1 to 20 carbon atoms, and more preferably a divalent linking group having 1 to 10 carbon atoms.

[0338] In addition, Q in Formula Z is preferably an alkylene group, an arylene group, an ester bond, an amide bond, or a group formed by combining two or more of these, and more preferably a phenylene group, an ester bond, or an amide bond.

[0339] The divalent group having a hydrophilic structure represented by W in Formula Z is preferably a polyalkyleneoxy group or a group in which $-CH_2CH_2NR^W-$ is bonded to one terminal of a polyalkyleneoxy group. R^W represents a hydrogen atom or an alkyl group.

[0340] The divalent group having a hydrophobic structure represented by W in Formula Z is preferably $-R^{WA}-$, $-O-R^{WA}-O-$, $-R^WN-R^{WA}-NR^W-$, $-OC(=O)-R^{WA}-O-$, or $-OC(=O)-R^{WA}-O-$. R^{WA}'s each independently represent a linear, branched, or cyclic alkylene group having 6 to 120 carbon atoms, a haloalkylene group having 6 to 120 carbon atoms, an arylene group having 6 to 120 carbon atoms, an alkarylene group having 7 to 120 carbon atoms (divalent group formed by removing one hydrogen atom from an alkylaryl group), or an aralkylene group having 7 to 120 carbon atoms.

[0341] The monovalent group having a hydrophilic structure represented by Y in Formula Z is preferably -OH, -C(=O)OH, a polyalkyleneoxy group having a hydrogen atom or an alkyl group on a terminal, or a group in which $-CH_2CH_2NR^W-$ is bonded to one terminal of a polyalkyleneoxy group having a hydrogen atom or an alkyl group on the other terminal.

[0342] The monovalent group having a hydrophobic structure represented by Y in Formula Z is preferably a linear, branched, or cyclic alkyl group having 6 to 120 carbon atoms, a haloalkyl group having 6 to 120 carbon atoms, an aryl group having 6 to 120 carbon atoms, an alkaryl group (alkylaryl group) having 7 to 120 carbon atoms, an aralkyl group having 7 to 120 carbon atoms, $-OR^{WB}$, $-C(=O)OR^{WB}$, or $-OC(=O)R^{WB}$. R^{WB} represents an alkyl group having 6 to 20 carbon atoms.

[0343] From the viewpoints of printing durability, receptivity, and on-press developability, in the polymer particles having a group represented by formula Z, W is preferably a divalent group having a hydrophilic structure, and it is more preferable that Q is a phenylene group, an ester bond, or an amide bond, W is a polyalkyleneoxy group, and Y is a polyalkyleneoxy group having a hydrogen atom or an alkyl group on a terminal.

[0344] From the viewpoints of printing durability and on-press developability, the polymer particles preferably include polymer particles having a polymerizable group, and more preferably include polymer particles having a polymerizable group on the particle surface.

[0345] Furthermore, from the viewpoint of printing durability, the polymer particles preferably include polymer particles having a hydrophilic group and a polymerizable group.

[0346] The polymerizable group may be a cationically polymerizable group or a radically polymerizable group and, from the viewpoint of reactivity, is preferably a radically polymerizable group.

[0347] The polymerizable group is not particularly limited as long as it is a polymerizable group, but from the viewpoint of reactivity, is preferably an ethylenically unsaturated group, more preferably a vinylphenyl group (styryl group), a (meth)acryloxy group, or a (meth)acrylamide group, and particularly preferably a (meth)acryloxy group.

[0348] In addition, the polymer in the polymer particles having a polymerizable group preferably has a constitutional unit having a polymerizable group.

[0349] The polymerizable group may be introduced into the surface of the polymer particles by a polymer reaction.

[0350] In addition, from the viewpoints of printing durability and on-press developability, the image-recording layer preferably contains, as the polymer particles, addition polymerization-type resin particles having a dispersible group which more preferably includes a group represented by Formula Z.

[0351] From the viewpoints of printing durability, receptivity, on-press developability, and suppressing the residues of development during on-press development, the polymer particles preferably contain a resin having a urea bond.

[0352] Suitable examples of the resin having a urea bond include those described in WO2020/262692A.

[0353] From the viewpoints of printing durability and on-press developability, the image-recording layer preferably contains thermoplastic resin particles.

[0354] The thermoplastic resin contained in the thermoplastic resin particles is not particularly limited, and examples thereof include polyethylene, polystyrene, polyvinyl chloride, polyvinylidene chloride, polymethyl (meth)acrylate, polyethyl (meth)acrylate, polybutyl (meth)acrylate, polyacrylonitrile, polyvinyl acetate, copolymers of these, and the like. The thermoplastic resin may be in the state of latex.

[0355] The thermoplastic resin according to the present disclosure is preferably a resin which melts or softens by heat generated in an exposure step that will be described later and thus forms a part or the entirety of a hydrophobic film forming the image-recording layer.

[0356] From the viewpoints of ink receptivity and printing durability, the thermoplastic resin preferably contains a resin having a constitutional unit formed of an aromatic vinyl compound and a constitutional unit having a cyano group.

[0357] Suitable examples of the resin having a constitutional unit formed of an aromatic vinyl compound and a constitutional unit having a cyano group include those described in WO2020/262692A.

[0358] From the viewpoints of printing durability and on-press developability, the thermoplastic resin contained in the thermoplastic resin particles preferably has a hydrophilic group.

[0359] The hydrophilic group is not particularly limited as long as it has a hydrophilic structure, and examples thereof include an acid group such as a carboxy group, a hydroxy group, an amino group, a cyano group, a polyalkylene oxide structure, and the like.

[0360] From the viewpoints of printing durability and on-press developability, the hydrophilic group is preferably a group having a polyalkylene oxide structure, a group having a polyester structure, or a sulfonic acid group, more preferably a group having a polyalkylene oxide structure or a sulfonic acid group, and even more preferably a group having a polyalkylene oxide structure.

[0361] From the viewpoint of on-press developability, the polyalkylene oxide structure is preferably a polyethylene oxide structure, a polypropylene oxide structure, or a poly(ethylene oxide/propylene oxide) structure.

[0362] In addition, from the viewpoint of on-press developability, among the hydrophilic groups, as a polyalkylene oxide structure, groups having a polypropylene oxide structure are preferable, and groups having a polyethylene oxide structure and a polypropylene oxide structure are more preferable.

[0363] From the viewpoint of on-press developability, the number of alkylene oxide structures in the polyalkylene oxide structure is preferably 2 or more, more preferably 5 or more, even more preferably 5 to 200, and particularly preferably 8 to 150.

[0364] From the viewpoint of on-press developability, the hydrophilic group is preferably a group represented by Formula Z.

[0365] From the viewpoints of printing durability and ink receptivity, the glass transition temperature (Tg) of the thermoplastic resin is preferably 60°C to 150°C, more preferably 80°C to 140°C, and even more preferably 90°C to 130°C.

[0366] In a case where the thermoplastic resin particles contain two or more kinds of thermoplastic resins, the value obtained by the FOX equation that will be described later is referred to as the glass transition temperature of the thermoplastic resin.

[0367] In the present disclosure, the glass transition temperature of a resin can be measured by differential scanning calorimetry (DSC).

[0368] Specifically, the glass transition temperature is measured according to the method described in JIS K 7121 (1987) or JIS K 6240 (2011). As the glass transition temperature in the present specification, an extrapolated glass transition initiation temperature (hereinafter, may be referred to as Tig) is used.

[0369] The method of measuring the glass transition temperature will be described in more detail.

[0370] In a case of determining the glass transition temperature, the device is kept at a temperature approximately 50°C lower than the expected Tg of the resin until the device stabilizes. Then, the resin is heated at a heating rate of 20 °C/min to a temperature approximately 30°C higher than the temperature at which the glass transition ends, and a differential thermal analysis (DTA) curve or a DSC curve is created.

[0371] The extrapolated glass transition initiation temperature (Tig), that is, the glass transition temperature Tg in the present specification is determined as a temperature at an intersection point between a straight line that is obtained by extending the baseline of a low temperature side in the DTA curve or the DSC curve to a high temperature side and a tangent line that is drawn at a point where the slope of the curve of a portion in which the glass transition changes stepwisely is maximum.

[0372] In a case where the thermoplastic resin particles contain two kinds of thermoplastic resins, Tg of the thermoplastic resin particles is determined as follows.

[0373] In a case where Tg1 (K) represents Tg of a first thermoplastic resin, W1 represents the mass ratio of the first thermoplastic resin to the total mass of thermoplastic resin components in the thermoplastic resin particles, Tg2 (K) represents Tg of a second thermoplastic resin, and W2 represents the mass ratio of the second resin to the total mass of thermoplastic resin components in the thermoplastic resin particles, Tg0 (K) of the thermoplastic resin particles can be estimated according to the following FOX equation.

$$\text{FOX expression: } 1/\mathrm{Tg0} = (\mathrm{W1}/\mathrm{Tg1}) + (\mathrm{W2}/\mathrm{Tg2})$$

[0374] In addition, in a case where the thermoplastic resin particles contain three or more kinds of resins or in a case where three or more kinds of thermoplastic resin particles each containing different types of thermoplastic resins are contained in a pretreatment liquid, similarly to the case described above, in a case where Tgn (K) represents Tg of nth resin and Wn represents the mass ratio of the nth resin to the total mass of resin components in the thermoplastic resin particles, Tg0 (K) of the thermoplastic resin particles can be estimated according to the following equation.

$$\text{FOX equation: } 1/\mathrm{Tg0} = (\mathrm{W1}/\mathrm{Tg1}) + (\mathrm{W2}/\mathrm{Tg2}) + (\mathrm{W3}/\mathrm{Tg3}) \cdots + (\mathrm{Wn}/\mathrm{Tgn})$$

[0375] As the differential scanning calorimeter (DSC), for example, EXSTAR 6220 manufactured by SII NanoTechnology Inc. can be used.

[0376] From the viewpoint of printing durability, the arithmetic mean particle diameter of the thermoplastic resin particles is preferably 1 nm or more and 200 nm or less, more preferably 3 nm or more and less than 80 nm, and even more preferably 10 nm or more and 49 nm or less.

[0377] Unless otherwise specified, the arithmetic mean particle diameter of the thermoplastic resin particles in the present disclosure refers to a value measured by a dynamic light scattering method (DLS). The measurement of the arithmetic mean particle diameter of the thermoplastic resin particles by DLS is carried out using Brookhaven BI-90 (manufactured by Brookhaven Instruments) according to the manual of the instrument.

[0378] The weight-average molecular weight of the thermoplastic resin contained in the thermoplastic resin particles is preferably 3,000 to 300,000, and more preferably 5,000 to 100,000.

[0379] The manufacturing method of the thermoplastic resin contained in the thermoplastic resin particles is not particularly limited, and the thermoplastic resin can be manufactured by known methods.

[0380] For example, the thermoplastic resin is obtained by polymerizing a styrene compound, an acrylonitrile compound, and at least one optional compound selected from the group consisting of an N-vinyl heterocyclic compound, a compound used for forming a constitutional unit having a ethylenically unsaturated group, a compound used for forming a constitutional unit having an acidic group, a compound used for forming a constitutional unit having a hydrophobic group, and a compound used for forming the other constitutional units, by known methods.

[0381] Specifically, suitable examples of the thermoplastic resin contained in the thermoplastic resin particles include those described in WO2020/262692A.

[0382] The average particle diameter of the particles is preferably 0.01 μm to 3.0 μm, more preferably 0.03 μm to 2.0 μm, and even more preferably 0.10 μm to 1.0 μm. In a case where the average particle diameter is in this range, excellent resolution and excellent temporal stability are obtained.

[0383] The average primary particle diameter of the particles in the present disclosure is obtained by measuring with a light scattering method or by imaging an electron micrograph of the particles, measuring the particle diameter of a total of 5,000 particles in the photograph, and calculating the average thereof. For non-spherical particles, the value of particle diameter of spherical particles having the same area as the area of the particles on the photograph is adopted as the particle diameter.

[0384] Unless otherwise specified, the average particle diameter in the present disclosure means a volume average particle diameter.

[0385] The image-recording layer may contain only one kind of particles, particularly, one kind of polymer particles or two or more kinds of polymer particles.

[0386] From the viewpoints of on-press developability and printing durability, the content of particles, particularly, the content of polymer particles in the image-recording layer with respect to the total mass of the image-recording layer is preferably 5% by mass to 90% by mass, more preferably 10% by mass to 90% by mass, even more preferably 20% by mass to 90% by mass, and particularly preferably 50% by mass to 90% by mass.

[0387] In addition, from the viewpoints of on-press developability and printing durability, the content of the polymer particles in the image-recording layer with respect to the total mass of components having a molecular weight of 3,000 or more in the image-recording layer is preferably 20% by mass to 100% by mass, more preferably 35% by mass to 100% by mass, even more preferably 50% by mass to 100% by mass, and particularly preferably 80% by mass to 100% by mass.

[Binder polymer]

[0388] The image-recording layer may contain a binder polymer.

[0389] The above-described polymer particles do not correspond to the binder polymer. That is, the binder polymer is a polymer that is not in the form of particles.

[0390] The binder polymer is preferably a (meth)acrylic resin, a polyvinyl acetal resin, or a polyurethane resin.

[0391] Among these, as the binder polymer, known binder polymers that can be used in an image-recording layer in lithographic printing plate precursors can be suitably used. As an example, a binder polymer that is used for an on-press development type lithographic printing plate precursor (hereinafter, also called binder polymer for on-press development) will be specifically described.

[0392] As the binder polymer for on-press development, a binder polymer having an alkylene oxide chain is preferable. The binder polymer having an alkylene oxide chain may have a poly(alkylene oxide) moiety in a main chain or side chain. In addition, the binder polymer may be a graft polymer having poly(alkylene oxide) in a side chain or a block copolymer of a block composed of a poly(alkylene oxide)-containing repeating unit and a block composed of an (alkylene oxide)-free repeating unit.

[0393] In a case where the binder polymer has a poly(alkylene oxide) moiety in the main chain, a polyurethane resin is preferable. In a case where the binder polymer has a poly(alkylene oxide) moiety in the side chain, examples of polymers include a (meth)acrylic resin, a polyvinyl acetal resin, a polyurethane resin, a polyurea resin, a polyimide resin, a polyamide resin, an epoxy resin, a polystyrene resin, a novolac-type phenol resin, a polyester resin, synthetic rubber, and natural rubber, and a (meth)acrylic resin is particularly preferable.

[0394] In addition, other preferred examples of the binder polymer include a polymer compound which has a polyfunctional thiol having functionalities of 6 or more and 10 or less as a nucleus and a polymer chain that is bonded to the nucleus by a sulfide bond and has a polymerizable group (hereinafter, this compound will be also called star-shaped polymer compound).

[0395] From the viewpoint of curing property, preferred examples of the star-shaped polymer compound include a star-shaped polymer compound having a polymerizable group such as an ethylenically unsaturated group on a main chain or a side chain, and more preferably on a side chain.

[0396] Examples of the star-shaped polymer compound include those described in JP2012-148555A or WO2020/262692A.

[0397] The molecular weight of the binder polymer that is a polystyrene-equivalent weight-average molecular weight (Mw) determined by GPC is preferably 2,000 or more, more preferably 5,000 or more, and even more preferably 10,000 to 300,000.

[0398] As necessary, a hydrophilic polymer such as polyacrylic acid or polyvinyl alcohol described in JP2008-195018A can be used in combination. In addition, a lipophilic polymer and a hydrophilic polymer can be used in combination.

[0399] From the viewpoints of printing durability and on-press developability, the image-recording layer preferably contains a polymer having a constitutional unit formed of an aromatic vinyl compound, and more preferably contains a polymer having a constitutional unit formed of an aromatic vinyl compound and an infrared absorber which decomposes by exposure to infrared.

[0400] In addition, for example, from the viewpoint of inhibiting on-press developability from deteriorating with the passage of time, the glass transition temperature (Tg) of the binder polymer used in the present disclosure is preferably 50°C or higher, more preferably 70°C or higher, even more preferably 80°C or higher, and particularly preferably 90°C or higher.

[0401] Furthermore, from the viewpoint of ease of permeation of water into the image-recording layer, the upper limit of the glass transition temperature of the binder polymer is preferably 200°C, and more preferably 120°C or lower.

[0402] From the viewpoint of further inhibiting on-press developability from deteriorating with the passage of time, the binder polymer having the above-described glass transition temperature is preferably polyvinyl acetal.

[0403] Polyvinyl acetal is a resin obtained by acetalizing a hydroxy group of polyvinyl alcohol with an aldehyde.

[0404] Particularly, polyvinyl butyral is preferable which is obtained by acetalizing (that is, butyralizing) a hydroxy group of polyvinyl alcohol with butyraldehyde.

[0405] From the viewpoint of improving printing durability, the polyvinyl acetal preferably has an ethylenically unsaturated group.

[0406] Suitable examples of the polyvinyl acetal include those described in WO2020/262692A.

[0407] The image-recording layer in the present disclosure preferably contains a resin having a fluorine atom, and more preferably contains a fluoroaliphatic group-containing copolymer.

[0408] In a case where the resin having a fluorine atom, particularly, the fluoroaliphatic group-containing copolymer is used, it is possible to inhibit surface abnormalities resulting from foaming during the formation of the image-recording layer and to improve the condition of the coated surface, and further to improve the ink receptivity of the formed image-recording layer.

[0409] In addition, the image-recording layer containing the fluoroaliphatic group-containing copolymer has high gradation and is highly sensitive, for example, to laser light. Therefore, the obtained lithographic printing plate exhibits excellent fogging property by scattered light, reflected light, and the like and has excellent printing durability.

[0410] As the fluoroaliphatic group-containing copolymer, those described in WO2020/262692A can be suitably used.

[0411] In the image-recording layer used in the present disclosure, one binder polymer may be used alone, or two or more binder polymers may be used in combination.

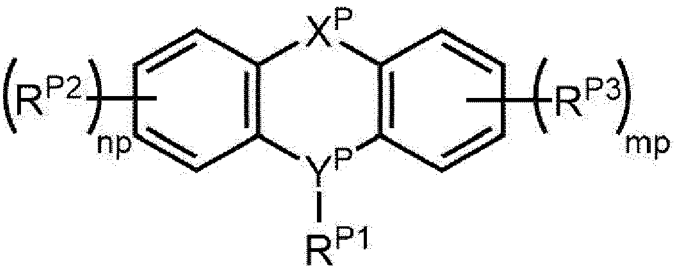
[0412] The content of the binder polymer to be contained in the image-recording layer can be optionally set, and the content of the binder polymer with respect to the total mass of the image-recording layer is preferably 1% by mass to 90% by mass and more preferably 5% by mass to 80% by mass.

[Polymerization Inhibitor]

[0413] From the viewpoint of temporal stability, the image-recording layer preferably contains a polymerization inhibitor. In a case where the image-recording layer contains a polymerization inhibitor, while the image-recording layer is being manufactured or stored, the polymerizable compound, particularly, the radically polymerizable compound can be prevented from undergoing unnecessary thermal polymerization.

[0414] Specifically, suitable examples of the polymerization inhibitor include hydroquinone, p-methoxyphenol, di-t-butyl-p-cresol, pyrogallol, t-butylcatechol, benzoquinone, 4,4'-thiobis(3-methyl-6-t-butylphenol), 2,2'-methylenebis(4-methyl-6-t-butylphenol), a N-nitroso-N-phenylhydroxylamine aluminum salt, and the like.

[0415] From the viewpoint of temporal stability, the polymerization inhibitor preferably includes a compound represented by Formula (Ph).



(Ph)

[0416] In Formula (Ph), X^P represents O, S, or NH, Y^P represents N or CH, R^{P1} represents a hydrogen atom or an alkyl group, R^{P2} and R^{P3} each independently represent a halogen atom, an alkylthio group, an arylthio group, an alkoxy group, an aryloxy group, an alkyl group, an aryl group, an acylthio group, or an acyl group, and mp and np each independently represent an integer of 0 to 4.

[0417] From the viewpoint of temporal stability, X^P in Formula (Ph) is preferably O or S and more preferably S.

[0418] From the viewpoint of temporal stability, Y^P in Formula (Ph) is preferably N.

[0419] From the viewpoint of temporal stability, R^{P1} in Formula (Ph) is preferably a hydrogen atom or a methyl group and more preferably a hydrogen atom.

[0420] R^{P2} and R^{P3} in Formula (Ph) each independently are preferably a halogen atom, an alkylthio group, an arylthio group, an alkoxy group, an aryloxy group, an alkyl group, or an aryl group.

[0421] From the viewpoint of temporal stability, mp and np in Formula (Ph) each independently are preferably an integer of 0 to 2, more preferably 0 or 1, and particularly preferably 0.

[0422] In the image-recording layer used in the present disclosure, only one polymerization inhibitor may be used, or

two or more polymerization inhibitors may be used in combination.
[0423] The content of the polymerization inhibitor with respect to the total mass of the image-recording layer is preferably 0.001% by mass to 5% by mass and more preferably 0.01% by mass to 1% by mass.

[Chain transfer agent]

[0424] The image-recording layer used in the present disclosure may contain a chain transfer agent. The chain transfer agent contributes to the improvement of printing durability of the lithographic printing plate.
[0425] The chain transfer agent is preferably a thiol compound, more preferably a thiol compound having 7 or more carbon atoms from the viewpoint of boiling point (low volatility), and even more preferably a compound having a mercapto group on an aromatic ring (aromatic thiol compound). The thiol compound is preferably a monofunctional thiol compound.
[0426] Specifically, suitable examples of the chain transfer agent include those described in WO2020/262692A.
[0427] Only one chain transfer agent may be added to the image-recording layer, or two or more chain transfer agents may be used in combination.
[0428] The content of the chain transfer agent with respect to the total mass of the image-recording layer is preferably 0.01% by mass to 50% by mass, more preferably 0.05% by mass to 40% by mass, and even more preferably 0.1% by mass to 30% by mass.

[Oil sensitizing agent]

[0429] In order to improve ink receptivity, the image-recording layer preferably further contains an oil sensitizing agent.
[0430] Examples of the oil sensitizing agent include an onium compound, a nitrogen-containing low-molecular-weight compound, an ammonium compound such as an ammonium group-containing polymer, and the like.
[0431] Particularly, in a case where an inorganic lamellar compound is contained in a protective layer, these compounds function as a surface coating agent for the inorganic lamellar compound and can inhibit the receptivity deterioration due to the inorganic lamellar compound in the middle of printing.
[0432] From the viewpoint of receptivity, the oil sensitizing agent is preferably an onium compound.
[0433] Examples of the onium compound include a phosphonium compound, an ammonium compound, a sulfonium compound, and the like. From the viewpoint described above, the onium compound is preferably at least one compound selected from the group consisting of a phosphonium compound and an ammonium compound.
[0434] Preferred examples of the ammonium compound can include a nitrogen-containing low-molecular-weight compound, an ammonium group-containing polymer, and the like.
[0435] Specifically, suitable examples of the oil sensitizing agent include those described in WO2020/262692A.
[0436] The content of the oil sensitizing agent with respect to the total mass of the image-recording layer is preferably 1% by mass to 40.0% by mass, more preferably 2% by mass to 25.0% by mass, and even more preferably 3% by mass to 20.0% by mass.
[0437] The image-recording layer may contain only one oil sensitizing agent, or two or more oil sensitizing agents may be used in combination.
[0438] One of the preferred aspects of the image-recording layer used in the present disclosure is an aspect in which the image-recording layer contains two or more compounds as an oil sensitizing agent.
[0439] Specifically, from the viewpoint of satisfying both the on-press developability and receptivity, the image-recording layer used in the present disclosure preferably uses all the phosphonium compound, the nitrogen-containing low-molecular-weight compound, and the ammonium group-containing polymer as an oil sensitizing agent, and more preferably uses all the phosphonium compound, the quaternary ammonium salts, and the ammonium group-containing polymer as an oil sensitizing agent.

[Other components]

[0440] As other components, the image-recording layer can contain a development accelerator, a surfactant, a higher fatty acid derivative, a plasticizer, an inorganic lamellar compound, and the like. Specifically, the description in paragraphs "0114" to "0159" of JP2008-284817A can be referred to.
[0441] In addition, as the development accelerator, for example, those described in WO2020/262692A may also be used.

[Formation of image-recording layer]

[0442] The image-recording layer in the lithographic printing plate precursor according to the present disclosure can be formed, for example, by preparing a coating liquid by dispersing or dissolving the necessary components described above in a known solvent, coating a support with the coating liquid by a known method such as bar coating, and drying the coating liquid, as described in paragraphs "0142" and "0143" of JP2008-195018A.

[0443] As the solvent, known solvents can be used. Specific examples thereof include water, acetone, methyl ethyl ketone (2-butanone), cyclohexane, ethyl acetate, ethylene dichloride, tetrahydrofuran, toluene, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol dimethyl ether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, acetylacetone, cyclohexanone, diacetone alcohol, ethylene glycol monomethyl ether acetate, ethylene glycol ethyl ether acetate, ethylene glycol monoisopropyl ether, ethylene glycol monobutyl ether acetate, 1-methoxy-2-propanol, 3-methoxy-1-propanol, methoxy methoxyethanol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, 3-methoxypropyl acetate, N,N-dimethylformamide, dimethyl sulfoxide, γ-butyrolactone, methyl lactate, ethyl lactate, and the like. Only one solvent may be used, or two or more solvents may be used in combination. The concentration of solid contents in the coating liquid is preferably 1% by mass to 50% by mass.

[0444] The coating amount (solid content) of the image-recording layer after coating and drying varies with uses, but from the viewpoint of obtaining excellent sensitivity and excellent film characteristics of the image-recording layer, is preferably 0.3 g/m^2 to 3.0 g/m^2.

[0445] In addition, the layer thickness of the image-recording layer is preferably 0.1 μm to 3.0 μm and more preferably 0.3 μm to 2.0 μm.

[0446] In the present disclosure, the layer thickness of each layer in the lithographic printing plate precursor is checked by preparing a slice by cutting the lithographic printing plate precursor in a direction perpendicular to the surface of the precursor and observing the cross section of the slice with a scanning electron microscope (SEM).

<Support>

[0447] The lithographic printing plate precursor according to the present disclosure has a support.

[0448] The support to be used can be appropriately selected from known supports for a lithographic printing plate precursor.

[0449] The support is preferably a support having a hydrophilic surface (hereinafter, also called "hydrophilic support").

[0450] As the support in the present disclosure, an aluminum plate is preferable which has been roughened using a known method and has undergone an anodization treatment. That is, the support in the present disclosure preferably has an aluminum plate and an aluminum anodic oxide film disposed on the aluminum plate.

[0451] In addition, it is preferable that the support has an aluminum plate and an anodic oxide film of aluminum disposed on the aluminum plate, the anodic oxide film is at a position closer to a side of the image-recording layer than the aluminum plate and has micropores extending in a depth direction from the surface of the anodic oxide film on the side of the image-recording layer, and the average diameter of the micropores within the surface of the anodic oxide film is more than 10 nm and 100 nm or less.

[0452] Furthermore, it is preferable that the micropores are each configured with a large diameter portion that extends to a position at a depth of 10 nm to 1,000 nm from the surface of the anodic oxide film and a small diameter portion that is in communication with a bottom portion of the large diameter portion and extends to a position at a depth of 20 nm to 2,000 nm from a communicate position, an average diameter of the large diameter portion within the surface of the anodic oxide film is preferably 15 nm to 100 nm, and an average diameter of the small diameter portion at the communicate position is preferably 13 nm or less.

[0453] In addition, it is preferable that the support has an aluminum plate and an anodic oxide film of aluminum disposed on the aluminum plate, the anodic oxide film is at a position closer to a side of the image-recording layer than the aluminum plate and has micropores extending in a depth direction from the surface of the anodic oxide film on the side of the image-recording layer, the micropores are each configured with a small diameter portion that extends to a position at a depth of 10 nm to 1,000 nm from the surface of the anodic oxide film and a large diameter portion that is in communication with the bottom portion of the small diameter portion and extends to a position at a depth of 20 nm to 2,000 nm from a communicate position, an average diameter of the small diameter portion within the surface of the anodic oxide film is 35 nm or less, and an average maximum diameter of the large diameter portion is 40 nm to 300 nm.

[0454] It is possible to easily prepare the support of the above aspect by using an aqueous phosphoric acid solution as a first-stage anodization treatment and using an aqueous sulfuric acid solution as a second-stage anodization treatment in the treatment that will be described later.

[0455] The tensile strength of the present support is preferably 160 MPa or more.

[0456] The tensile strength is measured using an autograph AGC-H5KN (manufactured by Shimadzu Corporation.) as a tensile strength measuring machine and using a sample: JIS metal material tensile test piece No. 5 at a tensile speed of 2 mm/min.

[0457] The tensile strength of the support is preferably 160 MPa or more, more preferably 170 MPa or more, and particularly preferably 190 MPa or more.

[0458] In addition, the maximum tensile strength of the support is not particularly limited, but is preferably 300 MPa or less, more preferably 250 MPa or less, and even more preferably 220 MPa or less.

[0459] There is no limit on how to obtain a support having a tensile strength of 160 MPa or more. For example, as will be described later, such a support is obtained by incorporating a specific amount of magnesium into the support and setting a reduction rate in a support rolling step to be equal to or more than a specific amount.

[0460] As the support, an aluminum support is preferable. The aluminum plate used in the aluminum support consists of a dimensionally stable metal containing aluminum as a main component, that is, aluminum or an aluminum alloy. It is preferable that the aluminum plate be selected from a pure aluminum plate and an alloy that contains aluminum as a main component and traces of foreign elements.

[0461] The foreign elements contained in the aluminum alloy include silicon, iron, manganese, copper, magnesium, chromium, zinc, bismuth, nickel, titanium, and the like. The content of the foreign elements in the alloy is 10% by mass or less. As the aluminum plate, a pure aluminum plate is suitable. However, the aluminum plate may be an alloy that contains traces of foreign elements, because it is difficult to manufacture perfectly pure aluminum by smelting technologies. The composition of the aluminum plate used for the aluminum support is not specified, and it is possible to appropriately use aluminum plates known in the related art, for example, JIS A 1050, JIS A 1100, JIS A 3103, and JIS A 3005 caused to have the above tensile strength.

[0462] It is preferable that the support is an aluminum support, and a magnesium content in the aluminum support is 0.020% by mass or more. Setting the magnesium content (content rate) in the aluminum support to be 0.020% by mass or more makes it possible to suitably obtain a support having a tensile strength of 160 MPa or more.

[0463] The magnesium content in the support is preferably 0.020% by mass or more, more preferably 0.040% by mass or more, and even more preferably 0.060% by mass or more.

[0464] The magnesium content in the support is not particularly limited, but is usually 0.200% by mass or less, preferably 0.150% by mass or less, and more preferably 0.100% by mass or less.

[0465] The magnesium content rate in the support was measured using an emission analysis apparatus (PDA-5500, manufactured by Shimadzu Corporation.) as a measurement apparatus.

[0466] In addition, it is preferable that the support is an aluminum support, and the aluminum support is configured with an aluminum plate that is subjected to a heat treatment at a temperature of 250°C or higher and then subjected to cold rolling at a reduction rate of 80% or more in the rolling step. In a case where this aspect is adopted, it is possible to suitably obtain a support having a tensile strength of 160 MPa or more.

[0467] Controlling the reduction rate in the cold rolling step following the heat treatment makes it possible to control the tensile strength of the support (preferably the aluminum support). The reduction rate is an amount calculated by $(h1 - h2)/h1$ where h1 represents a plate thickness of a material not yet being rolled and h2 represents a plate thickness of the material having been rolled. The reduction rate shows a processing degree of rolling, which is preferably 80% or more, more preferably 90% or more, and even more preferably 95% or more.

[0468] In addition, the reduction rate is preferably less than 99% and more preferably 98% or less.

[0469] The thickness of the support (preferably, the aluminum plate) is preferably about 0.1 mm to 0.6 mm.

[Anodic oxide film]

[0470] The support preferably has an anodic oxide film.

[0471] The anodic oxide film means an anodic oxide film (preferably an anodic aluminum oxide film) which is formed on the surface of a support (preferably an aluminum plate) by an anodization treatment and has supermicropores (also called micropores). The micropores extend from the surface of the anodic oxide film on the side opposite to the support along the thickness direction (support side, depth direction).

[0472] From the viewpoints of tone reproducibility, printing durability, and blanket stain property, the average diameter (average opening diameter) of the micropores within the surface of the anodic oxide film is preferably 7 nm to 150 nm, more preferably 10 nm to 100 nm, even more preferably 10 nm to 60 nm, particularly preferably 15 nm to 60 nm, and most preferably 18 nm to 40 nm.

[0473] The depth of the micropores is preferably 10 nm to 3,000 nm, more preferably 10 nm to 2,000 nm, and even more preferably 10 nm to 1,000 nm.

[0474] Usually, the micropores have a substantially straight tubular shape (substantially cylindrical shape) in which the diameter of the micropores substantially does not change in the depth direction (thickness direction). The micropores may also have a conical shape that continues to taper in the depth direction (thickness direction). The micropores may have a shape that discontinuously tapers along the depth direction (thickness direction).

[0475] Examples of the micropores having a shape that discontinuously tapers in the depth direction (thickness direction) include micropores each configured with a large diameter portion that extends along the depth direction from the surface of the anodic oxide film and a small diameter portion that is in communication with the bottom portion of the large diameter portion and extends along the depth direction from the communicate position.

[0476] Specifically, the micropores are preferable which are each configured with a large diameter portion that extends 10 nm to 1,000 nm in the depth direction from the surface of the anodic oxide film and a small diameter portion that is in communication with the bottom portion of the large diameter portion and extends 20 nm to 2,000 nm in the depth direction from the communicate position.

[0477] Hereinafter, the large diameter portion and the small diameter portion will be specifically described.

-Large diameter portion-

[0478] From the viewpoints of tone reproducibility, printing durability, and blanket stain property, the average diameter (average opening diameter) of the large diameter portion within the surface of the anodic oxide film is preferably 7 nm to 150 nm, more preferably 10 nm to 100 nm, even more preferably 15 nm to 100 nm, particularly preferably 15 nm to 60 nm, and most preferably 18 nm to 40 nm.

[0479] The average diameter of the large diameter portion is calculated by a method of observing the surface of the anodic oxide film with a field emission scanning electron microscope (FE-SEM) at 150,000X magnification (N = 4), measuring the sizes (diameters) of micropores (large diameter portions) existing in a range of 400 nm × 600 nm in the obtained 4 images, and calculating the arithmetic mean of the diameters.

[0480] In a case where the shape of the large diameter portion is not circular, the equivalent circle diameter is used. "Equivalent circular diameter" is a diameter determined on an assumption that the opening portion is in the form of a circle having the same projected area as the projected area of the opening portion.

[0481] The bottom portion of the large diameter portion is preferably in a position at a depth of 70 nm to 1,000 nm (hereinafter, also called depth A) from the surface of the anodic oxide film. That is, the large diameter portion is preferably a pore portion extending to a position at a depth of 70 nm to 1,000 nm from the surface of the anodic oxide film in the depth direction (thickness direction). Particularly, from the viewpoint of further improving the effect of the manufacturing method of a lithographic printing plate precursor, the depth A is more preferably 90 nm to 850 nm, even more preferably 90 nm to 800 nm, and particularly preferably 90 nm to 600 nm.

[0482] The depth is a value obtained by taking an image (150,000X magnification) of a cross section of the anodic oxide film, measuring the depths of 25 or more large diameter portions, and calculating the arithmetic mean thereof.

[0483] The shape of the large diameter portion is not particularly limited. Examples of the shape of the large diameter portion include a substantially straight tubular shape (substantially cylindrical shape) and a conical shape that tapers along the depth direction (thickness direction). Among these, a substantially straight tubular shape is preferable. The shape of the bottom portion of the large diameter portion is not particularly limited, and may be a curved (convex) or planar shape.

[0484] The inner diameter of the large diameter portion is not particularly limited, but is preferably as large as the diameter of the opening portion or smaller than the diameter of the opening portion. There may be a difference of about 1 nm to 10 nm between the inner diameter of the large diameter portion and the diameter of the opening portion.

-Small diameter portion-

[0485] The small diameter portion is a pore portion that is in communication with the bottom portion of the large diameter portion and further extends from the communicate position in the depth direction (thickness direction). Generally, one small diameter portion is in communication with one large diameter portion. However, two or more small diameter portions may be in communication with the bottom portion of one large diameter portion.

[0486] The average diameter of the small diameter portion at the communicate position is preferably less than 15 nm, more preferably 13 nm or less, even more preferably 11 nm or less, and particularly preferably 10 nm or less. The lower limit thereof is not particularly limited, but is preferably 5 nm.

[0487] The average diameter of the small diameter portion is obtained by observing the surface of the anodic oxide film with FE-SEM at 150,000X magnification (N = 4), measuring the sizes (diameters) of the micropores (small diameter portion) existing in a range of 400 nm × 600 nm in the obtained 4 images, and calculating the arithmetic mean of the diameters. In a case where the large diameter portion is deep, as necessary, the upper portion of the anodic oxide film (region where the large diameter portion is located) may be cut (for example, cut by using argon gas), then the surface of the anodic oxide film may be observed with FE-SEM described above, and the average diameter of the small diameter portion may be determined.

[0488] In a case where the shape of the small diameter portion is not circular, the equivalent circle diameter is used. "Equivalent circular diameter" is a diameter determined on an assumption that the opening portion is in the form of a circle having the same projected area as the projected area of the opening portion.

[0489] The bottom portion of the small diameter portion is preferably in a position 20 nm to 2,000 nm distant from the communicate position (corresponding to the depth A described above) with the large diameter portion in the depth direction. In other words, the small diameter portion is a pore portion that extends further from the communicate position with the large diameter portion in the depth direction (thickness direction), and the depth of the small diameter portion is preferably 20 nm to 2,000 nm, more preferably 100 nm to 1,500 nm, and particularly preferably 200 nm to 1,000 nm.

[0490] The depth is a value obtained by taking an image (150,000X magnification) of a cross section of the anodic oxide film, measuring the depths of 25 or more small diameter portions, and calculating the arithmetic mean thereof.

[0491] The shape of the small diameter portion is not particularly limited. Examples of the shape of the small diameter portion include a substantially straight tubular shape (substantially cylindrical shape) and a conical shape that tapers along the depth direction. Among these, a substantially straight tubular shape is preferable. The shape of the bottom portion of the small diameter portion is not particularly limited, and may be a curved (convex) or planar shape.

[0492] The inner diameter of the small diameter portion is not particularly limited, and may be the same as the diameter at the communicate position, or may be smaller or larger than the diameter at the communicate position. Generally, there may be a difference of about 1 nm to 10 nm between the inner diameter of the small diameter portion and the diameter of the opening portion.

[0493] The ratio of the average diameter of the large diameter portion within the surface of the anodic oxide film to the average diameter of the small diameter portion at the communicate position, (average diameter of large diameter portion within surface of anodic oxide film)/(average diameter of small diameter portion at communicate position) is preferably 1.1 to 13, and more preferably 2.5 to 6.5.

[0494] The ratio of the depth of the large diameter portion to the depth of the small diameter portion, (depth of large diameter portion)/(depth of small diameter portion) is preferably 0.005 to 50, and more preferably 0.025 to 40.

[0495] The micropores have a substantially straight tubular shape (substantially cylindrical shape) in which the diameter of the micropores substantially does not change in the depth direction (thickness direction). The micropores may also have a conical shape that continues to widen in the depth direction (thickness direction). The micropores may have a shape that discontinuously widens along the depth direction (thickness direction).

[0496] Examples of the micropores having a shape that discontinuously widens in the depth direction (thickness direction) include micropores each configured with a small diameter portion that extends along the depth direction from the surface of the anodic oxide film and a large diameter portion that is in communication with the bottom portion of the small diameter portion and extends along the depth direction from the communicate position.

[0497] Specifically, the micropores are preferable which are each configured with a small diameter portion that extends 10 nm to 1,000 nm in the depth direction from the surface of the anodic oxide film and a large diameter portion that is in communication with the bottom portion of the small diameter portion and extends 20 nm to 2,000 nm in the depth direction from the communicate position.

-Small diameter portion-

[0498] The average diameter (average opening diameter) of the small diameter portion within the surface of the anodic oxide film is not particularly limited, but is preferably 35 nm or less, more preferably 25 nm or less, and particularly preferably 20 nm or less. The lower limit thereof is not particularly limited, but is preferably 15 nm.

[0499] The average diameter of the small diameter portion is calculated by a method of observing the surface of the anodic oxide film with a field emission scanning electron microscope (FE-SEM) at 150,000X magnification (N = 4), measuring the sizes (diameters) of micropores (large diameter portions) existing in a range of 400 nm × 600 nm in the obtained 4 images, and calculating the arithmetic mean of the diameters.

[0500] In a case where the shape of the small diameter portion is not circular, the equivalent circle diameter is used. "Equivalent circular diameter" is a diameter determined on an assumption that the opening portion is in the form of a circle having the same projected area as the projected area of the opening portion.

[0501] The bottom portion of the small diameter portion is preferably in a position at a depth of 70 nm to 1,000 nm (hereinafter, also called depth A') from the surface of the anodic oxide film. That is, the small diameter portion is preferably a pore portion extending 70 nm to 1,000 nm in the depth direction (thickness direction) from the surface of the anodic oxide film.

[0502] The depth is a value obtained by taking an image (150,000X magnification) of a cross section of the anodic oxide film, measuring the depths of 25 or more large diameter portions, and calculating the arithmetic mean thereof.

[0503] The shape of the small diameter portion is not particularly limited. Examples of the shape of the large diameter portion include a substantially straight tubular shape (substantially cylindrical shape) and a conical shape that widens along the depth direction (thickness direction). Among these, a substantially straight tubular shape is preferable. The shape of the bottom portion of the small diameter portion is not particularly limited, and may be a curved (convex) or planar shape.

[0504] The inner diameter of the small diameter portion is not particularly limited, but is preferably as large as the diameter of the opening portion or smaller than the diameter of the opening portion. Generally, there may be a difference of about 1 nm to 10 nm between the inner diameter of the small diameter portion and the diameter of the opening portion.

-Large diameter portion-

[0505] The large diameter portion is a pore portion that is in communication with the bottom portion of the small diameter portion and further extends from the communicate position in the depth direction (thickness direction). Generally, the bottom portion of one large diameter portion may be in communication with two or more small diameter portions.

[0506] The average diameter of the large diameter portion at the communicate position is preferably 20 nm to 400 nm, more preferably 40 nm to 300 nm, even more preferably 50 nm to 200 nm, and particularly preferably 50 nm to 100 nm.

[0507] The average diameter of the large diameter portion is obtained by observing the surface of the anodic oxide film with FE-SEM at 150,000X magnification (N = 4), measuring the sizes (diameters) of the micropores (large diameter portion) existing in a range of 400 nm × 600 nm in the obtained 4 images, and calculating the arithmetic mean of the diameters. In a case where the small diameter portion is deep, as necessary, the upper portion of the anodic oxide film (region where the small diameter portion is located) may be cut (for example, cut by using argon gas), then the surface of the anodic oxide film may be observed with FE-SEM described above, and the average diameter of the large diameter portion may be determined.

[0508] In a case where the shape of the large diameter portion is not circular, the equivalent circle diameter is used. "Equivalent circular diameter" is a diameter determined on an assumption that the opening portion is in the form of a circle having the same projected area as the projected area of the opening portion.

[0509] The bottom portion of the large diameter portion is preferably in a position 20 nm to 2,000 nm distant from the communicate position (corresponding to the depth A' described above) with the small diameter portion in the depth direction. In other words, the large diameter portion is a pore portion that extends further from the communicate position with the small diameter portion in the depth direction (thickness direction), and the depth of the large diameter portion is preferably 20 nm to 2,000 nm, more preferably 100 nm to 1,500 nm, and particularly preferably 200 nm to 1,000 nm.

[0510] The depth is a value obtained by taking an image (150,000X magnification) of a cross section of the anodic oxide film, measuring the depths of 25 or more large diameter portions, and calculating the arithmetic mean thereof.

[0511] The shape of the large diameter portion is not particularly limited. Examples of the shape of the large diameter portion include a substantially straight tubular shape (substantially cylindrical shape) and a conical shape that tapers along the depth direction. Among these, a substantially straight tubular shape is preferable. The shape of the bottom portion of the large diameter portion is not particularly limited, and may be a curved (convex) or planar shape.

[0512] The inner diameter of the large diameter portion is not particularly limited, and may be the same as the diameter at the communicate position, or may be smaller or larger than the diameter at the communicate position. Generally, there may be a difference of about 1 nm to 10 nm between the inner diameter of the large diameter portion and the diameter of the opening portion.

[0513] It is preferable that the support preferably has an anodic oxide film, and

> the anodic oxide film has, in order from the surface of the anodic oxide film along the depth direction,
> an upper layer that has a thickness of 30 nm to 500 nm and has micropores having an average diameter of 20 nm to 100 nm,
> an intermediate layer that has a thickness of 100 nm to 300 nm and has micropores having an average diameter of 1/2 to 5 times the average diameter of the micropores in the micropore upper layer, and
> a lower layer that has a thickness of 300 nm to 2,000 nm and has micropores having an average diameter of 15 nm or less.

[0514] In an on-press development type lithographic printing plate precursor, from the viewpoint of improving image visibility, a support is useful in which the surface of an anodic oxide film (surface on which an image-recording layer is to be formed) has high brightness.

[0515] Usually, in a printing step using a lithographic printing plate, before the printing plate is mounted on a printer, the plate is inspected to check whether an image is printed as intended. For the on-press development type lithographic printing plate precursor, it is required to check the image at the stage where the image is exposed. Therefore, a unit generating a so-called printed image in an image exposure portion is used.

[0516] Examples of a method of quantitatively evaluating the visibility of an image area (image visibility) of the on-press development type lithographic printing plate precursor having undergone exposure of an image include a method of measuring the brightness of an image exposure portion and the brightness of a non-exposed portion and calculating the difference therebetween. As the brightness, a value of brightness L* in the CIEL*a*b* color system can be used. The brightness can be measured using a color difference meter (Spectro Eye, manufactured by X-Rite, Incorporated.). The larger the difference between the measured brightness of the image exposure portion and the measured brightness of the non-exposed portion is, the higher the visibility of the image area is.

[0517] It has been revealed that the larger the value of brightness L* of the surface of the anodic oxide film in the CIEL*a*b* color system is, the more effective it is to increase the difference between the brightness of the image exposure portion and the brightness of the non-exposed portion. That is, the value of the brightness L* is preferably 60 to 100.

[0518] As necessary, the support having an anodic oxide film may have a backcoat layer containing the organic high-molecular-weight compound described in JP1993-45885A (JP-H5-45885A), the alkoxy compound of silicon described in JP1994-35174A (JP-H6-35174A), or the like, on a surface opposite to the side where a constitutional layer containing a hydroxy acid compound having two or more hydroxyl groups is formed.

[Manufacturing of aluminum support having anodic oxide film]

[0519] The manufacturing method of an aluminum support having an anodic oxide film, which is an example of support, will be described.

[0520] The aluminum support having an anodic oxide film can be manufactured using known methods. The manufacturing method of the aluminum support having an anodic oxide film is not particularly limited. Examples of preferred aspects of the manufacturing method of the aluminum support having an anodic oxide film include a method including a step of performing a roughening treatment on an aluminum plate (roughening treatment step), a step of anodizing the aluminum plate having undergone the roughening treatment (anodization treatment step), and a step of bringing the aluminum plate having an anodic oxide film obtained by the anodization treatment step into contact with an acidic aqueous solution or an alkaline aqueous solution to increase the diameter of micropores in the anodic oxide film (pore widening treatment step).

[0521] Hereinafter, each step will be described in detail.

<<Roughening treatment step>>

[0522] The roughening treatment step is a step of performing a roughening treatment including an electrochemical roughening treatment on the surface of the aluminum plate. The roughening treatment step is preferably performed before the anodization treatment step which will be described later. However, in a case where the surface of the aluminum plate already has a preferable shape, the roughening treatment step may not be performed.

[0523] As the roughening treatment, only an electrochemical roughening treatment may be performed, or an electrochemical roughening treatment may be performed in combination with at least either a mechanical roughening treatment or a chemical roughening treatment.

[0524] In a case where the mechanical roughening treatment and the electrochemical roughening treatment are combined, it is preferable to perform the electrochemical roughening treatment after the mechanical roughening treatment.

[0525] The electrochemical roughening treatment is preferably performed in an aqueous solution of nitric acid or hydrochloric acid.

[0526] Generally, the mechanical roughening treatment is performed such that the aluminum plate has a surface roughness Ra of 0.35 μm to 1.0 μm.

[0527] The conditions of the mechanical roughening treatment are not particularly limited. For example, the mechanical roughening treatment can be performed according to the method described in JP1975-40047B (JP-S50-40047B). The mechanical roughening treatment can be performed by a brush graining treatment using a pumice stone suspension or by a transfer method.

[0528] The chemical roughening treatment is also not particularly limited, and can be performed according to known methods.

[0529] After the mechanical roughening treatment, it is preferable to perform the following chemical etching treatment.

[0530] By the chemical etching treatment performed after the mechanical roughening treatment, the edge portion of surface irregularities of the aluminum plate smoothed, such that ink clotting that may occur during printing is prevented, the antifouling property of the lithographic printing plate is improved, and unnecessary substances such as abrasive particles remaining on the surface are removed.

[0531] As the chemical etching treatment, etching with an acid and etching with an alkali are known. One of the examples of particularly efficient etching methods is a chemical etching treatment using an alkaline solution (hereinafter, also called "alkaline etching treatment").

[0532] The alkaline agent used in the alkaline solution is not particularly limited. Suitable examples thereof include caustic soda, caustic potash, sodium metasilicate, sodium carbonate, sodium aluminate, sodium gluconate, and the like.

[0533] The alkaline solution may contain aluminum ions. The concentration of the alkaline agent in the alkaline solution is preferably 0.01% by mass or more and more preferably 3% by mass or more. In addition, the concentration is preferably 30% by mass or less and more preferably 25% by mass or less.

[0534] The temperature of the alkaline solution is preferably equal to or higher than room temperature and more preferably 30°C or higher. In addition, the temperature is preferably 80°C or lower and more preferably 75°C or lower.

[0535] The etching amount is preferably 0.01 g/m^2 or more, and more preferably 0.05 g/m^2 or more. In addition, the etching amount is preferably 30 g/m^2 or less, and more preferably 20 g/m^2 or less.

[0536] The treatment time preferably is in a range of 2 seconds to 5 minutes depending on the etching amount. In view of improving productivity, the treatment time is more preferably 2 seconds to 10 seconds.

[0537] In a case where the alkaline etching treatment is performed after the mechanical roughening treatment, in order to remove products generated by the alkaline etching treatment, the chemical etching treatment by using a low-temperature acidic solution (hereinafter, also called "desmutting treatment") is preferably performed.

[0538] The acid used in the acidic solution is not particularly limited, and examples thereof include sulfuric acid, nitric acid, and hydrochloric acid. The concentration of the acidic solution is preferably 1% to 50% by mass. The temperature of the acidic solution is preferably 20°C to 80°C. In a case where the concentration and temperature of the acidic solution are in this range, the lithographic printing plate using an aluminum support becomes more resistant to dot-like stain.

[0539] Examples of preferred aspects of the roughening treatment step are as below.

-Aspect SA-

[0540] An aspect in which the following treatments (1) to (8) are performed in this order.

(1) Chemical etching treatment using an alkaline aqueous solution (first alkaline etching treatment)
(2) Chemical etching treatment using an acidic aqueous solution (first desmutting treatment)
(3) Electrochemical roughening treatment using aqueous solution containing nitric acid as main component (first electrochemical roughening treatment)
(4) Chemical etching treatment using an alkaline aqueous solution (second alkaline etching treatment)
(5) Chemical etching treatment using an acidic aqueous solution (second desmutting treatment)
(6) Electrochemical roughening treatment using aqueous solution containing hydrochloric acid as main component (second electrochemical roughening treatment)
(7) Chemical etching treatment using alkaline aqueous solution (third alkaline etching treatment)
(8) Chemical etching treatment using acidic aqueous solution (third desmutting treatment)

-Aspect SB-

[0541] An aspect in which the following treatments (11) to (15) are performed in this order.

(11) Chemical etching treatment using alkaline aqueous solution (fourth alkaline etching treatment)
(12) Chemical etching treatment using acidic aqueous solution (fourth desmutting treatment)
(13) Electrochemical roughening treatment using aqueous solution containing hydrochloric acid as main component (third electrochemical roughening treatment)
(14) Chemical etching treatment using alkaline aqueous solution (fifth alkaline etching treatment)
(15) Chemical etching treatment using acidic aqueous solution (fifth desmutting treatment)

[0542] As necessary, a mechanical roughening treatment may be performed before the treatment (1) of the aspect SA or before the treatment (11) of the aspect SB.

[0543] The amount of the aluminum plate dissolved by the first alkaline etching treatment and the fourth alkaline etching treatment is preferably 0.5 g/m^2 to 30 g/m^2 and more preferably 1.0 g/m^2 to 20 g/m^2.

[0544] Examples of the aqueous solution containing nitric acid as a main component used in the first electrochemical roughening treatment of the aspect SA include aqueous solutions used in the electrochemical roughening treatment using direct current or alternating current. Examples thereof include an aqueous solution obtained by adding aluminum nitrate, sodium nitrate, ammonium nitrate, or the like to a 1 g/L to 100 g/L aqueous nitric acid solution.

[0545] Examples of the aqueous solution containing hydrochloric acid as a main component used in the second electrochemical roughening treatment of the aspect SA and in the third electrochemical roughening treatment of the aspect SB include aqueous solutions used in the electrochemical roughening treatment using direct current or alternating current. Examples thereof include an aqueous solution obtained by adding 0 g/L to 30 g/L of sulfuric acid to a 1 g/L to 100 g/L aqueous hydrochloric acid solution. Nitrate ions such as aluminum nitrate, sodium nitrate, or ammonium nitrate; or hydrochloric acid ions such as aluminum chloride, sodium chloride, or ammonium chloride may be further added to the aqueous solution.

[0546] As the waveform of an alternating current power source for the electrochemical roughening treatment, a sine wave, a square wave, a trapezoidal wave, a triangular wave, or the like can be used. The frequency is preferably 0.1 Hz to 250 Hz.

[0547] Fig. 1 is a graph showing an example of an alternating waveform current waveform diagram used for an electrochemical roughening treatment.

[0548] In Fig. 1, ta represents an anodic reaction time, tc represents a cathodic reaction time, tp represents the time taken for current to reach a peak from 0, Ia represents the peak current on the anodic cycle side, and Ic represents the peak current on the cathodic cycle side. For a trapezoidal wave, the time tp taken for current to reach a peak from 0 is preferably 1 msec to 10 msec. Regarding the conditions of one cycle of alternating current used for the electrochemical roughening treatment, a ratio tc/ta of the cathodic reaction time tc to the anodic reaction time ta of the aluminum plate is preferably within a range of 1 to 20, a ratio Qc/Qa of an electricity quantity Qc during the cathodic reaction to an electricity quantity Qa during the anodic reaction of the aluminum plate is preferably within a range of 0.3 to 20, and the anodic reaction time ta is preferably within a range of 5 msec to 1,000 msec. The peak current density of the trapezoidal wave is preferably 10 to 200 A/dm^2 at both the anodic cycle side Ia and the cathodic cycle side Ic of the current. Ic/Ia is preferably 0.3 to 20. At a point in time when the electrochemical roughening treatment has ended, the total quantity of electricity that participates in the anodic reaction of the aluminum plate is preferably 25 C/dm^2 to 1,000 C/dm^2.

[0549] The electrochemical roughening treatment using alternating current can be performed using the device shown in Fig. 2.

[0550] Fig. 2 is a lateral view showing an example of a radial cell in an electrochemical roughening treatment using alternating current.

[0551] In Fig. 2, 50 represents a main electrolytic cell, 51 represents an alternating current power source, 52 represents a radial drum roller, 53a and 53b represent main poles, 54 represents an electrolytic solution supply port, 55 represents an electrolytic solution, 56 represents a slit, 57 represents an electrolytic solution channel, 58 represents an auxiliary anode, 60 represents an auxiliary anode cell, and W represents an aluminum plate. In a case where two or more electrolytic cells are used, the electrolysis conditions may be the same as or different from each other.

[0552] The aluminum plate W is wound around the radial drum roller 52 immersed and disposed in the main electrolytic cell 50. While being transported, the aluminum plate W is electrolyzed by the main poles 53a and 53b connected to the alternating current power source 51. From the electrolytic solution supply port 54, the electrolytic solution 55 is supplied to the electrolytic solution channel 57 between the radial drum roller 52 and the main poles 53a and 53b through the slit 56. The aluminum plate W treated in the main electrolytic cell 50 is then electrolyzed in the auxiliary anode cell 60. In the auxiliary anode cell 60, the auxiliary anode 58 is disposed to face the aluminum plate W. The electrolytic solution 55 is supplied to flow in the space between the auxiliary anode 58 and the aluminum plate W.

[0553] In view of easily manufacturing a predetermined lithographic printing plate precursor, the amount of the aluminum plate dissolved by the second alkaline etching treatment is preferably 1.0 g/m^2 to 20 g/m^2 and more preferably 2.0 g/m^2 to 10 g/m^2.

[0554] In view of easily manufacturing a predetermined lithographic printing plate precursor, the amount of the aluminum plate dissolved by the third alkaline etching treatment and the fifth alkaline etching treatment is preferably 0.01 g/m^2 to 0.8 g/m^2 and more preferably 0.05 g/m^2 to 0.3 g/m^2.

[0555] In the chemical etching treatment (first to fifth desmutting treatments) using an acidic aqueous solution, an acidic aqueous solution containing phosphoric acid, nitric acid, sulfuric acid, chromic acid, hydrochloric acid, or a mixed acid consisting of two or more of these acids is suitably used.

[0556] The concentration of the acid in the acidic aqueous solution is preferably 0.5% by mass to 60% by mass.

<<Anodization treatment step>>

[0557] The anodization treatment step is a step of performing an anodization treatment on the aluminum plate having undergone the roughening treatment such that an aluminum oxide film is formed on the surface of the aluminum plate. By the anodization treatment, an anodic oxide film of aluminum having micropores is formed on the surface of the aluminum plate.

[0558] The anodization treatment can be performed according to the method known in the field of the related art, by appropriately setting manufacturing conditions in consideration of the desired micropore shape.

[0559] In the anodization treatment step, an aqueous solution of sulfuric acid, phosphoric acid, oxalic acid, or the like can be mainly used as an electrolytic solution. In some cases, an aqueous solution or a non-aqueous solution of chromic acid, sulfamic acid, benzenesulfonic acid, or the like or an aqueous solution or a non-aqueous solution containing two or more kinds among the above acids can also be used. In a case where direct current or alternating current is applied to the aluminum plate in the electrolytic solution, an anodic oxide film can be formed on the surface of the aluminum plate. The electrolytic solution may contain aluminum ions. The content of the aluminum ions is not particularly limited, but is preferably 1 g/L to 10 g/L.

[0560] The conditions of the anodization treatment are appropriately set depending on the electrolytic solution used. Generally, the concentration of the electrolytic solution of 1% by mass to 80% by mass (preferably 5% by mass to 20% by mass), the liquid temperature of 5°C to 70°C (preferably 10°C to 60°C), the current density of 0.5 A/dm^2 to 60 A/dm^2 (preferably 5 A/dm^2 to 50 A/dm^2), the voltage of 1 V to 100 V (preferably 5 V to 50 V), and the electrolysis time of 1 second to 100 seconds (preferably 5 seconds to 60 seconds) are appropriate.

[0561] One of the preferred examples of the anodization treatment is the anodization method described in British

Patent 1,412,768, which is performed in a sulfuric acid at a high current density.

[0562] The anodization treatment can also be performed multiple times. It is possible to change one or more of conditions, such as the type, concentration, and liquid temperature of the electrolytic solution used in each anodization treatment, the current density, the voltage, and the electrolysis time. In a case where the anodization treatment is performed twice, sometime the firstly performed anodization treatment is called first anodization treatment, and the secondly performed anodization treatment is called second anodization treatment. Performing the first anodization treatment and the second anodization treatment makes it possible to form anodic oxide films having different shapes and to provide a lithographic printing plate precursor having excellent printing performance.

[0563] Furthermore, it is also possible to perform the following pore widening treatment after the anodization treatment and then perform the anodization treatment again. In this case, the first anodization treatment, the pore widening treatment, and the second anodization treatment are performed.

[0564] Using the method of performing the first anodization treatment, the pore widening treatment, and the second anodization treatment makes it possible to form micropores each configured with a large diameter portion that extends from the surface of the anodic oxide film along the depth direction and a small diameter portion that is in communication with the bottom portion of the large diameter portion and extends from the communicate position along the depth direction.

<<Pore widening treatment step>>

[0565] The pore widening treatment step is a treatment of enlarging the diameter of micropores (pore diameter) present in the anodic oxide film formed by the anodization treatment step (pore diameter enlarging treatment). By the pore widening treatment, the diameter of the micropores is enlarged, and an anodic oxide film having micropores having a larger average diameter is formed.

[0566] The pore widening treatment can be carried out by bringing the aluminum plate obtained by the anodization treatment step into contact with an acidic aqueous solution or an alkaline aqueous solution. The contact method is not particularly limited, and examples thereof include a dipping method and a spraying method. Among these, a dipping method is preferable.

[0567] In a case where an alkaline aqueous solution is used in the pore widening treatment step, it is preferable to use at least one alkaline aqueous solution selected from the group consisting of sodium hydroxide, potassium hydroxide, and lithium hydroxide. The concentration of the alkaline aqueous solution is preferably 0.1% by mass to 5% by mass. As a appropriate treatment method, the pH of the alkaline aqueous solution is adjusted to 11 to 13, and the aluminum plate is brought into contact with the alkaline aqueous solution for 1 second to 300 seconds (preferably 1 second to 50 seconds) under the condition of 10°C to 70°C (preferably 20°C to 50°C). At this time, the alkaline treatment liquid may contain a metal salt of a polyvalent weak acid such as carbonate, borate, or phosphate.

[0568] In a case where an acidic aqueous solution is used in the pore widening treatment step, it is preferable to use an aqueous solution of an inorganic acid such as sulfuric acid, phosphoric acid, nitric acid, or hydrochloric acid, or a mixture of these. The concentration of the acidic aqueous solution is preferably 1% by mass to 80% by mass and more preferably 5% by mass to 50% by mass. As a appropriate treatment method, the aluminum plate is brought into contact with the acidic aqueous solution for 1 second to 300 seconds (preferably 1 second to 150 seconds) under the condition of a liquid temperature of the acidic aqueous solution of 5°C to 70°C (preferably 10°C to 60°C).

[0569] The alkaline aqueous solution or the acidic aqueous solution may contain aluminum ions. The content of the aluminum ions is not particularly limited, but is preferably 1 g/L to 10 g/L.

[0570] The manufacturing method of the aluminum support having an anodic oxide film may include a hydrophilic treatment step of performing a hydrophilic treatment after the pore widening treatment step described above. As the hydrophilic treatment, it is possible to use the known method described in paragraphs "0109" to "0114" of JP2005-254638A.

[0571] The hydrophilic treatment is preferably performed by a method of immersing the aluminum plate in an aqueous solution of an alkali metal silicate such as sodium silicate or potassium silicate, a method of coating the aluminum plate with a hydrophilic vinyl polymer or a hydrophilic compound to form a hydrophilic undercoat layer, or the like.

[0572] The hydrophilic treatment using an aqueous solution of an alkali metal silicate such as sodium silicate or potassium silicate can be performed according to the method and procedure described in US2714066A and US3181461A.

<Undercoat layer>

[0573] The lithographic printing plate precursor according to the present disclosure preferably has an undercoat layer (also called interlayer in some cases) between the image-recording layer and the support. The undercoat layer enhances the adhesiveness between the support and the image-recording layer in an exposed portion, and enables the image-recording layer to be easily peeled from the support in a non-exposed portion. Therefore, the undercoat layer inhibits the deterioration of printing durability and contributes to the improvement of developability. In addition, in the case of exposure to infrared laser, the undercoat layer functions as a heat insulating layer and thus brings about an effect of preventing sensitivity reduction resulting from the diffusion of heat generated by exposure to the support.

[0574] Examples of compounds that are used in the undercoat layer include polymers having adsorbent groups that can be adsorbed onto the surface of the support and hydrophilic groups. In order to improve adhesiveness to the image-recording layer, polymers having adsorbent groups and hydrophilic groups plus crosslinking groups are preferable. The compounds that are used in the undercoat layer may be low-molecular-weight compounds or polymers. As necessary, as the compounds that are used in the undercoat layer, two or more compounds may be used by being mixed together.

[0575] In a case where the compound used in the undercoat layer is a polymer, a copolymer of a monomer having an adsorbent group, a monomer having a hydrophilic group, and a monomer having a crosslinking group is preferable.

[0576] As the adsorbent group that can be adsorbed onto the surface of the support, a phenolic hydroxy group, a carboxy group, $-PO_3H_2$, $-OPO_3H_2$, $-CONHSO_2-$, $-SO_2NHSO_2-$, and $-COCH_2COCH_3$ are preferable. As the hydrophilic groups, a sulfo group or salts thereof and salts of a carboxy group are preferable. As the crosslinking groups, an acryl group, a methacryl group, an acrylamide group, a methacrylamide group, an allyl group, and the like are preferable.

[0577] The polymer may have a crosslinking group introduced by the formation of a salt of a polar substituent of the polymer and a compound that has a substituent having charge opposite to that of the polar substituent and an ethylenically unsaturated bond, or may be further copolymerized with monomers other than the monomers described above and preferably with hydrophilic monomers.

[0578] Specifically, for example, silane coupling agents having addition polymerizable ethylenic double bond reactive groups described in JP1998-282679A (JP-H10-282679A) and phosphorus compounds having ethylenic double bond reactive groups described in JP1990-304441A (JP-H02-304441A) are suitable. The low-molecular-weight compounds or high-molecular-weight compounds having crosslinking groups (preferably ethylenically unsaturated groups), functional groups that interact with the surface of the support, and hydrophilic groups described in JP2005-238816A, JP2005-125749A, JP2006-239867A, and JP2006-215263A are also preferably used.

[0579] For example, the high-molecular-weight polymers having adsorbent groups that can be adsorbed onto the surface of the support, hydrophilic groups, and crosslinking groups described in JP2005-125749A and JP2006-188038A are more preferable.

[0580] The content of ethylenically unsaturated group in the polymer used in the undercoat layer is preferably 0.1 mmol to 10.0 mmol per gram of the polymer and more preferably 0.2 mmol to 5.5 mmol per gram of the polymer.

[0581] The weight-average molecular weight (Mw) of the polymer used in the undercoat layer is preferably 5,000 or more and more preferably 10,000 to 300,000.

[0582] In order to prevent contamination with the passage of time, the undercoat layer may contain, in addition to the compounds for the undercoat layer described above, a chelating agent, a secondary or tertiary amine, a polymerization inhibitor, a compound having an amino group or a functional group capable of inhibiting polymerization and a group that interacts with the surface of the support (for example, 1,4-diazabicyclo[2.2.2]octane (DABCO), 2,3,5,6-tetrahydroxy-p-quinone, chloranil, sulfophthalic acid, hydroxyethyl ethylenediaminetriacetic acid, dihydroxyethyl ethylenediaminediacetic acid, hydroxyethyl iminodiacetic acid, and the like), and the like.

[0583] The undercoat layer is formed by known coating methods. The coating amount (solid content) of the undercoat layer is preferably 0.1 mg/m^2 to 100 mg/m^2 and more preferably 1 mg/m^2 to 30 mg/m^2.

<Protective layer>

[0584] The lithographic printing plate precursor according to the present disclosure preferably has a protective layer (also called "overcoat layer" in some cases) on a surface of the image-recording layer that is opposite to the support side.

[0585] In addition, the lithographic printing plate precursor according to the present disclosure preferably has a support, an image-recording layer, and a protective layer in this order.

[0586] The protective layer may have a function of preventing the damage of the image-recording layer, and a function of preventing ablation during exposure to high-illuminance lasers, in addition to a function of suppressing the reaction inhibiting image formation by blocking oxygen.

[0587] The protective layer having such characteristics is described, for example, in US3458311A and JP1980-49729B (JP-S55-49729B). As polymers with low oxygen permeability that are used in the protective layer, any of water-soluble polymers and water-insoluble polymers can be appropriately selected. As necessary, two or more such polymers can be used by being mixed together. From the viewpoint of on-press developability, the polymers with low oxygen permeability preferably include a water-soluble polymer.

[0588] In the present disclosure, a water-soluble polymer means a polymer having a solubility of more than 5% by mass in water at 25°C.

[0589] Examples of the water-soluble polymer used in the protective layer include polyvinyl alcohol, modified polyvinyl alcohol, polyvinylpyrrolidone, a cellulose derivative, polyethylene glycol, poly(meth)acrylonitrile, and the like.

[0590] In addition, the water-soluble polymer preferably includes at least one selected from the group consisting of a modified polyvinyl alcohol and a cellulose derivative.

[0591] As the modified polyvinyl alcohol, acid-modified polyvinyl alcohol having a carboxy group or a sulfo group is preferably used. Specific examples thereof include modified polyvinyl alcohols described in JP2005-250216A and JP2006-259137A.

[0592] Examples of the cellulose derivative include methyl cellulose, hydroxypropyl methyl cellulose, carboxymethyl cellulose, and the like.

[0593] Among the above water-soluble polymers, a polymer containing polyvinyl alcohol is preferable, and a polymer containing polyvinyl alcohol having a saponification degree of 50% or more is more preferable.

[0594] The saponification degree is preferably 60% or more, more preferably 70% or more, and even more preferably 85% or more. The upper limit of the saponification degree is not particularly limited, and may be 100% or less.

[0595] The saponification degree is measured according to the method described in JIS K 6726: 1994.

[0596] As an aspect of the protective layer, for example, an aspect in which the protective layer contains polyvinyl alcohol and polyethylene glycol is also preferable.

[0597] In a case where the protective layer in the present disclosure contains the water-soluble polymer, the content of the water-soluble polymer with respect to the total mass of the protective layer is preferably 1% by mass to 99% by mass, more preferably 3% by mass to 97% by mass, and even more preferably 5% by mass to 95% by mass.

[0598] The protective layer preferably contains a hydrophobic polymer.

[0599] The hydrophobic polymer refers to a polymer that dissolves less than 5 g or does not dissolve in 100 g of pure water at 125°C.

[0600] Examples of the hydrophobic polymer include polyethylene, polystyrene, polyvinyl chloride, polyvinylidene chloride, polyalkyl (meth)acrylate ester (for example, polymethyl (meth)acrylate, polyethyl (meth)acrylate, polybutyl (meth)acrylate, and the like), a copolymer obtained by combining raw material monomers of these resins, and the like.

[0601] The hydrophobic polymer preferably includes a polyvinylidene chloride resin.

[0602] Furthermore, the hydrophobic polymer preferably includes a styrene-acrylic copolymer (also called styrene acrylic resin).

[0603] Moreover, from the viewpoint of on-press developability, the hydrophobic polymer is preferably hydrophobic polymer particles.

[0604] Only one hydrophobic polymer may be used, or two or more hydrophobic polymers may be used in combination.

[0605] In a case where the protective layer contains the hydrophobic polymer, the content of the hydrophobic polymer with respect to the total mass of the protective layer is preferably 1% by mass to 70% by mass, more preferably 5% by mass to 50% by mass, and even more preferably 10% by mass to 40% by mass.

[0606] In the present disclosure, the proportion of the area of the hydrophobic polymer occupying the surface of the protective layer is preferably 30 area% or more, more preferably 40 area% or more, and even more preferably 50 area% or more.

[0607] The upper limit of the proportion of the area of the hydrophobic polymer occupying the surface of the protective layer is, for example, 90 area%.

[0608] The proportion of the area of the hydrophobic polymer occupying the surface of the protective layer can be measured as follows.

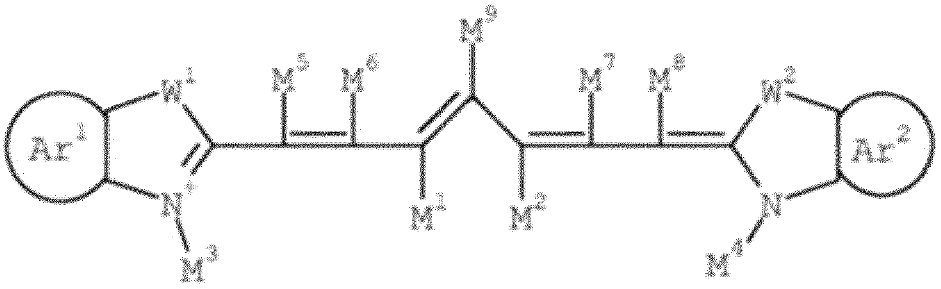
[0609] By using PHI nano TOFII time-of-flight secondary ion mass spectrometer (TOF-SIMS) manufactured by ULVAC-PHI, INCORPORATED., the surface of the protective layer is irradiated with Bi ion beams (primary ions) at an acceleration voltage of 30 kV, and the peak of ions (secondary ions) corresponding to a hydrophobic portion (that is, a region formed of the hydrophobic polymer) that are emitted from the surface is measured, so that the hydrophobic portion is mapped. By measuring the area of the hydrophobic portion in an area of 100 μm^2, the proportion of the area occupied by the hydrophobic portion is determined and adopted as "proportion of the area of the hydrophobic polymer occupying the surface of the protective layer".

[0610] For example, in a case where the hydrophobic polymer is an acrylic resin, the proportion is measured using the peak of $C_6H_{13}O^-$. In addition, in a case where the hydrophobic polymer is polyvinylidene chloride, the proportion is measured using the peak of $C_2H_2Cl^+$.

[0611] The proportion of occupied area can be adjusted by the amount of the hydrophobic polymer added or the like.

[0612] The protective layer preferably contains a second infrared absorber (hereinafter, also called a specific infrared absorber as distinguished from the infrared absorber contained in the image-recording layer) which includes a thermally decomposable group transformed into a group that is a stronger electron donor upon exposure to heat and/or infrared radiation, and which is capable of forming a print-out image upon exposure to heat and/or infrared radiation.

[0613] The specific infrared absorber is preferably a compound represented by the following Formula (VI).



(VI)

[0614] In Formula (VI), Ar^1 and Ar^2 each independently represent an optionally substituted aromatic hydrocarbon group or an aromatic hydrocarbon group having an optionally substituted benzene ring, W^1 and W^2 each independently represent a sulfur atom, an oxygen atom, or NR*, where R* represents an optionally substituted alkyl group, NH, or $-CM^{10}M^{11}$ group, where M^{10} and M^{11} each independently represent an optionally substituted aliphatic hydrocarbon group or an optionally substituted aryl group or heteroaryl group, M^1 and M^2 each independently represent a hydrogen atom, an optionally substituted aliphatic hydrocarbon group, or a group of atoms required to form an optionally substituted cyclic structure of M^1 and M^2, M^3 and M^4 each independently represent an optionally substituted aliphatic hydrocarbon group, M^5 to M^8 each independently represent a hydrogen atom, a halogen atom, or an optionally substituted aliphatic hydrocarbon group, and M^9 is a group which is converted into a group that is an electron donor stronger than M^9 by a chemical reaction induced by exposure to infrared or heat, and which increases an integrated light absorption of the compound represented by Formula (VI) in a wavelength range of 350 nm to 700 nm by this conversion, M^9 having optionally one or a plurality of counter ions in order to obtain an electrically neutral compound.

[0615] M^9 in Formula (VI) is preferably selected from any of $-(N=CR^{17})_a-NR^5-CO-R^4$, $-(N=CR^{17})_b-NR^5-SO_2-R^6$, $-(N=CR^{17})_c-NR^{11}-SO-R^{12}$, $-SO_2-NR^{15}R^{16}$, and $-S-CH_2-CR^7(H)_{1-d}(R^8)_d-NR^9-COOR^{18}$. Here, a, b, c, and d are each independently 0 or 1. In addition, M^9 may contain one or more counter ions in order to obtain an electrically neutral compound.

[0616] R^{17} represents a hydrogen atom, an optionally substituted aliphatic hydrocarbon group, an optionally substituted aryl group or heteroaryl group, or atomic groups necessary to form a cyclic structure together with R^5 or R^{11}.

[0617] R^4 represents $-OR^{10}$, $-NR^{13}R^{14}$, or $-CF_3$. Here, R^{10} represents an optionally substituted aryl group or heteroaryl group, or an aliphatic hydrocarbon group which may be branched.

[0618] R^{13} and R^{14} each independently represent a hydrogen atom, an optionally substituted aliphatic hydrocarbon group, an optionally substituted aryl group or heteroaryl group, or atomic groups necessary to form a cyclic structure together with R^{13} and R^{14}.

[0619] R^6 represents an optionally substituted aliphatic hydrocarbon group, an optionally substituted aryl group or heteroaryl group, $-OR^{10}$, $-NR^{13}R^{14}$, or $-CF_3$.

[0620] R^5 represents a hydrogen atom, an optionally substituted aliphatic hydrocarbon group, a SO_3^- group, a $-COOR^{18}$, an optionally substituted aryl group or heteroaryl group, or atomic groups necessary to form a cyclic structure together with at least one of R^{10}, R^{13}, and R^{14}.

[0621] R^{11} represents a hydrogen atom, an optionally substituted aliphatic hydrocarbon group, or an optionally substituted aryl group or heteroaryl group.

[0622] R^{15} and R^{16} each independently represent a hydrogen atom, an optionally substituted aliphatic hydrocarbon group, an optionally substituted aryl group or heteroaryl group, or atomic groups necessary to form a cyclic structure together with R^{15} and R^{16}.

[0623] R^{12} represents an optionally substituted aliphatic hydrocarbon group or an optionally substituted aryl group or heteroaryl group.

[0624] R^7 and R^9 each independently represent a hydrogen atom or an optionally substituted aliphatic hydrocarbon group.

[0625] R^8 represents -COO- or $-COOR^8$. Here, R^8 represents a hydrogen atom, an alkali metal cation, an ammonium ion, or a mono-, di-, tri-, or tetra-alkylammonium ion.

[0626] R^{18} represents an optionally substituted aryl group or heteroaryl group, or an α-branched aliphatic hydrocarbon group.

[0627] Ar^1 and Ar^2 in Formula (VI) each independently preferably represent an optionally substituted aryl group. The ring represented by Ar^1 and Ar^2 is preferably a benzene ring or a naphthalene ring.

[0628] W^1 and W^2 each preferably represent $-C(CH_3)_2$.

[0629] M^1 and M^2 preferably represent atomic groups necessary to form an optionally substituted 5-membered ring or benzene ring together.

[0630] M^3 and M^4 each independently preferably represent an optionally substituted aliphatic hydrocarbon group.

[0631] M^5, M^6, M^7, and M^8 each preferably represent a hydrogen atom.

[0632] M^9 preferably represents $-NR^5-CO-R^4$, $-NR^5-SO_2-R^6$, $-NR^1-SO-R^{12}$, or $-SO_2-NR^{15}R^{16}$. Here, R^4, R^5, R^6, R^{11}, R^{12}, R^{15} , and R^{16} have the same meaning as R^4, R^5, R^6, R^{11}, R^{12}, R^{15}, and R^{16}, which are described above. Particularly, M^9 more preferably represents $-NR^5-CO-R^4$ or $-NR^5-SO_2-R^6$. At this time, R^4 is preferably $-OR^{10}$, and R^{10} is preferably an aliphatic hydrocarbon group that may be branched. R^5 is a hydrogen atom, an optionally substituted aliphatic hydrocarbon group, or an optionally substituted aryl group or heteroaryl group, and R^6 is an optionally substituted aliphatic hydrocarbon group or an optionally substituted aryl group or heteroaryl group. In addition, M^9 optionally contains one or more counter ions to obtain an electrically neutral compound.

[0633] The specific infrared absorber, specifically, the compound represented by Formula (VI) may be a neutral dye, an anionic dye, or a cationic dye, depending on the type of the substituent and the number of each substituent.

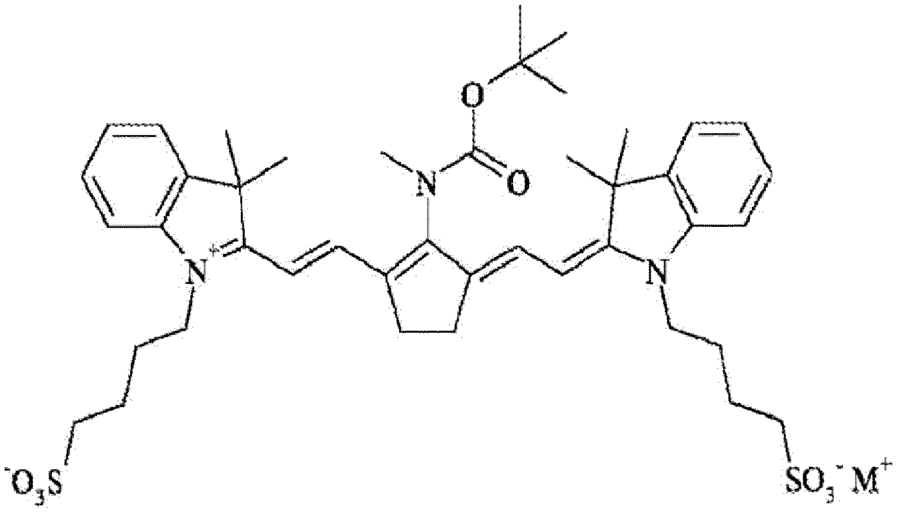
[0634] The compound represented by Formula (VI) preferably contains, in the structure, $-CO_2H$, $-CONHSO_2R^h$, $-SO_2NHCOR^1$, $-SO_2NHSO_2R^j$, $-PO_3H_2$, $-OPO_3H_2$, $-OSO_3H$, $-S-SO_3H$, $-SO_3H$, or an anionic group or acid group of salts thereof. Here, R^h, R^i, and R^j each independently represent an aryl group or an alkyl group, and is preferably a methyl group. Examples of the salt include an alkali metal salt or an ammonium salt, and a mono-, di-, tri-, or tetra-alkylammonium salt is preferable.

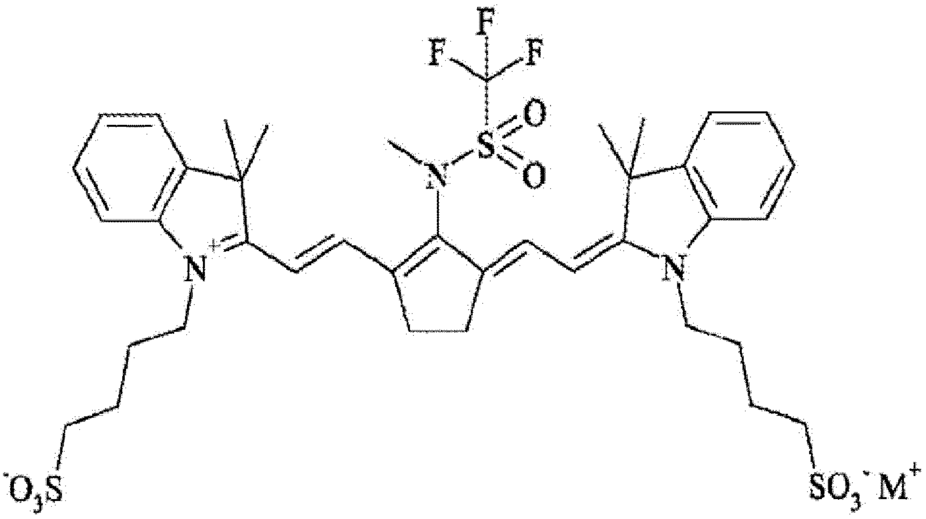
[0635] The anionic group or acid group is preferably present on the benzene ring of Ar^1 or Ar^2 or on the aliphatic hydrocarbon group of M^3 or M^4. The benzene ring of Ar^1 or Ar^2 or the aliphatic hydrocarbon group of M^3 or M^4 in which the anionic group or acid group is present may have another substituent. The other substituent can be selected from a halogen atom, a cyano group, a sulfone group, a carbonyl group, or a carboxylic acid ester group.

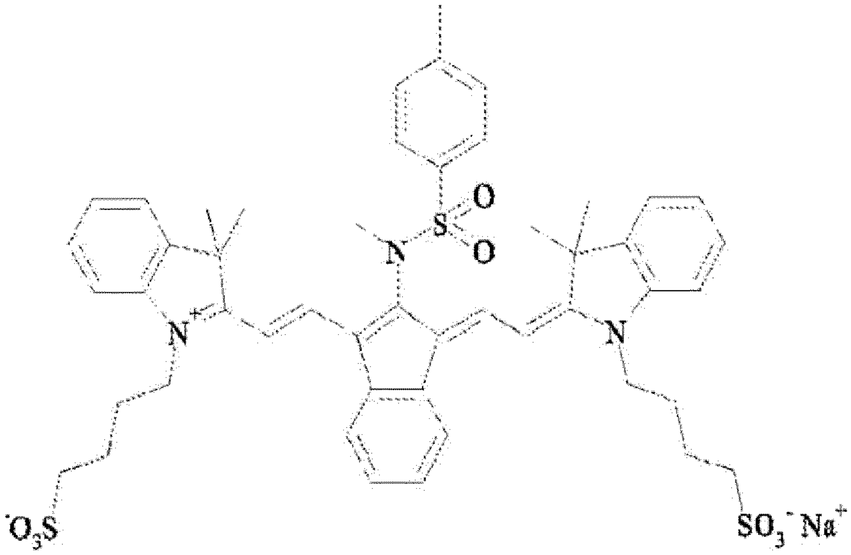
[0636] In particular, the compound represented by Formula (VI) preferably contains, on an aliphatic hydrocarbon group of M^3 or M^4, $-CO_2H$, $-CONHSO_2Me$, $-SO_2NHCOMe$, $-SO_2NHSO_2$, $-PO_3H_2$, $-SO_3$ group, or salts thereof. Here, Me represents a methyl group.

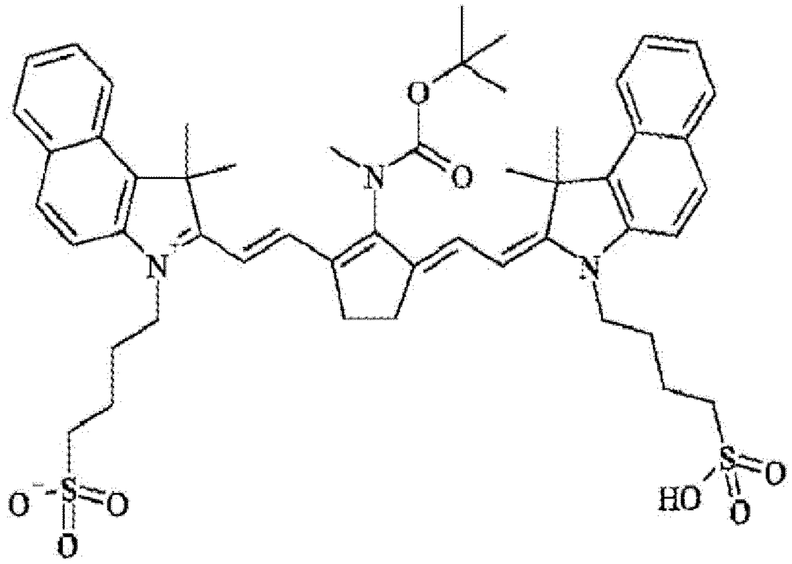
[0637] In the compound represented by Formula (VI), examples of any counter ions for obtaining an electrically neutral compound include an anion such as halogen, sulfonate, perfluorosulfonate, tosylate, tetrafluoroborate, hexafluorophosphate, aryl borate, and aryl sulfonate. In addition, examples of the salt structure of the compound represented by Formula (VI) include an alkali metal salt or an ammonium salt.

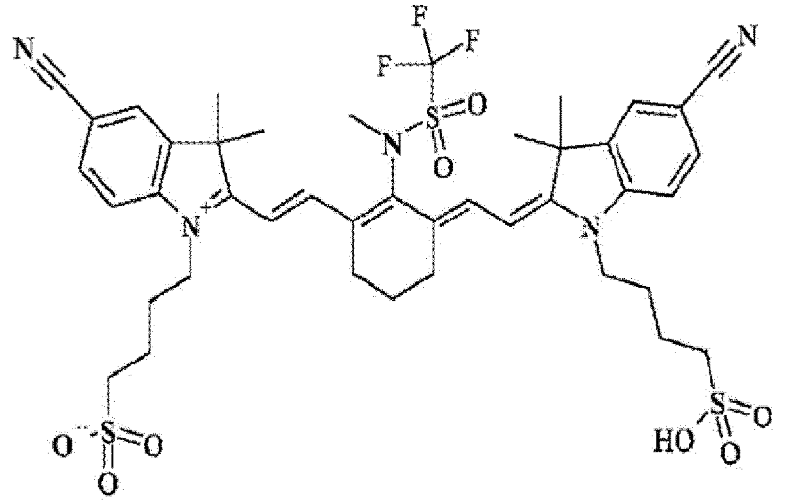
[0638] Specific examples of the compound represented by Formula (VI) are as follows. In the following specific examples, M^+ is L^+, Na^+, K^+, NH_4^+, or R_3NH^+, where R each independently represent a hydrogen atom, optionally substituted alkyl group, or an optionally substituted aryl group.

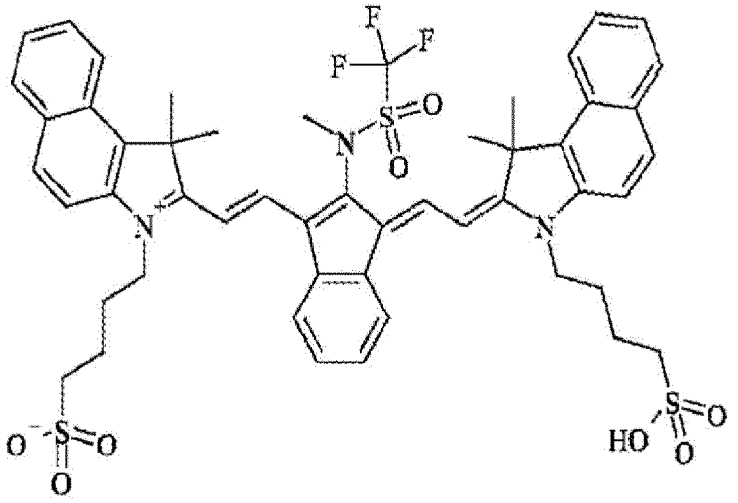












[0639] In a case where the protective layer contains a specific infrared absorber, the content of the infrared absorber with respect to the total mass of the protective layer is preferably 1% by mass to 40% by mass, more preferably 2% by mass to 20% by mass, and even more preferably 4% by mass to 10% by mass.

[0640] From the viewpoint of development defect suppressiveness, the protective layer preferably contains a filler.

[0641] Examples of the filler include inorganic particles, organic resin particles, and an inorganic lamellar compound, and the like. Among these, an inorganic lamellar compound is preferable. Using an inorganic lamellar compound makes it possible to effectively inhibit an attachment attached again from the roll surface from being directly attached to the surface of the image-recording layer.

[0642] Examples of the inorganic particles include metal oxide particles such as silica particles.

[0643] Examples of the organic resin particles include crosslinked resin particles.

[0644] The inorganic lamellar compound refers to particles in the form of a thin flat plate, and examples thereof include mica groups such as natural mica and synthetic mica, talc represented by Formula $3MgO \cdot 4SiO \cdot H_2O$, taeniolite, montmorillonite, saponite, hectorite, zirconium phosphate, and the like.

[0645] As the inorganic lamellar compound, a mica compound is preferably used. Examples of the mica compound include mica groups such as natural mica and synthetic mica, which are represented by Formula: $A(B, C)_{2\text{-}5}D_4O_{10}(OH, F, O)_2$ [here, A represents any of K, Na, and Ca, B and C represent any of Fe (II), Fe (III), Mn, Al, Mg, and V, and D represents Si or Al.].

[0646] In the mica group, examples of the natural mica include muscovite, soda mica, phlogopite, biotite, and lepidolite. Examples of synthetic mica include non-swelling mica such as fluorine phlogopite $KMg_3(AlSi_3O_{10})F_2$, potassium tetrasilic mica $KMg_{2.5}(Si_4O_{10})F_2$, and, Na tetrasilylic mica $NaMg_{2.5}(Si_4O_{10})F_2$, swelling mica such as Na or Li taeniolite $(Na, Li)Mg_2Li(Si_4O_{10})F_2$, montmorillonite-based Na or Li hectorite $(Na, Li)_{1/8}Mg_{2/5}Li_{1/8}(Si_4O_{10})F_2$. Furthermore, synthetic smectite is also useful.

[0647] Among the mica compounds, fluorine-based swelling mica is particularly useful. That is, swelling synthetic mica has a laminated structure consisting of unit crystal lattice layers having a thickness in a range of about 10Å to 15A (1A is equal to 0.1 nm), and metal atoms in lattices are more actively substituted than in any other clay minerals. As a result, positive charges are deficient in the lattice layers, and positive ions such as Li^+, Na^+, Ca^{2+}, and Mg^{2+} are adsorbed between the layers in order to compensate for the deficiency. Positive ions interposed between the layers are referred to as exchangeable positive ions and are exchangeable with various positive ions. Particularly, in a case where the positive ions between the layers are Li^+ and Na^+, the ionic radii are small, and thus the bonds between lamellar crystal lattices are weak, and mica is significantly swollen by water. In a case where shear is applied in this state, mica easily cleavages and forms a stable sol in water. Swelling synthetic mica is particularly preferably used because it clearly exhibits such a tendency.

[0648] From the viewpoint of diffusion control, regarding the shapes of the mica compounds, the thickness is preferably thin, and the planar size is preferably large as long as the smoothness and actinic ray-transmitting property of coated surfaces are not impaired. Therefore, the aspect ratio is preferably 20 or higher, more preferably 100 or higher, and particularly preferably 200 or higher. The aspect ratio is the ratio of the major diameter to the thickness of a particle, and it can be measured, for example, from a projection view obtained from the microphotograph of the particle. As the aspect ratio increases, the obtained effect is stronger.

[0649] Regarding the particle diameter of the mica compound, the average major diameter thereof is preferably 0.3 μm to 20 μm, more preferably 0.5 μm to 10 μm, and particularly preferably 1 μm to 5 μm. The average thickness of the particles is preferably 0.1 μm or less, more preferably 0.05 μm or less, and particularly preferably 0.01 μm or less. Specifically, for example, as a preferable aspect of swelling synthetic mica which is a representative compound, the thickness thereof is in a range of about 1 nm to 50 nm and the surface size (major diameter) is in a range of about 1 μm to 20 μm.

[0650] The content of the inorganic lamellar compound with respect to the total mass of the protective layer is preferably 1% by mass to 60% by mass and more preferably 3% by mass to 50% by mass. Even in a case where a plurality of kinds of inorganic lamellar compounds are used in combination, the total amount of the inorganic lamellar compounds preferable equals the content described above. In a case where the content is within the above range, the oxygen barrier property is improved, and excellent sensitivity is obtained. In addition, the deterioration of receptivity can be prevented.

[0651] The protective layer may contain known additives such as a plasticizer for imparting flexibility, a surfactant for improving coating property, and inorganic particles for controlling surface sliding property. In addition, the oil sensitizing agent described above regarding the image-recording layer may be contained in the protective layer.

[0652] The protective layer is formed by known coating methods. The coating amount (solid content) of the protective layer is preferably 0.01 g/m^2 to 10 g/m^2, more preferably 0.02 g/m^2 to 3 g/m^2, and particularly preferably 0.02 g/m^2 to 1 g/m^2.

[0653] The film thickness of the protective layer in the lithographic printing plate precursor according to the present disclosure is preferably 0.1 μm to 5.0 μm and more preferably 0.3 μm to 4.0 μm.

[0654] The lithographic printing plate precursor according to the present disclosure may have other layers in addition to those described above.

[0655] Known layers can be adopted as those other layers without particular limitations. For example, as necessary, a backcoat layer may be provided on a surface of the support that is opposite to the image-recording layer side.

(Method of preparing lithographic printing plate and lithographic printing method)

[0656] Although the method of preparing a lithographic printing plate according to the present disclosure is not particularly limited, but it is preferable that the method of preparing a lithographic printing plate include a step of exposing the lithographic printing plate precursor in the shape of an image (exposure step) and a step of removing the image-recording layer in a non-image area by supplying at least one selected from the group consisting of a printing ink and dampening water to the lithographic printing plate precursor having undergone exposure on a printer (on-press development step).

[0657] The lithographic printing method according to the present disclosure preferably includes a step of exposing the lithographic printing plate precursor in the shape of an image (exposure step), a step of removing the image-recording layer in a non-image area by supplying at least one selected from the group consisting of a printing ink and dampening water on a printer to prepare a lithographic printing plate (on-press development step), and a step of performing printing by using the obtained lithographic printing plate (hereinafter, also called "printing step").

<Exposure step>

[0658] The method of preparing a lithographic printing plate according to the present disclosure preferably includes an exposure step of exposing the lithographic printing plate precursor in the shape of an image to form an exposed portion and a non-exposed portion. The lithographic printing plate precursor according to the present disclosure is preferably exposed to a laser through a transparent original picture having a linear image, a halftone dot image, or the like or exposed in the shape of an image by laser light scanning according to digital data, or the like.

[0659] The wavelength of a light source to be used is preferably 750 nm to 1,400 nm. As the light source having a wavelength of 750 nm to 1,400 nm, a solid-state laser or a semiconductor laser that radiates infrared is suitable. In a case where an infrared laser is used, the output is preferably 100 mW or more, the exposure time per pixel is preferably 20 microseconds or less, and the amount of irradiation energy is preferably 10 mJ/cm^2 to 300 mJ/cm^2. In addition, in order to shorten the exposure time, a multibeam laser device is preferably used. The exposure mechanism may be any of an inner surface drum method, an external surface drum method, a flat head method, or the like.

[0660] The image exposure can be carried out by a common method using a platesetter or the like. In the case of on-press development, image exposure may be carried out on a printer after the lithographic printing plate precursor is mounted on the printer.

<On-press development step>

[0661] The method of preparing a lithographic printing plate according to the present disclosure preferably includes an on-press development step of removing the image-recording layer in a non-image area by supplying at least one selected from the group consisting of printing ink and dampening water on a printer.

[0662] Hereinafter, the on-press development method will be described.

[On-press development method]

[0663] In the on-press development method, the lithographic printing plate precursor having undergone image exposure is preferably supplied with an oil-based ink and an aqueous component on a printer such that the image-recording layer in a non-image area is removed and a lithographic printing plate is prepared.

[0664] That is, in a case where the lithographic printing plate precursor is subjected to image exposure and then mounted as it is on a printer without being subjected to any development treatment, or the lithographic printing plate precursor is mounted on a printer and then subjected to image exposure on the printer, and then an oil-based ink and an aqueous component is supplied to perform printing, at the initial stage in the middle of printing, in a non-image area, by either or both of the supplied oil-based ink and the aqueous component, a non-cured image-recording layer is dissolved or dispersed to remove, and the hydrophilic surface is exposed in the non-image area. Meanwhile, the image-recording layer cured by exposure forms an oil-based ink receiving areas having a lipophilic surface in the exposed portion. What is supplied first to the precursor surface may be any of the oil-based ink or the aqueous component. However, in view of preventing the plate from being contaminated by the components of the image-recording layer from which aqueous components are removed, it is preferable that the oil-based ink be supplied first. In the manner described above, the lithographic printing plate precursor is subjected to on-press development on a printer and used as it is for printing a number of sheets. As the oil-based ink and the aqueous component, ordinary printing ink and ordinary dampening water for lithographic printing are suitably used.

<Printing step>

[0665] The lithographic printing method according to the present disclosure includes a printing step of printing a recording medium by supplying a printing ink to the lithographic printing plate.

[0666] The printing ink is not particularly limited, and various known inks can be used as desired. In addition, preferred examples of the printing ink include oil-based ink or ultraviolet-curable ink (UV ink).

[0667] In the printing step, as necessary, dampening water may be supplied.

[0668] In addition, the printing step may be successively carried out after the on-press development step or the development step using a developer, without stopping the printer.

[0669] The recording medium is not particularly limited, and known recording media can be used as desired.

[0670] In the method of preparing a lithographic printing plate and the lithographic printing method according to the present disclosure, as necessary, the entire surface of the lithographic printing plate precursor may be heated before exposure, in the middle of exposure, or during a period of time from exposure to development. In a case where the lithographic printing plate precursor is heated as above, an image-forming reaction in the image-recording layer is accelerated, which can result in advantages such as improvement of sensitivity and printing durability, and stabilization of sensitivity. Heating before development is preferably carried out under a mild condition of 150°C or lower. In a case where this aspect is adopted, it is possible to prevent issues such as curing of a non-image area. For heating after development, it is preferable to use an extremely severe condition which is preferably in a range of 100°C to 500°C. In a case where the above range is adopted, a sufficient image-strengthening action is obtained, and it is also possible to inhibit issues such as the deterioration of the support or the thermal decomposition of the image area.

(Laminate)

[0671] The laminate according to the present disclosure is formed by at least laminating the lithographic printing plate precursors according to the present disclosure.

[0672] In addition, the laminate according to the present disclosure is preferably formed by laminating the lithographic printing plate precursors according to the present disclosure and preferably has a protective material that protects the lithographic printing plate precursor disposed on at least the uppermost portion of the laminated lithographic printing plate precursors, and a moisture content of the protective material is preferably 10% or less.

[0673] The lithographic printing plate precursor is in the form of one sheet of thin plate adopting a metal as a support. Therefore, in a case where scratches or deformation occurs in the corners, sides, inside, or the like of the lithographic printing plate precursor, unfortunately, images are likely to be blurred by photosensitization, or ink is likely to be non-uniformly distributed by printing.

[0674] Therefore, in a case where a plurality of precursors is laminated to constitute a laminate, in order to protect the lithographic printing plate precursor, generally, the protective material is disposed between a predetermined number of the precursors such that the precursors are reliably protected.

[0675] Furthermore, the precursors between which the protective material is disposed are packaged as they are with a packaging material to prepare a packaged substance, and handled (transported, stored, or the like). In a case where the protective material is disposed, deformation (such as bending) of the precursor is unlikely occur during, for example, handling, which prevents damage of the precursor. In addition, even though external force acts, the external force is partially absorbed into the protective material, which prevents deformation or scratches of the precursor.

[0676] Preferred aspects of the lithographic printing plate precursor in the laminate according to the present disclosure is the same as the preferred aspects of the lithographic printing plate precursor according to the present disclosure described above.

<Protective material>

[0677] The laminate according to the present disclosure preferably has a protective material that protects the lithographic printing plate precursor disposed on at least the uppermost portion of the laminated lithographic printing plate precursors, and a moisture content of the protective material is preferably 10% by mass or less.

[0678] From the viewpoint of development defect suppressiveness, the moisture content of the protective material is preferably 10% by mass or less, more preferably 7% by mass or less, and particularly preferably 3% by mass or less. The lower limit of the moisture content is 0% by mass.

[0679] The moisture content (equilibrium moisture content) of the protective material in the present disclosure is measured by the measuring method according to JIS P 8202 (1998).

[0680] Examples of the material of the protective material include thick paper, cardboard, plastic, and the like. Among these, from the viewpoint of development defect suppressiveness, cardboard or plastic is preferable, and plastic is more preferable.

[0681] As the plastic, a known polymer can be used, and examples thereof include polyester, polycarbonate, and polyolefin. Among these, polyester is preferable.

[0682] The size (length × width) of the protective material is not particularly limited and can be appropriately selected depending on the lithographic printing plate precursor to be used. For example, the size of the protective material is the same as or slightly larger than the size of the lithographic printing plate precursor.

[0683] The thickness of the protective material is not particularly limited. From the viewpoint of strength, moisture permeability, and development defect suppressiveness, the thickness of the protective material is preferably 10 μm to 10 mm and more preferably 100 μm to 5 mm.

[0684] In addition, it is preferable that the protective material be disposed not only in the uppermost portion of the laminate but also in the lowermost portion.

interleaving paper>

[0685] The laminate according to the present disclosure may have interleaving paper between two laminated lithographic printing plate precursors.

[0686] In addition, the interleaving paper may be between the lithographic printing plate precursor and the protective material.

[0687] Furthermore, the interleaving paper may be in the lowermost portion of the laminate.

[0688] In order to reduce the material cost, it is preferable to select low-cost raw materials as the material of the interleaving paper used in the present disclosure. For example, it is possible to use paper using wood pulp 100% by mass, paper using wood pulp together with synthetic pulp, paper composed of the above paper and a low-density or high-density polyethylene layer provided on the surface of the paper, and the like.

[0689] Specifically, examples thereof include acidic paper made of paper stock prepared by adding a sizing agent and a paper strengthening agent to paper stock obtained by beating bleached kraft pulp and then diluting the beaten pulp to a concentration of 4% by mass such that the amounts of the sizing agent and paper strengthening agent are 0.1% by mass and 0.2% by mass respectively with respect to the mass of the paper stock and then adding aluminum sulfate thereto until the pH reaches 5.0. It is preferable to use alkaline paper having a pH of 7 to 8 in which a neutral sizing agent, such as an alkyl ketene dimer (AKD) or an alkenyl succinic anhydride (ASA), is used as a sizing agent and calcium carbonate is used as a filler instead of aluminum sulfate.

[0690] As the interleaving paper, among these, paper is preferable, paper containing aluminum sulfate or calcium carbonate is more preferable, and paper containing calcium carbonate is particularly preferable.

[0691] The material of the interleaving paper is preferably paper containing 50% by mass or more of pulp, more preferably paper containing 70% by mass or more of pulp, and particularly preferably paper containing 80% by mass or more of pulp.

[0692] In the interleaving paper, the calcium content with respect to the total mass of the interleaving paper is preferably 0.15% by mass to 0.5% by mass, more preferably 0.2% by mass to 0.45% by mass, and particularly preferably 0.25% by mass to 0.4% by mass.

[0693] The calcium content of the interleaving paper is obtained by performing X-ray fluorescence spectrometry on the interleaving paper.

[0694] The calcium contained in paper is mainly calcium carbonate which is widely used as a filler for alkaline paper, and performs an action of increasing whiteness of the paper.

[0695] The basis weight of the interleaving paper (determined by measuring method specified in JIS P8124 (2011)) is not particularly limited, but from the viewpoints of printing durability and on-press developability, is preferably 29 g/m^2 to 80 g/m^2, more preferably 35 g/m^2 to 70 g/m^2, and particularly preferably 51 g/m^2 to 65 g/m^2.

[0696] From the viewpoints of UV printing durability and on-press developability, the basis weight of the interleaving paper is preferably 51 g/m^2 or more.

[0697] The thickness of the interleaving paper (determined by the measuring method specified in JIS P8118 (2014)) is not particularly limited, but is preferably 20 μm to 100 μm, more preferably 42 μm to 80 μm, even more preferably 45 μm to 65 μm, and particularly preferably 45 μm to 55 μm.

[0698] From the viewpoint of dot-like color defect suppressiveness, the moisture amount of the interleaving paper (moisture amount of the interleaving paper stored at 25°C/50% RH until the moisture amount of the interleaving paper is stabilized) with respect to the total mass of the interleaving paper is preferably 0% by mass to 20% by mass, more preferably 0% by mass to 15% by mass, and particularly preferably 0% by mass to 10% by mass.

[0699] As the interleaving paper, the interleaving paper described in JP2010-76336A can be suitably used.

[0700] The shape of the interleaving paper is not particularly limited, and examples thereof include a shape which is the same as or larger than the shape of the lithographic printing plate precursor in the plane direction.

[0701] The laminate according to the present disclosure may be entirely packaged by a known method.

Examples

[0702] Hereinafter, the present disclosure will be described in detail with reference to examples, but the present disclosure is not limited thereto. In the present examples, unless otherwise specified, "%" and "part" mean "% by mass" and "part by mass" respectively. Unless otherwise described, the molecular weight of a high-molecular-weight compound is a weight-average molecular weight (Mw), and the ratio of repeating constitutional units of a polymer compound is expressed as molar percentage. The weight-average molecular weight (Mw) is a polystyrene-equivalent molecular weight measured by gel permeation chromatography (GPC).

(Examples 1 to 97 and Comparative Examples 1 to 5)

<Preparation of support>

<<Surface treatment A»

(A-a) Mechanical roughening treatment (brush graining method)

[0703] By using the device as shown in Fig. 3, a pumice suspension (specific gravity: 1.1 g/cm^3) as an abrasive slurry was supplied to the surface of an aluminum plate, and in this state, a mechanical roughening treatment is performed using a rotating bundled brush. In Fig. 3, 1 represents an aluminum plate, 2 and 4 represent roller-shaped brushes (bundled brushes in the present example), 3 represents an abrasive slurry, and 5, 6, 7, and 8 represent support rollers.

[0704] In the mechanical roughening treatment, an abrasive having a median diameter (μm) of 30 μm and 4 brushes were used, and the rotation speed (rpm) of the brushes was set to 250 rpm. The bundled brush was made of 6 -10 nylon and consisted of bristles having a diameter of 0.3 mm and a length of 50 mm. The brush was prepared by making holes in a φ 300 mm stainless steel cylinder and densely implanting bristles therein. The distance between two support rollers (φ 200 mm) under the bundled brush was 300 mm. The bundled brush was pressed until the load of the drive motor for rotating the brush was 10 kW higher than the load applied before the bundled brush was pressed on the aluminum plate. The rotation direction of the brush was the same as the moving direction of the aluminum plate.

(A-b) Alkaline etching treatment

[0705] An aqueous solution of caustic soda having a caustic soda concentration of 26% by mass and an aluminum ion concentration of 6.5% by mass was sprayed from a spray tube onto the aluminum plate obtained above at a temperature of 70°C, thereby performing an etching treatment. Then, rinsing was performed by means of spraying. The amount of dissolved aluminum was 10 g/m^2.

(A-c) Desmutting treatment in acidic aqueous solution

[0706] Next, a desmutting treatment was performed in an aqueous nitric acid solution. As the aqueous nitric acid solution used in the desmutting treatment, the waste liquid of nitric acid used in the next step, electrochemical roughening, was used. The liquid temperature was 35°C. The desmutting treatment was performed for 3 seconds by spraying the desmutting liquid.

(A-d) Electrochemical roughening treatment

[0707] An electrochemical roughening treatment was continuously performed using nitric acid as an electrolyte at an alternating current voltage of 60 Hz. In this treatment, an electrolytic solution was used which was prepared by adding aluminum nitrate to 10.4 g/L aqueous nitric acid solution at a temperature of 35°C such that the aluminum ion concentration was adjusted to 4.5 g/L. By using an alternating current power source having the waveform shown in Fig. 1, alternating current having a trapezoidal rectangular waveform, and a carbon electrode as a counter electrode, an electrochemical roughening treatment was performed under the conditions of a time tp taken for the current value to reach the peak from zero of 0.8 msec and the duty ratio of 1:1. As an auxiliary anode, ferrite was used. The electrolytic cell shown in Fig. 2 was used. The peak current density was 30 A/dm^2, and 5% of the current coming from the power source was allowed to flow into the auxiliary anode. The electricity quantity (C/dm^2) was 185 C/dm^2, which is the total quantity of electricity used during the anodic reaction of the aluminum plate. Then, rinsing was performed by means of spraying.

(A-e) Alkaline etching treatment

[0708] An aqueous solution of caustic soda having a caustic soda concentration of 5% by mass and an aluminum ion concentration of 0.5% by mass was sprayed from a spray tube onto the aluminum plate obtained above at a temperature of 50°C, thereby performing an etching treatment. Then, rinsing was performed by means of spraying. The amount of dissolved aluminum was 0.5 g/m^2.

(A-f) Desmutting treatment in acidic aqueous solution

[0709] Next, a desmutting treatment was performed in an aqueous sulfuric acid solution. In the desmutting treatment, an aqueous sulfuric acid solution having a sulfuric acid concentration of 170 g/L and an aluminum ion concentration of 5 g/L was used. The liquid temperature was 30°C. The desmutting treatment was performed for 3 seconds by spraying the desmutting liquid.

(A-g) Electrochemical roughening treatment

[0710] An electrochemical roughening treatment was continuously performed using hydrochloric acid as an electrolyte at an alternating current voltage of 60 Hz. An electrolytic solution was used which was prepared by adding aluminum chloride to 6.2 g/L aqueous hydrochloric acid solution at a liquid temperature of 35°C such that the aluminum ion concentration was adjusted to 4.5 g/L. By using an alternating current power source having the waveform shown in Fig. 1, alternating current having a trapezoidal rectangular waveform, and a carbon electrode as a counter electrode, an electrochemical roughening treatment was performed under the conditions of a time tp taken for the current value to reach the peak from zero of 0.8 msec and the duty ratio of 1:1. As an auxiliary anode, ferrite was used. The electrolytic cell shown in Fig. 2 was used.

[0711] The peak current density was 25 A/dm^2, and the electricity quantity (C/dm^2) during the hydrochloric acid electrolysis was 63 C/dm^2 which is the total quantity of electricity used during the anodic reaction of the aluminum plate. Then, rinsing was performed by means of spraying.

(A-h) Alkaline etching treatment

[0712] An aqueous solution of caustic soda having a caustic soda concentration of 5% by mass and an aluminum ion concentration of 0.5% by mass was sprayed from a spray tube onto the aluminum plate obtained above at a temperature of 50°C, thereby performing an etching treatment. Then, rinsing was performed by means of spraying. The amount of dissolved aluminum was 0.1 g/m^2.

(A-i) Desmutting treatment in acidic aqueous solution

[0713] Next, a desmutting treatment was performed in an aqueous sulfuric acid solution. Specifically, by using a waste liquid generated in the anodization treatment step (170 g/L aqueous sulfuric acid solution containing dissolved aluminum ions at 5 g/L), the desmutting treatment was performed for 4 seconds at a liquid temperature of 35°C. The desmutting treatment was performed for 3 seconds by spraying the desmutting liquid.

(A-j) First-stage anodization treatment

[0714] By using the anodization device for direct current electrolysis having the structure shown in Fig. 4, a first-stage anodization treatment was performed. The anodization treatment was performed under the conditions shown in Table 1, thereby forming an anodic oxide film having a predetermined film thickness.

[0715] In the anodization treatment device 610, an aluminum plate 616 is transported as indicated by the arrow in Fig. 4. In a power supply tank 612 containing an electrolytic solution 618, the aluminum plate 616 is positively (+) charged by a power supply electrode 620. Then, the aluminum plate 616 is transported upwards by a roller 622 in the power supply tank 612, makes a turn downwards by a nip roller 624, then transported toward an electrolytic treatment tank 614 containing an electrolytic solution 626, and makes a turn by a roller 628 to move in the horizontal direction. Subsequently, the aluminum plate 616 is negatively (-) charged by an electrolysis electrode 630. As a result, an anodic oxide film is formed on the surface of the aluminum plate 616. The aluminum plate 616 exits from the electrolytic treatment tank 614 and is then transported for the next step. In the anodization treatment device 610, the roller 622, the nip roller 624, and the roller 628 constitute a direction change unit. Furthermore, in the inter-tank portion between the power supply tank 612 and the electrolytic treatment tank 614, the aluminum plate 616 is transported in a ridge shape and an inverted U shape by the rollers 622, 624, and 628. The power supply electrode 620 and the electrolysis electrode 630 are connected to a direct current power source 634.

(A-k) Pore widening treatment

[0716] Under the conditions shown in Table 1, the aluminum plate having undergone the above anodization treatment was immersed in an aqueous solution of caustic soda at a temperature of 35°C and having a caustic soda concentration of 5% by mass and an aluminum ion concentration of 0.5% by mass, thereby performing a pore widening treatment. Then, rinsing was performed by means of spraying.

(A-l) Second-stage anodization treatment

[0717] By using the anodization device for direct current electrolysis having the structure shown in Fig. 4, a second-stage anodization treatment was performed. The anodization treatment was performed under the conditions shown in Table 1, thereby forming an anodic oxide film having a predetermined film thickness.

(A-m) Third-stage anodization treatment

[0718] By using the anodization device for direct current electrolysis having the structure shown in Fig. 4, a third-stage anodization treatment was performed. The anodization treatment was performed under the conditions shown in Table 1, thereby forming an anodic oxide film having a predetermined film thickness.

[0719] By the above surface treatment A, the supports A shown in Tables 1 and 2 were obtained.

[0720] Table 2 shows the average diameter (nm) of the large diameter portion in the anodic oxide film within the surface of the anodic oxide film having micropores obtained after the second anodization treatment step, the average diameter (nm) of the small diameter portion at a communicate position, the depth (nm) of the large diameter portion and the small diameter portion, the pit density (micropore density, unit; number of micropores/μm^2), and the thickness (nm) of the anodic oxide film from the bottom portion of the small diameter portion to the surface of the aluminum plate.

[0721] The average diameter of the micropores (average diameter of the large diameter portion and the small diameter portion) is a value obtained by observing the surface of the large diameter portion and the surface of the small diameter portion with FE-SEM at 150,000X magnification (N= 4), and measuring the diameters of micropores (large diameter portion and small diameter portion) in a range of 400 nm x 600 nm in the obtained 4 images, and calculating the average thereof. In a case where the large diameter portion was deep and it was difficult to measure the diameter of the small diameter portion, and in a case where an enlarged diameter portion in the small diameter portion was measured, the upper portion of the anodic oxide film was cut, and then various diameters were calculated.

[0722] The depth of the micropores (depth of the large diameter portion and the small diameter portion) is a value obtained by observing the cross section of the support (anodic oxide film) with FE-SEM (observation of the depth of the large diameter portion: 150,000X magnification, observation of depth of small diameter portion: 50,000X magnification), measuring the depths of 25 random micropores in the obtained image, and calculating the average thereof.

[0723] In Table 1, film amount (AD) in the column of the first anodization treatment and film amount (AD) in the column of second anodization treatment represent the amount of film obtained by each treatment. As electrolytic solutions, the aqueous solutions containing the components in Table 1 were used.

[Table 1]

Support	Surface treatment	First anodization treatment							Pore widening treatment			Second anodization treatment						
		Liquid type	Liquid component	Component concentration	Temperature	Current density	Time	Film amount	Liquid component	Temperature	Time	Liquid type	Liquid component	Component concentration	Temperature	Current density	Time	Film amount
Support A	A	Sulfuric acid	H_2SO_4/Al	170/5	40	30	1.4	0.25	NaOH 5%/Al 0.5%	35	5	Sulfuric acid	H_2SO_4/Al	170/5	50	13	17	2.25

[Table 2]

Support	Large diameter portion				Small diameter portion			Thickness of anodic oxide film (nm)
	Average diameter (nm)	Shape	Micropore density (number of micropores/ μm^2)	Depth (nm)	Pore diameter at communication position (nm)	Shape	Depth (nm)	
Support A	35	Straight tubular shape	500	100	10	Straight tubular shape	900	1,000

[0724] Using the support A, an undercoat layer, an image-recording layer, and a protective layer were formed as follows to obtain a lithographic printing plate precursor.

<Formation of undercoat Layer>

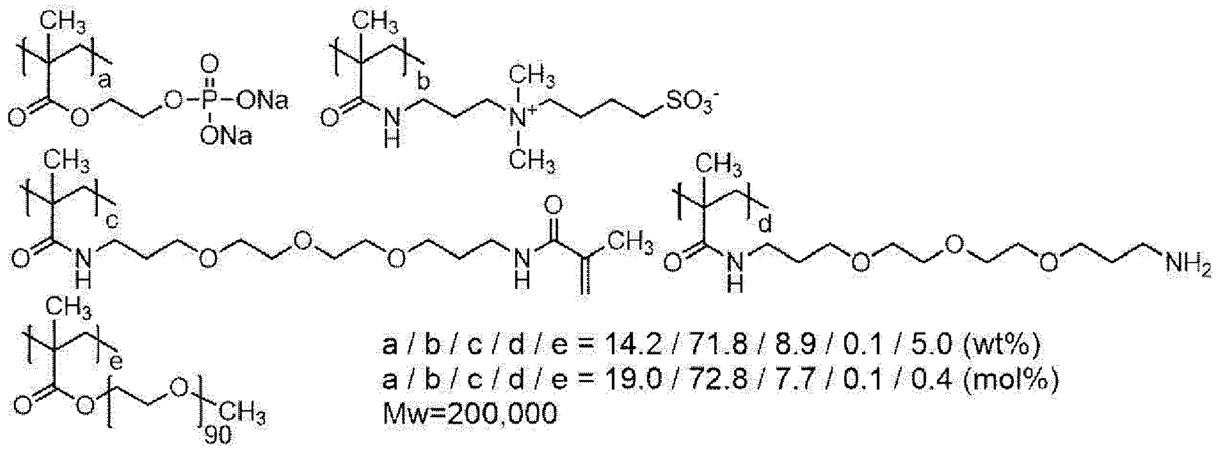
[0725] The obtained support A was coated with the undercoat layer coating liquid having the following composition such that the dry coating amount was 0.1 g/m^2, to form an undercoat layer.

-Undercoat layer coating liquid-

[0726]

·Compound for undercoat layer (the following U-1, 11% aqueous solution): 0.10502 parts
·Sodium gluconate: 0.0700 parts
·Surfactant (EMALEX (registered trademark) 710, manufactured by NIHON EMULSION Co., Ltd.): 0.00159 parts
·Preservative (BIOHOPE L, manufactured by K·I Chemical Industry Co., LTD.): 0.00149 parts
·Water: 2.8719 parts

(U-1)



a / b / c / d / e = 14.2 / 71.8 / 8.9 / 0.1 / 5.0 (wt%)
a / b / c / d / e = 19.0 / 72.8 / 7.7 / 0.1 / 0.4 (mol%)
Mw=200,000

<Formation of image-recording layer>

[0727] The undercoat layer 1 was bar-coated with the image-recording layer coating liquid, followed by drying in an oven at 120°C for 60 seconds, thereby forming an image-recording layer having a dry coating amount of 1.0 g/m^2.

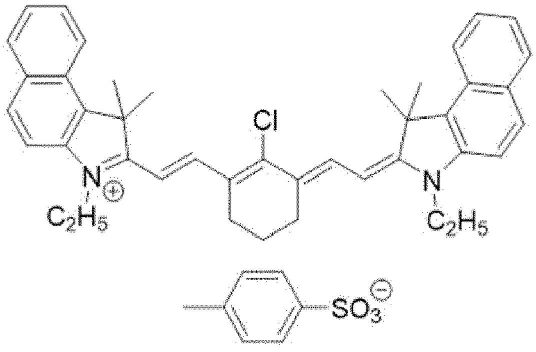
-Image-recording layer coating liquid-

[0728] The following components were dissolved in a mixed solution of 35% by volume methyl ethyl ketone (MEK) and 65% by volume 1-methoxy-2-propanol at a solid content concentration of 7.0% by mass to prepare the image-recording layer coating liquid 1.

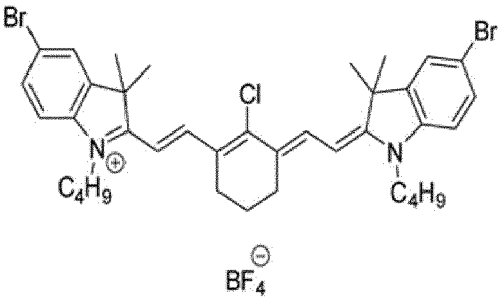
- ·Non-onium-based polymerization initiator (4-hydroxyphenyl-tribromomethylsulfone): 60 parts
- ·Borate compound (sodium tetraphenylborate (TPB)): no addition or 20 parts
- ·Infrared absorber (types shown in Tables 3 to 6): 20 parts
- ·Compound A (types shown in Tables 3 to 6): amounts (parts) shown in Tables 3 to 6
- ·Acid color forming agent (C-1, structure below): no addition or 50 parts
- ·Reaction product of 1 mole of 2,2,4-trimethylhexamethylene diisocyanate and 2 moles of hydroxyethyl methacrylate (82% by mass solution in MEK, FST 510, manufactured by AZ Electronics): 250 parts
- ·Epoxyacrylate oligomer (CN 104, manufactured by Arkema S.A.): 250 parts
- ·Non-ionic aliphatic polyether polyurethane (Ruco Coat EC4811, manufactured by Rudolf GmbH): 125 parts
- ·Polyvinyl butyral (vinyl butyral-co-vinyl acetate-co-vinyl alcohol, S-LEC BL-10, manufactured by Sekisui Chemical Company, Limited): 125 parts
- Poly ether siloxane copolymer (Tegoglide 410, manufactured by Evonik Resource Efficiency GmbH): 1.5 parts
- ·Polyethylene glycol monomethacrylate phosphate (JPA 528, manufactured by Johoku Chemical Co., Ltd.): 130 parts
- ·Copolymer of vinylphosphonic acid and acrylic acid (Albritect CP 30, manufactured by Rhodia, 20% by mass aqueous dispersion): 120 parts
- ·Phosphoric acid: 6.5 parts
- ·Hydrophilic fumed silica (Aerosil, manufactured by Evonik Resource Efficiency GmbH): 85 parts

[0729] The infrared absorber contained in the image-recording layer is as follows.

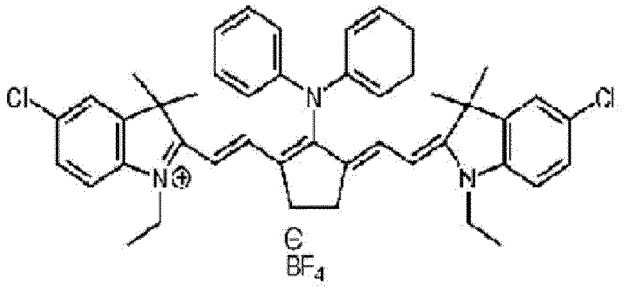
[0730] The following IR-4 is a salt of a cationic moiety of the infrared absorber and a borate anion (tetraphenyl borate anion).



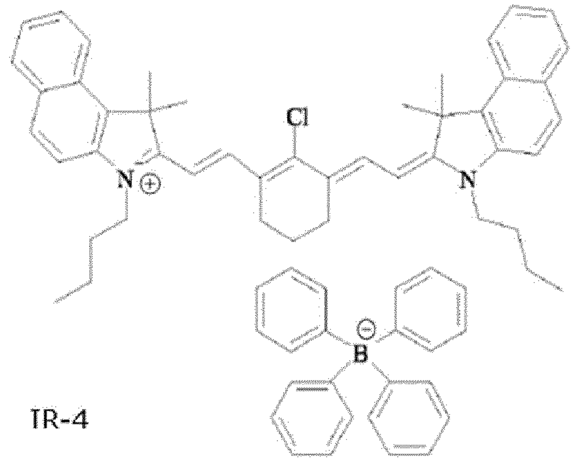
IR-1



IR-2



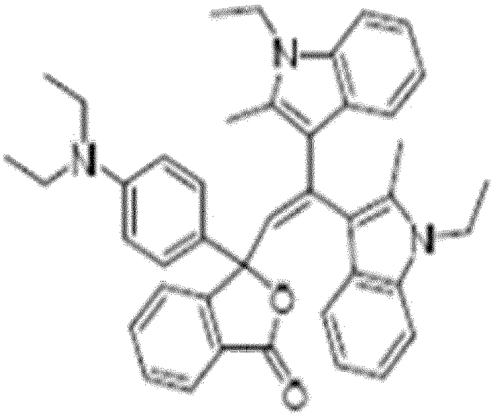
IR-3



IR-4

[0731] In addition, D1 to D31 in the compound A contained in the image-recording layer are the same compounds as D1 to D31 in the specific examples of the cations of the compound A described above.

[0732] Furthermore, the acid generator C-1 contained in the image-recording layer is a compound having the following structure.



C-1

<Formation of protective layer>

[0733] A protective layer was formed on the image-recording layer by the following forming method.

[0734] In Example 94 to 97, the protective layer was not formed.

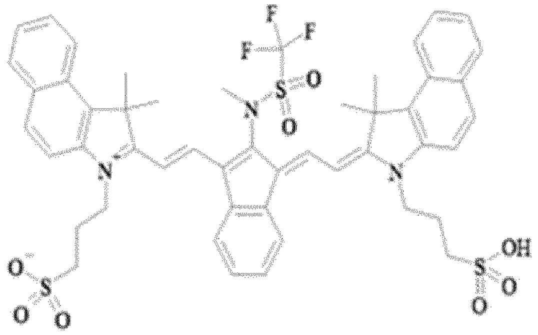
-Formation of protective layer-

[0735] The image-recording layer was bar-coated with the following coating liquid for a protective layer and dried in an oven at 110°C for 120 seconds, thereby forming a protective layer having a dry coating amount of 0.3 g/m^2. In this way, a lithographic printing plate precursor was prepared.

-Coating solution for protective layer-

[0736] The following components were mixed together, thereby preparing a coating liquid for a protective layer.

- ·Water: 2000 parts
- ·Polyvinyl alcohol (Mowiol 4-88TM, manufactured by KURARAY CO., LTD.): 160 parts
- ·Polyvinylidene chloride (Diofan A050, manufactured by Solvay S.A.): 296 parts
- ·ACTICIDE LA1206TM (manufactured by Thor): 1 part
- ·Surfactant (Lutensol A8TM, manufactured by BASF SE): 10 parts
- ·Specific infrared absorber (the following structure): 28 parts
- ·Potassium nitrate: 37 parts



<Evaluation of crystal precipitation>

[0737] The obtained lithographic printing plate precursor was come into contact with the rubber roller (diameter 2 cm) from the protective layer side, and pressured. The lithographic printing plate precursor after applying the contact pressure was stored for 3 days in a saturated atmosphere of 2-methoxypropanol using a vapor chamber. After storage for 3 days, the image-recording layer of the lithographic printing plate precursor was observed at 8X optical magnification, and the precipitates in the layers were evaluated.

-Evaluation indices-

[0738]

A: Crystal precipitate was not observed.
B: Some crystal precipitates were observed.
C: Many crystal precipitates were observed.

<Evaluation of printing durability>

[0739] The obtained lithographic printing plate precursor was exposed at a condition of 2400 dpi and an energy density of 90 mJ/cm^2 using an Avalon N8-20 platesetter (200 lpi Agfa Balancing Screening (ABS), manufactured by Agfa-Gevaert NV) with a 830 nm infrared laser.

[0740] The obtained exposed lithographic printing plate precursor was attached to the plate cylinder of the printer (manufactured by RYOBI LIMITED) without performing a development treatment. 50,000 sheets of printing were performed using non-coated offset paper (70 g) and a compressible blanket. For printing, TOYO FD LED UV EU3 cyan ink and a 3% by mass Prima AF S1 (manufactured by Agfa) aqueous solution as dampening water were used.

[0741] After that, the printing durability was evaluated using the number of printed sheets at a time when the reduction rate of the halftone portion density exceeded 8% with respect to the halftone portion density of the initial printed matter. The halftone portion density was measured using the Gretag macbeth densitometer.

[0742] The evaluation results are summarized in Tables 3 to 6.

[Table 3]

		Image-recording layer										Ratio (S_A/S_I)	Presence or absence of protective layer	Evaluation	
		Compound A						Infrared absorber		Acid color forming agent	Borate compound			Crystal precipitation	Printing durability
		Cation			Anion	Amountto be added [part]	*Molar content	Type	Shape index of cationic moiety (S_I)						
		Type	Shape index (S_A)	ClogP	Structure										
Examples	1	D1	0.45	5.1	TsO^-	0.03	1	IR-1	0.47	-	Present	0.96	Present	A	32000
	2	D2	0.43	5.6	TsO^-	0.03	1	IR-1	0.47	-	Present	0.91	Present	A	32000
	3	D3	0.39	6.5	TsO^-	0.03	1	IR-1	0.47	-	Present	0.83	Present	A	32000
	4	D4	0.46	7.9	TsO^-	0.03	1	IR-1	0.47	-	Present	0.98	Present	A	32000
	5	D5	0.38	5.6	TsO^-	0.03	1	IR-1	0.47	-	Present	0.82	Present	A	32000
	6	D6	0.60	3.6	TsO^-	0.03	1	IR-1	0.47	-	Present	1.28	Present	A	25000
	7	D7	0.60	2.1	TsO^-	0.03	1	IR-1	0.47	-	Present	1.28	Present	A	25000
	8	D8	0.53	62	TsO^-	0.03	1	IR-1	0.47	-	Present	1.13	Present	A	25000
	9	D9	0.52	9.8	TsO^-	0.03	1	IR-1	0.47	-	Present	1.11	Present	A	25000
	10	D10	0.29	5.7	TsO^-	0.03	1	IR-1	0.47	-	Present	0.62	Present	A	32000
	11	D11	0.56	2.5	TsO^-	0.03	1	IR-1	0.47	-	Present	1.18	Present	A	25000
	12	D12	0.38	4.3	TsO^-	0.03	1	IR-1	0.47	-	Present	0.82	Present	A	32000
	13	D13	0.52	9.5	TsO^-	0.03	1	IR-1	0.47	-	Present	1.10	Present	A	25000
	14	D14	0.36	6.6	TsO^-	0.03	1	IR-1	0.47	-	Present	0.77	Present	A	32000
	15	D15	0.56	2.5	TsO^-	0.03	1	IR-1	0.47	-	Present	1.19	Present	A	25000
	16	D16	0.52	13.5	TsO^-	0.03	1	IR-1	0.47	-	Present	1.10	Present	A	25000
	17	D17	0.60	-3.3	TsO^-	0.03	1	IR-1	0.47	-	Present	1.28	Present	A	25000
	18	D18	0.58	4.9	TsO^-	0.03	1	IR-1	0.47	-	Present	1.23	Present	A	25000
	19	D19	0.36	5.7	TsO^-	0.03	1	IR-1	0.47	-	Present	0.77	Present	A	32000

(continued)

	Image-recording layer										Ratio (S_A/S_I)	Presence or absence of protective layer	Evaluation	
	Compound A						Infrared absorber		Acid color forming agent	Borate compound			Crystal precipitation	Printing durability
	Cation			Anion	Amount to be added [part]	*Molar content	Type	Shape index of cationic moiety (S_I)						
	Type	Shape index (S_A)	ClogP	Structure										
20	D20	0.60	-0.1	TsO^-	0.03	1	IR-1	0.47	-	Present	1.28	Present	A	25000
21	D21	0.69	4.6	TsO^-	0.03	1	IR-1	0.47	-	Present	1.47	Present	A	25000
22	D22	0.64	3.5	TsO^-	0.03	1	IR-1	0.47	-	Present	1.37	Present	A	25000
23	D23	0.47	50	TsO^-	0.03	1	IR-1	0.47	-	Present	1.00	Present	A	32000
24	D24	0.45	40	TsO^-	0.03	1	IR-1	0.47	-	Present	0.96	Present	A	32000
25	D25	0.88	1.9	TsO^-	0.03	1	IR-1	0.47	-	Present	1.86	Present	B	20000
26	D26	0.82	-0.8	TsO^-	0.03	1	IR-1	0.47	-	Present	1.74	Present	B	20000
27	D27	0.75	2.0	TsO^-	0.03	1	IR-1	0.47	-	Present	1.60	Present	B	20000
28	D28	0.75	0.4	TsO^-	0.03	1	IR-1	0.47	-	Present	1.60	Present	B	20000
29	D29	0.36	4.4	TsO^-	0.03	1	IR-1	0.47	-	Present	0.77	Present	A	32000
30	D30	0.33	4.9	TsO^-	0.03	1	IR-1	0.47	-	Present	0.70	Present	A	32000
31	D31	0.33	4.9	TsO^-	0.03	1	IR-1	0.47	-	Present	0.70	Present	A	32000
32	D31	0.33	4.9	BF_4^-	0.03	1	IR-1	0.47	-	Present	0.70	Present	A	32000

*Molar content: molar content of cation of compound A with respect to molar content of anion of borate compound

[Table 4]

		Image-recording layer										Ratio (S_A/S_I)		Evaluation	
		Compound A						Infrared absorber		Acid color forming agent	Borate compound		Presence orabsence of protective layer	Crystal precipitation	Printing durability
		Cation			Anion	Amount to be added [part]	*Molar content	Type	Shape index of cationic moiety (S_I)						
		Type	Shape index (S_A)	ClogP	Structure										
Examples	33	D1	0.45	5.1	Br^-	0.03	1	IR-1	0.47	-	Present	0.96	Present	A	30000
	34	D1	0.45	5.1	BF_4^-	0.03	1	IR-1	0.47	-	Present	0.96	Present	A	32000
	35	D1	0.45	5.1	I^-	0.03	1	IR-1	0.47	-	Present	0.96	Present	A	30000
	36	D1	0.45	5.1	PF_6^-	0.03	1	IR-1	0.47	-	Present	0.96	Present	A	32000
	37	D1	0.45	5.1	Cl^-	0.03	1	IR-1	0.47	-	Present	0.96	Present	A	30000
	38	D1	0.45	5.1	Benzene sulfonate	0.03	1	IR-1	0.47	-	Present	0.96	Present	A	32000
	39	D1	0.45	5.1	1-Naphthalene sulfonate	0.03	1	IR-1	0.47	-	Present	0.96	Present	A	32000
	40	D1	0.45	5.1	2-Naphthalene sulfonate	0.03	1	IR-1	0.47	-	Present	0.96	Present	A	32000
	41	D1	0.45	5.1	Benzoate	0.03	1	IR-1	0.47	-	Present	0.96	Present	A	32000
	42	D1	0.45	5.1	Phenyl phosphate	0.03	1	IR-1	0.47	-	Present	0.96	Present	A	32000
	43	D1	0.45	5.1	Phenol salt	0.03	1	IR-1	0.47	-	Present	0.96	Present	A	32000
	44	D1	0.45	5.1	Thiophenol salt	0.03	1	IR-1	0.47	-	Present	0.96	Present	A	32000
	45	D1	0.45	5.1	Tetraphenylborate salt	0.03	1	IR-1	0.47	-	Present	0.96	Present	A	32000
	46	D1	0.45	5.1	TsO^-	0	0.1	IR-1	0.47	-	Present	0.96	Present	B	25000
	47	D1	0.45	5.1	TsO^-	0.01	0.3	IR-1	0.47	-	Present	0.96	Present	A	30000
	48	D1	0.45	5.1	TsO^-	0.02	0.7	IR-1	0.47	-	Present	0.96	Present	A	32000
	49	D1	0.45	5.1	TsO^-	0.04	1.3	IR-1	0.47	-	Present	0.96	Present	A	32000

(continued)

		Image-recording layer										Ratio (S_A/S_I)		Evaluation	
		Compound A						Infrared absorber		Acid color forming agent	Borate compound		Presence orabsence of protective layer	Crystal precipitation	Printing durability
		Cation			Anion	Amount to be added [part]	*Molar content	Type	Shape index of cationic moiety (S_I)						
		Type	Shape index (S_A)	ClogP	Structure										
	50	D1	0.45	5.1	TsO$^-$	0.06	2	IR-1	0.47	-	Present	0.96	Present	A	32000
	51	D1	0.45	5.1	TsO$^-$	0.08	2.7	IR-1	0.47	-	Present	0.96	Present	A	30000
	52	D1	0.45	5.1	TsO$^-$	0.1	3.3	IR-1	0.47	-	Present	0.96	Present	A	28000
	53	D1	0.45	5.1	TsO$^-$	0.15	5	IR-1	0.47	-	Present	0.96	Present	A	20000

*Molar content: molar content of cation of compound A with respect to molar content of anion of borate compound

[Table 5]

		Image-recording layer											Ratio (S_A/S_I)	Presence orabsence of protective layer	Evaluation	
		Compound A						Infrared absorber		Acid color forming agent	Borate compound				Crystal precipitation	Printing durability
		Cation			Anion	Amount to be added [part]	*Molar content									
		Type	Shape index (S_A)	ClogP	Structure			Type	Shape index of cationic moiety (Si)							
Examples	54	D12	0.38	4.3	BF_4^-	0.03	1	IR-1	0.47	-	Present		0.82	Present	A	32000
	55	D12	0.38	4.3	PF_6^-	0.03	1	IR-1	0.47	-	Present		0.82	Present	A	32000
	56	D12	0.38	4.3	Benzene sulfonate	0.03	1	IR-1	0.47	-	Present		0.82	Present	A	32000
	57	D12	0.38	4.3	1-Naphthalene sulfonate	0.03	1	IR-1	0.47	-	Present		0.82	Present	A	32000
	58	D12	0.38	4.3	2-Naphthalene sulfonate	0.03	1	IR-1	0.47	-	Present		0.82	Present	A	32000
	59	D12	0.38	4.3	Benzoate	0.03	1	IR-1	0.47	-	Present		0.82	Present	A	32000
	60	D12	0.38	4.3	Phenyl phosphate	0.03	1	IR-1	0.47	-	Present		0.82	Present	A	32000
	61	D12	0.38	4.3	Phenol salt	0.03	1	IR-1	0.47	-	Present		0.82	Present	A	32000
	62	D12	0.38	4.3	Thiophenol salt	0.03	1	IR-1	0.47	-	Present		0.82	Present	A	32000
	63	D12	0.38	4.3	Tetraphenylborate salt	0.03	1	IR-1	0.47	-	Present		0.82	Present	A	32000
	64	D1	0.45	5.1	TsO^-	0.03	1	IR-2	0.44	-	Present		1.02	Present	A	35000
	65	D1	0.45	5.1	BF_4^-	0.03	1	IR-2	0.44	-	Present		1.02	Present	A	35000
	66	D1	0.45	5.1	1-Naphthalene sulfonate	0.03	1	IR-2	0.44	-	Present		1.02	Present	A	35000
	67	D12	0.38	4.3	TsO^-	0.03	1	IR-2	0.44	-	Present		0.87	Present	A	35000
	68	D12	0.38	4.3	BF_4^-	0.03	1	IR-2	0.44	-	Present		0.87	Present	A	35000

(continued)

		Image-recording layer										Ratio (S_A/S_I)	Presence orabsence of protective layer	Evaluation	
		Compound A						Infrared absorber		Acid color forming agent	Borate compound			Crystal precipitation	Printing durability
		Cation			Anion	Amount to be added [part]	*Molar content	Type	Shape index of cationic moiety (Si)						
		Type	Shape index (S_A)	ClogP	Structure										
	69	D12	0.38	4.3	1-Naphthalene sulfonate	0.03	1	IR-2	0.44	-	Present	0.87	Present	A	35000
	70	D1	0.45	5.1	TsO^-	0.03	1	IR-3	0.38	-	Present	1.18	Present	A	35000
	71	D1	0.45	5.1	BF_4^-	0.03	1	IR-3	0.38	-	Present	1.18	Present	A	35000
	72	D1	0.45	5.1	1-Naphthalene sulfonate	0.03	1	IR-3	0.38	-	Present	1.18	Present	A	35000
	73	D12	0.38	4.3	TsO^-	0.03	1	IR-3	0.38	-	Present	1.01	Present	A	35000
	74	D12	0.38	4.3	BF_4^-	0.03	1	IR-3	0.38	-	Present	1.01	Present	A	35000
	75	D12	0.38	4.3	1-Naphthalene sulfonate	0.03	1	IR-3	0.38	-	Present	1.01	Present	A	35000

*Molar content: molar content of cation of compound A with respect to molar content of anion of borate compound

[Table 6]

		Image-recording layer										Ratio (S_A/S_I)	Presence or absence of protective layer	Evaluation	
		Compound A						Infrared absorber		Acid color forming agent	Borate compound			Crystal precipitation	Printing durability
		Cation			Anion	Amount to be added [part]	*Molar content								
		Type	Shape index (S_A)	ClogP	Structure			Type	Shape index of cationic moiety (Si)						
Examples	76	D1	0.45	5.1	TsO^-	0.03	1	IR-4	0.47	-	-	0.96	Present	A	32000
	77	D1	0.45	5.1	BF_4^-	0.03	1	IR-4	0.47	-	-	0.96	Present	A	32000
	78	D1	0.45	5.1	1-Naphthalene sulfonate	0.03	1	IR-4	0.47	-	-	0.96	Present	A	32000
	79	D12	0.38	4.3	TsO^-	0.03	1	IR-4	0.47	-	-	0.82	Present	A	32000
	80	D12	0.38	4.3	BF_4^-	0.03	1	IR-4	0.47	-	-	0.82	Present	A	32000
	81	D12	0.38	4.3	1-Naphthalene sulfonate	0.03	1	IR-4	0.47	-	-	0.82	Present	A	32000
	82	D12	0.38	4.3	BF_4^-	0	0.1	IR-1	0.47	-	Present	0.82	Present	B	25000
	83	D12	0.38	4.3	BF_4^-	0.01	0.3	IR-1	0.47	-	Present	0.82	Present	A	30000
	84	D12	0.38	4.3	BF_4^-	0.02	0.7	IR-1	0.47	-	Present	0.82	Present	A	32000
	85	D12	0.38	4.3	BF_4^-	0.04	1.3	IR-1	0.47	-	Present	0.82	Present	A	32000
	86	D12	0.38	4.3	BF_4^-	0.06	2	IR-1	0.47	-	Present	0.82	Present	A	32000
	87	D12	0.38	4.3	BF_4^-	0.08	2.7	IR-1	0.47	-	Present	0.82	Present	A	30000
	88	D12	0.38	4.3	BF_4^-	0.1	3.3	IR-1	0.47	-	Present	0.82	Present	A	28000
	89	D12	0.38	4.3	BF_4^-	0.15	5	IR-1	0.47	-	Present	0.82	Present	A	20000
	90	D1	0.45	5.1	TsO^-	0.03	1	IR-1	0.47	C-1	Present	0.96	Present	A	35000

(continued)

		Image-recording layer										Ratio (S_A/S_I)	Presence or absence of protective layer	Evaluation	
		Compound A						Infrared absorber		Acid color forming agent	Borate compound			Crystal precipitation	Printing durability
		Cation			Anion	Amount to be added [part]	*Molar content	Type	Shape index of cationic moiety (Si)						
		Type	Shape index (S_A)	ClogP	Structure										
	91	D1	0.45	5.1	BF_4^-	0.03	1	IR-1	0.47	C-1	Present	0.96	Present	A	35000
	92	D12	0.38	4.3	TsO^-	0.03	1	IR-1	0.47	C-1	Present	0.82	Present	A	35000
	93	D12	0.38	4.3	BF_4^-	0.03	1	IR-1	0.47	C-1	Present	0.82	Present	A	35000
	94	D1	0.45	5.1	TsO^-	0.03	1	IR-1	0.47	-	Present	0.96	Absent	A	35000
	95	D1	0.45	5.1	BF_4^-	0.03	1	IR-1	0.47	-	Present	0.96	Absent	A	35000
	96	D12	0.38	4.3	TsO^-	0.03	1	IR-1	0.47	-	Present	0.82	Absent	A	35000
	97	D12	0.38	4.3	BF_4^-	0.03	1	IR-1	0.47	-	Present	0.82	Absent	A	35000
Comparative examples	1	-	-	-	-	-	-	IR-1	0.47	-	Present	-	Present	C	16000
	2	-	-	-	-	-	-	IR-3	0.38	-	Present	-	Present	C	16000
	3	-	-	-	-	-	-	IR-4	0.47	-	-	-	Present	C	16000
	4	D25	0.88	1.9	TsO^-	0.03	1	IR-3	0.38	-	Present	2.30	Present	C	14000
	5	D26	0.82	-0.8	TsO^-	0.03	1	IR-3	0.38	-	Present	2.15	Present	C	14000

*Molar content: molar content of cation of compound A with respect to molar content of anion of borate compound

[0743] As is evident from Tables 3 to 6, it has been revealed that the lithographic printing plate precursors according to examples have excellent crystal precipitation suppressiveness, and further have excellent printing durability, compared to the lithographic printing plate precursors according to comparative examples.

Explanation of References

[0744]

1: aluminum plate
2, 4: roller-shaped brush
3: abrasive slurry
5, 6, 7, 8: support roller
50: main electrolytic cell
51: alternating current power source
52: radial drum roller
53a, 53b: main pole
54: electrolytic solution supply port
55: electrolytic solution
56: slit
57: electrolytic solution channel
58: auxiliary anode
60: auxiliary anode cell
610: anodization treatment device
612: power supply tank
614: electrolytic treatment tank
616: aluminum plate
618, 626: electrolytic solution
620: power supply electrode
622, 628: roller
624: nip roller
630: electrolysis electrode
632: cell wall
634: direct current power source
W: aluminum plate
S: liquid supply direction
Ex: electrolytic solution discharge direction
ta: anodic reaction time
tc: cathodic reaction time
tp: time taken for current to reach peak from 0
Ia: peak current on anodic cycle side
Ic: peak current on cathodic cycle side
AA: current of anodic reaction of aluminum plate
CA: current of cathodic reaction of aluminum plate

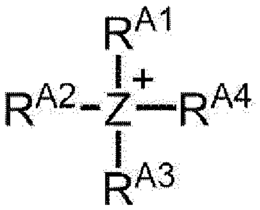
Claims

1. A lithographic printing plate precursor comprising:

a support; and
an image-recording layer on the support,
wherein the image-recording layer contains a non-onium-based polymerization initiator, a borate compound, an infrared absorber, and a compound A which is an onium salt with a cation having a shape index equal to or less than 2 times a shape index of a cationic moiety of the infrared absorber.

2. The lithographic printing plate precursor according to claim 1,

wherein the cation in the compound A is a cation represented by Formula (A),

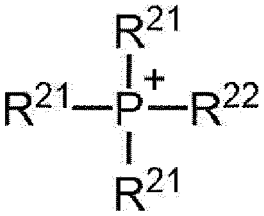


$$\begin{array}{c} R^{A1} \\ | \\ R^{A2}-\overset{+}{Z}-R^{A4} \\ | \\ R^{A3} \end{array} \qquad (A)$$

in Formula (A), Z represents P or N, and R^{A1} to R^{A4} each independently represent a hydrogen atom, an alkyl group, or an aryl group.

3. The lithographic printing plate precursor according to claim 1,

   wherein the cation in the compound A is a cation represented by Formula (2),

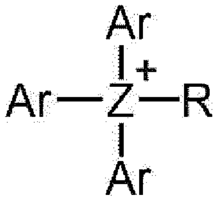


$$\begin{array}{c} R^{21} \\ | \\ R^{21}-\overset{+}{P}-R^{22} \\ | \\ R^{21} \end{array} \qquad (2)$$

   in Formula (2), R^{21}'s each independently represent an alkyl group and R^{22} represents a hydrogen atom or an alkyl group.

4. The lithographic printing plate precursor according to claim 1,

   wherein the cation in the compound A is a cation represented by Formula (1),



$$\begin{array}{c} Ar \\ | \\ Ar-\overset{+}{Z}-R \\ | \\ Ar \end{array} \qquad (1)$$

   in Formula (1), Z represents P or N, R represents an alkyl group, and Ar's each independently represent an aryl group.

5. The lithographic printing plate precursor according to any one of claims 1 to 4,
   wherein the cation in the compound A has a polymerizable group.

6. The lithographic printing plate precursor according to any one of claims 1 to 4,
   wherein clogP of the cation in the compound A is 0 or more and 10 or less.

7. The lithographic printing plate precursor according to any one of claims 1 to 4,
   wherein an anion in the compound A is a conjugate base of an organic acid.

8. The lithographic printing plate precursor according to any one of claims 1 to 4,

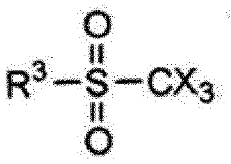
   wherein an anion in the compound A is at least one anion selected from the group consisting of $R^1SO_3^-$, $R^1SO_2^-$, $R^1R^2PO_2^-$, $R^1PO_3^{2-}$, $R^1CO_2^-$, R^1O^-, R^1S^-, $(R^1SO2)_2N^-$, and $R^1R^2R^3R^4B^-$, and
   R^1 to R^4 each independently represent a hydrogen atom, an alkyl group, or an aryl group.

9. The lithographic printing plate precursor according to any one of claims 1 to 4,
   wherein a molar content of the cation in the compound A is 0.2 times to 4 times a molar content of an anion in the

borate compound.

10. The lithographic printing plate precursor according to any one of claims 1 to 4,

wherein the non-onium-based polymerization initiator includes a compound represented by Formula (II),



$$R^3-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-CX_3$$

(II)

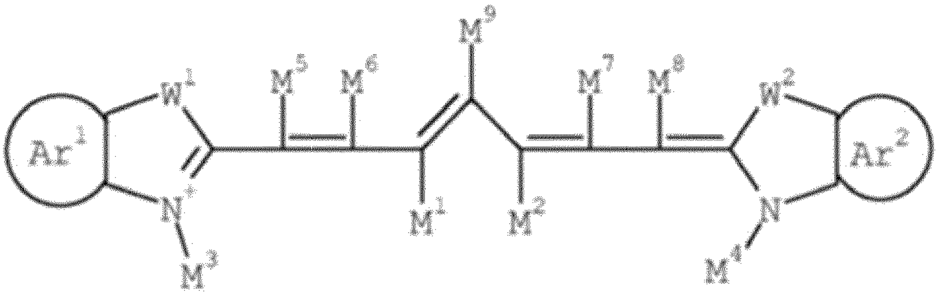
in Formula (II), X's each independently represent a halogen atom, and R^3 represents an aryl group.

11. The lithographic printing plate precursor according to any one of claims 1 to 4, further comprising: a protective layer on the image-recording layer.

12. The lithographic printing plate precursor according to claim 11, wherein the protective layer contains a second infrared absorber which includes a thermally decomposable group transformed into a group that is a stronger electron donor upon exposure to heat and/or infrared radiation, and which is capable of forming a print-out image upon exposure to heat and/or infrared radiation.

13. The lithographic printing plate precursor according to claim 12,

wherein the second infrared absorber is a compound represented by Formula (VI),



(VI)

in Formula (VI), Ar^1 and Ar^2 each independently represent an optionally substituted aromatic hydrocarbon group or an aromatic hydrocarbon group having an optionally substituted benzene ring, W^1 and W^2 each independently represent a sulfur atom, an oxygen atom, or NR*, where R* represents an optionally substituted alkyl group, NH, or $-CM^{10}M^{11}$ group, where M^{10} and M^{11} each independently represent an optionally substituted aliphatic hydrocarbon group or an optionally substituted aryl group or heteroaryl group, M^1 and M^2 each independently represent a hydrogen atom, an optionally substituted aliphatic hydrocarbon group, or a group of atoms required to form an optionally substituted cyclic structure of M^1 and M^2, M^3 and M^4 each independently represent an optionally substituted aliphatic hydrocarbon group, M^5 to M^8 each independently represent a hydrogen atom, a halogen atom, or an optionally substituted aliphatic hydrocarbon group, and M^9 is a group which is converted into a group that is an electron donor stronger than M^9 by a chemical reaction induced by exposure to infrared or heat, and which increases an integrated light absorption of the compound represented by Formula (VI) in a wavelength range of 350 nm to 700 nm by the conversion, M^9 having optionally one or a plurality of counter ions in order to obtain an electrically neutral compound.

14. A method of preparing a lithographic printing plate, comprising:

a step of exposing the lithographic printing plate precursor according to any one of claims 1 to 4 in a shape of an image; and a step of supplying at least one material selected from the group consisting of a printing ink and dampening water on a printer to remove the image-recording layer in a non-image area.

15. A lithographic printing method comprising:

a step of exposing the lithographic printing plate precursor according to any one of claims 1 to 4 in a shape of an image;
a step of supplying at least one material selected from the group consisting of a printing ink and dampening water to remove the image-recording layer in a non-image area on a printer and to prepare a lithographic printing plate; and
a step of performing printing by using the obtained lithographic printing plate.

FIG. 1

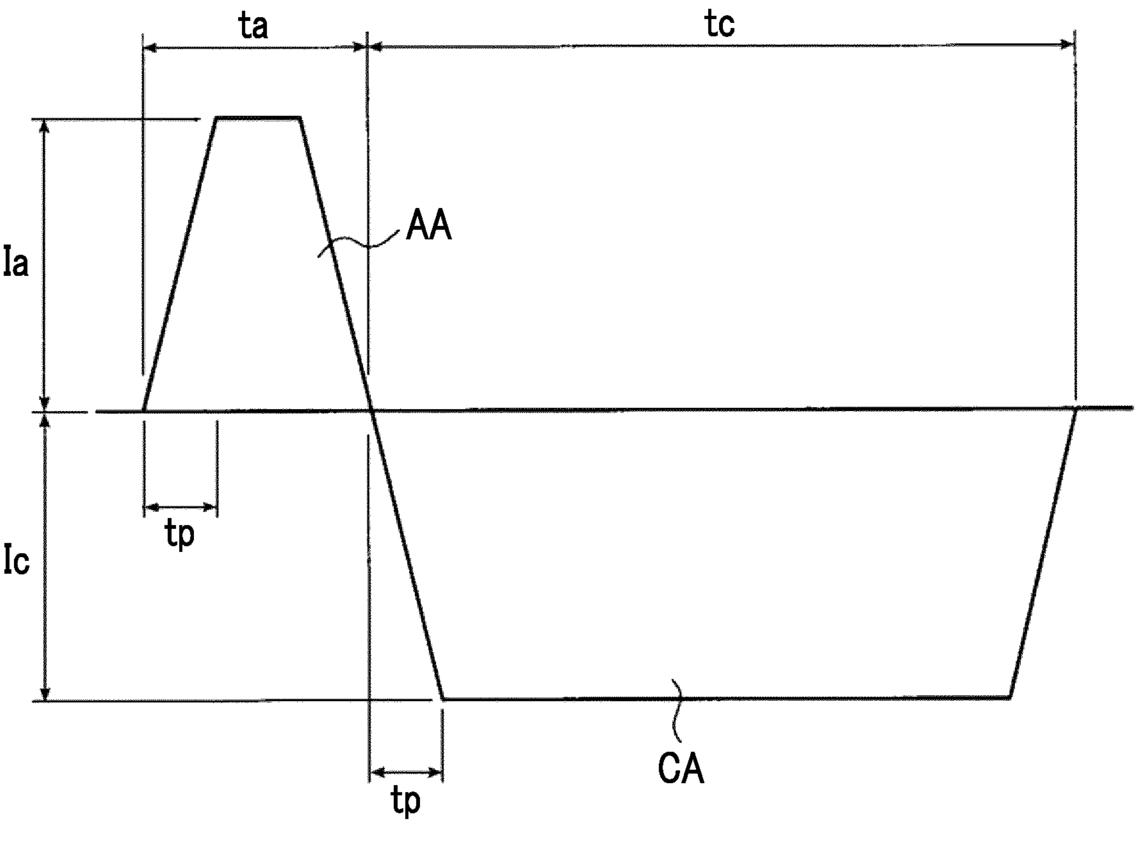


FIG. 2

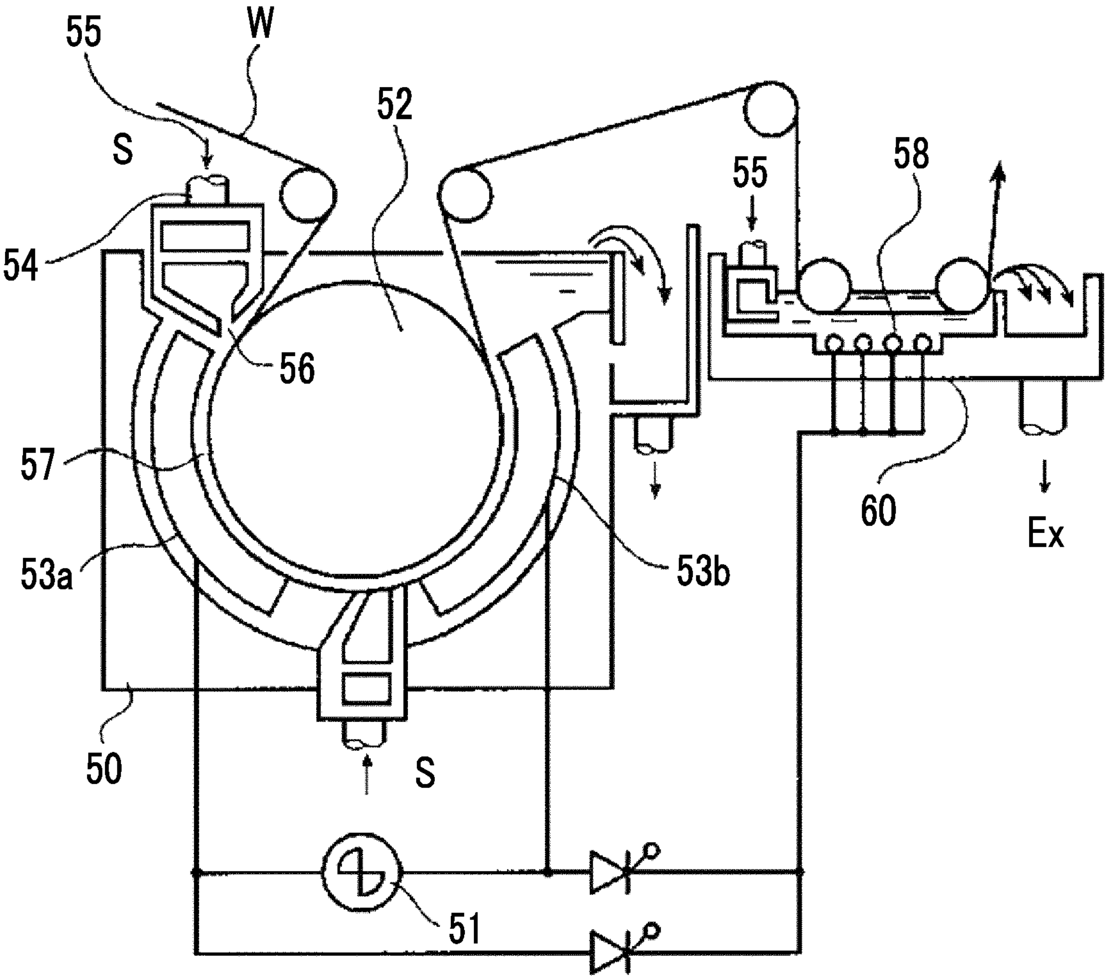


FIG. 3

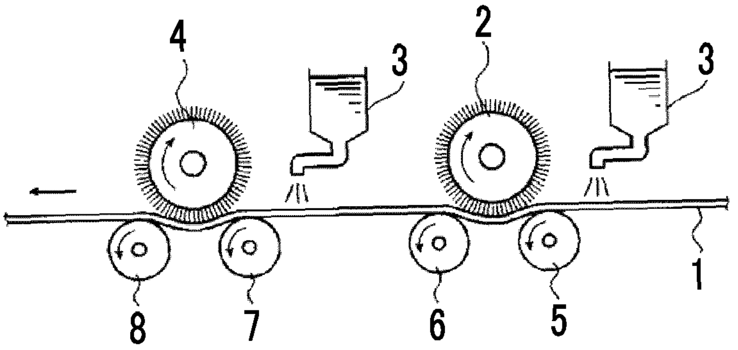
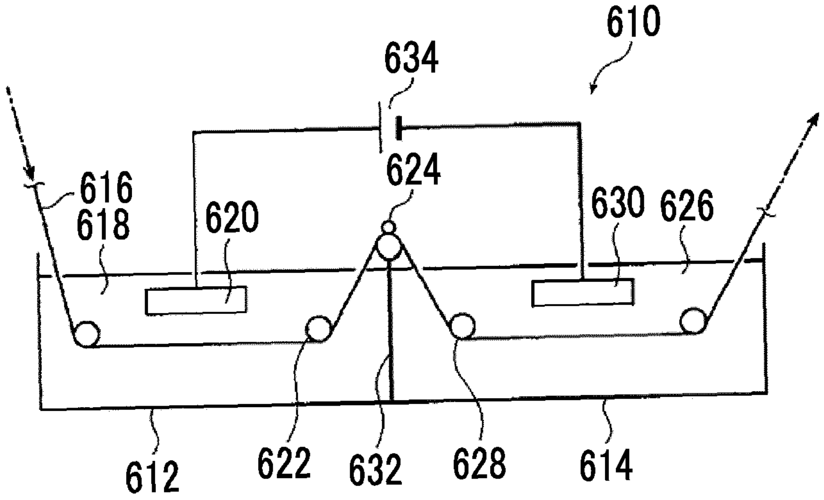


FIG. 4



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EUROPEAN SEARCH REPORT

Application Number
EP 23 20 4033

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	5 February 2024	Vogel, Thomas

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