



(11) **EP 2 275 257 A2**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
**19.01.2011 Bulletin 2011/03**

(51) Int Cl.:  
**B41C 1/10 (2006.01)**

(21) Application number: **10158357.3**

(22) Date of filing: **30.03.2010**

(84) Designated Contracting States:  
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR  
HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL  
PT RO SE SI SK SM TR**  
Designated Extension States:  
**AL BA ME RS**

(30) Priority: **31.03.2009 JP 2009088555**

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(54) **Lithographic printing plate precursor and method of preparing lithographic printing plate**

(57) A lithographic printing plate precursor includes, in the following order: a support; an intermediate layer containing a polyvalent cation and a polymer compound having at least one of an acid group selected from a sulfonic acid group, a carboxylic acid group and a phosphor-

ic acid group and a salt thereof; an image-recording layer containing (i) a polymerization initiator, (ii) a polymerizable compound and (iii) a binder polymer; and a protective layer.

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**Description**FIELD OF THE INTENTION

5 **[0001]** The present invention relates to a lithographic printing plate precursor and a method of preparing a lithographic printing plate.

BACKGROUND OF THE INTENTION

10 **[0002]** In general, a lithographic printing plate has a surface composed of an oleophilic image area and a hydrophilic non-image area. Lithographic printing is a printing method comprising supplying alternately dampening water and oily ink on the surface of lithographic printing plate, making the hydrophilic non-image area a dampening water-receptive area (ink unreceptive area) and depositing the oily ink only on the oleophilic image area by utilizing the nature of water and oil to repel with each other, and then transferring the ink to a printing material, for example, paper.

15 **[0003]** In order to produce the lithographic printing plate, a lithographic printing plate precursor (PS plate) comprising a hydrophilic support having provided thereon an oleophilic photosensitive layer (image-recording layer) has heretofore been broadly used. Ordinarily, a lithographic printing plate is obtained by conducting plate making by a method of exposing the lithographic printing plate precursor through an original, for example, a lith film, and then treating the exposed lithographic printing plate precursor to remove the photosensitive layer in the unnecessary non-image area by  
20 dissolving with an alkaline developer or an organic solvent thereby revealing a surface of the hydrophilic support to form the non-image area while leaving the photosensitive layer in the image area.

**[0004]** In the hitherto known plate making process of lithographic printing plate precursor, after the exposure, the step of removing the unnecessary photosensitive layer by dissolving, for example, with a developer is required. However, it is one of the subjects to simplify such an additional wet treatment as described above. As one means for the simplification,  
25 it has been desired to conduct the development with a nearly neutral aqueous solution or simply with water.

**[0005]** On the other hand, digitalized technique of electronically processing, accumulating and outputting image information using a computer has been popularized in recent years, and various new image outputting systems responding to the digitalized technique have been put into practical use. Correspondingly, attention has been drawn to a computer-to-plate technique of carrying the digitalized image information on highly converging radiation, for example, laser light  
30 and conducting scanning exposure of a lithographic printing plate precursor with the light thereby directly preparing a lithographic printing plate without using a lith film. Thus, it is one of the important technical subjects to obtain a lithographic printing plate precursor adaptable to the technique described above.

**[0006]** Based on the background described above, adaptation of plate making operation to both simplification and digitalization has been demanded strongly more and more than ever before.

35 **[0007]** It is known that in a lithographic printing plate precursor having a photopolymerizable image-recording layer on a support, an intermediate layer containing a compound having a polymerization reactive group and a support adsorbing group is provided between the support and the image-recording layer in order to improve an adhesion property (see, for example, JP-A-7-159983 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), JP-A-9-296593, JP-A-2000-235254 and JP-A-2008-77078). However, any of the hitherto known techniques  
40 has a problem in that when the adhesion property is increased, stain resistance in the unexposed area (non-image area) degrades although printing durability of the exposed area (image area) of the image-recording layer is improved, and it is difficult to achieve a good balance between the printing durability of the exposed area and the stain resistance in the unexposed area.

**[0008]** It is also known that an intermediate layer containing a compound having a functional group of high hydrophilicity in order to improve the stain resistance in the non-image area (see, for example, JP-A-2006-239867). However, the hitherto known technique has a problem in that when the hydrophilicity of the functional group increases, the hydrophilicity of the intermediate layer increases to cause decrease in the adhesion property to the image-recording layer (image area) having high hydrophobicity, resulting in degradation of the printing durability of the image area.

50 SUMMARY OF THE INVENTION

**[0009]** An object of the present invention is to provide a lithographic printing plate precursor which can provide a lithographic printing plate which is excellent in the printing durability in the image area while maintaining good stain resistance in the non-image area and a method of preparing the lithographic printing plate.

55 **[0010]** The above-described object can be achieved by providing an intermediate layer containing a polymer compound having an anionic functional group and a polyvalent cation between the support and the image-recording layer. Specifically, the present invention includes the following items.

(1) A lithographic printing plate precursor comprising: a support; an intermediate layer containing a polymer compound having at least one of an acid group selected from a sulfonic acid group, a carboxylic acid group and a phosphoric acid group and a salt thereof and a polyvalent cation; an image-recording layer containing (i) a polymerization initiator, (ii) a polymerizable compound and (iii) a binder polymer; and a protective layer in this order.

(2) The lithographic printing plate precursor as described in (1) above, wherein the acid group contained in the polymer compound is a carboxylic acid group or a sulfonic acid group.

(3) The lithographic printing plate precursor as described in (1) or (2) above, wherein the polymer compound further contains a support adsorbing group.

(4) The lithographic printing plate precursor as described in (3) above, wherein the support adsorbing group is any one of an onium salt group, a phosphoric acid group, a phosphonic acid group, a boric acid group and a  $\beta$ -diketone group.

(5) The lithographic printing plate precursor as described in (4) above, wherein the support adsorbing group is a phosphoric acid group or a phosphonic acid group.

(6) The lithographic printing plate precursor as described in any one of (1) to (5) above, wherein the polymer compound further contains an ethylenically unsaturated bond group.

(7) The lithographic printing plate precursor as described in any one of (1) to (6) above, wherein the polyvalent cation is a divalent or higher valent alkaline earth metal or transition metal ion.

(8) The lithographic printing plate precursor as described in (7) above, wherein the polyvalent cation is a calcium ion, a magnesium ion, a copper (II) ion, an aluminum ion or an iron (II) ion.

(9) The lithographic printing plate precursor as described in any one of (1) to (8) above, wherein the intermediate layer is formed by coating a coating solution containing the polymer compound and the polyvalent cation.

(10) The lithographic printing plate precursor as described in any one of (1) to (8) above, wherein the intermediate layer is formed by coating a coating solution containing the polymer compound and then coating a coating solution containing the polyvalent cation.

(11) The lithographic printing plate precursor as described in any one of (1) to (8) above, wherein the intermediate layer is formed by coating a coating solution containing the polymer compound and then treating with a treatment solution containing the polyvalent cation.

(12) The lithographic printing plate precursor as described in any one of (1) to (8) above, wherein the intermediate layer is formed by treating with a treatment solution containing the polymer compound and then coating a coating solution containing the polyvalent cation.

(13) The lithographic printing plate precursor as described in any one of (1) to (8) above, wherein the intermediate layer is formed by treating with a treatment solution containing the polymer compound and then treating with a treatment solution containing the polyvalent cation.

(14) The lithographic printing plate precursor as described in any one of (1) to (8) above, wherein the intermediate layer is formed by treating with a treatment solution containing the polymer compound and the polyvalent cation.

(15) A method of preparing a lithographic printing plate comprising processing the lithographic printing plate precursor as described in any one of (1) to (14) above with a developer having pH of 2 to 11.

(16) The method of preparing a lithographic printing plate as described in (15) above, wherein the developer contains a carbonate ion and a hydrogen carbonate ion.

**[0011]** According to the present invention, a lithographic printing plate precursor which can provide a lithographic printing plate which is excellent in the printing durability in the image area while maintaining good stain resistance in the non-image area and a method of preparing the lithographic printing plate can be provided.

#### BRIEF DESCRIPTION OF THE DRAWINGS

#### **[0012]**

Fig. 1 is a view schematically showing a configuration of an automatic development processor.

[Description of reference numerals and signs]

#### **[0013]**

- 1: Rotating brush roller
- 2: Backing roller
- 3: Transport roller
- 4: Transport guide plate

- 5: Spray pipe  
 6: Pipe line  
 7: Filter  
 8: Plate supply table  
 5 9: Plate discharge table  
 10: Developer tank  
 11: Circulating pump  
 12: Plate

## 10 DETAILED DESCRIPTION OF THE INVENTION

[Lithographic printing plate precursor]

15 **[0014]** First, the lithographic printing plate precursor according to the invention will be described below. The lithographic printing plate precursor according to the invention has an intermediate layer between an image-recording layer and a support.

<Intermediate layer>

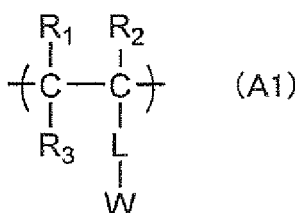
20 **[0015]** The intermediate layer according to the invention is characterized by containing a polymer compound (hereinafter, also referred to as a specific polymer compound for intermediate layer) having at least one of an acid group selected from a sulfonic acid group, a carboxylic acid group and a phosphoric acid group and a salt thereof and a polyvalent cation.

25 **[0016]** The specific polymer compound for intermediate layer is not particularly restricted as far as it is a polymer compound having at least one of an acid group selected from a sulfonic acid group, a carboxylic acid group and a phosphoric acid group and a salt thereof. Of the acid groups, a sulfonic acid group or a carboxylic acid group is preferable in view of the electrostatic interaction with the polyvalent cation.

30 **[0017]** It is preferred that the specific polymer compound for intermediate layer has adsorptivity to a surface of the support. Whether the adsorptivity to the surface of support is present or not can be evaluated, for example, by the following method.

35 **[0018]** Specifically, the specific polymer compound for intermediate layer (test compound) is dissolved in a solvent in which the test compound is easily soluble to prepare a coating solution, and the coating solution is coated and dried on a support so as to have the coating amount after drying of 30 mg/m<sup>2</sup>. After thoroughly washing the support coated with the test compound using the solvent in which the test compound is easily soluble, the residual amount of the test compound that has not been removed by the washing is measured to calculate the adsorption amount to the support. For measurement of the residual amount, the amount of the residual test compound may be directly determined, or it may be calculated from the amount of the test compound dissolved in the washing solution. The determination for the compound can be performed, for example, by fluorescent X-ray measurement, reflection spectral absorbance measurement or liquid chromatography measurement. The compound having the adsorptivity to support means a compound that remains by 0.1 mg/m<sup>2</sup> or more even after conducting the washing treatment described above.

40 **[0019]** The specific polymer compound for intermediate layer is preferably a polymer compound containing a repeating unit represented by formula (A1) shown below.



55 **[0020]** In formula (A1), R<sub>1</sub> to R<sub>3</sub> each independently represents a hydrogen atom, an alkyl group having from 1 to 6 carbon atoms or a halogen atom. L represents a single bond or a divalent connecting group selected from the group consisting of -CO-, -O-, -NH-, a divalent aliphatic group, a divalent aromatic group and a combination thereof. W represents -COOM<sub>1</sub>, -SO<sub>3</sub>M<sub>1</sub> or -OPO(OM<sub>1</sub>)(OM<sub>2</sub>). M<sub>1</sub> and M<sub>2</sub> each independently represents a hydrogen atom, a metal atom or

an ammonium group.

**[0021]** Specific examples of the combination of groups represented by L are set forth below. In each of the specific examples shown below, the left side connects to the main chain.

- L1: -CO-NH-divalent aliphatic group-O-CO-
- L2: -CO-divalent aliphatic group-O-CO-
- L3: -CO-O-divalent aliphatic group-O-CO-
- L4: -divalent aliphatic group-O-CO-
- L5: -CO-NH-divalent aromatic group-O-CO-
- L6: -CO-divalent aromatic group-O-CO-
- L7: -divalent aromatic group-O-CO-
- L8: -CO-O-divalent aliphatic group-CO-O-divalent aliphatic group-O-CO-
- L9: -CO-O-divalent aliphatic group-O-CO-divalent aliphatic group-O-CO-
- L10: -CO-O-divalent aromatic group-CO-O-divalent aliphatic group-O-CO-
- L11: -CO-O-divalent aromatic group-O-CO-divalent aliphatic group-O-CO-
- L12: -CO-O-divalent aliphatic group-CO-O-divalent aromatic group-O-CO-
- L13: -CO-O-divalent aliphatic group-O-CO-divalent aromatic group-O-CO-
- L14: -CO-O-divalent aromatic group-CO-O-divalent aromatic group-O-CO-
- L15: -CO-O-divalent aromatic group-O-CO-divalent aromatic group-O-CO-
- L16: -CO-O-divalent aromatic group-O-CO-NH-divalent aliphatic group-O-CO-
- L17: -CO-O-divalent aliphatic group-O-CO-NH-divalent aliphatic group-O-CO-

**[0022]** The divalent aliphatic group includes an alkylene group, a substituted alkylene group, an alkenylene group, a substituted alkenylene group, an alkynylene group, a substituted alkynylene group and a polyalkyleneoxy group. Among them, an alkylene group, a substituted alkylene group, an alkenylene group and a substituted alkenylene group are preferable, and an alkylene group and a substituted alkylene group are more preferable.

**[0023]** Of the divalent aliphatic groups, a chain structure is preferable than a cyclic structure, and further a straight chain structure is more preferable than a branched chain structure.

**[0024]** A number of carbon atoms included in the divalent aliphatic group is preferably from 1 to 20, more preferably from 1 to 15, still more preferably from 1 to 12, yet still more preferably from 1 to 10, and most preferably from 1 to 8.

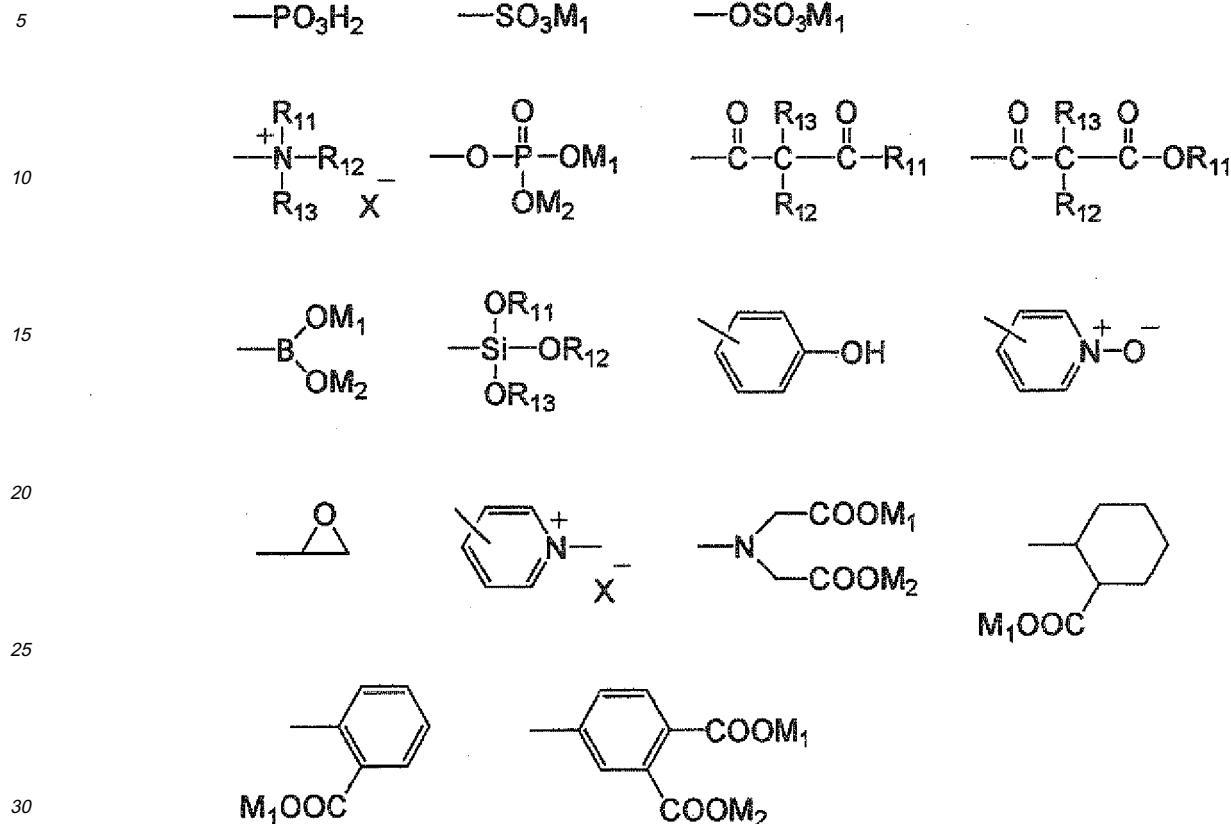
**[0025]** Examples of the substituent for the divalent aliphatic group include a halogen atom (e.g., F, Cl, Br or I), a hydroxy group, a carboxyl group, an amino group, a cyano group, an aryl group, an alkoxy group, an aryloxy group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, an acyloxy group, a monoalkylamino group, a dialkylamino group, a monoarylamino group and a diarylamino group.

**[0026]** The divalent aromatic group includes an arylene group and a substituted arylene group. It preferably includes a phenylene group, a substituted phenylene group, a naphthylene group and a substituted naphthylene group.

**[0027]** Examples of the substituent for the divalent aromatic group include an alkyl group in addition to the substituents described for the divalent aliphatic group described above.

**[0028]** Of L1 to L17 described above, L1, L3, L5, L7 and L17 are preferable.

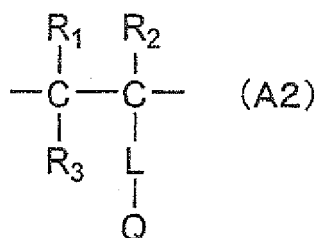
**[0029]** It is preferred that the specific polymer compound for intermediate layer further contains a support adsorbing group. The support adsorbing group includes a group capable of forming a bond, for example, a covalent bond, an ionic bond or a hydrogen bond and a group capable of undergoing interaction, for example, polar interaction, with metal, a metal oxide, a hydroxy group or the like present on the support. Specific examples of the support adsorbing group are set forth below.



**[0030]** In the above-formulae,  $R_{11}$  to  $R_{13}$  each independently represents a hydrogen atom, an alkyl group, an aryl group, an alkynyl group or an alkenyl group,  $M_1$  and  $M_2$  each independently represents a hydrogen atom, a metal atom or an ammonium group, and  $X^-$  represents a counter anion.

**[0031]** As the support adsorbing group, an onium group (for example, an ammonium group or a pyridinium group), a phosphoric acid group ( $-OPO_3H_2$ ), a phosphonic acid group, a boric acid group and a  $\beta$ -diketone group (for example, an acetylacetone group) is preferable. In particular, a phosphoric acid group and a phosphonic acid group are preferable. The phosphoric acid group is a group having a function of interacting with the polyvalent cation as described above and also has a function as the support adsorbing group.

**[0032]** The specific polymer compound for intermediate layer containing a support adsorbing group is preferably a polymer compound containing a repeating unit represented by formula (A2) shown below.



**[0033]** In formula (A2),  $R_1$  to  $R_3$  and  $L$  have the same meanings as  $R_1$  to  $R_3$  and  $L$  defined in formula (A1), respectively.  $Q$  represents a support adsorbing group.

**[0034]** Specific examples of the combination of groups represented by  $L$  include the groups set forth below in addition to the specific examples set forth for  $L$  in formula (A1). In each of the specific examples shown below, the left side

connects to the main chain.

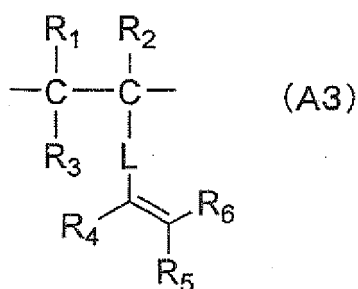
L18: -CO-NH-

L19: -CO-O-

L20: -divalent aromatic group-

**[0035]** It is preferred that the specific polymer compound for intermediate layer further contains an ethylenically unsaturated bond group.

**[0036]** The specific polymer compound for intermediate layer containing an ethylenically unsaturated bond group is preferably a polymer compound containing a repeating unit represented by formula (A3) shown below.



**[0037]** In formula (A3),  $R_1$  to  $R_3$  have the same meanings as  $R_1$  to  $R_3$  defined in formula (A1), respectively. L has the same meaning as the divalent connecting group represented by L defined in formula (A1).  $R_4$  to  $R_6$  each independently represents a hydrogen atom, an alkyl group having from 1 to 6 carbon atoms, a halogen atom, an acyl group or an acyloxy group. Alternatively,  $R_4$  and  $R_5$  or  $R_5$  and  $R_6$  may be combined with each other to form a ring.

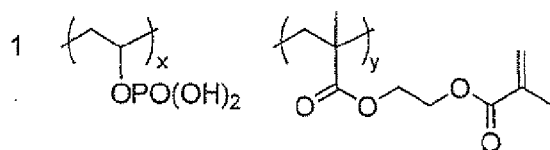
**[0038]** As the specific polymer compound for intermediate layer, a polymer compound containing the repeating unit represented by formula (A1) is preferable, a polymer compound containing the repeating unit represented by formula (A2) or the repeating unit represented by formula (A3) in addition to the repeating unit represented by formula (A1) is more preferable, and a polymer compound containing the repeating unit represented by formula (A2) and the repeating unit represented by formula (A3) in addition to the repeating unit represented by formula (A1) is still more preferable.

**[0039]** In the specific polymer compound for intermediate layer, the content of a monomer corresponding to the repeating unit represented by formula (A1) is preferably from 5 to 100% by mole, more preferably from 30 to 90% by mole, still more preferably from 50 to 85% by mole, based on the total polymerization monomer. The content of a monomer corresponding to the repeating unit represented by formula (A2) is preferably from 5 to 80% by mole, more preferably from 10 to 50% by mole, based on the total polymerization monomer. The content of a monomer corresponding to the repeating unit represented by formula (A3) is preferably from 5 to 80% by mole, more preferably from 10 to 50% by mole, based on the total polymerization monomer.

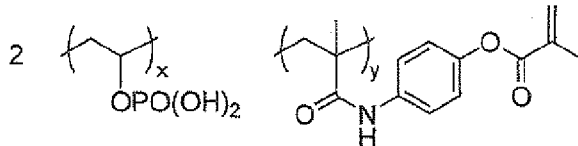
**[0040]** The weight average molecular weight of the specific polymer compound for intermediate layer is preferably from 10,000 to 500,000 and more preferably from 50,000 to 200,000.

**[0041]** Specific examples of the specific polymer compound for intermediate layer for use in the invention are set forth below, but the invention should not be construed as being limited thereto.

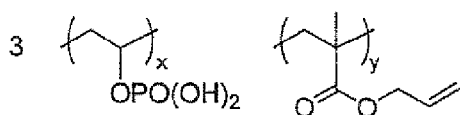
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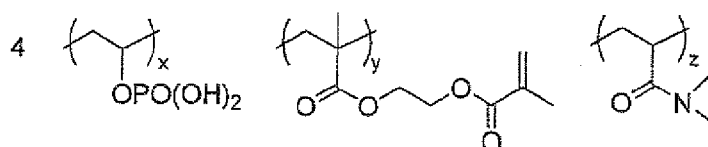
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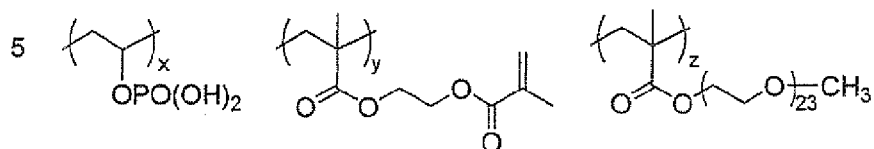
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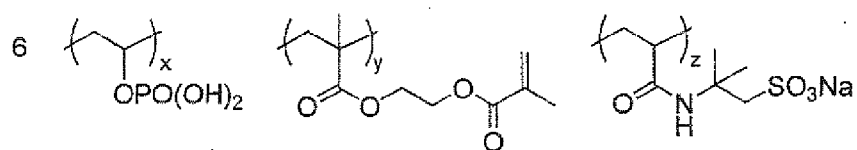
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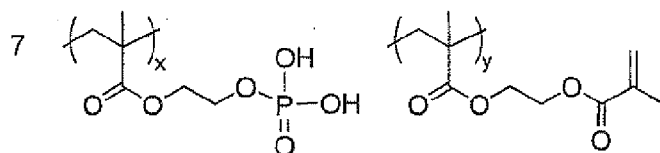
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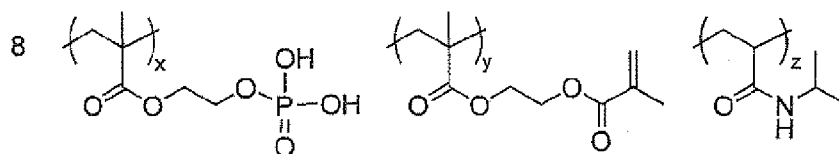
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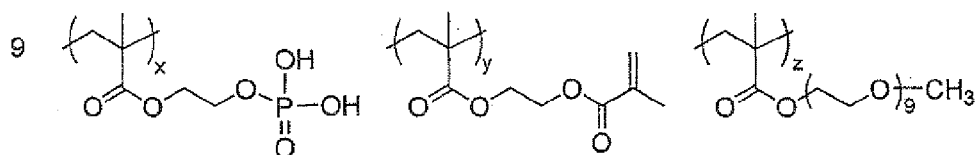
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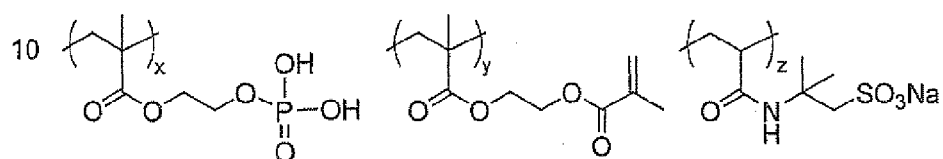
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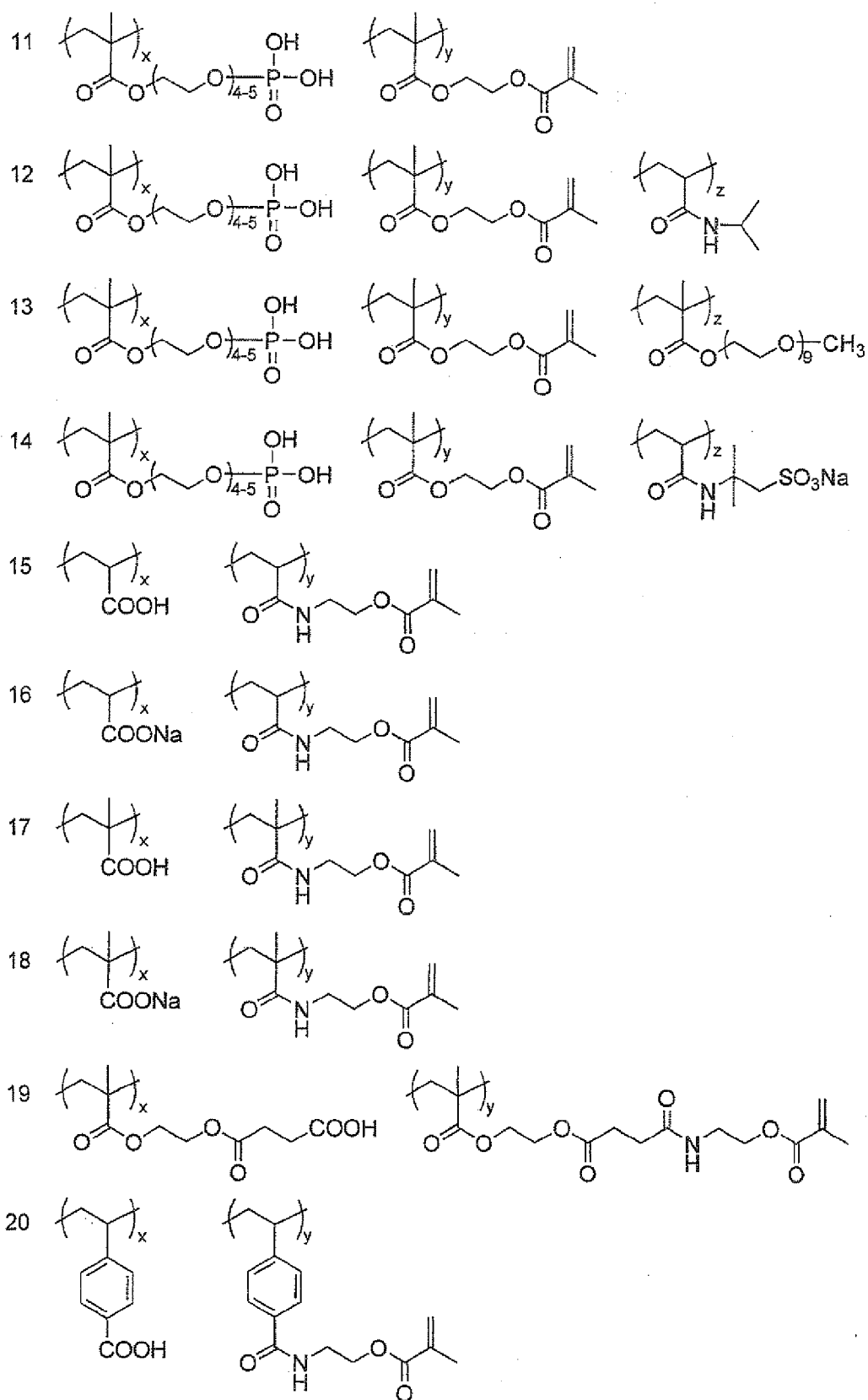


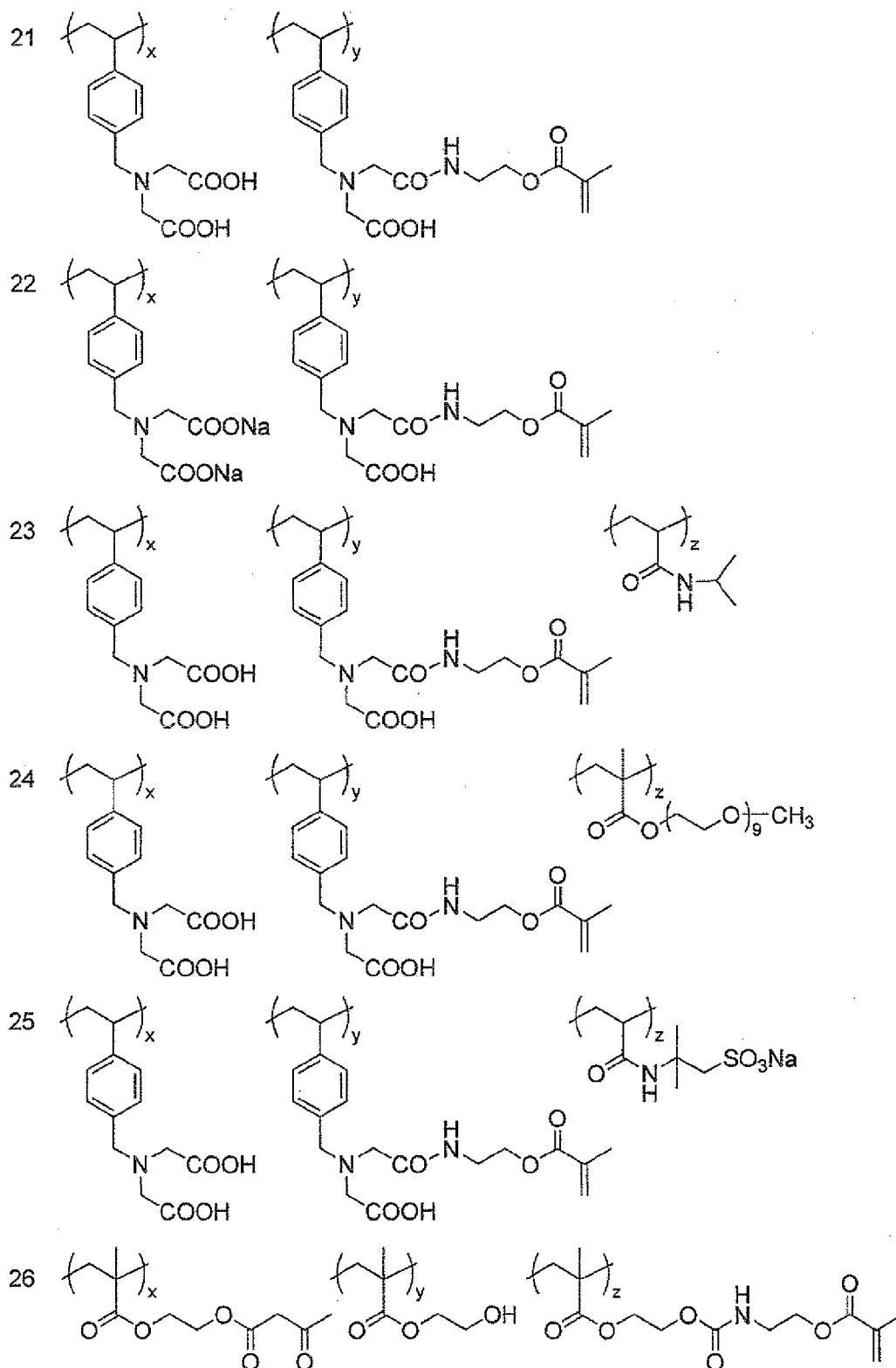
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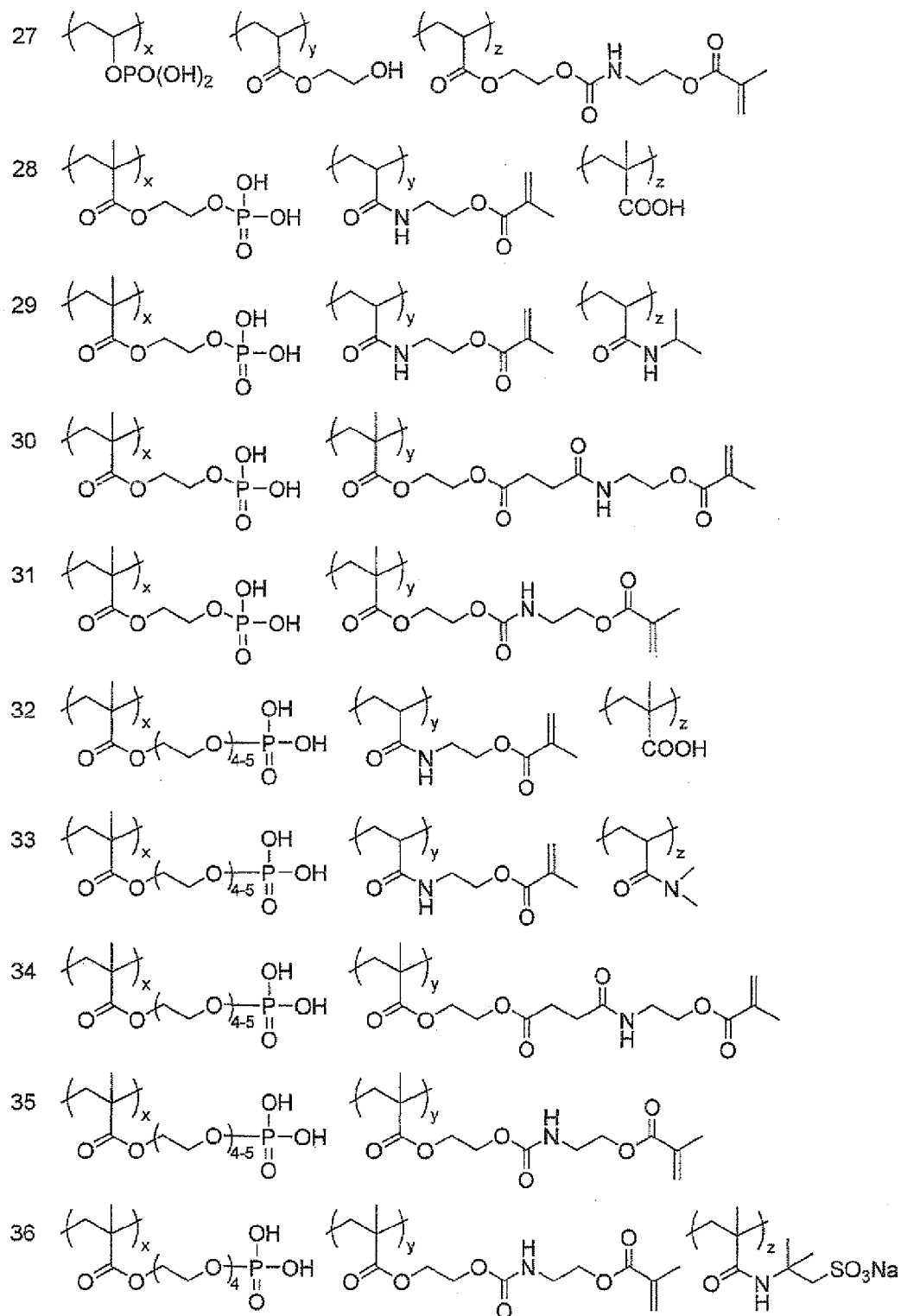


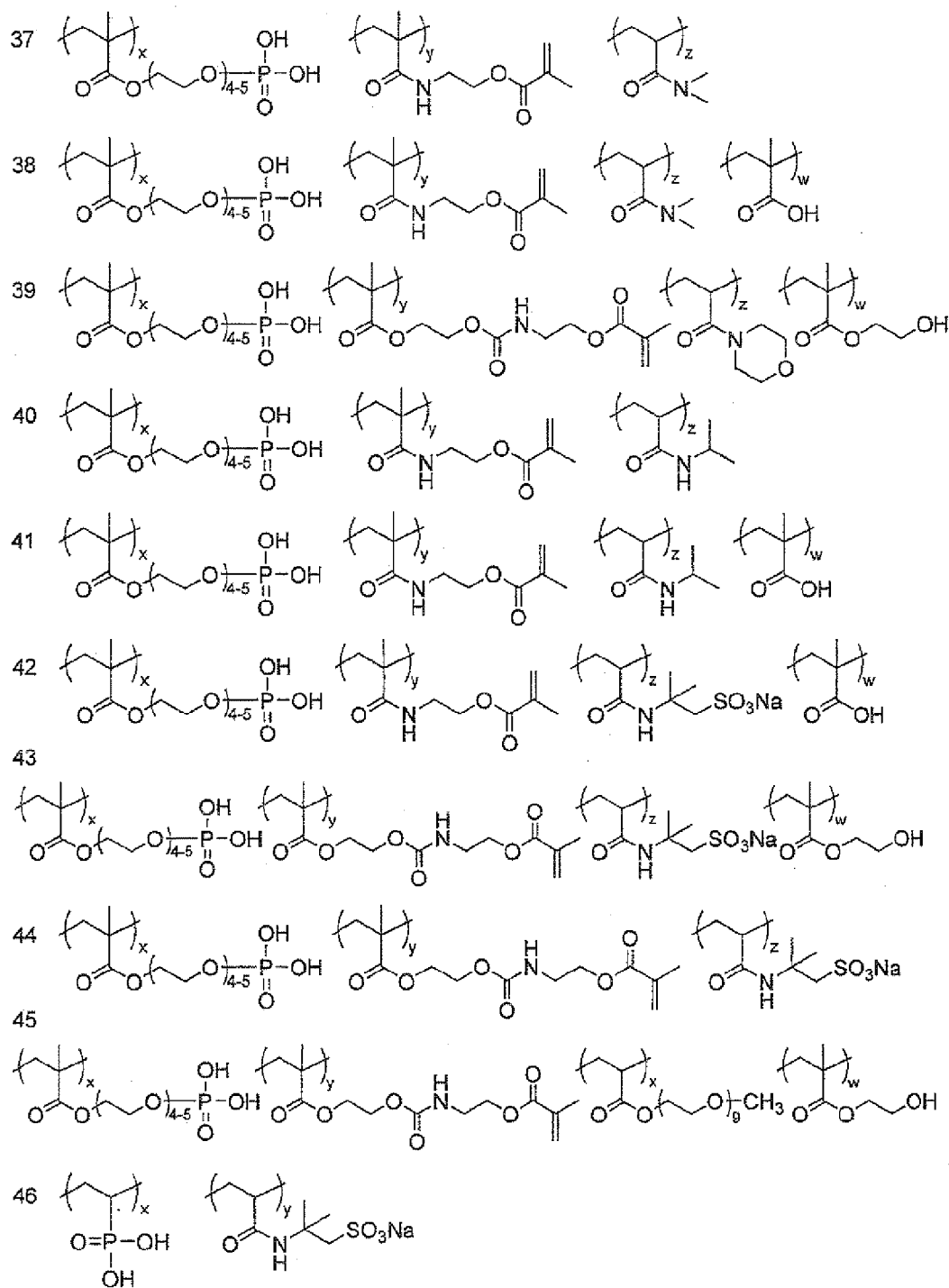
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**[0042]** The polyvalent cation contained in the intermediate layer according to the invention is a divalent or higher valent cation and includes, for example, an alkaline earth metal ion and a transition metal ion. In particular, a calcium ion, a magnesium ion, a copper (II) ion, an aluminum ion or an iron (II) ion is preferably used.

**[0043]** The intermediate layer can be formed by providing the specific polymer compound for intermediate layer and the polyvalent cation individually or in combination on the support. Specifically, the intermediate layer can be formed by a method where a solution containing the specific polymer compound for intermediate layer and/or the polyvalent cation in water, an organic solvent, for example, methanol, ethanol or methyl ethyl ketone or a mixed solvent thereof is coating on a support and dried, a method where a support is treated with a solution containing the specific polymer compound for intermediate layer and/or the polyvalent cation in water, an organic solvent, for example, methanol, ethanol or methyl ethyl ketone or a mixed solvent thereof and dried, or a combination of these methods. In order to treat the support with the solution containing the specific polymer compound for intermediate layer and/or the polyvalent cation, for example, a method of immersing the support in the solution is preferably used. After the treatment with the solution, the support may be washed, for example, with water, if desired. It is preferred that the specific polymer compound for intermediate layer is provided on the support prior to or simultaneously with the polyvalent cation.

**[0044]** More specifically, for example, (a) method of coating a coating solution containing the specific polymer compound for intermediate layer and the polyvalent cation, (b) method of coating a coating solution containing the specific polymer compound for intermediate layer and then coating a coating solution containing the polyvalent cation, (c) method of coating a coating solution containing the specific polymer compound for intermediate layer and then treating with a treatment solution containing the polyvalent cation, (d) method of treating with a treatment solution containing the specific polymer compound for intermediate layer and then coating a coating solution containing the polyvalent cation, (e) method of treating with a treatment solution containing the specific polymer compound for intermediate layer and then treating with a treatment solution containing the polyvalent cation, or (f) method of treating with a treatment solution containing the specific polymer compound for intermediate layer and the polyvalent cation is preferably used.

**[0045]** In the method of using the coating solution, the solution of each component having concentration of about 0.005 to about 10% by weight is coated according to known various methods. Any method, for example, bar coater coating, spin coating, spray coating or curtain coating can be used. In the method of using the treatment solution, the concentration of each component is ordinarily from about 0.01 to about 20% by weight, and preferably from about 0.05 to about 5% by weight, the temperature of the treatment solution is ordinarily from about 20 to about 90°C, and preferably from about 25 to about 50°C, and the treatment time is ordinarily from about 0.1 second to about 20 minutes, and preferably from about 2 seconds to about 1 minute.

**[0046]** The coating amount of the specific polymer compound for intermediate layer is preferably from 1 to 100 mg/m<sup>2</sup>, more preferably from 1.0 to 50 mg/m<sup>2</sup> still more preferably from 5.0 to 20 mg/m<sup>2</sup>, in terms of dry weight. The coating amount of the polyvalent cation is preferably from 0.1 to 10 mg/m<sup>2</sup>, more preferably from 0.5 to 5.0 mg/m<sup>2</sup>, still more preferably from 1.0 to 3.0 mg/m<sup>2</sup>, in terms of dry weight.

**[0047]** The intermediate layer may contain a surfactant for the purpose of improving state of the coated surface, if desired. For example, compounds described in Paragraph Nos. [0161] to [0201] of JP-A-2007-206217 are used.

<Image-recording layer>

**[0048]** The image-recording layer (hereinafter, also referred to as a photosensitive layer) of the lithographic printing plate precursor according to the invention contains (i) a polymerization initiator, (ii) a polymerizable compound and (iii) a binder polymer.

(Polymerization initiator)

**[0049]** As the polymerization initiator (hereinafter, also referred to as an initiator compound) contained in the image-recording layer according to the invention, a radical polymerization initiator is preferably used.

**[0050]** As the initiator compound according to the invention, initiator compounds known to those skilled in the art can be used without limitation. Specifically, the initiator compound includes, for example, a trihalomethyl compound, a carbonyl compound, an organic peroxide, an azo compound, an azide compound, a metallocene compound, a hexaarylbiimidazole compound, an organic boron compound, a disulfone compound, an oxime ester compound, an onium salt and a iron arene complex. Among them, at least one compound selected from the hexaarylbiimidazole compound, onium salt, trihalomethyl compound and metallocene compound is preferable, and the hexaarylbiimidazole compound is particularly preferable.

**[0051]** The hexaarylbiimidazole compound includes, for example, lophine dimers described in JP-B-45-37377 (the term "JP-B" as used herein means an "examined Japanese patent publication") and JP-B-44-86516, specifically, 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetraphenylbiimidazole, 2,2'-bis(o-bromophenyl)-4,4',5,5'-tetraphenylbiimidazole,

2,2'-bis(o,p-dichlorophenyl)-4,4',5,5'-tetraphenylbiimidazole,  
 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetra(m-methoxyphenyl)biimidazole,  
 2,2'-bis(o,o'-dichlorophenyl)-4,4',5,5'-tetraphenylbiimidazole,  
 2,2'-bis(o-nitrophenyl)-4,4',5,5'-tetraphenylbiimidazole,

2,2'-bis(o-methylphenyl)-4,4',5,5'-tetraphenylbiimidazole and

2,2'-bis(o-trifluoromethylphenyl)-4,4',5,5'-tetraphenylbiimidazole. The hexaarylbiimidazole compound is particularly preferably used together with a sensitizing dye having an absorption maximum in a wavelength range of 300 to 450 nm described hereinafter.

**[0052]** The onium salt preferably used in the invention includes a sulfonium salt, an iodonium salt and a diazonium salt. Particularly, a diaryliodonium salt and a triarylsulfonium salt are preferably used. The onium salt is particularly preferably used together with an infrared absorbing agent having an absorption maximum in a wavelength range of 750 to 1,400 nm.

**[0053]** In addition, polymerization initiators described in Paragraph Nos. [0071] to [0129] of JP-A-2007-206217 are preferably used.

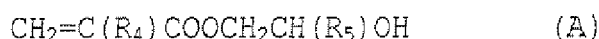
**[0054]** The polymerization initiators are preferably used individually or in combination of two or more thereof. The amount of the polymerization initiator used in the photosensitive layer is preferably from 0.01 to 20% by weight, more preferably from 0.1 to 15% by weight, still more preferably from 1.0 to 10% by weight, based on the total solid content of the photosensitive layer.

(Polymerizable compound)

**[0055]** The polymerizable compound for use in the photosensitive layer according to the invention is an addition-polymerizable compound having at least one ethylenically unsaturated double bond and it is selected from compounds having at least one, preferably two or more, terminal ethylenically unsaturated double bonds. The polymerizable compound has a chemical form, for example, a monomer, a prepolymer, specifically, a dimer, a trimer or an oligomer, or a mixture thereof. Examples of the monomer include unsaturated carboxylic acids (for example, acrylic acid, methacrylic acid, itaconic acid, crotonic acid, isocrotonic acid or maleic acid) and esters or amides thereof. Preferably, esters of an unsaturated carboxylic acid with a polyhydric alcohol compound and amides of an unsaturated carboxylic acid with a polyvalent amine compound are used. An addition reaction product of an unsaturated carboxylic acid ester or amide having a nucleophilic substituent, for example, a hydroxy group, an amino group or a mercapto group, with a monofunctional or polyfunctional isocyanate or epoxy compound, or a dehydration condensation reaction product of the unsaturated carboxylic acid ester or amide with a monofunctional or polyfunctional carboxylic acid is also preferably used. Moreover, an addition reaction product of an unsaturated carboxylic acid ester or amide having an electrophilic substituent, for example, an isocyanate group or an epoxy group with a monofunctional or polyfunctional alcohol, amine or thiol, or a substitution reaction product of an unsaturated carboxylic acid ester or amide having a releasable substituent, for example, a halogen atom or a tosyloxy group with a monofunctional or polyfunctional alcohol, amine or thiol is also preferably used. In addition, compounds in which the unsaturated carboxylic acid described above is replaced by an unsaturated phosphonic acid, styrene, vinyl ether or the like can also be used.

**[0056]** Specific examples of the monomer, which is an ester of a polyhydric alcohol compound with an unsaturated carboxylic acid, include, as an acrylic acid ester, for example, ethylene glycol diacrylate, 1,3-butanediol diacrylate, tetramethylene glycol diacrylate, propylene glycol diacrylate, trimethylolpropane triacrylate, hexanediol diacrylate, tetraethylene glycol diacrylate, pentaerythritol tetraacrylate, sorbitol triacrylate, isocyanuric acid ethylene oxide (EO) modified triacrylate and polyester acrylate oligomer. As a methacrylic acid ester, for example, tetramethylene glycol dimethacrylate, neopentyl glycol dimethacrylate, trimethylolpropane trimethacrylate, ethylene glycol dimethacrylate, pentaerythritol trimethacrylate, bis[p-(3-methacryloxy-2-hydroxypropoxy)phenyl]dimethylmethane and bis[p-(methacryloxyethoxy)phenyl]dimethylmethane are exemplified. Specific examples of the monomer, which is an amide of a polyvalent amine compound with an unsaturated carboxylic acid, include methylene bisacrylamide, methylene bismethacrylamide, 1,6-hexamethylene bisacrylamide, 1,6-hexamethylene bismethacrylamide, diethylenetriamine trisacrylamide, xylylene bisacrylamide and xylylene bismethacrylamide.

**[0057]** Urethane type addition-polymerizable compounds produced using an addition reaction between an isocyanate and a hydroxy group are also preferably used and specific examples thereof include vinylurethane compounds having two or more polymerizable vinyl groups per molecule obtained by adding a vinyl monomer containing a hydroxy group represented by formula (A) shown below to a polyisocyanate compound having two or more isocyanate groups per molecule, described in JP-B-48-41708.



wherein  $R_4$  and  $R_5$  each independently represents H or  $CH_3$ .

**[0058]** Also, urethane acrylates described in JP-A-51-37193, JP-B-2-32293 and JP-B-2-16765, and urethane compounds having an ethylene oxide skeleton described in JP-B-58-49860, JP-B-56-17654, JP-B-62-39417 and JP-B-62-39418 are preferably used.

**[0059]** Details of the method of using the polymerizable compound, for example, selection of the structure, individual or combination use or an amount added, can be appropriately determined in accordance with the characteristic design of the final lithographic printing plate precursor. The polymerizable compound is used preferably in a range of 5 to 75% by weight, more preferably in a range of 25 to 70% by weight, particularly preferably in a range of 30 to 60% by weight, based on the total solid content of the photosensitive layer.

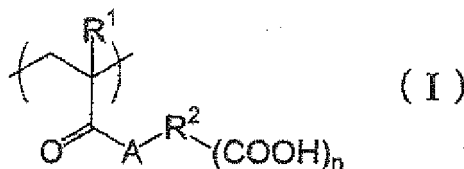
(Binder polymer)

**[0060]** The photosensitive layer according to the invention contains a binder polymer. As the binder polymer, a polymer capable of holding the components of photosensitive layer on a support and capable of being removed by a developer is used. The binder polymer used includes a (meth)acrylic polymer, a polyurethane resin, a polyvinyl alcohol resin, a polyvinyl butyral resin, a polyvinyl formal resin, a polyamide resin, a polyester resin and an epoxy resin. Particularly, a (meth)acrylic polymer and a polyurethane resin are preferably used.

**[0061]** The term "(meth) acrylic polymer" as used herein means a copolymer containing as a polymerization component, (meth)acrylic acid or a (meth)acrylic acid derivative, for example, a (meth)acrylate (including, for example, an alkyl ester, aryl ester and allyl ester), (meth)acrylamide or a (meth) acrylamide derivative. The term "polyurethane resin" as used herein means a polymer formed by a condensation reaction of a compound having two or more isocyanate groups and a compound having two or more hydroxy groups. The term "polyvinyl butyral resin" as used herein means a polymer synthesized by a reaction (acetalization reaction) of polyvinyl alcohol obtained by partial or full saponification of polyvinyl acetate with butylaldehyde under an acidic condition and includes a polymer wherein an acid group or the like is introduced

by a method of reacting the remaining hydroxy group with a compound having the acid group or the like.

**[0062]** One preferable example of the binder polymer according to the invention is a copolymer containing a repeating unit having an acid group. Examples of the acid group include a carboxylic acid group, a sulfonic acid group, a phosphonic acid group, a phosphoric acid group and a sulfonamido group. Particularly, a carboxylic acid group is preferable. A polymer having a repeating unit represented by formula (I) shown below is preferably used.



**[0063]** In formula (I),  $R^1$  represents a hydrogen atom or a methyl group,  $R^2$  represents a single bond or an  $n+1$  valent connecting group, A represents an oxygen atom or  $\text{---NR}^3\text{---}$ , wherein  $R^3$  represents a hydrogen atom or a monovalent hydrocarbon group having from 1 to 10 carbon atoms, and  $n$  represents an integer of 1 to 5.

**[0064]** The connecting group represented by  $R^2$  in formula (I) is constructed from a carbon atom, a hydrogen atom, an oxygen atom, a nitrogen atom, a sulfur atom and a halogen atom and preferably contains from 1 to 80 atoms. Specific examples of the connecting group include an alkylene group, a substituted alkylene group, an arylene group and a substituted arylene group. The connecting group may have a structure wherein a plurality of such divalent groups is connected to each other via an amido bond or an ester bond.  $R^2$  is preferably a single bond, an alkylene group or a substituted alkylene group, more preferably a single bond, an alkylene group having from 1 to 5 carbon atoms or a substituted alkylene group having from 1 to 5 carbon atoms, and most preferably a single bond, an alkylene group having from 1 to 3 carbon atoms or a substituted alkylene group having from 1 to 3 carbon atoms.

**[0065]** Examples of the substituent include a monovalent non-metallic atomic group exclusive of a hydrogen atom, for example, a halogen atom (e.g.,  $\text{---F}$ ,  $\text{---Br}$ ,  $\text{---Cl}$  or  $\text{---I}$ ), a hydroxy group, an alkoxy group, an aryloxy group, a mercapto group, an acyl group, a carboxyl group and a conjugate base group thereof, an alkoxy carbonyl group, an aryloxy carbonyl group, a carbamoyl group, an aryl group, an alkenyl group and an alkynyl group.

**[0066]**  $R^3$  is preferably a hydrogen atom or a hydrocarbon group having from 1 to 5 carbon atoms, more preferably a hydrogen atom or a hydrocarbon group having from 1 to 3 carbon atoms, and most preferably a hydrogen atom or a methyl group.  $n$  is preferably from 1 to 3, more preferably 1 or 2, and most preferably 1.

**[0067]** A ratio of the copolymerization component having a carboxylic acid group in the total copolymerization components of the binder polymer is preferably from 1 to 70% by mole in view of developing property. Considering good compatibility between the developing property and printing durability, it is more preferably from 1 to 50% by mole, and particularly preferably from 1 to 30% by mole.

**[0068]** It is preferred that the binder polymer for use in the invention further contains a crosslinkable group. The term "crosslinkable group" as used herein means a group capable of crosslinking the binder polymer in the process of a radical polymerisation reaction which is caused in the photosensitive layer, when the lithographic printing plate precursor is exposed to light. The crosslinkable group is not particularly restricted as long as it has such a function and includes, for example, an ethylenically unsaturated bonding group, an amino group or an epoxy group as a functional group capable of undergoing an addition polymerization reaction. Also, a functional group capable of forming a radical upon irradiation with light may be used and such a crosslinkable group includes, for example, a thiol group and a halogen atom. Among them, the ethylenically unsaturated bonding group is preferable. The ethylenically unsaturated bonding group preferably includes a styryl group, a (meth)acryloyl group and an allyl group.

**[0069]** In the binder polymer, for example, a free radical (a polymerization initiating radical or a propagating radical in the process of polymerization of the polymerizable compound) is added to the crosslinkable functional group to cause an addition-polymerization between the polymers directly or through a polymerization chain of the polymerizable compound, as a result, crosslinking is formed between the polymer molecules to effect curing. Alternatively, an atom (for example, a hydrogen atom on the carbon atom adjacent to the functional crosslinkable group) in the polymer is withdrawn by a free radical to produce a polymer radical and the polymer radicals combine with each other to form crosslinking between the polymer molecules to effect curing.

**[0070]** The content of the crosslinkable group (content of radical-polymerizable unsaturated double bond determined by iodine titration) in the binder polymer is preferably from 0.01 to 10.0 mmol, more preferably from 0.05 to 5.0 mmol, and most preferably from 0.1 to 2.0 mmol, per g of the binder polymer.

**[0071]** The binder polymer for use in the invention may contain a polymerization unit of alkyl (meth)acrylate or aralkyl (meth)acrylate besides the polymerization unit having an acid group and the polymerization unit having a crosslinkable group. The alkyl group in the alkyl (meth)acrylate is preferably an alkyl group having from 1 to 5 carbon atoms and more preferably a methyl group. The aralkyl (meth)acrylate includes, for example, benzyl (meth)acrylate.

**[0072]** The binder polymer preferably has a weight average molecular weight of 5,000 or more, more preferably from 10,000 to 300,000, and a number average molecular weight of 1,000 or more, more preferably from 2,000 to 250,000. The polydispersity (weight average molecular weight/number average molecular weight) is preferably from 1.1 to 10.

**[0073]** The binder polymers may be used individually or in combination of two or more thereof. The content of the binder polymer is preferably from 5 to 75% by weight, more preferably from 10 to 70% by weight, still more preferably from 10 to 60% by weight, based on the total solid content of the photosensitive layer, from the standpoint of good strength of the image area and good image-forming property.

**[0074]** The total content of the polymerizable compound and the binder polymer is preferably 80% by weight or less based on the total solid content of the photosensitive layer. When it exceeds 80% by weight, decrease in the sensitivity and deterioration in the developing property may be caused sometimes. The total content is more preferably from 35 to 75% by weight.

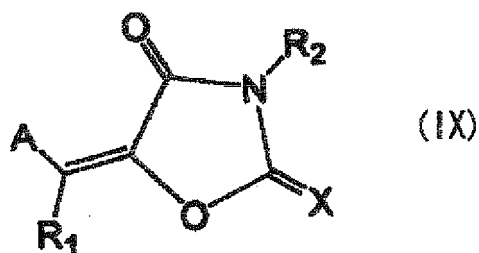
(Sensitizing dye)

**[0075]** The photosensitive layer according to the invention preferably contains a sensitizing dye. The sensitizing dye can be used without particular limitation as far as it absorbs light at the image exposure to form the excited state and provides energy to the polymerization initiator described hereinbefore with electron transfer, energy transfer or heat generation thereby improving the polymerization initiation function. Particularly, a sensitizing dye having an absorption maximum in a wavelength range of 300 to 450 nm or 750 to 1,400 nm is preferably used.

**[0076]** Examples of the sensitizing dye having an absorption maximum in a wavelength range of 300 to 450 nm include merocyanines, benzopyranes, coumarins, aromatic ketones and anthracenes.

**[0077]** Of the sensitizing dyes having an absorption maximum in a wavelength range of 300 to 450 nm, a dye represented by formula (IX) shown below is more preferable in view of high sensitivity.





**[0078]** In formula (IX), A represents an aromatic cyclic group which may have a substituent, X represents an oxygen atom, a sulfur atom or =N(R<sub>3</sub>), and R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> each independently represents a monovalent non-metallic atomic group, or A and R<sub>1</sub> or R<sub>2</sub> and R<sub>3</sub> may be combined with each other to form an aliphatic or aromatic ring.

**[0079]** In the formula (IX), R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> each independently represents a monovalent non-metallic atomic group, preferably a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted aromatic heterocyclic residue, a substituted or unsubstituted alkoxy group, a substituted or unsubstituted alkylthio group, a hydroxy group or a halogen atom.

**[0080]** A represents an aromatic cyclic group which may have a substituent or a heterocyclic group which may have a substituent. The aromatic cyclic group which may have a substituent and heterocyclic group which may have a substituent are same as the substituted or unsubstituted aryl group and substituted or unsubstituted aromatic heterocyclic residue described for any one of R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> above, respectively.

**[0081]** As such a sensitizing dye, compounds described in Paragraph Nos. [0047] to [0053] of JP-A-2007-58170 are preferably used.

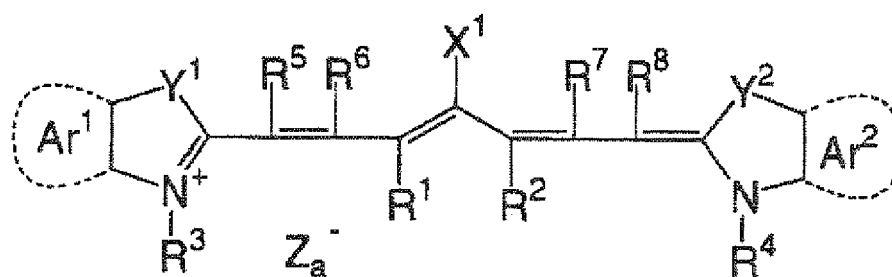
**[0082]** Further, sensitizing dyes described in JP-A-2007-171906, JP-A-2007-206216, JP-A-2007-206217, JP-A-2007-225701, JP-A-2007-225702, JP-A-2007-316582 and JP-A-2007-328243 are also preferably used.

**[0083]** As the sensitizing dye having an absorption maximum in a wavelength range of 750 to 1,400 (hereinafter, also referred to as an "infrared absorbing agent") preferably used in the invention, a dye or pigment is preferably used.

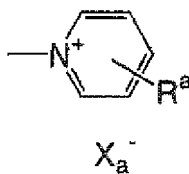
**[0084]** As the dye, commercially available dyes and known dyes described in literatures, for example, Senryo Binran (Dye Handbook) compiled by The Society of Synthetic Organic Chemistry, Japan (1970) can be used. Specifically, the dyes includes azo dyes, metal complex azo dyes, pyrazolone azo dyes, naphthoquinone dyes, anthraquinone dyes, phthalocyanine dyes, carbonium dyes, quinoneimine dyes, methine dyes, cyanine dyes, squarylium dyes, pyrylium salts and metal thiolate complexes.

**[0085]** Of the dyes, cyanine dyes, squarylium dyes, pyrylium dyes, nickel thiolate complexes and indolenine cyanine dyes are particularly preferred. Further, cyanine dyes and indolenine cyanine dyes are more preferred. As particularly preferable examples of the dye, cyanine dyes represented by formula (a) shown below are exemplified.

Formula (a) :



**[0086]** In formula (a), X<sup>1</sup> represents a hydrogen atom, a halogen atom, -NPh<sub>2</sub>, X<sup>2</sup>-L<sup>1</sup> or a group shown below. X<sup>2</sup> represents an oxygen atom, a nitrogen atom or a sulfur atom, L<sup>1</sup> represents a hydrocarbon group having from 1 to 12 carbon atoms, an aromatic cyclic group containing a hetero atom (a nitrogen atom, a sulfur atom, an oxygen atom, a halogen atom or a selenium atom) or a hydrocarbon group having from 1 to 12 carbon atoms and containing a hetero atom. X<sup>a</sup> has the same meaning as Z<sup>a</sup> defined hereinafter. R<sup>a</sup> represents a hydrogen atom, an alkyl group, an aryl group, a substituted or unsubstituted amino group or a halogen atom.



**[0087]** R<sup>1</sup> and R<sup>2</sup> each independently represents a hydrocarbon group having from 1 to 12 carbon atoms. In view of the preservation stability of a coating solution for photosensitive layer, it is preferred that R<sup>1</sup> and R<sup>2</sup> each represents a hydrocarbon group having two or more carbon atoms. It is also preferred that R<sup>1</sup> and R<sup>2</sup> are combined with each other to form a 5-membered or 6-membered ring.

**[0088]** Ar<sup>1</sup> and Ar<sup>2</sup>, which may be the same or different, each represents an aromatic hydrocarbon group which may have a substituent. Preferable examples of the aromatic hydrocarbon group include a benzene ring group and a naphthalene ring group. Preferable examples of the substituent include a hydrocarbon group having 12 or less carbon atoms, a halogen atom and an alkoxy group having 12 or less carbon atoms. Y<sup>1</sup> and Y<sup>2</sup>, which may be the same or different, each represents a sulfur atom or a dialkylmethylene group having 12 or less carbon atoms. R<sup>3</sup> and R<sup>4</sup>, which may be the same or different, each represents a hydrocarbon group having 20 or less carbon atoms, which may have a substituent. Preferable examples of the substituent include an alkoxy group having 12 or less carbon atoms, a carboxyl group and a sulfo group. R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup>, which may be the same or different, each represents a hydrogen atom or a hydrocarbon group having 12 or less carbon atoms. In view of the availability of raw materials, a hydrogen atom is preferred. Z<sup>a-</sup> represents a counter anion. However, Z<sup>a-</sup> is not necessary when the cyanine dye represented by formula (a) has an anionic substituent in the structure thereof and neutralization of charge is not needed. Preferable examples of the counter ion for Z<sup>a-</sup> include a halide ion, a perchlorate ion, a tetrafluoroborate ion, a hexafluorophosphate ion and a sulfonate ion, and particularly preferable examples thereof include a perchlorate ion, a hexafluorophosphate ion and an arylsulfonate ion in view of the preservation stability of a coating solution for photosensitive layer.

**[0089]** Specific examples of the cyanine dye represented by formula (a) include those described in Paragraph Nos. [0017] to [0019] of JP-A-2001-133969.

**[0090]** Further, other particularly preferable examples include specific indolenine cyanine dyes described in JP-A-2002-278057.

**[0091]** Examples of the pigment for use in the invention include commercially available pigments and pigments described in Colour Index (C.I.), Saishin Ganryo Binran (Handbook of the Newest Pigments) compiled by Pigment Technology Society of Japan (1977), Saishin Ganryo Oyou Gijutsu (Newest Application on Technologies for Pigments), CMC Publishing Co., Ltd. (1986) and Insatsu Ink Gijutsu (Printing Ink Technology), CMC Publishing Co., Ltd. (1984).

**[0092]** The amount of the sensitizing dye added is preferably from 0.05 to 30 parts by weight, more preferably from 0.1 to 20 parts by weight, most preferably from 0.2 to 10 parts by weight, per 100 parts by weight of the total solid content of the photosensitive layer.

(Other components of photosensitive layer)

**[0093]** The photosensitive layer preferably further contains a chain transfer agent. As the chain transfer agent, for example, compounds having SH, PH, SiH or GeH in their molecules are used. The compound donates hydrogen to a low active radical species to generate a radical or is oxidized and deprotonized to generate a radical.

**[0094]** In particular, a thiol compound (for example, a 2-mercaptobenzimidazole, a 2-mercaptobenzothiazole, a 2-mercaptobenzoxazole, a 3-mercaptotriazole or a 5-mercaptotetrazole) is preferably used as the chain transfer agent in the photosensitive layer. Specific examples of the thiol compound include, for example, those described in Paragraph Nos. [0212] to [0216] of JP-A-2008-276155.

**[0095]** Into the photosensitive layer, various additives can be further incorporated, if desired. Examples of the additive include a surfactant for progressing the developing property and improving the surface state of coated layer, a microcapsule for providing good compatibility between developing property and printing durability, a hydrophilic polymer for improving the developing property and dispersion stability of microcapsule, a coloring agent or print-out agent for visually distinguishing the image area from the non-image area, a polymerization inhibitor for preventing undesirable thermal polymerization of the radical polymerizable compound during the production and preservation of the photosensitive layer, a higher fatty acid derivative for avoiding polymerization inhibition due to oxygen, a fine inorganic particle for increasing strength of the cured layer in the image area, a hydrophilic low molecular weight compound for improving the developing property, a co-sensitizer for increasing sensitivity, and a plasticizer for improving plasticity. As the additives, known compounds are used and, for example, compounds described in Paragraph Nos. [0161] to [0215] of JP-A-

2007-206217 are used.

(Formation of photosensitive layer)

**[0096]** The photosensitive layer is formed by dispersing or dissolving each of the necessary constituting components described above in a solvent to prepare a coating solution and coating the solution. The solvent includes, for example, methyl ethyl ketone, ethylene glycol monomethyl ether, 1-methoxy-2-propanol, 2-methoxyethyl acetate, 1-methoxy-2-propyl acetate and  $\gamma$ -butyrolactone, but the invention should not be construed as being limited thereto. The solvents may be used individually or as a mixture thereof. The solid content concentration of the coating solution is preferably from 1 to 50% by weight.

**[0097]** The coating amount (solid content) of the photosensitive layer on the support after the coating and drying is preferably from 0.3 to 3.0 g/m<sup>2</sup>. Various methods can be used for the coating. Examples of the method include bar coater coating, spin coating, spray coating, curtain coating, dip coating, air knife coating, blade coating and roll coating.

<Protective layer>

**[0098]** In the lithographic printing plate precursor according to the invention, a protective layer (oxygen-blocking layer) is provided on the photosensitive layer in order to prevent penetration and diffusion of oxygen which inhibits the polymerization reaction at the time of exposure. In the protective layer, a water-soluble polymer compound relatively excellent in crystallizability is preferably used. Specifically, when polyvinyl alcohol is used as a main component, the preferable results can be obtained in the fundamental characteristics, for example, oxygen-blocking property and removability by development.

**[0099]** The polyvinyl alcohol for use in the protective layer may be partially substituted with ester, ether or acetal as long as it contains unsubstituted vinyl alcohol units for achieving the necessary oxygen-blocking property and water solubility. Also, polyvinyl alcohol may partly have other copolymerization component. Polyvinyl alcohol is obtained by hydrolysis of polyvinyl acetate. As specific examples of the polyvinyl alcohol, those having a hydrolysis degree of 71 to 100% by mole and a polymerization repeating unit number of 300 to 2,400 are exemplified. Specific examples thereof include PVA-105, PVA-110, PVA-117, PVA-117H, PVA-120, PVA-124, PVA-124H, PVA-CS, PVA-CST, PVA-HC, PVA-203, PVA-204, PVA-205, PVA-210, PVA-217, PVA-220, PVA-224, PVA-217EE, PVA-217E, PVA-220E, PVA-224E, PVA-405, PVA-420, PVA-613 and L-8 (produced by Kuraray Co., Ltd.). The polyvinyl alcohols can be used individually or as a mixture thereof. The content of polyvinyl alcohol in the protective layer is preferably from 20 to 95% by weight, and more preferably from 30 to 90% by weight.

**[0100]** Also, known modified polyvinyl alcohol can be preferably used. Particularly, an acid-modified polyvinyl alcohol having a carboxylic acid group or a sulfonic acid group is preferably used. As a component used as a mixture with polyvinyl alcohol, polyvinyl pyrrolidone or a modified product thereof is preferable from the viewpoint of the oxygen-blocking property and removability by development. The content thereof is ordinarily from 3.5 to 80% by weight, preferably from 10 to 60% by weight, more preferably from 15 to 30% by weight, in the protective layer.

**[0101]** In to the protective layer, glycerin, dipropylene glycol or the like can be added in an amount corresponding to several % by weight of the binder to provide flexibility. Further, an anionic surfactant, for example, sodium alkylsulfate or sodium alkylsulfonate, an amphoteric surfactant, for example, alkylaminocarboxylate and alkylaminodicarboxylate, or a nonionic surfactant, for example, polyoxyethylene alkyl phenyl ether can be added in an amount corresponding to several % by weight of the binder.

**[0102]** Further, it is also preferred to incorporate an inorganic stratiform compound into the protective layer of the lithographic printing plate precursor according to the invention for the purpose of improving the oxygen-blocking property and property for protecting the surface of photosensitive layer. Of the inorganic stratiform compounds, fluorine based swellable synthetic mica, which is a synthetic inorganic stratiform compound, is particularly useful.

**[0103]** The coating amount of the protective layer is preferably in a range of 0.05 to 10 g/m<sup>2</sup> in terms of the coating amount after drying. When the protective layer contains the inorganic stratiform compound, it is more preferably in a range of 0.1 to 5 g/m<sup>2</sup>, and when the protective layer does not contain the inorganic stratiform compound, it is more preferably in a range of 0.5 to 5 g/m<sup>2</sup>.

<Support>

**[0104]** The support for use in the lithographic printing plate precursor according to the invention is not particularly restricted as long as it is a dimensionally stable plate-like hydrophilic support. Particularly, an aluminum plate is preferable. In advance of the use of an aluminum plate, the aluminum plate is preferably subjected to a surface treatment, for example, roughening treatment or anodizing treatment. The roughening treatment of the surface of the aluminum plate is conducted by various methods and includes, for example, mechanical roughening treatment, electrochemical rough-

ening treatment (roughening treatment of electrochemically dissolving the surface) and chemical roughening treatment (roughening treatment of chemically dissolving the surface selectively). With respect to the treatments, methods described in Paragraph Nos. [0241] to [0245] of JP-2007-206217 are preferably used.

**[0105]** The center line average roughness of support is preferably from 0.10 to 1.2  $\mu\text{m}$ . In the range described above, good adhesion property to the photosensitive layer, good printing durability and good resistance to stain are achieved.

**[0106]** The color density of the support is preferably from 0.15 to 0.65 in terms of the reflection density value. In the range described above, good image-forming property by preventing halation at the image exposure and good aptitude for plate inspection after development are achieved.

**[0107]** The thickness of the support is preferably from 0.1 to 0.6 mm, more preferably from 0.15 to 0.4 mm, and still more preferably from 0.2 to 0.3 mm.

(Hydrophilizing treatment of surface of support)

**[0108]** As for the lithographic printing plate precursor according to the invention, in order to increase hydrophilicity of the non-image area and to prevent printing stain, it is preferred to further conduct hydrophilizing treatment of the surface of support.

**[0109]** The hydrophilizing treatment of the surface of support includes an alkali metal silicate treatment method wherein the support is subjected to an immersion treatment or an electrolytic treatment in an aqueous solution, for example, of sodium silicate, a method of treating with potassium fluorozirconate and a method of treating with polyvinylphosphonic acid. An immersion treatment in an aqueous polyvinylphosphonic acid solution is preferably used.

<Backcoat layer>

**[0110]** In the lithographic printing plate precursor according to the invention, a backcoat layer can be provided on the back surface of the support, if desired. The backcoat layer preferably includes, for example, a coating layer comprising an organic polymer compound described in JP-A-5-45885 and a coating layer comprising a metal oxide obtained by hydrolysis and polycondensation of an organic metal compound or an inorganic metal compound described in JP-A-6-35174. Among them, use of an alkoxy compound of silicon, for example,  $\text{Si}(\text{OCH}_3)_4$ ,  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ,  $\text{Si}(\text{OC}_3\text{H}_7)_4$  or  $\text{Si}(\text{OC}_4\text{H}_9)_4$  is preferred since the starting material is inexpensive and easily available.

[Method of preparing lithographic printing plate]

**[0111]** The lithographic printing plate precursor according to the invention is exposed imagewise and then subjected to development processing to prepare a lithographic printing plate.

<Image exposure>

**[0112]** The lithographic printing plate precursor is imagewise exposed with laser through a transparent original having a line image, a halftone dot image or the like, or imagewise exposed, for example, by scanning of laser beam based on digital data.

**[0113]** The wavelength of the exposure light source is preferably from 300 to 450 nm or from 750 to 1,400 nm. In case of exposing with light of 300 to 450 nm, the lithographic printing plate precursor having a photosensitive layer containing a sensitizing dye having an absorption maximum in the wavelength range is used. In case of exposing with light of 750 to 1,400 nm, the lithographic printing plate precursor containing an infrared absorbing agent which is a sensitizing dye having an absorption maximum in the wavelength range is used. As the light source of 300 to 450 nm, a semiconductor laser is preferably used. As the light source of 750 to 1,400 nm, a solid laser or semiconductor laser emitting an infrared ray is preferably used. The exposure mechanism may be any of an internal drum system, an external drum system and a flat bed system.

<Development processing>

**[0114]** The development processing ordinarily includes (1) a method of developing with an alkali developer (having pH higher than 11), (2) a method of developing with a developer having pH of 2 to 11, and (3) a method of developing (on-press development) by supplying dampening water and ink on a printing machine.

**[0115]** According to the developing process using the alkali developer as in the method (1), it is necessary that a protective layer is removed in a pre-water washing step, the alkali development is conducted, the alkali is removed by washing with water in a post-water washing step, gum solution treatment is conducted and drying is conducted in a drying step. According to the method of developing using the developer having pH of 2 to 11 as in the method (2), the

development and gum solution treatment can be conducted at the same time by incorporating a surfactant or a water-soluble polymer compound into the developer. Thus, the post-water washing step is not particularly necessary, and after conducting the development and gum solution treatment with one solution, the drying step can be performed. Moreover, the pre-water washing step is also not particularly necessary and the removal of protective layer can also be conducted simultaneously with the development and gum solution treatment. It is preferred that after the development and gum treatment, the excess developer is removed using a squeeze roller, followed by conducting drying. The developing method (2) has an advantage in that it is free from the measures against development scum resulting from the protective layer and/or photosensitive layer at the time of printing encountered in the on-press development of the method (3).

**[0116]** According to the invention, the method of developing with a developer having pH of 2 to 11 is preferably used.

**[0117]** Specifically, in the method of preparing a lithographic printing plate according to the invention, the lithographic printing plate precursor is subjected to the development processing with the developer having pH of 2 to 11 to remove together a protective layer and the unexposed area of the photosensitive layer so that the resulting lithographic printing plate can be immediately mounted on a printing machine to perform printing. The development of the lithographic printing plate precursor according to the invention is performed at temperature from 0 to 60°C, preferably from about 15 to about 40°C in a conventional manner, for example, by a method wherein the imagewise exposed lithographic printing plate precursor is immersed in the developer and rubbed with a brush or a method wherein the developer is splayed to the imagewise exposed lithographic printing plate precursor and the lithographic printing plate precursor is rubbed with a brush.

**[0118]** The development processing according to the invention is preferably performed by an automatic development processor equipped with a supplying means for a developer and a rubbing member. An automatic development processor using a rotating brush roll as the rubbing member is particularly preferred. Further, the automatic development processor is preferably provided with a means for removing the excess developer, for example, a squeeze roller or a drying means, for example, a hot air apparatus, subsequently to the development processing means.

**[0119]** The developer for use in the invention is preferably an aqueous solution containing water as the main component (containing 60 by weight or more of water). In particular, an aqueous solution containing a surfactant (for example, an anionic, nonionic, cationic or amphoteric surfactant) or an aqueous solution containing a water-soluble polymer compound is preferable. An aqueous solution containing both the surfactant and the water-soluble polymer compound is also preferable. The pH of the developer is preferably from 2 to 11, more preferably from 5 to 10.7, still more preferably from 6 to 10.5, and most preferably from 7.5 to 10.3.

**[0120]** The anionic surfactant for use in the developer is not particularly limited and includes, for example, fatty acid salts, abietic acid salts, hydroxyalkanesulfonic acid salts, alkanesulfonic acid salts, dialkylsulfosuccinic acid salts, straight-chain alkylbenzenesulfonic acid salts, branched alkylbenzenesulfonic acid salts, alkyl-naphthalenesulfonic acid salts, alkyl-diphenylether (di)sulfonic acid salts, alkylphenoxy polyoxyethylene propylsulfonic acid salts, polyoxyethylene alkyl-sulfophenyl ether salts, N-methyl-N-oleytaurine sodium salt, N-alkylsulfosuccinic acid monoamide disodium salts, petroleum sulfonic acid salts, sulfated castor oil, sulfated beef tallow oil, sulfate ester salts of fatty acid alkyl ester, alkyl sulfate ester salts, polyoxyethylene alkyl ether sulfate ester salts, fatty acid monoglyceride sulfate ester salts, polyoxyethylene allyl phenyl ether sulfate ester salts, polyoxyethylene styryl phenyl ether sulfate ester salts, alkyl phosphate ester salts, polyoxyethylene alkyl ether phosphate ester salts, polyoxyethylene alkyl phenyl ether phosphate ester salts, partially saponified products of styrene-maleic anhydride copolymer, partially saponified products of olefin-maleic anhydride copolymer and naphthalene sulfonate formalin condensates. Of the compounds, alkylbenzenesulfonic acid salts, alkyl-naphthalenesulfonic acid salts and alkyl-diphenylether (di)sulfonic acid salts are particularly preferably used.

**[0121]** The cationic surfactant for use in the developer is not particularly limited and, for example, alkylamine salts, quaternary ammonium salts, polyoxyethylene alkyl amine salts and polyethylene polyamine derivatives are preferably used.

**[0122]** The nonionic surfactant for use in the developer is not particularly limited and includes, for example, polyethylene glycol type higher alcohol ethylene oxide adducts, alkylphenol ethylene oxide adducts, alkyl-naphthol ethylene oxide adducts, phenol ethylene oxide adducts, naphthol ethylene oxide adducts, fatty acid ethylene oxide adducts, polyhydric alcohol fatty acid ester ethylene oxide adducts, higher alkylamine ethylene oxide adducts, fatty acid amide ethylene oxide adducts, ethylene oxide adducts of fat, polypropylene glycol ethylene oxide adducts, dimethylsiloxane-ethylene oxide block copolymers, dimethylsiloxane-(propylene oxide-ethylene oxide) block copolymers, fatty acid esters of polyhydric alcohol type glycerol, fatty acid esters of pentaerythritol, fatty acid esters of sorbitol and sorbitan, fatty acid esters of sucrose, alkyl ethers of polyhydric alcohols and fatty acid amides of alkanolamines. Of the compounds, those having an aromatic ring and an ethylene oxide chain are preferable and alkyl-substituted or unsubstituted phenol ethylene oxide adducts and alkyl-substituted or unsubstituted naphthol ethylene oxide adducts are more preferable.

**[0123]** The amphoteric surfactant for use in the developer is not particularly limited and includes, for example, amine oxide type, for example, alkyl-dimethylamine oxide, betaine type, for example, alkyl betaine and amino acid type, for example, sodium salt of alkylamino fatty acid. In Particular, alkyl-dimethylamine oxide which may have a substituent, alkyl carboxy betaine which may have a substituent and alkyl sulfo betaine which may have a substituent are preferably

used. Specific examples of the compound are described, for example, in Paragraph Nos. [0255] to [0278] of JP-A-2008-203359 and Paragraph Nos. [0028] to [0052] of JP-A-2008-276166. Specific examples of the more preferable compound include 2-alkyl-N-carboxymethyl-N-hydroxyethyl imidazolinium betaine, alkylidiaminoethylglycine hydrochloride, lauryldimethylaminoacetic acid betaine, N-lauric acid amidopropyldimethyl betaine and N-lauric acid amidopropyldimethylamine oxide.

**[0124]** Two or more of the surfactants may be used in combination. The content of the surfactant in the developer is preferably from 0.01 to 20% by weight, and more preferably from 0.1 to 10% by weight.

**[0125]** The water-soluble polymer compound for use in the developer includes, for example, soybean polysaccharide, modified starch, gum arabic, dextrin, a cellulose derivative (for example, carboxymethyl cellulose, carboxyethyl cellulose or methyl cellulose) or a modified product thereof, plulan, polyvinyl alcohol or a derivative thereof, polyvinyl pyrrolidone, polyacrylamide, an acrylamide copolymer, a vinyl methyl ether/maleic anhydride copolymer, a vinyl acetate/maleic anhydride copolymer and a styrene/maleic anhydride copolymer.

**[0126]** As the soybean polysaccharide, known soybean polysaccharide can be used. For example, as a commercial product, Soyafive (trade name, produced by Fuji Oil Co., Ltd.) is available and various grade products can be used. The soybean polysaccharide preferably used is that having viscosity in a range of 10 to 100 mPa/sec in the 10% by weight aqueous solution thereof.

**[0127]** As the modified starch, known modified starch can be used. The modified starch can be prepared, for example, by a method wherein starch, for example, of corn, potato, tapioca, rice or wheat is decomposed, for example, with an acid or an enzyme to an extent that the number of glucose residue per molecule is from 5 to 30 and then oxypropylene is added thereto in an alkali.

**[0128]** Two or more of the water-soluble polymer compounds may be used in combination. The content of the water-soluble polymer compound in the developer is preferably from 0.1 to 20% by weight, and more preferably from 0.5 to 10% by weight.

**[0129]** Into the developer, a pH buffer agent may further be incorporated. As the pH buffer agent, a pH buffer agent exhibiting a pH buffer function at pH of 2 to 11 is used without particular restriction. In the invention, a weak alkaline buffer agent is preferably used and includes, for example, (a) a combination of a carbonate ion and a hydrogen carbonate ion, (b) a borate ion, (c) a combination of a water-soluble amine compound and an ion of the water-soluble amine compound. By the function of the pH buffer agent, fluctuation of the pH of developer is prevented even when the developer is used for a long period of time. As a result, for example, the deterioration of developing property resulting from the fluctuation of pH and the occurrence of development scum are restrained. The combination of a carbonate ion and a hydrogen carbonate ion is particularly preferable.

**[0130]** In order for a carbonate ion and a hydrogen carbonate ion to be present in the developer, a carbonate and a hydrogen carbonate may be added to the developer or a carbonate ion and a hydrogen carbonate ion may be generated by adding a carbonate or a hydrogen carbonate to the developer and then adjusting the pH. The carbonate or hydrogen carbonate used is not particularly restricted and it is preferably an alkali metal salt thereof. Examples of the alkali metal include lithium, sodium and potassium and sodium is particularly preferable. The alkali metals may be used individually or in combination of two or more thereof. The total amount of the carbonate ion and hydrogen carbonate ion is preferably from 0.05 to 5 mole/l, more preferably from 0.1 to 2 mole/l, particularly preferably from 0.2 to 1 mole/l, in the developer.

**[0131]** The developer according to the invention may contain an organic solvent. As the organic solvent, for example, an aliphatic hydrocarbon (e.g., hexane, heptane, Isopar E, Isopar H, Isopar G (produced by Esso Chemical Co., Ltd.), gasoline or kerosene), an aromatic hydrocarbon (e.g., toluene or xylene), a halogenated hydrocarbon (methylene dichloride, ethylene dichloride, trichloroethylene or monochlorobenzene) or a polar solvent is exemplified. Examples of the polar solvent include an alcohol (e.g., methanol, ethanol, propanol, isopropanol, benzyl alcohol, ethylene glycol monomethyl ether, 2-ethoxyethanol, diethylene glycol monoethyl ether, diethylene glycol monohexyl ether, triethylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol monomethyl ether, polyethylene glycol monomethyl ether, polypropylene glycol, tetraethylene glycol, ethylene glycol monobutyl ether, ethylene glycol monobenzyl ether, ethylene glycol monophenyl ether, propylene glycol monophenyl ether, methyl phenyl carbinol, n-amyl alcohol or methylamyl alcohol), a ketone (e.g., acetone, methyl ethyl ketone, ethyl butyl ketone, methyl isobutyl ketone or cyclohexanone), an ester (e.g., ethyl acetate, propyl acetate, butyl acetate, amyl acetate, benzyl acetate, methyl lactate, butyl lactate, ethylene glycol monobutyl acetate, polyethylene glycol monomethyl ether acetate, diethylene glycol acetate, diethyl phthalate or butyl levulinate) and others (e.g., triethyl phosphate, tricresyl phosphate, N-phenylethanolamine or N-phenyldiethanolamine).

**[0132]** When the organic solvent is insoluble in water, it may be employed by being solubilized in water using a surfactant or the like. In the case where the developer contains an organic solvent, the concentration of the organic solvent is desirably less than 40% by weight in view of safety and inflammability.

**[0133]** The developer may contain a preservative, a chelating agent, a defoaming agent, an organic acid, an inorganic acid, an inorganic salt or the like in addition the components described above. Specifically, compounds described in Paragraph Nos. [0266] to [0270] of JP-A-2007-206217 are preferably used.

**[0134]** The developer can be used as a developer and a development replenisher for the exposed lithographic printing plate precursor and it is preferably applied to the automatic development processor described above. In the case of conducting the development processing using an automatic development processor, the developer becomes fatigued in accordance with the processing amount, and hence the processing ability may be restored using a replenisher or a fresh developer.

**[0135]** In the method of preparing a lithographic printing plate according to the invention, the lithographic printing plate precursor may be heated its entire surface between the exposure and the development, if desired. By the heating, the image-forming reaction in the photosensitive layer is accelerated and advantages, for example, improvement in the sensitivity and printing durability and stabilization of the sensitivity are achieved. For the purpose of increasing the image strength and printing durability, it is also effective to perform entire after-heating or entire exposure of the image after the development. Ordinarily, the heating before the development is preferably performed under a mild condition of 150°C or lower. When the temperature is too high, a problem may arise sometimes in that the unexposed area is also cured. On the other hand, the heating after the development can be performed using very strong conditions and is ordinarily carried out in a temperature range of 100 to 500°C. When the temperature is too low, a sufficient effect of strengthening the image may not be obtained, whereas when it is excessively high, problems of deterioration of the support and thermal decomposition of the image area may occur sometimes.

### EXAMPLES

**[0136]** The present invention will be described in more detail with reference to the following examples, but the invention should not be construed as being limited thereto.

#### Examples 1 to 12 and Comparative Examples 1 to 10

[Preparation of Lithographic printing plate precursor]

##### (1) Preparation of Support

**[0137]** An aluminum plate (material: JIS A1050) having a thickness of 0.3 mm was dipped in an aqueous 10% by weight sodium hydroxide solution at 60°C for 25 seconds to effect etching, washed with running water, neutralized and cleaned with an aqueous 20% by weight nitric acid solution and then washed with water. The aluminum plate was subjected to an electrolytic surface roughening treatment in an aqueous 1 % by weight nitric acid solution using an alternating current with a sinusoidal waveform at an anode time electricity of 300 coulomb/dm<sup>2</sup>. Subsequently, the aluminum plate was dipped in an aqueous 1% by weight sodium hydroxide solution at 40°C for 5 seconds, dipped in an aqueous 30% by weight sulfuric acid solution at 60°C for 40 seconds to effect a desmut treatment, and then subjected to an anodizing treatment in an aqueous 20% by weight sulfuric acid solution for 2 minutes at a current density of 2 A/ctm<sup>2</sup> to form an anodic oxide film having a thickness of 2.7 g/m<sup>2</sup>, thereby preparing a support. The center line average roughness of the support was measured using a stylus having a diameter of 2 μm and found to be 0.25 μm (Ra indication according to JIS B0601).

##### (2) Formation of Intermediate layer

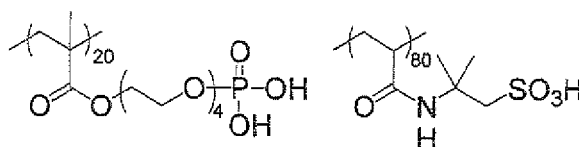
Intermediate layers 1 to 8 for comparison

**[0138]** A water/methanol (1/9 weight ratio) solution containing any one of Polymer Compounds A-1 to A-8 shown below in an appropriate concentration (about 0.1% by weight) so as to have a coating amount after drying of 10 mg/m<sup>2</sup> was prepared, coated on the support described above by a bar and dried in an oven at 80°C for 10 seconds to form Intermediate layers 1 to 8 for comparison, respectively.

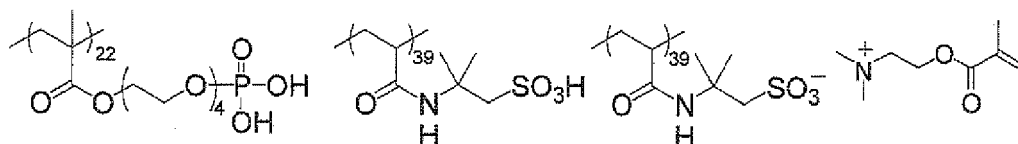
A-1 shown below (weight average molecular weight: 100,000)

A-2 shown below (weight average molecular weight: 100,000)

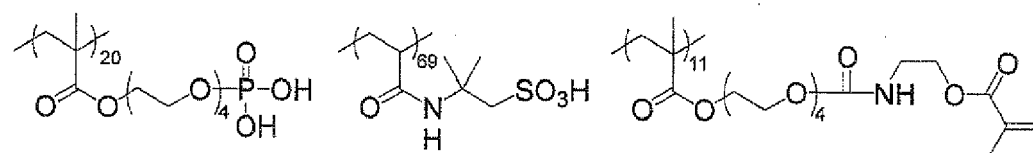
A-3 shown below (weight average molecular weight: 100,000)



A-1



A-2



A-3

A-4: Specific polymer compound for intermediate layer 11 shown hereinbefore (weight average molecular weight: 100,000, composition ratio:  $x = 100$ ,  $y = 0$ )

A-5: Specific polymer compound for intermediate layer 11 shown hereinbefore (weight average molecular weight: 100,000, composition ratio:  $x = 90$ ,  $y = 10$ )

A-6: Specific polymer compound for intermediate layer 32 shown hereinbefore (weight average molecular weight: 100,000, composition ratio:  $x = 20$ ,  $y = 0$ ,  $z = 80$ )

A-7: Specific polymer compound for intermediate layer 32 shown hereinbefore (weight average molecular weight: 100,000, composition ratio:  $x = 20$ ,  $y = 10$ ,  $z = 70$ )

A-8: Specific polymer compound for intermediate layer 46 shown hereinbefore (weight average molecular weight: 100,000, composition ratio:  $x = 20$ ,  $y = 80$ )

Intermediate layers 9 to 16

**[0139]** A water/methanol (1/9 weight ratio) solution containing any one of Polymer Compounds A-1 to A-8 shown above in an appropriate concentration (about 0.1% by weight) so as to have a coating amount of 10 mg/m<sup>2</sup> after drying was prepared, coated on the support described above by a bar and dried in an oven at 80°C for 10 seconds. Then, an aqueous solution containing calcium chloride in an appropriate concentration (from 0.05 to 0.2% by weight) so as to have a calcium ion amount of 1. mg/m<sup>2</sup> on the support after drying was coated by a bar and dried in an oven at 80°C for 10 seconds to form Intermediate layers 9 to 16, respectively.

Intermediate layers 17 to 20

**[0140]** A water/methanol (1/9 weight ratio) solution containing Polymer Compound A-1 or A-8 shown above in an appropriate concentration (about 0.1% by weight) so as to have a coating amount of 10 mg/m<sup>2</sup> after drying was prepared, coated on the support described above by a bar and dried in an oven at 80°C for 10 seconds. Then, an aqueous solution containing copper (II) chloride or aluminum chloride in an appropriate concentration (from 0.05 to 0.2% by weight) so



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as to have a cation amount of 1.8 mg/m<sup>2</sup> on the support after drying was coated by a bar and dried in an oven at 80°C for 10 seconds to form Intermediate layers 17 to 20, respectively.

Intermediate layers 21 to 22

**[0141]** A water/methanol (1/9 weight ratio) solution containing Polymer Compound A-1 or A-8 shown above in an appropriate concentration (about 0.1% by weight) so as to have a coating amount of 10 mg/m<sup>2</sup> after drying was prepared, coated on the support described above by a bar and dried in an oven at 80°C for 10 seconds. Then, the support was immersed in an aqueous solution containing calcium chloride in an appropriate concentration (from 0.05 to 0.2% by weight) so as to have a calcium ion amount of 1.8 mg/m<sup>2</sup> on the support after drying at 20°C for 10 seconds, rinsed with desalted water at 20°C for 2 seconds and dried to form Intermediate layers 21 to 22, respectively.

Intermediate layers 23 to 24

**[0142]** To a water/methanol (1/9 weight ratio) solution containing Polymer Compound A-1 or A-8 shown above in an appropriate concentration (about 0.1% by weight) so as to have a coating amount of 10 mg/m<sup>2</sup> after drying was added calcium chloride in an appropriate concentration (from 0.05 to 0.2% by weight) so as to have a calcium ion amount of 1.8 mg/m<sup>2</sup> on the support after drying to prepare a solution and the solution was coated on the support described above by a bar and dried in an oven at 80°C for 10 seconds to form Intermediate layers 23 to 24, respectively.

Intermediate layers 25 to 26 for comparison

**[0143]** The support described above was immersed in a water/methanol (1/9 weight ratio) solution containing Polymer Compound A-1 or A-8 shown above in an appropriate concentration (from 0.3 to 0.6% by weight) so as to have a coating amount of 10 mg/m<sup>2</sup> after drying at 40°C for 10 seconds, rinsed with desalted water at 20°C for 2 seconds and dried to form Intermediate layers 25 to 26 for comparison, respectively.

Intermediate layers 27 to 28

**[0144]** The support described above was immersed in a water/methanol (1/9 weight ratio) solution containing Polymer Compound A-1 or A-8 shown above in an appropriate concentration (from 0.3 to 0.6% by weight) so as to have a coating amount of 10 mg/m<sup>2</sup> after drying at 40°C for 10 seconds, rinsed with desalted water at 20°C for 2 seconds and dried. Then, the support was immersed in an aqueous solution containing calcium chloride in an appropriate concentration (from 0.05 to 0.2% by weight) so as to have a calcium ion amount of 1.8 mg/m<sup>2</sup> on the support after drying at 20°C for 10 seconds, rinsed with desalted water at 20°C for 2 seconds and dried to form Intermediate layers 27 to 28, respectively.

Intermediate layers 29 to 30

**[0145]** The support described above was immersed in a water/methanol (1/9 weight ratio) solution containing Polymer Compound A-1 or A-8 shown above in an appropriate concentration (from 0.3 to 0.6% by weight) so as to have a coating amount of 10 mg/m<sup>2</sup> after drying at 40°C for 10 seconds, rinsed with desalted water at 20°C for 2 seconds and dried. Then, an aqueous solution containing calcium chloride in an appropriate concentration (from 0.05 to 0.2% by weight) so as to have a calcium ion amount of 1.8 mg/m<sup>2</sup> on the support after drying was coated by a bar and dried in an oven at 80°C for 10 seconds to form Intermediate layers 29 to 30, respectively.

Intermediate layers 31 to 32

**[0146]** To a water/methanol (1/9 weight ratio) solution containing Polymer Compound A-1 or A-8 shown above in an appropriate concentration (from 0.3 to 0.6% by weight) so as to have a coating amount of 10 mg/m<sup>2</sup> after drying was added calcium chloride in an appropriate concentration (from 0.05 to 0.2% by weight) so as to have a calcium ion amount of 1.8 mg/m<sup>2</sup> on the support after drying to prepare a solution. The support described above was immersed in the solution at 40°C for 10 seconds, rinsed with desalted water at 20°C for 2 seconds and dried to prepare Intermediate layers 31 to 32, respectively.

(3) Formation of Image-recording layer and Protective layer

**[0147]** Coating solution (1) for image-recording layer shown below was coated on the support having the intermediate layer formed above using a bar and dried in an oven at 100°C for 44 seconds to form an image-recording layer having

a dry coating amount of 1.3 g/m<sup>2</sup>. Coating solution (1) for protective layer shown below was coated on the image-recording layer using a bar so as to have a dry coating amount of 0.8 g/m<sup>2</sup> and dried at 125°C for 70 seconds, whereby a lithographic printing plate precursor was prepared.

<Coating solution (1) for image-recording layer>

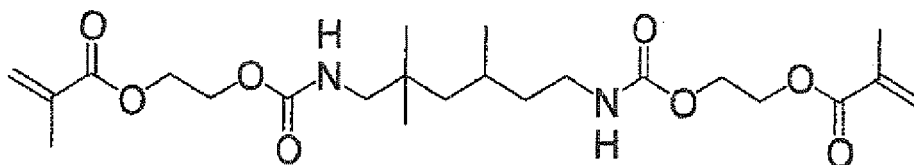
**[0148]**

Binder Polymer (1) shown below (weight average molecular weight: 120,000)	0.54 g
Polymerizable Compound (1) shown below	0.40 g
Sensitizing Dye (1) shown below	0.06 g
Polymerization Initiator (1) shown below	0.18 g
Chain Transfer Agent (1) shown below	0.07 g
Dispersion of $\epsilon$ -phthalocyanine pigment	0.40 g

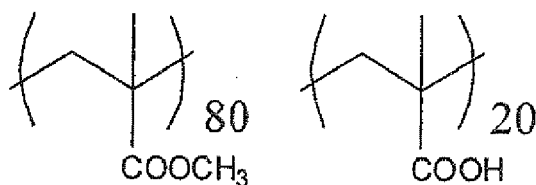
[pigment: 15 parts by weight; dispersing agent (allyl methacrylate/methacrylic acid copolymer (copolymerization molar ratio: 83/17, weight average molecular weight: 60,000)): 10 parts by weight; solvent (cyclohexanone/methoxypropyl acetate/1-methoxy-2-propanol = 15 parts by weight/20 parts by weight/40 parts by weight)]

Thermal polymerization inhibitor	0.01 g
N-nitrosophenylhydroxylamine aluminum salt	
Fluorine-Based Surfactant (1) shown below (weight average molecular weight: 11,000)	0.001 g
Polyoxyethylene-polyoxypropylene condensate (Pluronic L44, produced by ADEKA Corp.)	0.04 g
Tetraethylamine hydrochloride	0.01 g
1-Methoxy-2-propanol	3.5 g
Methyl ethyl ketone	8.0 g

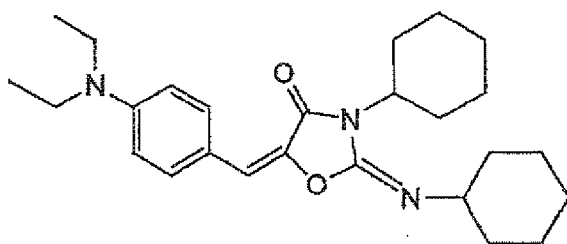
**[0149]** Polymerizable Compound (1):



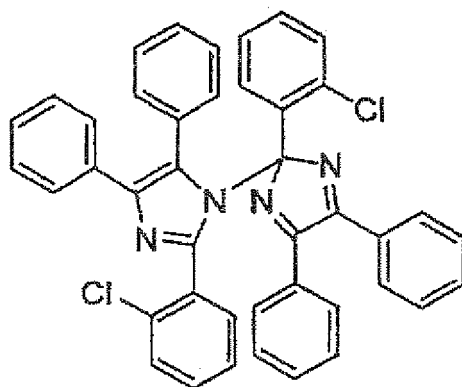
**[0150]** Binder Polymer (1):



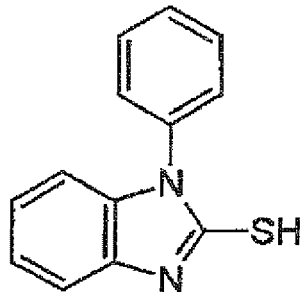
**[0151]** Sensitizing Dye (1):



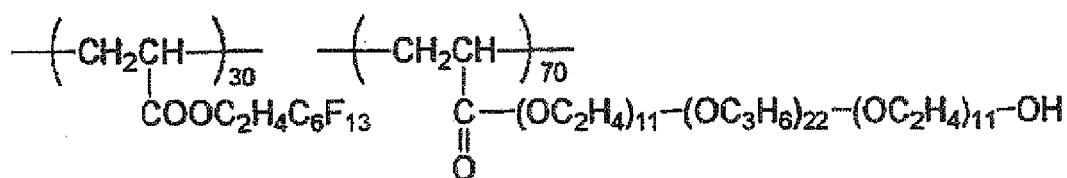
[0152] Polymerization Initiator (1)



[0153] Chain Transfer Agent (1):



[0154] Fluorine-Based Surfactant (1):



&lt;Coating solution (1) for protective layer&gt;

[0155]

Dispersion of Mica (1) shown below

13.0 g

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(continued)

	Polyvinyl alcohol (saponification degree: 98% by mole; polymerization degree: 500)	1.3 g
	Sodium 2-ethylhexylsulfosuccinate	0.2 g
5	Vinyl pyrrolidone/vinyl acetate copolymer (molar ratio: 1/1, weight average molecular weight: 70,000)	0.05 g
	Surfactant (Emalex 710, produced by Nihon-Emulsion Co., Ltd.)	0.05 g
	Water	133 g

(Preparation of Dispersion of Mica (1))

**[0156]** In 368 g of water was added 32 g of synthetic mica (SOMASIF ME-100, produced by CO-OP Chemical Co., Ltd.; aspect ratio: 1, 000 or more) and the mixture was dispersed using a homogenizer until the average particle diameter (measured by a laser scattering method) became 0.5  $\mu\text{m}$  to obtain Dispersion of Mica (1).

[Preparation of Lithographic printing plate]

<Exposure, Development and Printing>

**[0157]** Each of the lithographic printing plate precursors was subjected to image exposure by Violet semiconductor laser plate setter Vx9600 (having InGaN semiconductor laser (emission wavelength: 405 nm  $\pm$  10 nm/output: 30 mW)) produced by FFEI Ltd. The image drawing was performed at resolution of 2, 438 dpi using FM screen (TAFETA 20, produced by Fuji Film Co., Ltd.) in a plate surface exposure amount of 0.05 mJ/cm<sup>2</sup>.

**[0158]** The exposed lithographic printing plate precursor was subjected to preheating at 100°C for 30 seconds and then subjected to development processing in an automatic development processor having a structure as shown in Fig. 1 using a developer having the composition shown below. The automatic development processor had two rotating brush rollers. The first brush roller was a brush roller having an outer diameter of 50 mm and being implanted with fiber of polybutylene terephthalate (bristle diameter: 200  $\mu\text{m}$ , bristle length: 17 mm), and the brush roller was rotated at 200 rpm (peripheral velocity at the tip of brush: 0.52 m/sec) in the same direction as the transporting direction. The second brush roller was a brush roller having an outer diameter of 50 mm and being implanted with fiber of polybutylene terephthalate (bristle diameter: 200  $\mu\text{m}$ , bristle length: 17 mm), and the brush roller was rotated at 200 rpm (peripheral velocity at the tip of brush: 0.52 m/sec) in the opposite direction to the transporting direction. The transportation of the lithographic printing plate precursor was performed at transporting speed of 100 cm/min.

**[0159]** The developer was supplied on the surface of the lithographic printing plate precursor by showering from a spray pipe using a circulation pump. The tank volume for the developer was 10 liters.

Developer (pH: 9.8)

**[0160]**

40	Water	7620 g
	Sodium carbonate anhydride	100 g
	Sodium hydrogen carbonate	50 g
	Softazoline LPB-R (amphoteric surfactant, produced by Kawaken Fine Chemicals Co, Ltd.)	1500 g
45	Softazoline LAO (amphoteric surfactant, produced by Kawaken Fine Chemicals Co, Ltd.)	360 g
	Sodium gluconate	150 g
	TSA 739 (defoaming agent, produced by Momentive Performance Materials Inc.)	20 g
	Ethylenediaminedisuccinate	200 g
	2-Bromo-2-nitropropane-1,3-diol	0.1 g
50	2-Methyl-4-isothiazolin-3-one	0.1 g

**[0161]** The lithographic printing plate obtained by the development processing was mounted on a printing machine (SOR-M, produced by Heidelberg) and printing was performed at a printing speed of 6,000 sheets per hour using dampening water (Vegraviolet, produced by Vegra)/water/isopropyl alcohol = 2/88/10 (by volume ratio)) and Hostmann (N) black ink (produced by Hostmann). With each lithographic printing plate, printing durability of the image area and stain resistance of the non-image area were evaluated in the manner shown below. The results obtained are shown in Table 1. In Table 1, with respect to the indication of formation method of intermediate layer, A1 represents coating of

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the solution of polymer compound, A2 represents immersion in the solution of polymer compound, B1 represents coating of the solution of polyvalent cation, B2 represents immersion in the solution of polyvalent cation, AB1 represents coating of the solution containing the polymer compound and polyvalent cation, and AB2 represents immersion in the solution containing the polymer compound and polyvalent cation.

<Printing durability>

**[0162]** As increase in the number of printing sheets in the course of printing as described above, the image-recording layer was gradually abraded to cause decrease in the ink receptivity, resulting in decrease of ink density on printing paper. A number of printed materials obtained until the ink density (reflection density) decreased by 0.1 from that at the initiation of printing was determined to evaluate the printing durability.

<Stain resistance>

**[0163]** On the 500th sheet of the printed material, the stain resistance of the non-image area was evaluated on 11-point scale from 1.0 to 6.0. On the scale, 4.0 or larger is in the acceptable level and as the number increases, the stain resistance is excellent.

TABLE 1

	Intermediate Layer				Printing Durability (x 10 <sup>4</sup> sheets)	Stain Resistance
	Number	Polymer Compound	Polyvalent Cation	Formation Method		
Example 1	9	A-1	Ca <sup>2+</sup>	A1 + B1	8	6
Example 2	10	A-2	Ca <sup>2+</sup>	A1 + B1	8	6
Example 3	11	A-3	Ca <sup>2+</sup>	A1 + B1	8.5	5
Example 4	12	A-4	Ca <sup>2+</sup>	A1 + B1	7.5	5
Example 5	13	A-5	Ca <sup>2+</sup>	A1 + B1	7.5	5
Example 6	14	A-6	Ca <sup>2+</sup>	A1 + B1	8	5.5
Example 7	15	A-7	Ca <sup>2+</sup>	A1 + B1	8.5	5
Example 8	16	A-8	Ca <sup>2+</sup>	A1 + B1	8.5	6
Example 9	17	A-1	Cu <sup>2+</sup>	A1 + B1	8	5
Example 10	18	A-8	Cu <sup>2+</sup>	A1 + B1	8.5	6
Example 11	19	A-1	Al <sup>3+</sup>	A1 + B1	9	5
Example 12	20	A-8	Al <sup>3+</sup>	A1 + B1	9	5
Example 13	21	A-1	Ca <sup>2+</sup>	A1 + B2	8	5
Example 14	22	A-8	Ca <sup>2+</sup>	A1 + B2	8.5	6
Example 15	23	A-1	Ca <sup>2+</sup>	AB1	7.5	5
Example 16	24	A-8	Ca <sup>2+</sup>	AB1	8	5.5
Example 17	27	A-1	Ca <sup>2+</sup>	A2 + B2	8	5
Example 18	28	A-8	Ca <sup>2+</sup>	A2 + B2	8.5	6
Example 19	29	A-1	Ca <sup>2+</sup>	A2 + B1	8	5
Example 20	30	A-8	Ca <sup>2+</sup>	A2 + B1	8.5	6
Example 21	31	A-1	Ca <sup>2+</sup>	AB2	7.5	5
Example 22	32	A-8	Ca <sup>2+</sup>	AB2	8	5.5
Comparative Example 1	1	A-1	None	A1	5	5

(continued)

	Intermediate Layer				Printing Durability (x 10 <sup>4</sup> sheets)	Stain Resistance
	Number	Polymer Compound	Polyvalent Cation	Formation Method		
Comparative Example 2	2	A-2	None	A1	5.5	5
Comparative Example 3	3	A-3	None	A1	6.5	4
Comparative Example 4	4	A-4	None	A1	5	5
Comparative Example 5	5	A-5	None	A1	6	4
Comparative Example 6	6	A-6	None	A1	5	6
Comparative Example 7	7	A-7	None	A1	6.5	5
Comparative Example 8	8	A-8	None	A1	5	6
Comparative Example 9	25	A-1	None	A2	5.5	4.5
Comparative Example 10	26	A-8	None	A2	5	4.5

[0164] From the results shown in Table 1, it can be seen that the lithographic printing plates having the intermediate layer containing the polyvalent cation exhibit the improved printing durability in comparison with the lithographic printing plates having the intermediate layer containing no polyvalent cation. This effect is recognized even when the kind of the acid group included in the polymer compound for intermediate layer and the kind of the polyvalent cation are varied. It is believed that this is because the acid group included in the polymer compound for intermediate layer and a carboxylic acid group which is an acid group contained in the binder polymer of the image-recording layer undergo electrostatic interaction through the polyvalent cation to achieve higher adhesion property in the image area. This effect is also recognized even when the application method of the polymer compound for intermediate layer and polyvalent cation is varied. Further, it is understood that the larger effect (more improved printing durability) can be obtained by first applying the polymer compound for intermediate layer and then applying the polyvalent cation in comparison with the simultaneous application of the polymer compound for intermediate layer and polyvalent cation, for example, from the comparison of Examples 1, 13, 17 and 19 with Examples 15 and 21. This result indicates that it is more preferable for the polyvalent cation to exist at the interface between the intermediate layer and the image-recording layer. It is also believed that the reason for the improvement in the printing durability without accompanying the degradation of the stain resistance is that the electrostatic interaction through the polyvalent cation dissolves at the time of development processing.

[0165] Moreover, it can be seen that the stain resistance is somewhat improved. This is an unexpected result. It is known that the component of the image-recording layer, for example, the binder polymer, adsorbs to the support to cause the stain. However, it is believed that due to the presence of the polyvalent cation at the interface, the component of the image-recording layer interacts with the polyvalent cation rather than the surface of the support to be removed together with the polyvalent cation at the development.

[0166] From the results described above, it can be understood that the lithographic printing plate precursor excellent in the balance between the stain resistance and the printing durability can be obtained by the intermediate layer containing the polymer compound for intermediate layer having an acid group and the polyvalent cation.

## Claims

1. A lithographic printing plate precursor comprising, in the following order:

a support;

an intermediate layer comprising a polyvalent cation and a polymer compound having at least one of an acid group selected from a sulfonic acid group, a carboxylic acid group and a phosphoric acid group and a salt thereof;

an image-recording layer comprising (i) a polymerization initiator, (ii) a polymerizable compound and (iii) a binder polymer; and

a protective layer.

2. The lithographic printing plate precursor as claimed in claim 1, wherein the acid group contained in the polymer compound is a carboxylic acid group or a sulfonic acid group.

3. The lithographic printing plate precursor as claimed in claim 1 or 2, wherein the polymer compound further has a support adsorbing group.

4. The lithographic printing plate precursor as claimed in claim 3, wherein the support adsorbing group is one of an onium salt group, a phosphoric acid group, a phosphonic acid group, a boric acid group and a  $\beta$ -diketone group.

5. The lithographic printing plate precursor as claimed in claim 4, wherein the support adsorbing group is a phosphoric acid group or a phosphonic acid group.

6. The lithographic printing plate precursor as claimed in any one of claims 1 to 5, wherein the polymer compound further has an ethylenically unsaturated bond group.

7. The lithographic printing plate precursor as claimed in any one of claims 1 to 6, wherein the polyvalent cation is a divalent or higher valent alkaline earth metal or transition metal ion.

8. The lithographic printing plate precursor as claimed in claim 7, wherein the polyvalent cation is a calcium ion, a magnesium ion, a copper (II) ion, an aluminum ion or an iron (II) ion.

9. The lithographic printing plate precursor as claimed in any one of claims 1 to 8, wherein the intermediate layer is formed by applying a coating solution containing the polymer compound and the polyvalent cation.

10. The lithographic printing plate precursor as claimed in any one of claims 1 to 8, wherein the intermediate layer is formed by applying a coating solution containing the polymer compound and then applying a coating solution containing the polyvalent cation.

11. The lithographic printing plate precursor as claimed in any one of claims 1 to 8, wherein the intermediate layer is formed by applying a coating solution containing the polymer compound and then treating with a treatment solution containing the polyvalent cation.

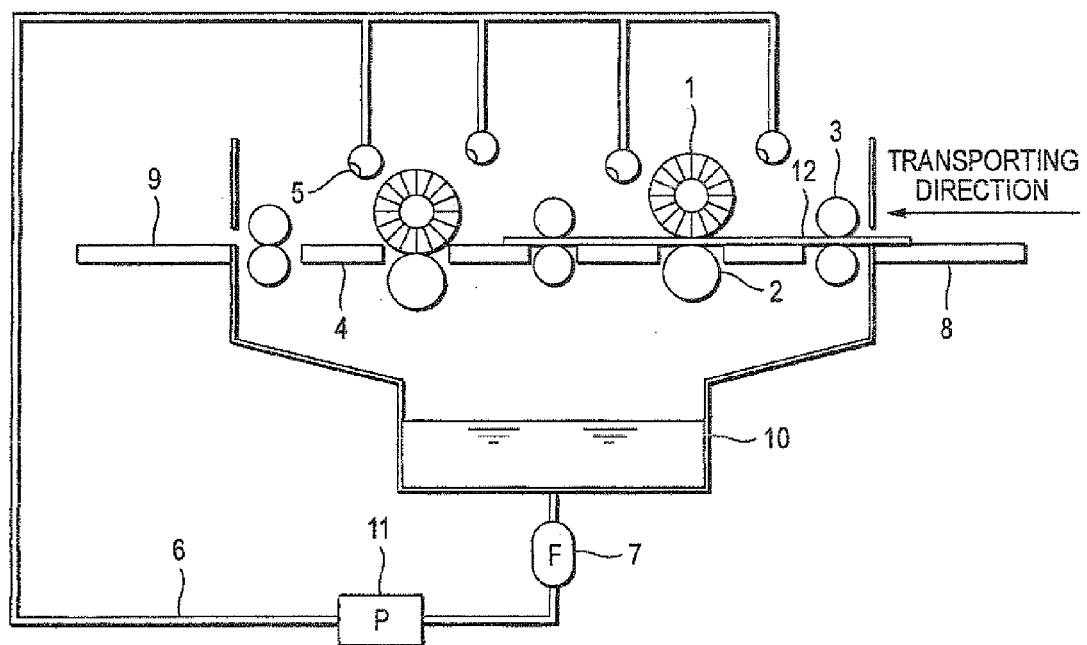
12. The lithographic printing plate precursor as claimed in any one of claims 1 to 8, wherein the intermediate layer is formed by treating with a treatment solution containing the polymer compound and then applying a coating solution containing the polyvalent cation.

13. The lithographic printing plate precursor as claimed in any one of claims 1 to 8, wherein the intermediate layer is formed by treating with a treatment solution containing the polymer compound and then treating with a treatment solution containing the polyvalent cation.

14. The lithographic printing plate precursor as claimed in any one of claims 1 to 8, wherein the intermediate layer is formed by treating with a treatment solution containing the polymer compound and the polyvalent cation.

15. A method of preparing a lithographic printing plate comprising processing the lithographic printing plate precursor as claimed in any one of Claims 1 to 14 with a developer having pH of from 2 to 11.

FIG. 1





## REFERENCES CITED IN THE DESCRIPTION

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