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(54) **LITHOGRAPHIC PRINTING PLATE PRECURSOR AND PROCESS FOR MAKING
LITHOGRAPHIC PRINTING PLATE**

(57) An object of the present invention is to provide a lithographic printing plate precursor that has excellent printing durability and developability and that has stain resistance, in particular resistance to staining of a non-image area of a printed material that occurs due to the operation of a slip mechanism of a dampener, and a process for making a lithographic printing plate using the lithographic printing plate precursor.

Disclosed is a lithographic printing plate precursor comprising, in order above a support, an intermediate

layer and an image recording layer,
the intermediate layer comprising, as Component A, a specific copolymer,
the image recording layer comprising an infrared absorbing agent,
either the intermediate layer or the image recording layer comprising, as Component B, a specific polymer compound, and
the mass ratio of Component A and Component B being Component A:Component B = 1:0.5 to 1:5.

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Description

[0001] The present invention relates to a lithographic printing plate precursor and a process for making a lithographic printing plate.

[0002] In the field of lithographic printing plate precursors, high-output and small-sized solid-state, semiconductor, and gas lasers that emit UV light, visible light, and infrared light having a wavelength of 300 nm to 1,200 nm have become easily available, and these lasers are very useful as a recording light source when making a plate directly from digital data from a computer, etc. Various investigations have been carried out into recording materials that respond to these various types of laser light; as representatives, a positive-working recording material and a negative-working recording material can first be cited as materials that enable recording to be carried out with an infrared laser having an image recording wavelength of at least 760 nm. There can secondly be cited a radically polymerizable negative-working recording material, etc. as a recording material that is responsive to a UV light or visible light laser of 300 nm to 700 nm.

[0003] On the other hand, in the field of lithographic printing methods, for the purpose of improving productivity by means of a reduction in time or a reduction in the amount of waste paper at the start of printing, uniformity of water lift of dampening water for printing, and removability, etc. of dirt or paper dust due to printing paper, the application of a slip mechanism to a dampener of a lithographic printer has been carried out in recent years. As one example, there can be cited a method in which a slip mechanism is applied to a dampening form roller. The slip mechanism of the dampening form roller is a mechanism that enables a dampening form roller to be rotated at different surface speed from that of a plate cylinder. When this mechanism is operated, the dampening form roller and the plate cylinder rotate at different surface speeds, thus temporarily causing slippage between the two.

[0004] For a lithographic printing plate precursor, it is important to achieve both printing durability and stain resistance of a printing plate at the same time, and in order to meet this requirement a lithographic printing plate precursor in which a hydrophilic layer having higher adhesion to a support surface is provided to thus improve both printing durability and stain resistance is known. For example, JP-A-2008-250226 (JP-A denotes a Japanese unexamined patent application publication) discloses a lithographic printing plate precursor comprising, in order above a support, a layer comprising a compound containing an ethylenically unsaturated bond and a functional group that interacts with the support surface and a polymer compound containing an ethylenically unsaturated bond, a functional group that interacts with the support surface, and a hydrophilic functional group, and an image formation layer. JP-A-2013-205569 discloses a lithographic printing plate precursor comprising, in order above a support, a layer comprising a polyfunctional ethylenically unsaturated compound and a polymer compound having a polymer having a polyalkyleneoxy bond in a side chain, and an image formation layer.

[0005] A lithographic printing method comprising a step of carrying out processing by rotating a dampening form roller and a plate cylinder at different surface speeds is described in JP-A-2004-284223.

[0006] However, it has been found that these known techniques have the problem that, when aging occurs under a high humidity atmosphere, the developability in particular of an on-machine development type lithographic printing plate precursor, for which development is carried out using dampening water and/or ink on a printer, is greatly degraded. It has also been found that, when printing is carried out using an on-machine development type lithographic printing plate precursor by operating a slip mechanism of a dampener, if a large number of prints are made, staining on a non-image area of a printed material (scumming) occurs and, furthermore, staining also occurs in a section, other than the printing paper, of a blanket cylinder or a pressure cylinder of the printer, which is a new problem. Furthermore, it has been found that there is the problem that due to the operation of the dampener slip mechanism the printing durability is degraded.

[0007] Therefore, it is an object of the present invention to provide a lithographic printing plate precursor that has excellent printing durability and developability and that has stain resistance, in particular resistance to staining of a non-image area of a printed material that occurs due to the operation of a slip mechanism of a dampener, and a process for making a lithographic printing plate using the lithographic printing plate precursor.

[0008] The above object of the present invention has been achieved by the following means of <1> and <11> to <12>. Preferable embodiments <2> to <10> will also be described below.

<1> A lithographic printing plate precursor comprising, in order above a support, an intermediate layer and an image recording layer, the intermediate layer comprising, as Component A, a copolymer comprising constituent repeating unit 1-1 comprising a phosphonic acid structure, a phosphonic acid salt structure, a phosphoric acid ester structure, or a phosphoric acid ester salt structure in a side chain and constituent repeating unit 1-2 comprising a zwitterionic structure in a side chain, the image recording layer comprising an infrared absorbing agent, either the intermediate layer or the image recording layer comprising, as Component B, a water-soluble polymer compound that does not have a phosphonic acid structure, a phosphonic acid salt structure, a phosphoric acid ester structure, or a phosphoric acid ester salt structure, and the mass ratio of Component A and Component B being Component A:Component B = 1:0.5 to 1:5,

<2> the lithographic printing plate precursor according to <1>, wherein Component B has a weight-average molecular

weight of at least 1,000 but no greater than 200,000,

<3> the lithographic printing plate precursor according to <1> or <2>, wherein Component B comprises as a constituent repeating unit at least one selected from the group consisting of a hydroxy group-containing structure, a carboxy group-containing structure, a pyrrolidone group-containing structure, and an oxyalkylene group-containing structure,

<4> the lithographic printing plate precursor according to <3>, wherein Component B comprises an oxyalkylene group-containing structure as a constituent repeating unit,

<5> the lithographic printing plate precursor according to any one of <1> to <4>, wherein Component A further comprises constituent repeating unit 1-3 comprising an ethylenically unsaturated double bond in a side chain,

<6> the lithographic printing plate precursor according to any one of <1> to <5>, wherein constituent repeating unit 1-2 has a content of at least 50 mass% but no greater than 90 mass% relative to the total mass of Component A,

<7> the lithographic printing plate precursor according to any one of <1> to <6>, wherein constituent repeating units 1-1 and 1-2 have a total content of at least 70 mass% but no greater than 95 mass% relative to the total mass of Component A,

<8> the lithographic printing plate precursor according to any one of <1> to <7>, wherein the image recording layer further comprises a polymerizable compound as Component C, a binder as Component D, and a polymerization initiator as Component E,

<9> the lithographic printing plate precursor according to any one of <1> to <8>, wherein the image recording layer comprises hydrophobic thermoplastic polymer particles,

<10> the lithographic printing plate precursor according to any one of <1> to <9>, wherein the image recording layer is removable with dampening water composition and/or a printing ink,

<11> a process for making a lithographic printing plate comprising, an exposure step of imagewise exposing the lithographic printing plate precursor according to any one of <1> to <10>, and

a development step of removing a non-exposed area of the image recording layer of the lithographic printing plate precursor in the presence of a developer having a pH of 2 to 14,

<12> a process for making a lithographic printing plate comprising, an exposure step of imagewise exposing the lithographic printing plate precursor according to any one of <1> to <10>, and a development step of removing a non-exposed area of the image recording layer of the lithographic printing plate precursor by supplying a printing ink and dampening water on a printer.

[0009] The lithographic printing plate precursor of the present invention is a lithographic printing plate precursor comprising an image recording layer that can be developed with a dampening water composition and/or a printing ink, the precursor comprising, in order above a support, an intermediate layer and an image recording layer, the intermediate layer comprising, as Component A, a copolymer comprising constituent repeating unit 1-1 comprising a phosphonic acid structure, a phosphonic acid salt structure, a phosphoric acid ester structure, or a phosphoric acid ester salt structure in a side chain and constituent repeating unit 1-2 comprising a zwitterionic structure in a side chain, the image recording layer comprising an infrared absorbing agent, either the intermediate layer or the image recording layer comprising, as Component B, a water-soluble polymer compound that does not have a phosphonic acid structure, a phosphonic acid salt structure, a phosphoric acid ester structure, or a phosphoric acid ester salt structure, and the mass ratio of Component A and Component B being Component A:Component B = 1:0.5 to 1:5.

[0010] Since Component A has a zwitterionic structure and also has a phosphonic acid structure, a phosphonic acid salt structure, a phosphoric acid ester structure, or a phosphoric acid ester salt structure on the support surface, it is surmised that it has an effect in further diffusing dampening water at the support interface.

[0011] Component B does not have a phosphonic acid structure, a phosphonic acid salt structure, a phosphoric acid ester structure, or a phosphoric acid ester salt structure, has little interaction with the support, does not stay on the support surface, and is present more easily in the intermediate layer or the image recording layer. Furthermore, due to its high water solubility, it is believed to have the function of increasing the amount of dampening water that can reach the support interface and also have the function of making the support surface hydrophilic. Because of this, Component B has an effect in promoting development, and is believed to exhibit the effects of the present invention.

[0012] Furthermore, since an on-machine development type lithographic printing plate precursor does not include a processing step in which a developer or a gumming liquid is used after imagewise exposure or a hydrophilization treatment step, removal of a non-image area and hydrophilization become insufficient, and when printing is carried out by contacting a dampening form roller and/or an ink-application roller having a surface speed that is different from the surface speed of a plate material, there is a possibility that the ink will become attached to a non-image area, but by the use of the two types of polymer compounds above in combination it is possible to suppress the attachment of ink to a non-image area.

[0013] By the use of these two types of polymer compounds in combination, it is possible to impart stable developability after aging while maintaining high printing durability, and in a method in which printing is carried out by contacting a dampening form roller and/or an ink-application roller having a surface speed that is different from the surface speed of

a plate material, it is possible to enable printing to be carried out without staining a printed material, a blanket, or a pressure cylinder.

[0014] In accordance with the present invention, there can be provided a lithographic printing plate precursor that has excellent printing durability and developability and that has stain resistance, in particular resistance to staining of a non-image area of a printed material that occurs due to the operation of a slip mechanism of a dampener, and a process for making a lithographic printing plate using the lithographic printing plate precursor.

FIG. 1 A schematic diagram of the constitution of one example of an automatic processor used in the present invention.

FIG. 2 A schematic diagram of the constitution of another example of an automatic processor used in the present invention.

4: lithographic printing plate precursor, 6, development section, 10: heater, 11: transport path, 16: inlet roller, 20: processing tank, 22: pair of in-solution rollers, 24: brush roller, 26: pair of transport-out rollers, 28: pair of transport-out rollers, 36: support roller, 38: pair of transport-out rollers, 50: external tank, 51: overflow opening, 52: upper limit liquid level meter, 53: lower limit liquid level meter, 54: filter section, 55: developer supply pump, 71: replenishing water tank, 72: water replenishing pump, 100: automated processor, 200: preheating section, 202: machine frame, 208: heating chamber, 210: comb-shaped roller, 212: inlet, 214: heater, 216: circulating fan, 218: outlet, 300: development section, 304: pair of inlet rollers, 306: processing tank, 308: development tank, 310: outer panel, 312: slit-shaped inlet, 316: pair of in-solution rollers, 318: pair of transport-out rollers, 322: pair of brush rollers, 324: shielding lid, 326: pair of brush rollers, 330: spray pipe, 332: partition plate, 334: slit-shaped inlet, 336: liquid temperature sensor, 338: liquid surface level meter, 342: guide member, 344: guide roller, 400: drying section, 402: support roller, 404: discharge opening, 406: pair of transport rollers, 408: pair of transport rollers, 410, 412: duct, 414: slit, C1: first circulation pipe, C2: second circulation pipe, C3: third circulation pipe

[0015] The present invention will be explained in detail below. While the explanation will occasionally be based on representative embodiments of the present invention, the present invention is not limited to these embodiments. Note in this specification that the wording "to" with preceding and succeeding numerals is used for indicating a numerical range with the lower and upper limits thereof respectively given by these numerals.

[0016] As used herein, any reference to a group in a compound represented by a general formula without indicating that the group is substituted or unsubstituted includes the group not only unsubstituted but also substituted if the group may be further substituted, unless otherwise specified. For example, the reference in a formula that "R represents alkyl, aryl or heterocyclyl" means that "R represents unsubstituted alkyl, substituted alkyl, unsubstituted aryl, substituted aryl, unsubstituted heterocyclyl or substituted heterocyclyl". As used herein, "(meth)acrylamide" refers to the concept including both methacrylamide and acrylamide. Further, in the present invention, "mass %" and "weight %" have the same meaning, and "part(s) by mass" and "part(s) by weight" have the same meaning. Furthermore, 'a copolymer comprising constituent repeating unit 1-1 comprising a phosphonic acid structure, a phosphonic acid salt structure, a phosphoric acid ester structure, or a phosphoric acid ester salt structure in a side chain and constituent repeating unit 1-2 comprising a zwitterionic structure in a side chain', etc. is also simply called 'Component A', etc., and the 'constituent repeating unit 1-1 comprising a phosphonic acid structure, a phosphonic acid salt structure, a phosphoric acid ester structure, or a phosphoric acid ester salt structure in a side chain', etc. is also simply called 'repeating unit 1-1', etc.

(Lithographic printing plate precursor)

[0017] A lithographic printing plate precursor of the present invention is characterized by that it comprises, in order above a support, an intermediate layer and an image recording layer, the intermediate layer comprising, as Component A, a copolymer comprising constituent repeating unit 1-1 comprising a phosphonic acid structure, a phosphonic acid salt structure, a phosphoric acid ester structure, or a phosphoric acid ester salt structure in a side chain and constituent repeating unit 1-2 comprising a zwitterionic structure in a side chain, the image recording layer comprising an infrared absorbing agent, either the intermediate layer or the image recording layer comprising, as Component B, a water-soluble polymer compound that does not have a phosphonic acid structure, a phosphonic acid salt structure, a phosphoric acid ester structure, or a phosphoric acid ester salt structure, and the mass ratio of Component A and Component B being Component A:Component B = 1:0.5 to 1:5.

<Intermediate layer>

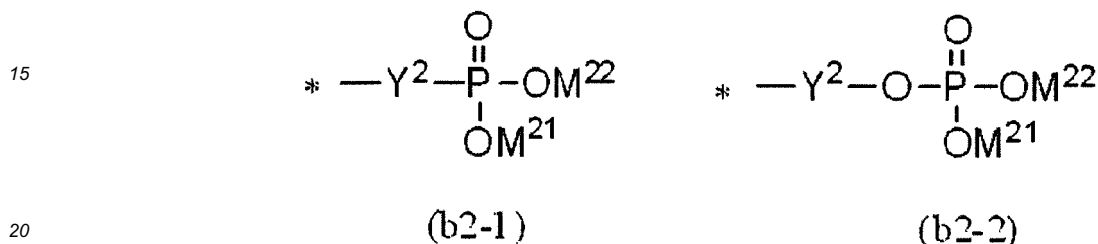
[0018] A lithographic printing plate precursor of the present invention has an intermediate layer between the support and the image recording layer and the intermediate layer comprises, as Component A, a copolymer comprising constituent repeating unit 1-1 comprising a phosphonic acid structure, a phosphonic acid salt structure, a phosphoric acid ester structure, or a phosphoric acid ester salt structure in a side chain and constituent repeating unit 1-2 comprising a

zwitterionic structure in a side chain

<Copolymer>

- 5 Constituent repeating unit 1-1 comprising phosphonic acid structure, phosphonic acid salt structure, phosphoric acid ester structure, or phosphoric acid ester salt structure in side chain

10 **[0019]** Component A in the present invention comprises constituent repeating unit 1-1 comprising a phosphonic acid structure, a phosphonic acid salt structure, a phosphoric acid ester structure, or a phosphoric acid ester salt structure in a side chain. Specifically, constituent repeating unit 1-1 preferably has a structure represented by Formula b2-1 or b2-2 below.



25 **[0020]** M²¹ and M²² independently denote a hydrogen atom, a metal atom belonging to the alkali metals or alkaline earth metals, or ammonium. Y² denotes a single bond or a divalent linking group selected from the group consisting of -CO-, -O-, -NH-, a divalent aliphatic group, a divalent aromatic group, and a combination thereof. * denotes a site bonded to a main chain of a polymer compound. Furthermore, the numerical value on the right-hand side of the parentheses denotes repeat number.

[0021] Preferred specific examples of Y² formed from the combination are listed below. In the examples below, the left-hand side is bonded to a main chain.

L201: -CO-O-divalent aliphatic group-

30 L202: -CO-O-divalent aromatic group-

L203: -CO-NH-divalent aliphatic group-

L204: -CO-NH-divalent aromatic group-

35 **[0022]** The divalent aliphatic group in L201 to L204 means an alkylene group, a substituted alkylene group, an alkenylene group, a substituted alkenylene group, an alkynylene group, a substituted alkynylene group, or 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.

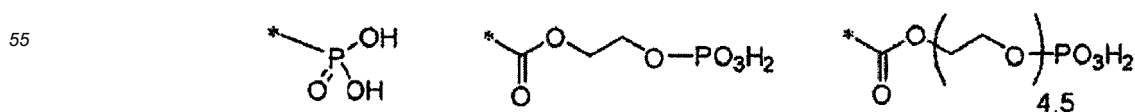
40 **[0023]** The divalent aliphatic group is preferably a chain-form structure rather than a cyclic structure, and is more preferably a straight-chain structure rather than a branched chain-form structure. The number of carbon atoms in the divalent aliphatic group is preferably 1 to 20, more preferably 1 to 15, yet more preferably 1 to 12, still more preferably 1 to 10, and most preferably 1 to 8.

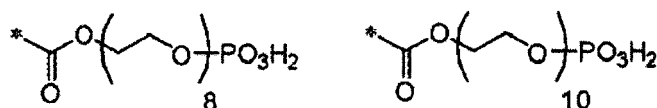
[0024] Preferred examples of the substituent on the divalent aliphatic group include a halogen atom (F, Cl, Br, I), a hydroxy group, a carboxy group, an amino group, a cyano group, an aryl group, an alkoxy group, an aryloxy group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, an acyloxy group, a monoalkylamino group, a dialkylamino group, an arylamino group, and a diarylamino group.

45 **[0025]** Preferred examples of the divalent aromatic group in L201 to L204 include a phenylene group, a substituted phenylene group, a naphthalene group, and a substituted naphthalene group, and a phenylene group is more preferable.

[0026] Preferred examples of the substituent of the divalent aromatic group include, in addition to the examples cited for the substituent of the divalent aliphatic group, an alkyl group.

50 **[0027]** Preferred specific examples of Formulae b2-1 and b2-2 include the structures below. The present invention should not be construed as being limited to the structures below. In the formulae below, * denotes a site bonded to a main chain of a polymer compound. The numerical value next to the repeating unit of the side chain means the repeat number of the repeating unit.

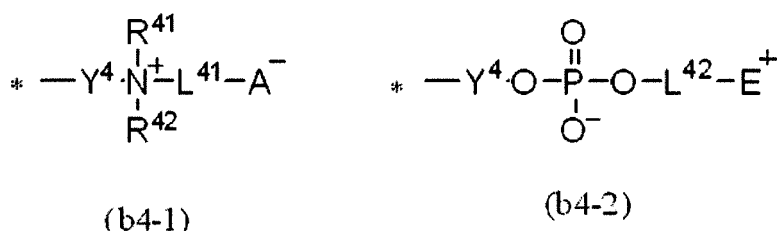




[0028] The content of constituent repeating unit 1-1 relative to the total mass of Component A used in the present invention is preferably in the range of 1 to 40 from the viewpoint of printing durability, stain resistance, and developability, more preferably in the range of 3 to 30 mass%, and yet more preferably in the range of 5 to 20 mass%.

Constituent repeating unit 1-2 comprising zwitterionic structure in side chain

[0029] Component A in the present invention further comprises constituent repeating unit 1-2 comprising a zwitterionic structure in a side chain. Specifically, constituent repeating unit 1-2 preferably comprises a structure represented by Formulae b4-1 or b4-2 below.



[0030] In Formula b4-1 and Formula b4-2, R^{41} and R^{42} independently denote a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, an aryl group, or a heterocyclic group, R^{41} and R^{42} may be bonded to each other to form a ring structure, L^{41} and L^{42} denote a linking group, A^- denotes a structure having an anion, and E^+ denotes a structure having a cation. Y^4 denotes a divalent linking group bonded to a main chain of a polymer compound. * denotes the site bonded to the main chain of a polymer compound.

[0031] Formula b4-1 is first explained. In Formula b4-1, the number of carbons of the alkyl group, alkenyl group, alkynyl group, aryl group, or heterocyclic group denoted by R^{41} and R^{42} , including the number of carbons of a substituent that is described later, is preferably 1 to 30 carbons, more preferably 1 to 20 carbons, particularly preferably 1 to 15 carbons, and most preferably 1 to 8 carbons.

[0032] The ring structure formed by R^{41} and R^{42} bonding to each other may have a heteroatom such as an oxygen atom and is preferably a 5- to 10-membered ring, and more preferably a 5- or 6-membered ring.

[0033] Preferred examples of R^{41} or R^{42} are the same as those described in JP-A-2013-205569. Particularly preferred examples of R^{41} and R^{42} include a hydrogen atom, a methyl group, and an ethyl group from the viewpoint of the effect and ready availability.

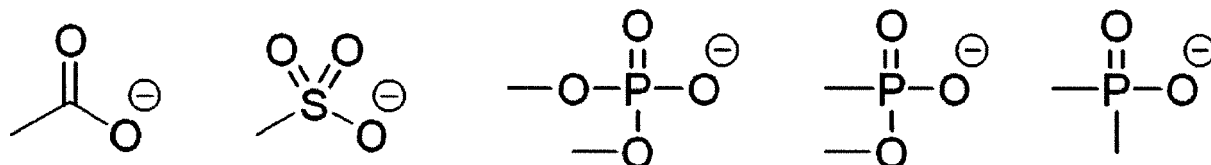
[0034] In Formula b4-1, preferred examples of the divalent linking group denoted by Y^4 are the same as those described in JP-A-2013-205569. It is preferably a single bond, -CO- , a divalent aliphatic group, a divalent aromatic group, $\text{L401: -CO-O-divalent aliphatic group-}$, $\text{L402: -CO-O-divalent aromatic group-}$, $\text{L403: -CO-NH-divalent aliphatic group-}$, or $\text{L404: -CO-NH-divalent aromatic group-}$. From the viewpoint of stain resistance, Y^4 is preferably L404 or L403 , and more preferably L403 . Furthermore, the divalent aliphatic group of L403 is preferably a straight-chain alkylene group having 2 to 4 carbons, and most preferably a straight-chain alkylene group having 3 carbons from the viewpoint of synthetic suitability.

[0035] In Formula b4-2, preferred examples of L^{41} are the same as those described in JP-A-2013-205569. It is preferably -CO- , -O- , -NH- , a divalent aliphatic group, a divalent aromatic group, or a linking group formed by a combination thereof, the linking group, including the number of carbons of a substituent that is described later, preferably having no greater than 30 carbons. Specific examples thereof include an alkylene group (preferably 1 to 20 carbons, and more preferably 1 to 10 carbons), and an arylene group such as phenylene or xylylene (preferably 6 to 15 carbons, and more preferably 6 to 10 carbons). Among them, from the viewpoint of stain resistance, L^{41} is preferably a straight-chain alkylene group having 3 to 5 carbons, more preferably a straight-chain alkylene group having 4 or 5 carbons, and most preferably a straight-chain alkylene group having 4 carbons.

[0036] In Formula b4-1, A^- is preferably a carboxylate anion, a sulfonate anion, a phosphate anion, a phosphonate anion, or a phosphinate anion.

[0037] Specifically, the anions below can be cited as preferred examples.

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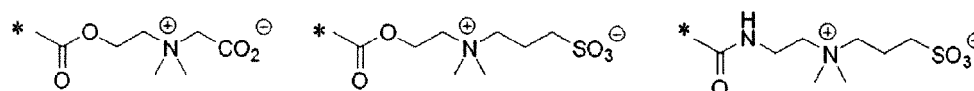
[0038] From the viewpoint of stain resistance, A^- is most preferably a sulfonate anion. Furthermore, in Formula b4-1 a combination in which L^{41} is a straight-chain alkylene group having 4 or 5 carbons and A^- is a sulfonate anion is preferable, and a combination in which L^{41} is a straight-chain alkylene group having 4 carbons and A^- is a sulfonate anion is most preferable.

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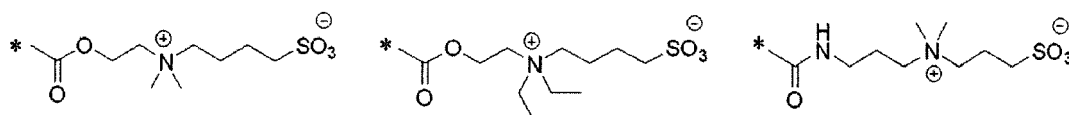
[0039] A combination in which Y^4 is L401 or L403, R^{41} and R^{42} are independently an ethyl group or a methyl group, L^{41} is a straight-chain alkylene group having 4 or 5 carbons, and A^- is a sulfonate anion is preferable. Furthermore, a combination in which Y^4 is L403, R^{41} and R^{42} are methyl groups, L^{41} is a straight-chain alkylene group having 4 carbons, and A^- is a sulfonate anion is more preferable.

[0040] Preferred specific examples of the zwitterionic structure represented by Formula b4-1 include the structures below. * in the Formulae below denotes a site bonded to a polymer main chain of Component A.

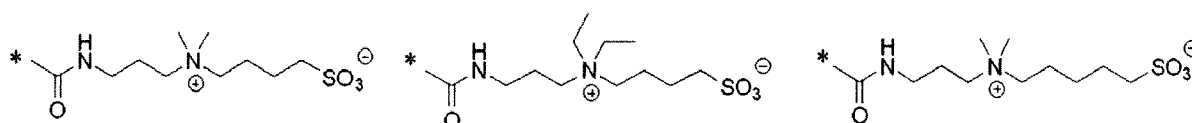
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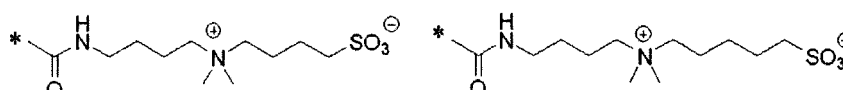
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[0041] The zwitterionic structure represented by Formula b4-2 is now explained.

[0042] In Formula b4-2, L^{42} has the same meaning as that of L^{41} in Formula b4-1, and preferred embodiments are also the same. Y^4 has the same meaning as that of Y^4 in Formula b4-1, and preferred embodiments are also the same.

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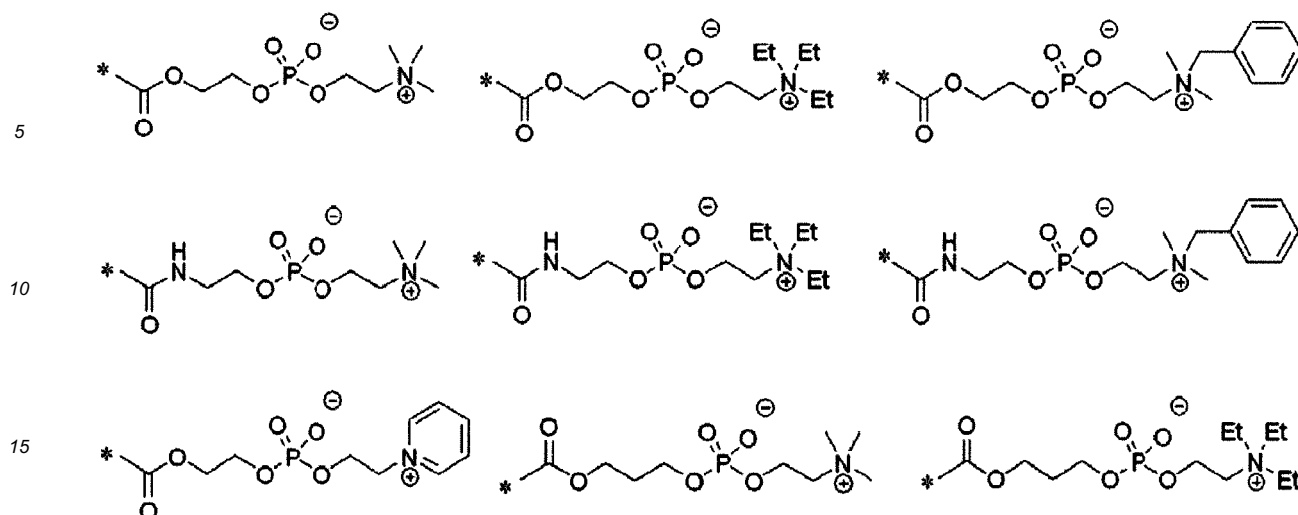
[0043] E^+ denotes a structure having a cation, and preferably a structure having ammonium, phosphonium, iodonium, or sulfonium. It is more preferably a structure having ammonium or phosphonium, and particularly preferably a structure having ammonium. Specific examples of the structure having a cation include a trimethylammonio group, a triethylammonio group, a tributylammonio group, a benzyltrimethylammonio group, a diethylhexylammonio group, a (2-hydroxyethyl)dimethylammonio group, a pyridinio group, an *N*-methylimidazolio group, an *N*-acridinio group, a trimethylphosphonio group, a triethylphosphonio group, and a triphenylphosphonio group.

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[0044] A most preferred combination of L^{42} , Y^4 , and E^+ is a combination in which L^{42} is an alkylene group having 2 to 4 carbons, Y^4 is L401 or L403, and E^+ is a trimethylammonio group or a triethylammonio group.

[0045] Preferred specific examples of the zwitterionic structure represented by Formula b4-2 include the structures below. In the formulae below, * denotes a site bonded to a polymer main chain of Component A, and Et denotes an ethyl group.

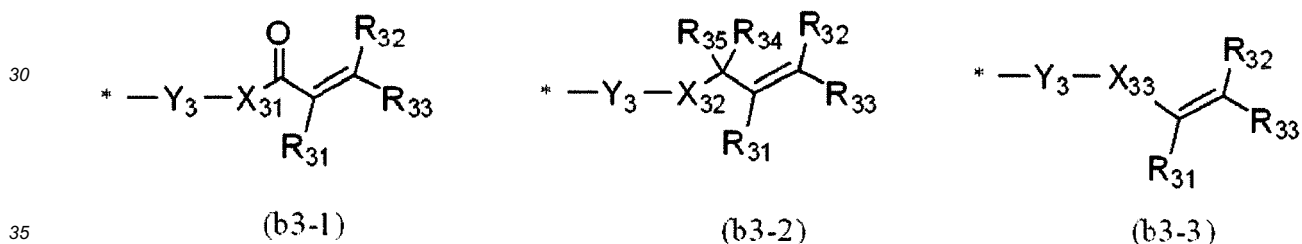
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[0046] In the present invention, from the viewpoint of stain resistance and developability, the content of the constituent repeating unit 1-2 comprising a zwitterionic structure in a side chain is preferably in the range of 50 to 95 mass% relative to the total mass of Component A, more preferably in the range of 60 to 90 mass%, and yet more preferably in the range of 70 to 85 mass%.

[0047] Constituent repeating unit 1-3 comprising ethylenically unsaturated double bond in side chain

[0048] Component A used in the present invention preferably comprises constituent repeating unit 1-3 comprising an ethylenically unsaturated double bond in a side chain in order to improve the film strength of an image area. Constituent repeating unit 1-3 preferably has at least one of the structures represented by Formulae b3-1, b3-2, and b3-3 below.



[0049] In the Formulae, X_{31} and X_{32} independently denote an oxygen atom, a sulfur atom, or $-N(R_{36})-$. X_{33} denotes an oxygen atom, a sulfur atom, $-N(R_{37})-$, or a phenylene group. The Y_3 s independently denote a single bond or a divalent linking group selected from the group consisting of $-CO-$, $-O-$, $-NH-$, a divalent aliphatic group, a divalent aromatic group, and a combination thereof. R_{31} to R_{37} independently denote a monovalent substituent, and * denotes a site bonded to a main chain of a polymer compound.

[0050] In Formula b3-1 to Formula b3-3, X_{31} and X_{32} are oxygen atoms, sulfur atoms, or $-N(R_{36})-$, and preferably oxygen atoms or $-N(R_{36})-$. X_{33} is an oxygen atom, a sulfur atom, $-N(R_{37})-$, or a phenylene group, and preferably an oxygen atom or $-N(R_{37})-$.

[0051] In Formula b3-1 to Formula b3-3, Y_3 is a single bond or a divalent linking group selected from the group consisting of $-CO-$, $-O-$, $-NH-$, a divalent aliphatic group, a divalent aromatic group, and a combination thereof.

[0052] Preferred specific examples of Y_3 formed from the above combination include those below. In the examples, the left-hand side is bonded to a main chain.

L301: $-CO-O-$ divalent aliphatic group-

L302: $-CO-O-$ divalent aromatic group-

L303: $-CO-NH-$ divalent aliphatic group-

L304: $-CO-NH-$ divalent aromatic group-

L305: $-CO-O-$ divalent aliphatic group- $O-CO-NH-$ divalent aliphatic group-

L306: $-CO-O-$ divalent aliphatic group- $O-CO-NH-$ divalent aromatic group-

L307: $-CO-O-$ divalent aromatic group- $O-CO-NH-$ divalent aliphatic group-

L308: $-CO-O-$ divalent aromatic group- $O-CO-NH-$ divalent aromatic group-

L309: $-CO-NH-$ divalent aliphatic group- $NH-CO-NH-$ divalent aliphatic group-

L310: $-CO-NH-$ divalent aliphatic group- $NH-CO-NH-$ divalent aromatic group-

L311:-CO-NH-divalent aromatic group-NH-CO-NH-divalent aliphatic group-

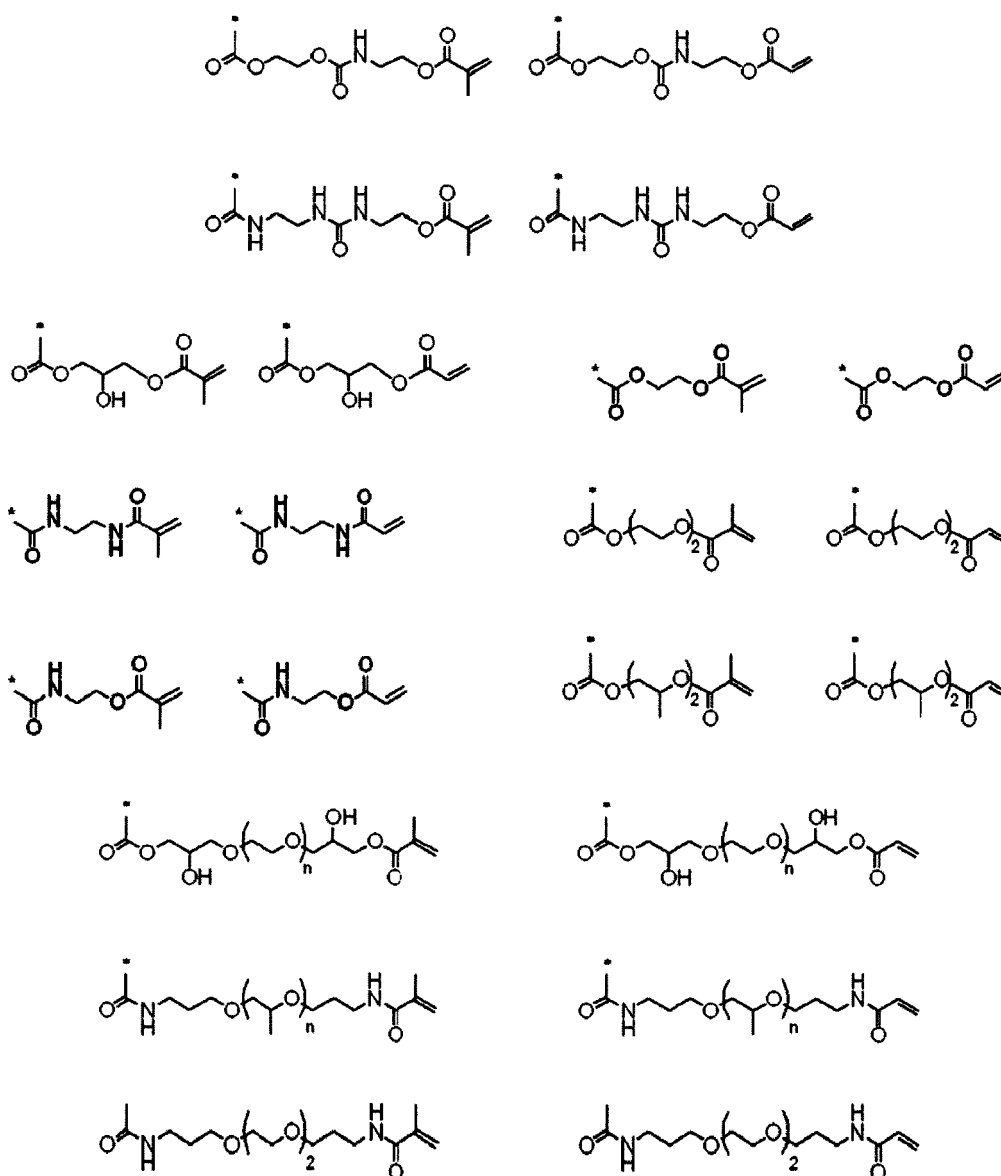
L312:-CO-NH-divalent aromatic group-NH-CO-NH-divalent aromatic group-

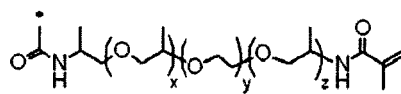
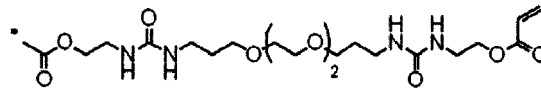
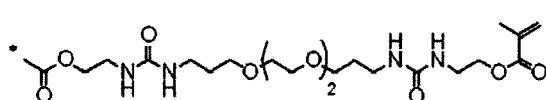
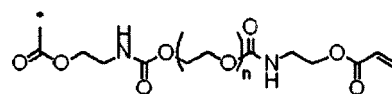
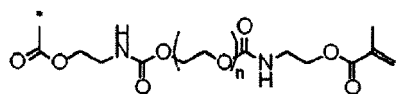
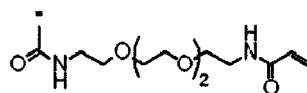
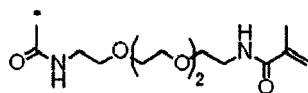
[0053] In L301 to L312, the divalent aliphatic group has the same meaning as that of the divalent aliphatic group in L201 to L204, and preferred embodiments are also the same. In L301 to L312, the divalent aromatic group has the same meaning as that of the divalent aromatic group in L201 to L204, and preferred embodiments are also the same.

[0054] In Formula b3-1 to Formula b3-3, Y_3 is preferably a single bond, -CO-, a divalent aliphatic group, a divalent aromatic group, or the above L301 to L312. Furthermore, from the viewpoint of stain resistance, Y_3 is preferably the above L301, L303, L305, or L309. The divalent aliphatic group of L301, L303, L305, or L309 is yet more preferably an alkylene group having 1 to 10 carbons or a divalent linking group having 1 to 10 carbons in which 2 or more alkylene groups are bonded via an oxygen atom linking group (the alkylene groups being independently optionally substituted). The divalent linking group in which 2 or more alkylene groups are bonded via an oxygen atom linking group is particularly preferably an ethylene oxide chain, a propylene oxide chain, or a combination thereof.

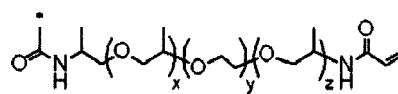
[0055] Among the structures of Formula b3-1 to Formula b3-3, from the viewpoint of stain resistance and printing durability, constituent repeating unit 1-3 comprising an ethylenically unsaturated group in a side chain is preferably a constituent repeating unit having a structure represented by b3-1.

[0056] Preferred specific examples of the structure represented by Formula b3-1 to Formula b3-3 include the structures below. The present invention should not be construed as being limited to the structures below. In the Formulae below, * denotes a site bonded to a main chain of a polymer compound.

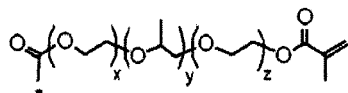




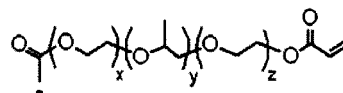
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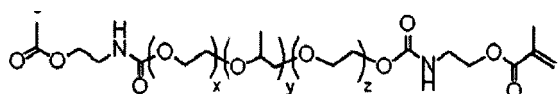
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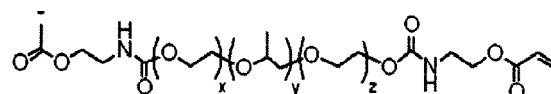
$$y=35, x+z=5$$



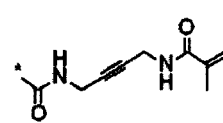
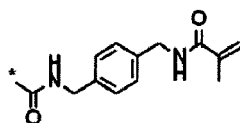
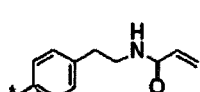
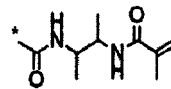
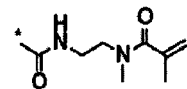
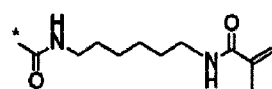
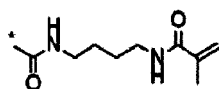
$$y=35, x+z=5$$



$$y=25, x+z=22$$



$$y=25, x+z=22$$



[0057] The content of constituent repeating unit 1-3 is preferably in the range of 1 to 30 mass% relative to the total mass of the entire constituent units of Component A from the viewpoint of printing durability and stain resistance, more preferably in the range of 3 to 20 mass%, and yet more preferably in the range of 5 to 15 mass%.

[0058] In the present invention, the total content of constituent repeating units 1-1 and 1-2 relative to the total mass of Component A, from the viewpoint of stain resistance and developability, is preferably in the range of 50 to 95 mass%, more preferably in the range of 70 to 95 mass%, and yet more preferably in the range of 70 to 90 mass%.

[0059] The weight-average molecular weight (Mw) of Component A used in the present invention may be set freely by the performance design of the lithographic printing plate precursor. From the viewpoint of printing durability and stain resistance, the weight-average molecular weight is preferably 2,000 to 1,000,000, more preferably 2,000 to 500,000, and most preferably 8,000 to 300,000.

[0060] The weight-average molecular weight (Mw) may be measured by a gel permeation chromatography (GPC) method with polyethylene glycol as a reference substance.

[0061] Component A used in the present invention may also be synthesized by a known method, the synthesis preferably employing a radical polymerization method and, subsequently, a ureation reaction between an amino group of

the polymer side chain and an isocyanate having a radically polymerizable reactive group or an amidation reaction between an amino group of the polymer side chain and an acid anhydride having a radically polymerizable reactive group.

[0062] A standard radical polymerization method may be referred to in for example 'Shin-kobunshi Jikken-gaku 3' (New Polymer Experiments 3) (edited by the Society of Polymer Science, Japan, Kyoritsu Publishing, published on 28th March 1996), 'Kobunshi-no Gosei-to-Hannou' (Synthesis and Reactions of Polymers 1) (edited by the Society of Polymer Science, Japan, Kyoritsu Publishing, published on May 1992), 'Shin-jikken Kagaku-koza 19, Kobunshi Kagaku' (I) (New Experimental Chemistry Lecture, Polymer Chemistry (I)) (Ed. by Chemical Society of Japan, Maruzen Co., Ltd., published on 20th November 1980), 'Busshitsu-kogaku-koza Kobunshi Gosei-kagaku' (Material Engineering Lecture, Polymer Synthetic Chemistry) (Tokyo Denki University Publishing, published on September 1995).

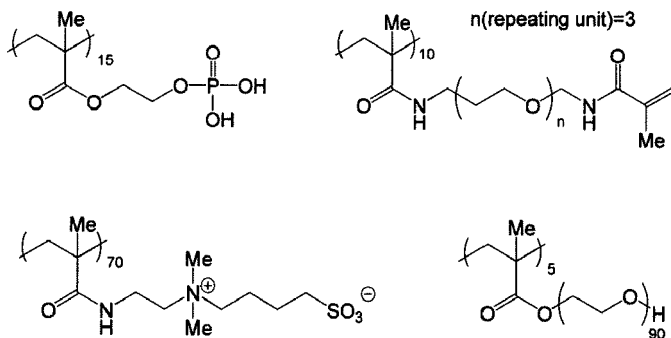
[0063] With regard to Component A in the intermediate layer used in the present invention, one type may be used on its own or two or more types may be used in combination.

[0064] The content of Component A in the intermediate layer used in the present invention is preferably 50 to 99.9 mass% relative to the total mass of the total solids content, excluding volatile components, in the intermediate layer, more preferably 60 to 99.9 mass%, and yet more preferably 70 to 99.9 mass%.

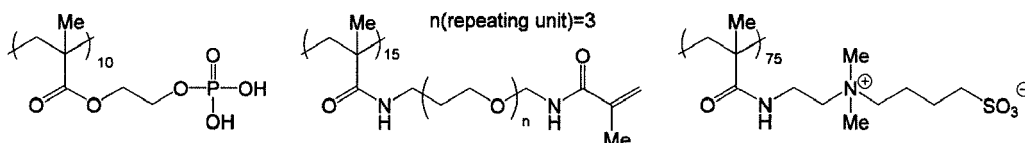
[0065] As mentioned above, the coat weight (total solids content mass) of the intermediate layer used in the present invention is preferably 0.1 to 100 mg/m², and more preferably 1 to 30 mg/m².

[0066] Preferred specific examples of Component A used in the present invention are shown together with the weight-average molecular weight, but the present invention should not be construed as being limited to these examples. Furthermore, the compositional ratio of the polymer structure (content ratio of constituent units) is expressed as mass percent.

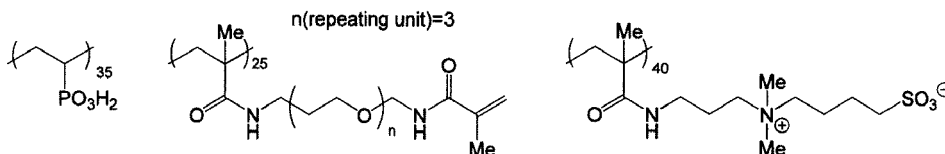
P-1 Mw:100,000



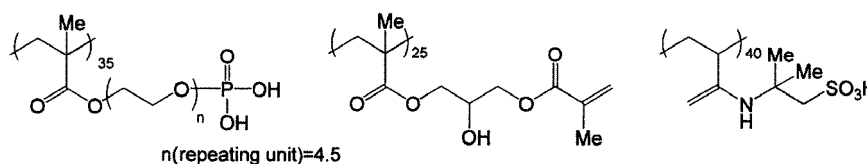
P-2 Mw:200,000



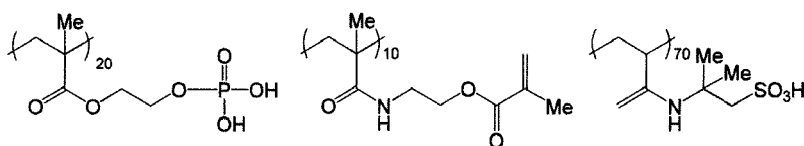
P-3 Mw:10,000



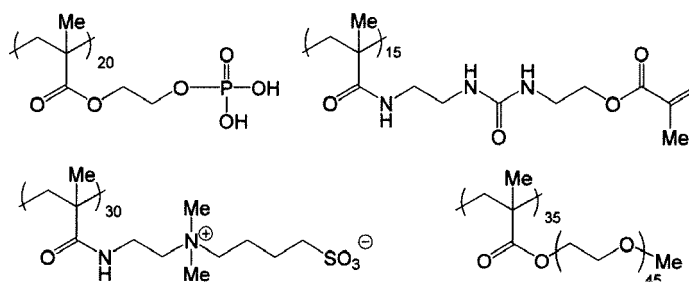
P-4 Mw:230,000



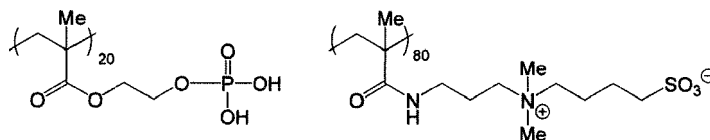
P-5 Mw:100,000



P-6 Mw:210,000



P-7 Mw:150,000



[0067] In the present invention, as Component B a water-soluble polymer compound that does not have a phosphonic acid structure, a phosphonic acid salt structure, a phosphoric acid ester structure, or a phosphoric acid ester salt structure is contained in the intermediate layer or the image recording layer. The water-soluble polymer compound is preferably a polymer compound of which at least 1 g dissolves in 100 g of water at 25°C, more preferably a polymer compound of which at least 5 g dissolves in 100 g of water at 25°C, and yet more preferably a polymer compound of which at least 10 g dissolves in 100 g of water at 25°C.

[0068] Component B is contained in at least one of the intermediate layer and the image recording layer. It is preferable for the image recording layer to contain Component B because Component B has the function of efficiently increasing the amount of dampening water penetrating into the support interface when Component B is contained within the image recording layer.

[0069] The water-soluble polymer preferably comprises as a repeating unit at least one selected from the group consisting of a hydroxy group-containing structure, a carboxy group-containing structure, a pyrrolidone group-containing structure, and an oxyalkylene group-containing structure, which have affinity toward water in particular, and more preferably comprises as a constituent repeating unit an oxyalkylene group-containing structure.

[0070] Specific examples of the hydroxy group-containing water-soluble polymer include gum arabic, gum soya, carboxymethylcellulose, hydroxymethylcellulose, hydroxyethylcellulose, polyhydroxyethylated cellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose, glyoxalated hydroxypropylmethylcellulose, hydroxypropylmethylcellulose phthalate, methylcellulose, α -cyclodextrin, β -cyclodextrin, γ -cyclodextrin, white dextrin, red dextrin, pullulan, enzymatically-decomposed etherified dextrin, maltose-modified cyclodextrin, pregelatinized starch, grafted starch, dialdehyde starch, periodic acid-modified starch, hydroxyether-modified starch, cationic starch ether, alkali cellulose, industrial cationic starch, and polyvinyl alcohol.

[0071] Specific examples of the carboxy group-containing water-soluble polymer include polyacrylic acid, carboxyethylcellulose, alginic acid, sodium alginate, ammonium alginate, alginic acid propylene glycol ester, xanthan gum, a copolymer containing acrylic acid units, polymethacrylic acid, and a copolymer containing methacrylic acid units.

[0072] Specific examples of the pyrrolidone group-containing water-soluble polymer include polyvinylpyrrolidone and a copolymer of vinylpyrrolidone and vinyl acetate.

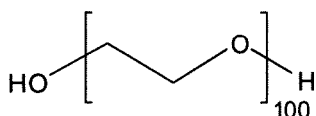
[0073] Specific examples of the oxyalkylene group-containing water-soluble polymer include a polyalkylene glycol such as polyethylene glycol, polypropylene glycol, or polyoxyethylene polyoxypropylene glycol (also called a polyoxyethylene-polyoxypropylene condensation product), a polyoxyalkylene monoalkyl or aryl ether such as poly(ethylene

glycol) methyl ether or poly(ethylene glycol) phenyl ether, a polyoxyethylene polyoxypropylene alkyl ether, a polyglycerol or an ether thereof such as polyglycerol, polyoxyethylene glycerol, polyoxypropylene glyceryl ether, or polyoxyethylene polyoxypropylene glyceryl ether, and an ester having a polyoxyalkylene structure such as a polyoxyethylene monoester, a polyoxyethylene alkyl ether ester, polyoxyethylene glyceryl isostearate, polyoxyethylene glyceryl triisostearate, polyoxyethylene glyceryl triisostearate, polyoxyethylene trimethylolpropane distearate, a polyoxyethylene sorbitan monofatty acid ester, a polyoxyethylene sorbitan fatty acid ester, polyoxyethylene hardened castor oil, a polyoxyethylene hardened castor oil monofatty acid ester, polyoxyethylene hardened castor oil succinate, polyoxyethylene castor oil, polyoxyethylene sorbitol tetraoleate, polyoxyethylene sorbitol tetraisostearate, or polyoxyethylene sorbitol isostearate.

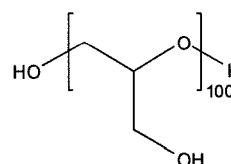
[0074] Among them, a polyoxyalkylene monoalkyl ether is preferable, and poly(ethylene glycol) methyl ether is more preferable.

[0075] Preferred specific examples of Component B used in the present invention are listed together with the weight-average molecular weight, but the present invention should not be construed as being limited thereto. Furthermore, the compositional ratio of the polymer structure (content ratio of constituent units) is expressed as mass percent.

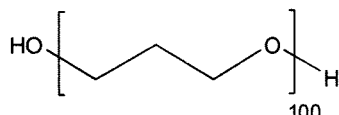
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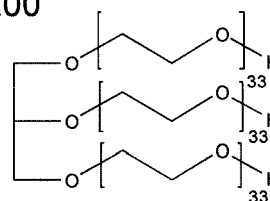
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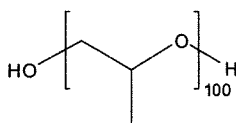
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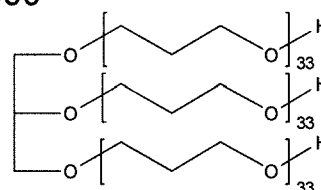
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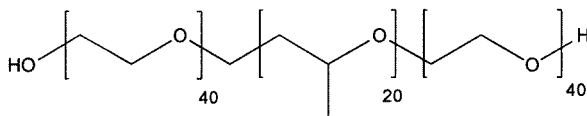
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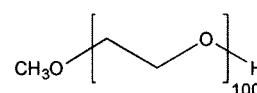
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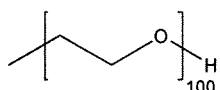
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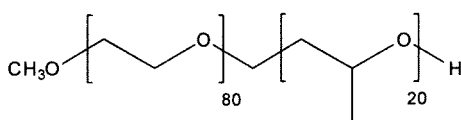
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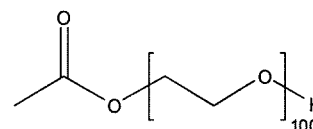
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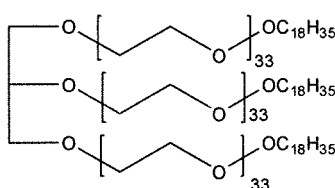
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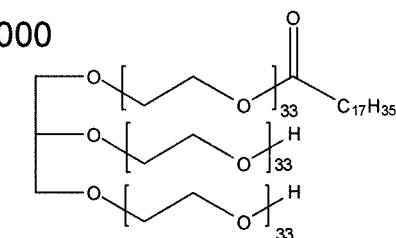
Mw : 3000



Mw : 3000



Mw : 3000



[0076] The weight-average molecular weight (Mw) of Component B used in the present invention may be set freely

by the performance design of the lithographic printing plate precursor. The weight-average molecular weight (Mw) is preferably in the range of 1,000 to 200,000. The weight-average molecular weight (Mw) is more preferably 3,000 to 100,000, and yet more preferably 3,000 to 50,000. When the weight-average molecular weight (Mw) is at least 1,000 an effect in suppressing the degradation of developability over time may be sufficiently exhibited, and when it is no greater than 200,000 the printing durability is also excellent. It may be measured by a gel permeation chromatography (GPC) method with polyethylene glycol as a reference substance.

[0077] In the present invention, the mass ratio of Component A and Component B is Component A:Component B = 1:0.5 to 1:5. When it is less than 0.5 the developability is insufficient, and when it exceeds 5 the printing durability is degraded. It is more preferably 1:0.7 to 1:4, and yet more preferably 1:0.8 to 1:3.

<Image recording layer>

[0078] A image recording layer in the lithographic printing plate precursor of the present invention contains an infrared absorbing agent.

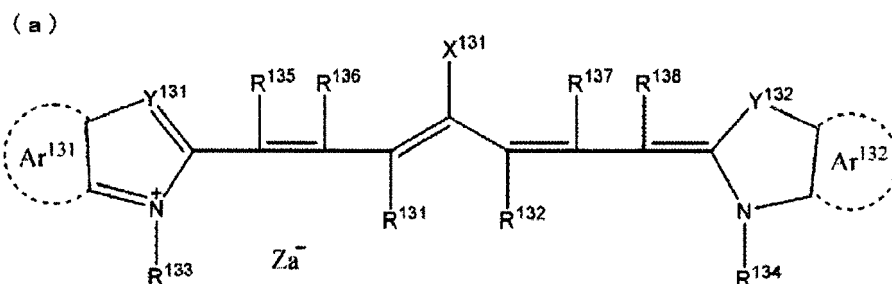
<Infrared absorbing agent>

[0079] The infrared absorbing agent used in the present invention has a maximum absorption in a wavelength region of 750 to 1,400 nm. In particular, since an on-machine development type lithographic printing plate precursor might undergo on-machine development in a printer under a white lamp, use of a sensitizing dye having a maximum absorption in a wavelength region of 750 to 1,400 nm enables a lithographic printing plate precursor having excellent developability to be obtained.

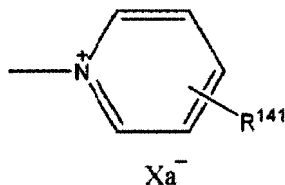
[0080] As the infrared absorbing agent, a dye or a pigment is preferably used.

[0081] As the above dye, commercial dyes and known dyes described in the literature such as 'Senryo Binran' (Dye Handbook) (Ed. The Society of Synthetic Organic Chemistry, Japan, 1970), etc. may be used.

[0082] Among these dyes, a cyanine dye, a squarylium dye, a pyrylium salt, a nickel thiolate complex, and an indolenine cyanine dye are exemplified. A cyanine dye and an indolenine cyanine dye are more preferable, and a cyanine dye represented by Formula (a) below is particularly preferable.



[0083] In Formula (a), X^{131} denotes a hydrogen atom, a halogen atom, $-NPh_2$, $-X^{132}-L^{131}$, or the group shown below. Here, Ph denotes a phenyl group



[0084] In Formula (a), X^{132} denotes an oxygen atom, a nitrogen atom, or a sulfur atom, L^{131} denotes a hydrocarbon group having 1 to 12 carbon atoms, a hetero atom (N, S, O, a halogen atom, or Se)-containing aryl group, or a hetero atom-containing hydrocarbon group having 1 to 12 carbon atoms. X_a^- is defined in the same manner as for Z_a^- , which is described later, and R^{141} denotes a hydrogen atom or a substituent selected from the group consisting of an alkyl group, an aryl group, a substituted or unsubstituted amino group, and a halogen atom.

[0085] Preferable examples of the substituent are the same as those described in JP-A-2013-205569.

[0086] With regard to such infrared absorbing dyes, only one type may be used or two or more types may be used in combination, and an infrared absorbing agent other than an infrared absorbing dye, such as a pigment, may be used in

combination. As the pigment, compounds described in paragraphs. 0072 to 0076 of JP-A-2008-195018 are preferable.

[0087] The amount of the infrared absorbing dyes added is preferably 0.05 to 30 parts by mass relative to 100 parts by mass of the total solids content of the image recording layer, more preferably 0.1 to 20 parts by mass, and yet more preferably 0.2 to 10 parts by mass.

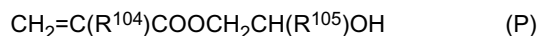
[0088] The image recording layer in the lithographic printing plate precursor of the present invention preferably contains a polymerizable compound as Component C, a binder as Component D and a polymerization initiator as Component E. The image recording layer in the lithographic printing plate precursor of the present invention is preferably a photo-sensitive layer (hereinafter, the image recording layer is also called a 'photosensitive layer'). (C) Polymerizable compound

[0089] The image recording layer in the lithographic printing plate precursor of the present invention preferably contains a polymerizable compound as Component C. The polymerizable compound described in JP-A-2013-205569 may be used.

[0090] These are described in Published Japanese translation 2006-508380 of a PCT application, JP-A-2002-287344, JP-A-2008-256850, JP-A-2001-342222, JP-AH9-179296, JP-A-H9-179297, JP-A-H9-179298, JP-A-2004-294935, JP-A-2006-243493, JP-A-2002-275129, JP-A-2003-64130, JP-A-2003-280187, JP-A-10-333321 etc.

[0091] Specific examples of a monomer that is an ester of a polyhydric alcohol compound and an unsaturated carboxylic acid include a (meth)acrylic acid ester such as ethylene glycol di(meth)acrylate, etc. Specific examples of a monomer that is an amide of a polyamine compound and an unsaturated carboxylic acid include methylene-bis-(meth)acrylamide.

[0092] Furthermore, a urethane-based addition-polymerizable compound produced by an addition reaction of an isocyanato group and a hydroxy group is also suitable, and specific examples thereof include a vinylurethane compound containing two or more polymerizable vinyl groups per molecule in which a hydroxy group-containing vinyl monomer represented by Formula (P) below is added to a polyisocyanate compound having two or more isocyanato groups per molecule described in JP-B-48-41708.



R^{104} and R^{105} independently denote H or CH_3 .

[0093] Among the above, in the case of a lithographic printing plate precursor applied to on-machine development, from the viewpoint of achieving a balance between the hydrophilicity involved in on-machine developability and the polymerizability involved in printing durability, an isocyanuric acid ethylene oxide-modified (meth)acrylate such as tris((meth)acryloyloxyethyl) isocyanurate or bis((meth)acryloyloxyethyl)hydroxyethyl isocyanurate is particularly preferable.

[0094] Details of the structure of Component C and the method of use such as its use on its own or in combination or the amount added can be freely set in accordance with the final performance design of the lithographic printing plate precursor.

[0095] In the present invention the content of Component C is preferably 5 to 75 mass% relative to the total solids content mass of the photosensitive layer, more preferably 25 to 70 mass%, and particularly preferably 30 to 60 mass%.

(D) Binder

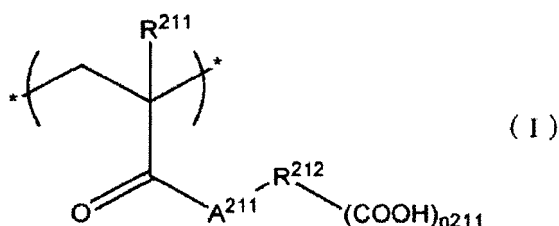
[0096] The image recording layer (photosensitive layer) in the lithographic printing plate precursor of the present invention preferably contains a binder as Component D. The binder described in JP-A-2013-205569 may be used.

[0097] As Component D contained in the photosensitive layer in the lithographic printing plate precursor of the present invention, a binder is preferably a polymer binder resin having a molecular weight of at least 2,000, more preferably 2,000 to 500,000 and yet more preferably 10,000 to 300,000. Furthermore, Component D does not include Component B.

[0098] As Component D, one that can support a photosensitive layer component above a support and that can be removed by a developer is used.

[0099] Preferably examples of Component D include 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, etc. Among them, a (meth)acrylic polymer, a polyurethane resin and a polyvinyl butyral resin are more preferable and a (meth)acrylic polymer, a polyurethane resin and a polyvinyl butyral resin are yet more preferable.

[0100] Preferred examples of the (meth)acrylic polymer as Component D in the present invention include a copolymer comprising a repeating unit comprising 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 sulfonamide group, and a carboxylic acid group is particularly preferable. A polymer comprising (meth)acrylic acid as a polymerization monomer or a polymer comprising a repeating unit derived from (meth)acrylic acid and represented by Formula (I) below, described in JP-A-2013-205569, is particularly preferably used.



[0101] In Formula (I), R^{211} denotes a hydrogen atom or a methyl group, and R^{212} denotes a single bond or an $(n211+1)$ -valent linking group. A^{211} denotes an oxygen atom or $\text{---NR}^3\text{---}$, and R^3 denotes a hydrogen atom or a monovalent hydrocarbon group having 1 to 10 carbons. $n211$ denotes an integer of 1 to 5.

[0102] The proportion (mole%) of carboxylic acid group-containing copolymerization components in the total copolymerization components of Component D is, from the viewpoint of developability, preferably 1% to 70%. From the viewpoint of a balance being achieved between developability and printing durability, it is more preferably 1% to 50%, and particularly preferably 1% to 30%.

[0103] Component D used in the present invention preferably has the crosslinkable group. The crosslinkable group referred to here is a group that crosslinks Component D in the process of a radical polymerization reaction occurring in the photosensitive layer when the lithographic printing plate precursor is exposed. The group is not particularly limited as long as it has the above function, and examples thereof include, as a functional group that can undergo an addition polymerization reaction, an ethylenically unsaturated bond group, an amino group, and an epoxy group. It may be a functional group that can become a radical upon exposure to light, and examples of such a crosslinkable group include a thiol group, and a halogen group. Among them, an ethylenically unsaturated bond group is preferable, and as the ethylenically unsaturated bond group, a styryl group, a (meth)acryloyl group, and an allyl group are preferable.

[0104] The content of the crosslinkable group (content of radically polymerizable unsaturated double bond determined by iodine titration) in Component D is preferably 0.01 to 10.0 mmol, more preferably 0.05 to 9.0 mmol, and yet more preferably 0.1 to 8.0 mmol, per g of the Component D.

[0105] Component D used in the present invention may have a constituent unit derived from a monomer such as a (meth)acrylic acid alkyl or aralkyl ester, (meth)acrylamide or a derivative thereof, α -hydroxymethyl acrylate, or a styrene derivative, in addition to the acid group-containing constituent unit and crosslinkable group-containing constituent unit. Preferred examples of the monomer include examples described in JP-A-2013-205569.

[0106] Furthermore, when the lithographic printing plate precursor of the present invention is a lithographic printing plate precursor to which on-machine development is applied, Component D preferably has a hydrophilic group. The hydrophilic group contributes to the imparting of on-machine developability to the photosensitive layer. In particular, due to the coexistence of the crosslinkable group and the hydrophilic group, printing durability and on-machine developability can be achieved at the same time.

[0107] Examples of the hydrophilic group that Component D may have include a hydroxy group, a carboxy group, an alkylene oxide structure, an amino group, an ammonium group, an amide group, a sulfo group, and a phosphoric acid group, among them an alkylene oxide structure having 1 to 9 alkylene oxide units having 2 or 3 carbons being preferable. Imparting a hydrophilic group to a binder is carried out for example by copolymerization of a monomer having a hydrophilic group.

[0108] Component D preferably has a weight-average molecular weight of 2,000 or more, and more preferably 10,000 to 300,000, and a number-average molecular weight of 1,000 or more, and more preferably 2,000 to 250,000. The polydispersity (weight-average molecular weight/number-average molecular weight) is preferably 1.1 to 10.

[0109] Component D may be used singly or in a combination of two or more types as a mixture.

[0110] From the view point of good strength for an image area and good image formation properties, the content of Component D is preferably 5 to 75 mass % relative to the total solids content of the photosensitive layer, more preferably 10 to 70 mass %, and yet more preferably 10 to 60 mass %.

[0111] Furthermore, the total content of Component C and Component D is preferably no greater than 90 mass % relative to the total solids content of the photosensitive layer, and more preferably 35 to 80 mass %. When in the above-mentioned range, sensitivity and developability are excellent.

(E) Polymerization initiator

[0112] The image recording layer in the lithographic printing plate precursor of the present invention preferably contains a polymerization initiator as Component E. It is not particularly limited in the present invention, the polymerization initiator described in JP-A-2013-205569 is preferably used. Among them, an onium salt is preferably used. The polymerization initiator may be used singly or in a combination of two or more types.

[0113] Examples of an onium salt include an iodonium salt and a sulfonium salt.

[0114] Specific examples of these compounds are shown below, but the present invention is not limited by these examples.

[0115] Examples of an iodonium salt preferably include a diphenyliodonium salt, in particular, more preferably a diphenyl iodonium salt substituted by an electron-releasing group such as an alkyl group and an alkoxyl group and yet more preferably an asymmetric diphenyl iodonium salt. Examples of the diphenyliodonium salt include diphenyliodonium hexafluorophosphate, 4-methoxyphenyl-4-(2-methylpropyl)phenyliodonium hexafluorophosphate, 4-(2-methylpropyl)phenyl-p-tryliodonium hexafluorophosphate, 4-hexyloxyphenyl-2,4,6-trimethoxyphenyliodonium hexafluorophosphate, 4-hexyloxyphenyl-2,4-dietoxyphenyliodonium tetrafluoroborate, 4-octyloxyphenyl-2,4,6-trimethoxyphenyliodonium 1-perfluorobutanesulfonate, 4-octyloxyphenyl-2,4,6-trimethoxyphenyliodonium hexafluorophosphate and bis(4-*t*-butylphenyl)iodonium tetraphenylborate.

[0116] Examples of the sulfonium salt include triphenylsulfonium hexafluorophosphate, triphenylsulfonium benzoylfomate, bis(4-chlorophenyl)phenylsulfonium benzoylfomate, bis(4-chlorophenyl)-4-methylphenylsulfonium tetrafluoroborate, tris(4-chlorophenyl)sulfonium 3,5-bis(metoxycarbonyl)benzenesulfonate, tris(4-chlorophenyl)sulfonium hexafluorophosphate.

[0117] Among them, an iodonium salt is preferable. An onium salt is particularly preferably used in a combination with an infrared absorbing agent having a maximum absorption in a wavelength region of 750 to 1,400 nm.

[0118] The polymerization initiator is preferably used singly or in a combination of two or more types.

[0119] The content of Component E is preferably 0.01 to 20 mass % relative to the total solids content of the photosensitive layer, more preferably 0.1 to 15 mass %, and yet more preferably 1.0 to 10 mass %.

(F) Low-molecular-weight hydrophilic compound

[0120] The image recording layer of the lithographic printing plate precursor of the present invention preferably comprises a low-molecular-weight hydrophilic compound as Component F. In the present invention, Component F is preferably contained since on-machine developability can be improved without degrading the printing durability of the lithographic printing plate precursor of the present invention.

[0121] Component F is the same as those described in paragraph 0100 et seq. of JP-A-2013-205569. Among them, it is preferable for at least one selected from a polyol, an organic sulfate, an organic sulfonate, and a betaine to be contained.

[0122] Since the compound cited as a preferred example of Component F has a small-structured hydrophobic moiety and hardly any surface activity, the hydrophobicity or the film strength of an image area is not degraded due to dampening water penetrating into an exposed image recording layer portion (image area), and ink acceptance and printing durability of a photosensitive layer can be maintained well.

[0123] The content of Component F is preferably 0.5 to 20 mass % relative to the total solids content of the photosensitive layer, more preferably 1 to 15 mass %, and yet more preferably 2 to 10 mass %. Component F is preferably used singly or in a combination of two or more types.

(G) Oleophilizing agent

[0124] The image recording layer of the lithographic printing plate precursor of the present invention may comprise as Component G an oleophilizing agent.

[0125] In the present invention, the image recording layer may preferably comprise Component G, such as a phosphonium compound, a nitrogen-containing low-molecular-weight compound, or an ammonium group-containing polymer, in order to improve laydown. In particular, when a protective layer of the lithographic printing plate precursor of the present invention comprises an inorganic lamellar compound, Component G functions as a surface covering agent for the inorganic lamellar compound, thereby preventing degradation of laydown during printing due to the inorganic lamellar compound. A phosphonium compound, a quaternary ammonium salt, or a pyridinium salt is preferable. Preferred oleophilizing agents are the same as those described in JP-A-2013-205569.

[0126] The content of Component G is preferably 0.01 to 30.0 mass % relative to the total solids content of the photosensitive layer, more preferably 0.1 to 15.0 mass %, and yet more preferably 1 to 5 mass %.

(H) Hydrophobizing precursor

[0127] The image recording layer of the lithographic printing plate precursor of the present invention may comprise as Component H a hydrophobizing precursor.

[0128] In the present invention, the photosensitive layer may comprise as Component H a hydrophobizing precursor in order to improve the on-machine developability.

[0129] The hydrophobizing precursor means particles that can convert the photosensitive layer into being hydrophobic when heat is applied.

[0130] The particles are preferably at least one type selected from hydrophobic thermoplastic polymer particles, thermoreactive polymer particles, polymerizable group-containing polymer particles, hydrophobic compound-encapsulating microcapsules, and a microgel (crosslinked polymer particles). Among them, polymerizable group-containing polymer particles and a microgel are preferable. From the viewpoint of developability, it is preferable for it to comprise hydrophobic thermoplastic polymer particles.

[0131] Such a hydrophobizing precursor is the same as one described in JP-A-2013-205569.

[0132] More preferred examples include polystyrene, a styrene- and acrylonitrile-containing copolymer, and polymethyl methacrylate.

[0133] The average particle size of the hydrophobic thermoplastic polymer particles used in the present invention is preferably 0.01 to 2.0 μm .

[0134] Examples of the thermoreactive polymer particles used in the present invention include thermoreactive group-containing polymer particles, and they form a hydrophobizing region due to crosslinking by a thermal reaction and change of a functional group at that time.

[0135] Preferred examples of the thermoreactive group in the thermoreactive group-containing polymer particles used in the present invention include a polymerizable group described in JP-A-2013-20556, an isocyanate group for carrying out an addition reaction or a blocked form thereof, an epoxy group, a vinyloxy group, and an active hydrogen atom-containing functional group that reacts with the above (e.g. an amino group, a hydroxy group, a carboxy group, etc.), a carboxy group for carrying out a condensation reaction and a hydroxy group or amino group that react with the above, and an acid anhydride for carrying out a ring-opening addition reaction and an amino group or hydroxy group that react with the above.

[0136] Examples of the microcapsules used in the present invention include those in which the whole or part of the constituent components of the photosensitive layer is encapsulated in microcapsules as described in JP-A-2001-277740 or JP-A-2001-277742. The constituent components of the photosensitive layer may also be contained outside the microcapsules. Furthermore, a preferred embodiment is one in which the microcapsule-containing photosensitive layer includes a hydrophobic constituent component within the microcapsules, and contains a hydrophilic constituent component outside the microcapsules.

[0137] The microgel used in the present invention may comprise part of the constituent components of the photosensitive layer in at least one of the interior and the surface of the microgel. In particular, an embodiment in which a reactive microgel is formed by having a radically polymerizable group on the surface is particularly preferable from the viewpoint of image formation sensitivity and printing durability.

[0138] Making microcapsules or a microgel using the constituent components of the photosensitive layer may be carried out by a known method.

[0139] The average particle size of the microcapsules or the microgel is preferably 0.01 to 3.0 μm , more preferably 0.05 to 2.0 μm , and particularly preferably 0.10 to 1.0 μm . Good resolution and aging stability are obtained within this range.

[0140] The content of Component H is preferably 5 to 90 mass % relative to the total solids content of the photosensitive layer.

(I) Other photosensitive layer components

[0141] The image recording layer of the lithographic plate precursor in the present invention may comprise the (I) other photosensitive layer components other than Component A to Component H above.

[0142] The content of component I is preferably 0.01 to 20 mass % relative to the total solids content of the photosensitive layer, more preferably 1 to 10 mass %, and yet more preferably 1 to 5 mass %.

[0143] The photosensitive layer may further contain various additives as necessary. The additives described in JP-A-2013-205569 may be used.

<Formation of image recording Layer>

[0144] The method for forming the image recording layer (photosensitive layer) in the printing plate precursor of the present invention is not particularly limited and may be a known method. The photosensitive layer according to the invention is formed by dissolving or dispersing each of the necessary components described above in an appropriate solvent to prepare a coating solution and coating the coating solution. The solvents used include, for example, methyl ethyl ketone, ethylene glycol monomethyl ether, 1-methoxy-2-propanol, 2-methoxyethyl acetate, 1-methoxy-2-propyl acetate and γ -butyrolactone, but the invention should not be construed as being limited thereto. The solvents are preferably used singly or in a combination of two or more types. The solid content concentration of the coating solution is preferably

from 1 to 50 mass %.

[0145] The coating amount (solid content) of the photosensitive layer is preferably from 0.3 to 3.0 g/m². 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.

[0146] The image recording layer used in the lithographic printing plate precursor of the present invention is preferably removable with a dampening water composition and/or a printing ink.

<Support>

[0147] The support used for the lithographic printing plate precursor of the present invention is not particularly limited and may be a dimensionally stable plate-form hydrophilic support. Particularly, an aluminum plate is preferable. Examples of the support described in JP-A-2013-205569, which may be appropriately used.

Hydrophilization treatment

[0148] In the lithographic printing plate precursor of the present invention, in order to improve the hydrophilicity of a non-image region to thus prevent printing stains, it is preferable to subject a support surface to a hydrophilization treatment.

[0149] Examples of the hydrophilization treatment of a support surface include a treatment with an alkali metal silicate in which a support is immersed or electrolyzed in an aqueous solution of sodium silicate, etc., a treatment with potassium fluorozirconate, and a treatment with polyvinylphosphonic acid; a treatment method involving immersion in an aqueous solution of polyvinylphosphonic acid is preferably used.

<Protective Layer>

[0150] In the lithographic printing plate precursor of the present invention, a protective layer (oxygen-blocking layer) is preferably provided on the photosensitive layer in order to prevent diffusion and penetration of oxygen, which inhibits a polymerization reaction at the time of exposure.

[0151] As a material that can be used in the protective layer, either a water-soluble polymer or a water-insoluble polymer may be used by appropriate selection, and two or more types may be mixed as necessary and used. Specific examples include polyvinyl alcohol, a modified polyvinyl alcohol, polyvinylpyrrolidone, a water-soluble cellulose derivative, and a poly(meth)acrylonitrile. Among them, it is preferable to use a water-soluble polymer compound having relatively good crystallinity. Specifically, use of polyvinyl alcohol as a main component can give the best results in terms of basic characteristics such as oxygen barrier properties and development removability.

[0152] Examples of the polyvinylalcohol are described in paragraphs 0216 to 0217 of JP-A-2013-205569, and may be appropriately used.

[0153] Furthermore, it is also preferable for an inorganic layered compound to be contained in the protective layer for the purpose of improving the oxygen-blocking properties and the photosensitive layer surface protection properties. Among inorganic layered compounds, a fluorine-based swelling synthetic mica, which is a synthetic inorganic layered compound, is particularly useful. Specific preferred examples include inorganic layered compounds described in JP-A-2005-119273.

[0154] The coat weight of the protective layer is preferably in the range of 0.05 to 10 g/m². When the protective layer contains the inorganic layered compound, it is more preferably in the range of 0.1 to 5 g/m², and when the protective layer does not contain the inorganic layered compound, it is more preferably in the range of 0.5 to 5 g/m².

<Backcoat layer>

[0155] In the lithographic printing plate precursor of the present invention, a backcoat layer may as necessary be provided on the back surface of the support.

[0156] As the backcoat layer, there can preferably be cited, 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 such as Si(OCH₃)₄, Si(OC₂H₅)₄, Si(OC₃H₇)₄, or Si(OC₄H₉)₄ is preferable since starting materials are inexpensive and readily available.

(Process for making lithographic printing plate)

[0157] A lithographic printing plate may be made by processing the lithographic printing plate precursor of the present invention by imagewise exposure.

[0158] A first embodiment of the process for making a lithographic printing plate of the present invention comprises an exposure step of imagewise exposing the lithographic printing plate precursor of the present invention and a development step of removing a non-exposed area of the image recording layer of the lithographic printing plate precursor in the presence of a developer having a pH of 2 to 14.

[0159] A second embodiment of the process for making a lithographic printing plate of the present invention comprises an exposure step of imagewise exposing the lithographic printing plate precursor of the present invention and a development step of removing a non-exposed area of the image recording layer of the lithographic printing plate precursor by supplying a printing ink and dampening water on a printer.

[0160] With regard to the process for making a lithographic printing plate of the present invention, preferred embodiments for each step are explained below in sequence. In accordance with the process for making a lithographic printing plate of the present invention, the lithographic printing plate precursor of the present invention may also be made into a lithographic printing plate when a water washing step is contained in the development step.

<Exposure step>

[0161] The process for making a lithographic printing plate of the present invention preferably comprises an exposure step of imagewise exposing the lithographic printing plate precursor of the present invention. The lithographic printing plate precursor of the present invention is preferably exposed to a laser through a transparent original image having a line image, a halftone image, etc., or imagewise exposed by laser light scanning using digital data.

[0162] The wavelength of the light source employed is preferably 750 to 1,400 nm. As a light source at 750 to 1,400 nm, a solid-state laser and a semiconductor laser that emit infrared are suitable. With regard to the infrared laser, the output is preferably at least 100 mW, the exposure time per pixel is preferably within 20 microseconds, and the illumination energy level is preferably 10 to 300 mJ/cm². Furthermore, in order to shorten the exposure time it is preferable to use a multi-beam laser device. The exposure mechanism may be any of a drum inner face method, a drum outer face method, a flat bed method, etc.

[0163] Imagewise exposure may be carried out by a standard method using a plate setter, etc. In the case of on-machine development, after a lithographic printing plate precursor is mounted on a printer, imagewise exposure may be carried out on the printer.

<Development step>

[0164] The process for making a lithographic printing plate of the present invention preferably comprises a development step of removing a non-exposed area of the image recording layer of the lithographic printing plate precursor in the presence of a developer having a pH of 2 to 14. Furthermore, the process for making a lithographic printing plate of the present invention preferably comprises a development step of removing a non-exposed area of the image recording layer of the lithographic printing plate precursor by supplying a printing ink and dampening water on a printer. The process for making a lithographic printing plate of the present invention preferably comprises either one of the two steps as the development step. That is, in the process for making a lithographic printing plate of the present invention, processing is preferably carried out by (1) a method in which development is carried out using a developer having a pH of 2 to 14 (developer processing method) or (2) a method in which development is carried out while applying dampening water and an ink on a printer (on-machine development method).

[0165] The developer processing method and the on-machine development method are explained below.

(Solution development method)

[0166] In the solution developing process, the lithographic printing plate precursor is treated using the developer of pH 2 to 14, so as to remove the photosensitive layer in non-exposed areas, and thereby lithographic printing plate is manufactured.

[0167] In a general process of development using a strong alkaline developer (pH12 or above), the protective layer is removed by pre-water washing, subjected to alkaline development, post-water washing for removing alkali by water washing, gum solution treatment, and drying process, to thereby obtain the lithographic printing plate.

[0168] According to a first preferable embodiment of the present invention, the developer used herein has pH value of 2 to 14. In this embodiment, the developer preferably contains a surfactant or water-soluble polymer compound, so as to concomitantly allow the development and gum solution treatment to proceed. Accordingly, the post-water washing is not indispensable, and the development and the gum solution treatment may be proceeded in a single solution.

[0169] Also the pre-water washing is not indispensable, so that also the removal of the protective layer may be proceeded concomitantly with the gum solution treatment. In the process for making the lithographic printing plate of the present invention, it is preferred not to include the water washing step before and after the solution development

step. In the process for making the lithographic printing plate of the present invention, the development and gum solution treatment is preferably followed by removal of excessive developer using a squeeze roller for example, and drying.

[0170] The development by developer in the lithographic printing plate precursor of the present invention may be proceeded as usual at 0 to 60° C., preferably 15 to 40° C. or around, typically by a method of dipping the exposed lithographic printing plate precursor into a developer followed by rubbing with a brush, or a method of spraying a developer followed by rubbing with a brush.

[0171] The development using the developer is successfully implemented on an automatic processor, equipped with a developer feeder and a rubbing member. The automatic processor having rotating brush rollers as the rubbing member is particularly preferable. The automatic processor preferably has a unit for removing excessive developer, such as squeeze rollers, and a drying unit such as a hot air blower, on the downstream side of the developing unit. Moreover, the automatic processor may have a pre-heating unit for heating the exposed lithographic printing plate precursor, on the upstream side of the developing unit.

[0172] The example of the automatic processor used for the method of manufacturing a lithographic printing plate of the present invention is illustrated in FIG. 1.

[0173] The automatic processor 100 illustrated in FIG. 1 is composed of a chamber shaped by an equipment frame 202, and has a pre-heating section 200, a developing section 300 and a drying section 400 aligned in line in the direction of a feed path 11 along which the lithographic printing plate precursor is fed (indicated by arrow A).

[0174] The pre-heating section 200 has a heating chamber 208 with a feeding port 212 and an output port 218, and has tandem rollers 210, heaters 214 and a circulating fan 216 arranged therein.

[0175] The developing section 300 is partitioned by an outer panel 310 from the pre-heating section 200, and the outer panel 310 has an insertion slit 312.

[0176] Inside the developing section 300, there is provided a process tank 306 having therein a developing tank 308 filled with a developer, and an insertion roller pair 304 for guiding the lithographic printing plate precursor into the process tank 306. The upper portion of the developing tank 308 is covered with a shielding lid 324.

[0177] Inside the developing tank 308, there is provided a guide roller 344 and a guiding member 342, an immersed roller pair 316, a brush roller pair 322, a brush roller pair 326, and an output roller pair 318 which are aligned in sequence from the upstream side of the feeding direction. The lithographic printing plate precursor brought into the developing tank 308 is dipped in the developer, and allowed to pass through the rotating brush roller pairs 322, 326, to be removed with the non-image-forming area.

[0178] Below the brush roller pairs 322, 326, there is provided a spray 330. The spray pipe 330 is connected to a pump (not illustrated), and the developer in the developing tank 308 sucked up by the pump is ejected through the spray pipe 330 into the developing tank 308.

[0179] On the sidewall of the developing tank 308, there is provided an overflow port 51 opened at the top end portion of a first circulating pipe C1, so as to allow an excessive portion of the developer to flow into the overflow port 51, run down through the first circulating pipe C1, to be discharged into an external tank 50 provided outside the developing section 300.

[0180] The external tank 50 is connected to a second circulating pipe C2. The second circulating pipe C2 is provided with a filter unit 54 and a developer feed pump 55. By the developer feed pump 55, the developer is fed from the external tank 50 to the developing tank 308. The external tank 50 is provided with an upper level gauge 52 and a lower level gauge 53.

[0181] The developing tank 308 is connected through a third circulating pipe C3 to a supplementary water tank 71. The third circulating pipe C3 is provided with a water supplement pump 72 by which water reserved in the supplementary water tank 71 is fed to the developing tank 308.

[0182] A liquid temperature sensor 336 is provided on the upstream side of the immersed roller pair 316, and a level gauge 338 is provided on the upstream side of the output roller pair 318.

[0183] A partition board 332 placed between the developing section 300 and the drying section 400 has an insertion slit 334 provided thereto. On a path between the developing section 300 and the drying section 400, there is provided a shutter (not illustrated) which closes the path when the lithographic printing plate precursor 11 does not travel on the path.

[0184] The drying section 400 has a support roller 402, ducts 410, 412, a feed roller pair 406, ducts 410, 412, and a feed roller pair 408 aligned therein in sequence. Each of the ducts 410, 412 has a slit hole 414 provided to the tip thereof.

[0185] The drying section 400 has provided thereto an unillustrated drying unit such as a hot air blower, heat generator or the like. The drying section 400 has a discharge port 404, through which the lithographic printing plate 11 dried by the drying unit is ejected.

[0186] In the present invention the developer used in development processing comprises an aqueous solution having a pH of 2 to 14 or a surfactant. The developer is preferably an aqueous solution containing water as a main component (containing at least 60 mass% of water), and particularly preferably an aqueous solution containing a surfactant (anionic, nonionic, cationic, amphoteric, etc.) or an aqueous solution containing a water-soluble polymer compound. An aqueous solution containing both a surfactant and a water-soluble polymer compound is preferable. The pH of the developer is more preferably 2.0 to 10.0, yet more preferably 3.5 to 10.0, and particularly preferably 6.5 to 10.0. In particular, in a

method in which a developer having a pH of 2.0 to 10.0 is used, it is very difficult to satisfy all of stain resistance, printing durability, and suppression of degradation of stain resistance after aging. The reason therefor can be explained as follows. That is, when the same material for a lithographic printing plate precursor is used but the type of developer is changed, compared with an alkali developer having a pH of 12 to 13, which has been used conventionally, a developer having a pH of 2.0 to 10.0 degrades the stain resistance of an unexposed portion. When the hydrophilicity of a material is increased in an attempt to improve the stain resistance when using a developer having a pH of 2.0 to 10.0, the printing durability tends to be degraded. In accordance with use of the lithographic printing plate precursor of the present invention, such a developer having a pH of 2.0 to 10.0 can preferably be used.

[0187] The anionic surfactant to be comprised in the above developer in the present invention is not particularly limited but examples thereof include fatty acid salts, abietates, hydroxyalkanesulfonates, alkanesulfonates, dialkylsulfosuccinates, linear alkylbenzenesulfonates, branched alkylbenzenesulfonates, alkyl-naphthalenesulfonates, alkyl-diphenylether (di)sulfonates, alkylphenoxy-polyoxyethylene alkylsulfonates, salts of polyoxyethylene alkylsulfophenyl ether, sodium N-methyl-N-oleyltaurates, monoamide disodium N-alkylsulfosuccinates, petroleum sulfonates, sulfated castor oil, sulfated tallow oil, salts of sulfuric ester of fatty acid alkyl ester, salts of alkylsulfuric ester, salts of sulfuric ester of polyoxyethylene alkyl ether, salts of sulfuric ester of fatty acid monoglyceride, salts of sulfuric ester of polyoxyethylene alkylphenyl ether, salts of sulfuric ester of polyoxyethylene styrylphenyl ether, salts of alkylphosphoric ester, salts of phosphoric ester of polyoxyethylene alkyl ether, salts of phosphoric ester of polyoxyethylene alkylphenyl ether, partially saponified products of styrene-maleic anhydride copolymer, partially saponified products of olefin-maleic anhydride copolymer, and naphthalene sulfonate formalin condensates. Among these, alkylbenzenesulfonates, alkyl-naphthalenesulfonates and alkyl-diphenylether (di)sulfonates are preferably used.

[0188] The cationic surfactant to be comprised in the above developer in the present invention is not particularly limited and a conventionally known cationic surfactant may be used. Examples thereof include alkylamine salts, quaternary ammonium salts, alkylimidazolium salts, polyoxyethylene alkylamine salts and polyethylene polyamine derivatives.

[0189] The nonionic surfactant to be comprised in the above developer in the present invention is not particularly limited, but examples thereof include a polyethylene glycol-type higher alcohol ethylene oxide adduct, an alkylphenol ethylene oxide adduct, an alkyl-naphthol ethylene oxide adduct, a phenol ethylene oxide adduct, a naphthol ethylene oxide adduct, a fatty acid ethylene oxide adduct, a polyhydric alcohol fatty acid ester ethylene oxide adduct, a higher alkylamine ethylene oxide adduct, a fatty acid amide ethylene oxide adduct, a fatty oil ethylene oxide adduct, a polypropylene glycol ethylene oxide adduct, a dimethylsiloxane-ethylene oxide block copolymer, a dimethylsiloxane-(propylene oxide-ethylene oxide) block copolymer, a fatty acid ester of polyhydric alcohol-type glycerol, a fatty acid ester of pentaerythritol, a fatty acid ester of sorbitol or sorbitan, a fatty acid ester of sucrose, an alkyl ether of polyhydric alcohol, and a fatty acid amide of alkanolamines. Among these, those having an aromatic ring and an ethylene oxide chain are preferred, and an alkyl-substituted or unsubstituted phenol ethylene oxide adduct and an alkyl-substituted or unsubstituted naphthol ethylene oxide adduct are more preferred.

[0190] The zwitterionic surfactant to be comprised in the above developer in the present invention is not particularly limited but includes an amine oxide type such as alkyl-dimethylamine oxide, a betaine type such as alkylbetaine, and an amino acid type such as alkylamino-fatty acid sodium salt. In particular, an alkyl-dimethylamine oxide which may have a substituent, an alkylcarboxybetaine which may have a substituent, and an alkylsulfobetaine which may have a substituent, are preferably used. As for specific examples thereof, a compound represented by formula (2) in paragraph 0256 of JP-A-2008-203359, compounds represented by formulae (I), (II) and (VI) in paragraph 0028 of JP-A-2008-276166, and compounds illustrated in paragraphs 0022 to 0029 of JP-A-2009-47927 may be used.

[0191] The surfactant may be used singly or in a combination of two or more types as a mixture. And the proportion of the surfactant in the developer is preferably from 0.01 to 20 mass %, more preferably from 0.1 to 10 mass %.

[0192] The water-soluble polymer compound for use in the developer according to the invention 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, pullulan, 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, a styrene/maleic anhydride copolymer, polyvinylsulfonic acid or a salt thereof and a polystyrenesulfonic acid or a salt thereof.

[0193] 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 from 10 to 100 mPa/sec in the 10% by weight aqueous solution thereof.

[0194] 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.

[0195] Two or more 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 mass.

[0196] Into the developer for use in the invention, a pH buffer agent may be incorporated. A pH buffer agent exhibiting a pH buffer function at pH from 2 to 14 is used without particular restriction in the developer according to the invention. In the invention, a weak alkaline buffer agent is preferably used and includes, for example, (a) a carbonate ion and a hydrogen carbonate ion, (b) a borate ion, (c) a water-soluble amine compound and an ion of the water-soluble amine compound, and combinations thereof. Specifically, for example, (a) a combination of a carbonate ion and a hydrogen carbonate ion, (b) a borate ion, or (c) a combination of a water-soluble amine compound and an ion of the water-soluble amine compound exhibits a pH buffer function in the developer to prevent fluctuation of the pH even when the developer is used for a long period of time. As a result, for example, the deterioration of development 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 preferred.

[0197] 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.

[0198] The total amount of the carbonate ion and hydrogen carbonate ion is preferably from 0.05 to 5 mole/l, more preferably from 0.07 to 2 mole/l, particularly preferably from 0.1 to 1 mole/l, in the developer.

[0199] The developer for use in, the present invention may contain an organic solvent. As the organic solvent to be contained, for example, an aliphatic hydrocarbon (e.g., hexane, heptane, Isopar E, Isopar H, Isopar G (produced by Esso Chemical Co., Ltd.)), an aromatic hydrocarbon (e.g., toluene or xylene), a halogenated hydrocarbon (methylene dichloride, ethylene dichloride, trichlene or monochlorobenzene) or a polar solvent is exemplified. Examples of the polar solvent include an alcohol (e.g., methanol, ethanol, propanol, isopropanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 2-octanol, 2-ethyl-1-hexanol, 1-nonanol, 1-decanol, 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, 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, N-phenyldiethanolamine, N-methyldiethanolamine, N-ethyldiethanolamine, 4-(2-hydroxyethyl)morpholine, N,N-dimethylacetamide or N-methylpyrrolidone).

[0200] The organic solvents are preferably used singly or in a combination of two or more types. 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. The developer according to the invention may contain a preservative, a chelating agent, a defoaming agent, an organic acid, an inorganic acid, an inorganic salt or the like in addition to the components described above. Specifically, compounds described in Paragraphs 0266 to 0270 of JP-A-2007-206217 are preferably used.

[0201] The developer for use in the invention can be used as a developer and a development replenisher for the exposed lithographic printing plate precursor. Also, 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.

<On-machine development method>

[0202] In the on-machine development method, an oil-based ink and an aqueous component are supplied to a lithographic printing plate precursor that has been imagewise exposed on the printer to thus remove the photosensitive layer of a non-image area, thereby making a lithographic printing plate.

[0203] That is, a lithographic printing plate precursor is imagewise exposed and then mounted on a printer as it is without any processing, or a lithographic printing plate precursor is mounted on a printer and then imagewise exposed on the printer; printing is subsequently carried out by supplying an oil-based ink and an aqueous component, in the initial stage of printing uncured photosensitive layer is dissolved or decomposed by the supplied oil-based ink and/or aqueous component in a non-image area and removed, and a hydrophilic surface is exposed in that area. On the other hand, in

an exposed portion, the photosensitive layer cured by exposure forms an oil-based ink-receiving area having an oleophilic surface. It may be either an oil-based ink or an aqueous component that is first supplied to a plate surface, but from the viewpoint of preventing an aqueous component from being contaminated with a photosensitive layer component that has been removed, it is preferable to first supply an oil-based ink. In this way, the lithographic printing plate precursor is subjected to on-machine development on the printer and used as it is for printing of a large number of sheets. As the oil-based ink and the aqueous component, a usual printing ink and dampening water for lithographic printing are suitably used.

[0204] In the process for making a lithographic printing plate using the lithographic printing plate precursor of the present invention, regardless of the development method, the entire face of the lithographic printing plate precursor may be heated as necessary before exposure, during exposure, or during the period after exposure but before development. Such heating promotes an image formation reaction in the photosensitive layer, thereby resulting in advantages such as improvement of sensitivity and printing durability and stabilization of sensitivity. Furthermore, in the case of a developer processing method, it is also effective, for the purpose of improving image strength and printing durability, to subject an image after processing to heating of the whole face or exposure of the whole face. It is usually preferable to carry out heating prior to development under mild conditions of 150°C or lower. When the temperature is too high, the problem of a non-image area being cured might occur. Heating after development utilizes very strong conditions for heating. It is usually in the range of 100°C to 500°C. When the temperature is low, a sufficient image strengthening effect cannot be obtained, and when it is too high, there might be problems such as degradation of the support and thermal decomposition of the image area.

[0205] Aspects of the present invention are explained more specifically by reference to Examples below. The materials, amounts used, proportions, processing details, processing procedure, etc. shown in the Examples below may be modified as appropriate as long as the modifications do not depart from the spirit of the present invention. Therefore, the scope of the present invention should not be construed as being limited by the specific examples shown below.

[0206] Unless otherwise specified, 'parts' and '%' below means 'parts by mass' and 'mass%'.

[0207] Compounds A-1 to A-7 used in the Examples are the same compounds as Compounds A-1 to A-7 described above.

(1) Preparation of lithographic printing plate precursor

<Preparation of aluminum support 1>

[0208] In order to remove rolling oil on the surface of a 0.3 mm thick aluminum plate (material: JIS A1050), it was subjected to a degreasing treatment using a 10 mass% aqueous solution of sodium aluminate at 50°C for 30 seconds, and the aluminum surface was grained using three nylon brushes implanted with bundled bristles having a diameter of 0.3mm and an aqueous suspension of pumice having a median diameter of 25 μm (specific gravity 1.1 g/cm³) and washed well with water. This plate was immersed in a 25 mass% aqueous solution of sodium hydroxide at 45°C for 9 seconds to thus carry out etching, washed with water, then immersed in a 20 mass% aqueous solution of nitric acid at 60°C for a further 20 seconds, and washed with water. The amount of etching of the grained surface here was about 3 g/m².

[0209] Subsequently, an electrochemical surface roughening treatment was continuously carried out using 60 Hz AC voltage. The electrolyte used here was a 1 mass% aqueous solution of nitric acid (containing aluminum ions at 0.5 mass%), and the liquid temperature was 50°C. An electrochemical surface roughening treatment was carried out with a carbon electrode as a counter electrode using an AC power source waveform with a trapezoidal rectangular wave AC having a time TP for the current value to reach a peak from zero of 0.8 msec and a duty ratio of 1:1. Ferrite was used as an auxiliary anode. The electric current density was 30 A/dm² as a peak current value, and 5% of the current flowing from a power source was diverted to the auxiliary anode.

[0210] With regard to the quantity of electricity in nitric acid electrolysis, the quantity of electricity when the aluminum plate was the anode was 175 C/dm².

[0211] Subsequently, washing with water using a spray was carried out.

[0212] Next, an electrochemical surface roughening treatment was carried out in a 0.5 mass% aqueous solution of hydrochloric acid (containing aluminum ions at 0.5 mass%) as an electrolyte at a liquid temperature of 50°C under conditions in which the quantity of electricity when the aluminum plate was the anode was 50 C/dm² in the same method as that for nitric acid electrolysis, and then washed with water using a spray. A 2.5 g/m² direct current anodized film was provided on the aluminum plate under conditions of an electric current density of 15 A/dm² using a 15 mass% aqueous solution of sulfuric acid (containing aluminum ions at 0.5 mass%) as an electrolyte, and the plate was then washed with water, dried, and treated with a 1 mass% aqueous solution of sodium silicate at 20°C for 10 seconds, thus producing aluminum support 1. The surface roughness was measured and found to be 0.54 μm (RA expressed in accordance with JIS B0601).

<Preparation of aluminum support 2>

[0213] A 0.24 mm thick aluminum plate (material 1050, temper H16) was immersed in a 5% aqueous solution of sodium hydroxide maintained at 65°C, subjected to a degreasing treatment for 1 minute, and then washed with water. This aluminum plate was immersed in a 10% aqueous solution of hydrochloric acid maintained at 25°C for 1 minute so as to carry out neutralization, and then washed with water. Subsequently, this aluminum plate was electrolytically roughened in a 0.3 mass% aqueous solution of hydrochloric acid at 25°C under conditions of an electric current density of 100 A/dm² using alternating current for 60 seconds, and then subjected to a desmutting treatment in a 5% aqueous solution of sodium hydroxide maintained at 60°C for 10 seconds. This aluminum plate was subjected to anodization in a 15% aqueous solution of sulfuric acid at 25°C under conditions of an electric current density of 10 A/dm² and a voltage of 15 V for 1 minute, thus producing aluminum support 2. The surface roughness thereof was measured and found to be 0.44 μm (RA expressed in accordance with JIS B0601).

<Preparation of aluminum support 3>

[0214] A 0.19 mm thick aluminum plate was degreased by immersing it in a 40 g/L sodium hydroxide aqueous solution at 60°C for 8 seconds and washed with desalted water for 2 seconds. Subsequently, the aluminum plate was subjected to an electrochemical surface roughening treatment in an aqueous solution containing 12 g/L hydrochloric acid and 38 g/L aluminum sulfate (octadecahydrate) using alternating current for 15 seconds at a temperature of 33°C and an electric current density of 130 A/dm². After washing with desalted water for 2 seconds, the aluminum plate was subjected to desmutting by etching using a 155 g/L aqueous solution of sulfuric acid at 70°C for 4 seconds, and washed with desalted water at 25°C for 2 seconds. The aluminum plate was subjected to anodization in 155 g/L sulfuric acid in an aqueous solution for 13 seconds at a temperature of 45°C and an electric current density of 22 A/dm², and washed with desalted water for 2 seconds. Furthermore, it was post-treated using a 4 g/L aqueous solution of polyvinylphosphonic acid at 40°C for 10 seconds, washed with desalted water at 20°C for 2 seconds, and dried. The support thus obtained had a surface roughness Ra of 0.21 μm and an anodized film amount of 4 g/m².

<Formation of intermediate layer>

[0215] Aluminum supports 1 to 3 were coated with an intermediate layer coating solution having the formulation below using a bar coater and dried at 100°C for 1 minute, thus forming an undercoat layer. The dry coat weight of the intermediate layer was 18 mg/m².

<Intermediate layer coating solution>

[0216]

Component A described in Table 1, or comparative polymer compounds R-1 and R-2 below: 0.50 parts

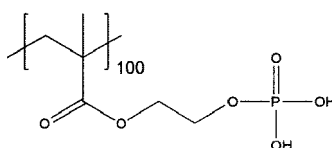
Component B described in Table 1, or comparative compounds R-2, R-3, and R-4 below: amount added described in Table 1

Methanol: 90.0 parts

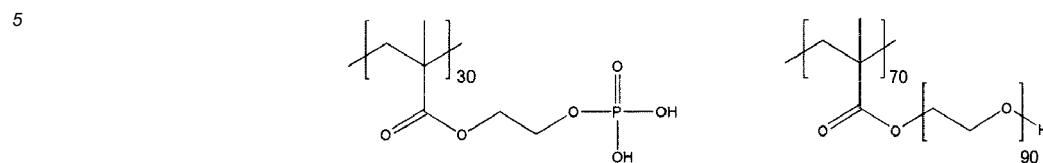
Pure water: 10.0 parts

[0217] The structures of comparative compounds R-1 to R-4 are shown below. In the compound examples below, the numerical value written by the side of each repeating unit (numerical value written by the side of main chain repeating unit) denotes the mole percent of the repeating unit. The numerical value written by the side of the repeating unit in a side chain denotes the repeat number of the repeating unit.

R-1 Mw : 20,000

[0218]

R-2 Mw : 170,000

[0219]

R-3 Mw:200

[0220]

R-4 Mw : 250000

[0221]

<Formation of image recording layer>

[0222] The intermediate layer formed as above was bar-coated with image recording layer coating solution (1-1) having the formulation below, and oven drying was carried out at 100°C for 60 seconds, thus forming an image recording layer having a dry coat weight of 1.0 g/m².

[0223] Image recording layer coating solution (1-1) was obtained by mixing and stirring photosensitive liquid (1-1) and microgel liquid (1) below immediately prior to coating.

<Photosensitive liquid (1-1)>

[0224]

Binder polymer (1) (structure below): 0.240 parts

IR-absorbing dye (1) (structure below): 0.030 parts

Radical-generating agent (1) (structure below): 0.162 parts

Radically polymerizable compound Tris(acryloyloxyethyl) isocyanurate

(NK Ester A-9300, Shin-Nakamura Chemical Co., Ltd.): 0.192 parts Low-molecular-weight hydrophilic compound

Tris(2-hydroxyethyl) isocyanurate: 0.062 parts

Low-molecular-weight hydrophilic compound (1) (structure below): 0.050 parts Oleophilizing agent Phosphonium

compound (1) (structure below): 0.055 parts

Oleophilizing agent

[0225] Benzyltrimethyloctylammonium hexafluorophosphate: 0.018 parts Oleophilizing agent Ammonium group-containing polymer (structure below, reduced specific viscosity 44 cSt/g/ml): 0.035 parts Fluorine-based surfactant (1) (structure below): 0.001 parts

2-Butanone: 1.091 parts

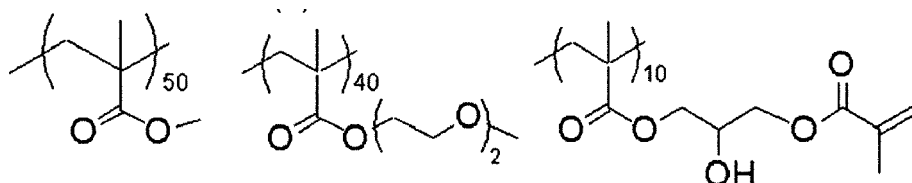
1-Methoxy-2-propanol: 8.609 parts

<Microgel liquid (1)>

[0226] Microgel (1): 2.640 parts

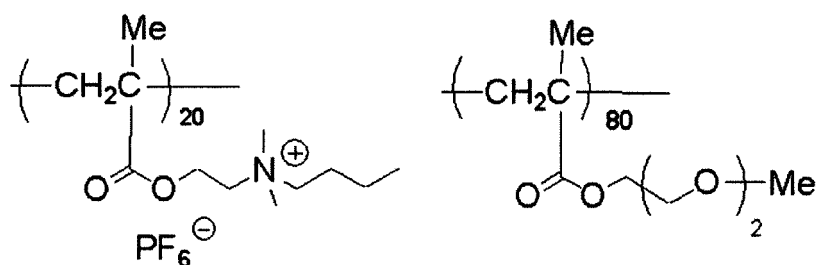
Distilled water: 2.425 parts

[0227] The structures of binder polymer (1), IR-absorbing dye (1), radical-generating agent (1), phosphonium compound (1), low-molecular-weight hydrophilic compound (1), ammonium group-containing polymer, and fluorine-based surfactant (1) described above are as follows.

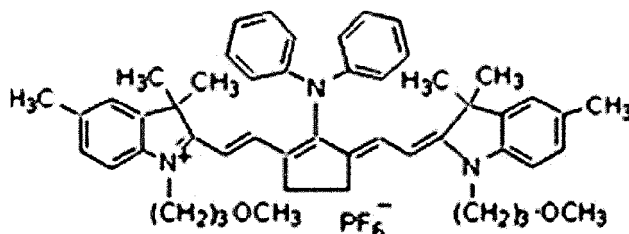


Binder polymer (1)

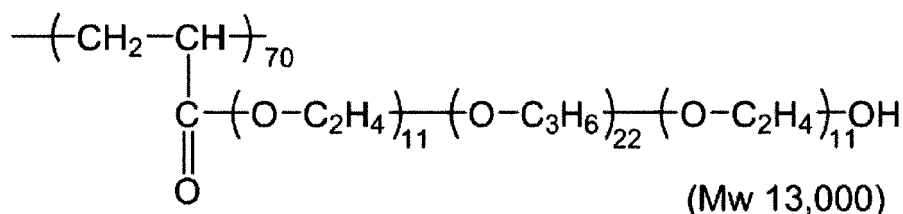
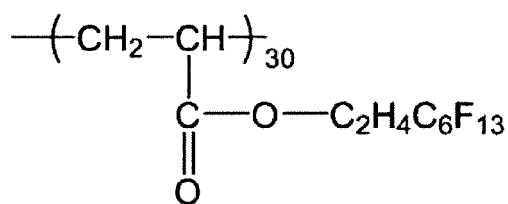
(Mw70,000)



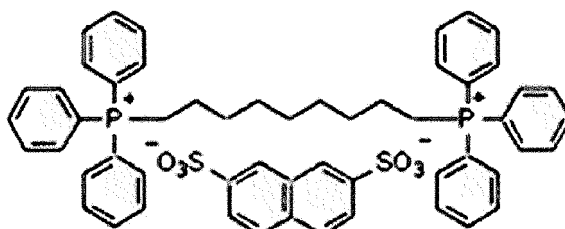
Ammonium group-containing polymer



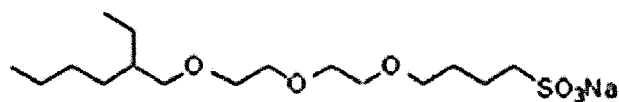
IR-absorbing dye (1)



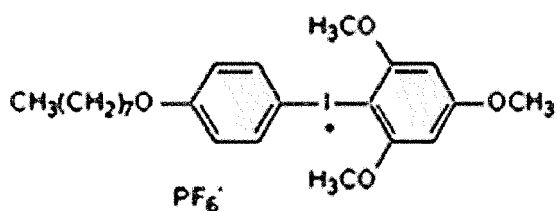
Fluorine-based surfactant (1)



Phosphonium compound (1)



Low-molecular-weight hydrophilic compound (1)



Radical-generating agent (1)

Synthesis of microgel (1)

[0228] As an oil phase component, 10 g of trimethylolpropane xylene diisocyanate adduct (Mitsui Chemicals Polyurethanes, Inc., Takenate D-110N), 3.15 g of pentaerythritol triacrylate (Nippon Kayaku Co., Ltd., SR444), and 0.1 g of Pionin A-41C (Takemoto Oil & Fat Co., Ltd.) were dissolved in 17 g of ethyl acetate. As an aqueous phase component, 40 g of a 4 mass% aqueous solution of PVA-205 was prepared. The oil phase component and the aqueous phase component were mixed and emulsified using a homogenizer at 12,000 rpm for 10 minutes. The emulsion thus obtained was added to 25 g of distilled water, stirred at room temperature for 30 minutes, and then stirred at 50°C for 3 hours. The microgel liquid thus obtained was diluted with distilled water so that the solids content concentration became 15 mass%, and this was defined as microgel (1) above. The average particle size of the microgel was measured by a light

scattering method and found to be 0.2 μm .

<Formation of image recording layer>

5 **[0229]** Image recording layer coating solution (1-2) having the formulation below was applied to the intermediate layer by bar coating and then oven-dried at 100°C for 60 seconds, thus forming an image recording layer having a dry coat weight of 1.0 g/m². Image recording layer coating solution (1-2) was obtained by mixing and stirring photosensitive liquid (1-2) below and microgel liquid (1) immediately prior to coating.

10 <Photosensitive liquid (1-2)>

[0230]

15 Binder polymer (1): 0.240 parts
 IR-absorbing dye (1): 0.030 parts
 Radical-generating agent (1): 0.162 parts
 Radically polymerizable compound Tris(acryloyloxyethyl) isocyanurate
 (NK Ester A-9300, Shin-Nakamura Chemical Co., Ltd.): 0.192 parts Low-molecular-weight hydrophilic compound
 Tris(2-hydroxyethyl) isocyanurate: 0.062 parts Low-molecular-weight hydrophilic compound (1): 0.050 parts Ole-
 20 ophilizing agent Phosphonium compound (1): 0.055 parts Oleophilizing agent
 Benzyltrimethylammonium hexafluorophosphate: 0.018 parts Oleophilizing agent Ammonium group-containing
 polymer (structure below, reduced specific viscosity 44cSt/g/ml): 0.035 parts Fluorine-based surfactant (1): 0.001
 parts
 2-Butanone: 1.091 parts
 25 1-Methoxy-2-propanol: 8.609 parts
 B-1 (corresponding to Component B of the present invention) poly(ethylene glycol) methyl ether (SIGMA-ALDRICH):
 amount added was such that the ratio of Component B relative to Component A was 1

<Formation of image recording layer 2>

30 **[0231]** Image recording layer coating solution (2) having the formulation below was applied to the intermediate layer by bar coating and then oven-dried at 70°C for 60 seconds, thus forming image recording layer 2 having a dry coat weight of 0.6 g/m².

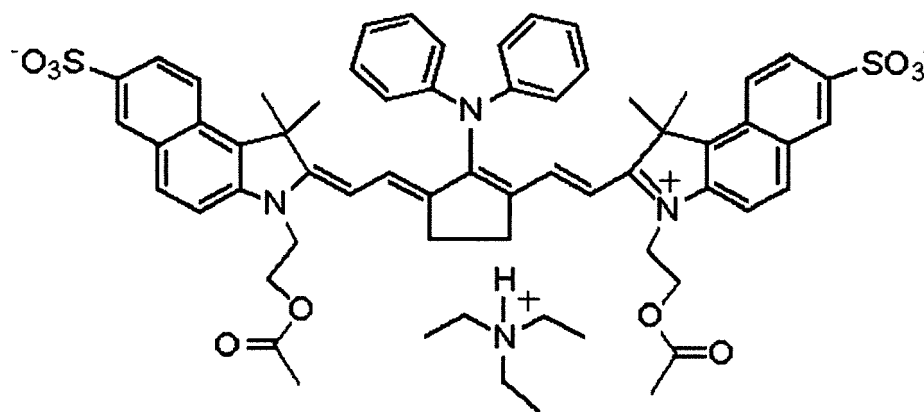
35 <Image recording layer coating solution (2)>

[0232]

40 Polymer microparticle aqueous dispersion (1): 20.0 parts
 IR-absorbing dye (2) (structure below): 0.2 parts
 Radical-generating agent Irgacure 250 (Ciba Speciality Chemicals): 0.5 parts
 Radically polymerizable compound SR-399 (Sartomer Company Inc.): 1.50 parts
 Mercapto-3-triazole: 0.2 parts
 Byk336 (Byk Chemie): 0.4 parts
 45 Klucel M (Hercules): 0.05 parts
 ELVACITE 4026 (Ineos AcrylicA): 2.5 parts
n-Propanol: 55.0 parts
 2-Butanone: 17.0 parts

50 **[0233]** Compounds described by the product name in the formulations are as follows.

Irgacure 250: (4-methoxyphenyl)[4-(2-methylpropyl)phenyl]iodonium hexafluorophosphate (75 mass% propylene carbonate solution) SR-399: dipentaerythritol pentaacrylate
 Byk336: modified dimethylpolysiloxane copolymer (25 mass% xylene/methoxypropyl acetate solution)
 55 Klucel M: hydroxypropylcellulose (2 mass% aqueous solution)
 ELVACITE 4026: highly branched polymethyl methacrylate (10 mass% 2-butanone solution)



IR-absorbing dye (2)

(Production of polymer microparticle aqueous dispersion (1))

[0234] A four-necked flask equipped with a stirrer, a thermometer, a dropping funnel, a nitrogen inlet, and a reflux condenser was charged with 20 g of polyethylene glycol methyl ether methacrylate (PEGMA average ethylene glycol repeat unit 50), 200 g of distilled water, and 200 g of *n*-propanol and heated to an internal temperature of 70°C while subjecting it to oxygen removal by introducing nitrogen gas. Subsequently, a mixture of 10 g of styrene (St), 80 g of acrylonitrile (AN), and 0.8 g 2,2'-azobisisobutyronitrile, which was mixed in advance, was added dropwise over 1 hour. After completion of the dropwise addition, the reaction was continued as it was for 5 hours, 0.4 g of 2,2'-azobisisobutyronitrile was added, and the internal temperature was increased to 80°C. Subsequently, 0.5 g of 2,2'-azobisisobutyronitrile was added over 6 hours. When the reaction had been carried out for a total of 20 hours polymerization had proceeded to at least 98%, and polymer microparticle aqueous dispersion (1) having a PEGMA/St/AN mass ratio of 10/10/80 was obtained. The particle size distribution of the polymer microparticles had a maximum value at a particle size of 150 nm.

[0235] Here, the particle size distribution was determined by taking an electron microscope photograph of the polymer microparticles, measuring the particle size of a total of 5,000 microparticles on the photograph, splitting a section from zero to the maximum value of the particle size measurement into 50 on a log scale, and plotting the frequency of occurrence of each particle size. As for non-spherical particles, the particle size of a spherical particle having the same particle area as the particle area of the non-spherical particles on the photograph was defined as the particle size.

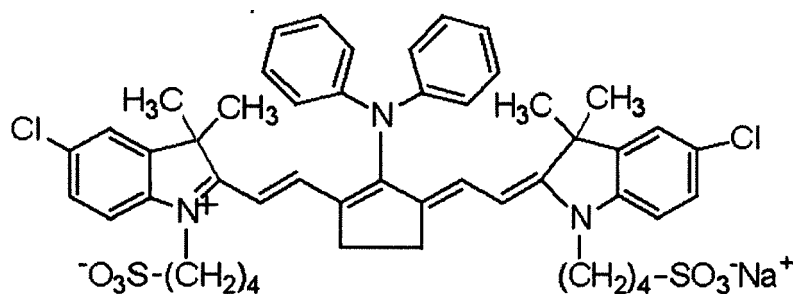
<Formation of image recording layer 3>

[0236] The support having an intermediate layer was bar-coated with image recording layer coating solution (3) below and oven-dried at 70°C for 60 seconds, thus producing an image recording layer having a dry coat weight of 0.6 g/m².

<Image recording layer coating solution (3)>

[0237]

Polymer microparticle aqueous dispersion (2): 33.0 parts
 IR-absorbing dye (3) (structure below): 1.0 part
 Polyacrylic acid (mass average molar mass 20,000): 0.05 parts
 Disodium 1,5-naphthalenedisulfonate: 0.1 parts
 Methanol: 16.0 parts



IR-absorbing dye (3)

(Production of polymer microparticle aqueous dispersion (2))

[0238] A four-necked flask equipped with a stirrer, a thermometer, a dropping funnel, a nitrogen inlet, and a reflux condenser was charged with 350 mL of distilled water and heated to an internal temperature of 80°C while carrying out removal of oxygen by introducing nitrogen gas. 1.5 g of sodium dodecyl sulfate was added as a dispersant, 0.45 g of ammonium persulfide was further added as an initiator, and 45.0 g of styrene was then added dropwise from a dropping funnel over about 1 hour. After completion of the dropwise addition, the reaction was carried out as it was for a further 5 hours, and unreacted monomer was then removed by steam distillation. Subsequently, the mixture was cooled, the pH was adjusted to 6 using aqueous ammonia, and finally pure water was added to give a non-volatile content of 15 mass%, thus giving polymer microparticle aqueous dispersion (2). The particle size distribution of the polymer microparticles measured in the same manner as for polymer microparticle aqueous dispersion (1) had a maximum value at a particle size of 60 nm.

<Formation of image recording layer 4>

[0239] The support having an intermediate layer was bar-coated with image recording layer coating solution (4) below and oven-dried at 50°C for 60 seconds, thus producing an image recording layer having a dry coat weight of 0.8 g/m².

<Image recording layer coating solution (4)>

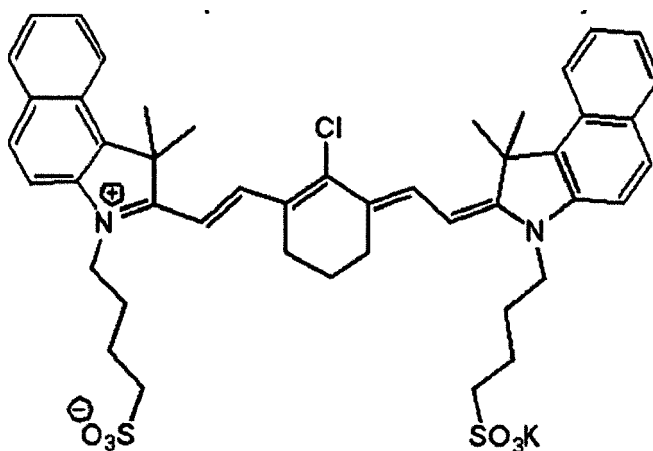
[0240] Thermoplastic microparticle polymer SAN: styrene/acrylonitrile copolymer (molar ratio 50/50), T_g: 99°C, average particle size: 60 nm: 0.7 parts

Polyglycerol compound PG-1: polyglycerol PGL 10 (number of repeating units: 10)

(Daicel): 0.005 parts

Infrared absorbing agent (structure below): 0.12 x 10⁻³ parts

[0241] The pH of the mixture was adjusted to 3.6 by adding water.



<Formation of image recording layer 5>

[0242] Image recording layer coating solution (5) having the formulation below was applied by bar coating and oven-dried at 82°C for 90 seconds, thus forming an image recording layer having a dry coat weight of 1.2 g/m².

<Image recording layer coating solution (5)>

[0243] Binder polymer (structure below): 1.75 parts

HyBridur 580 (urethane-acrylic hybrid polymer dispersion (40%), Air Products And Chemicals): 2.34 parts as solids content

SR399 (dipentaerythritol pentaacrylate available from Sartomer Company Inc. Japan): 2.66 parts

NK-Ester A-DPH (dipentaerythritol hexaacrylate available from Nakamura Chemical Co., Ltd.): 2.66 parts

CD9053 (trifunctional organic acid ester compound available from Sartomer Company Inc. Japan): 0.53 parts

bis-*tert*-Butylphenyliodonium tetraphenylborate: 0.96 parts

Fluor N2900 (surfactant available from Cytnix): 0.11 parts

Pigment 1: 0.73 parts

IR-absorbing agent (2) below: 0.27 parts

Ion-exchanged water: 13.77 parts

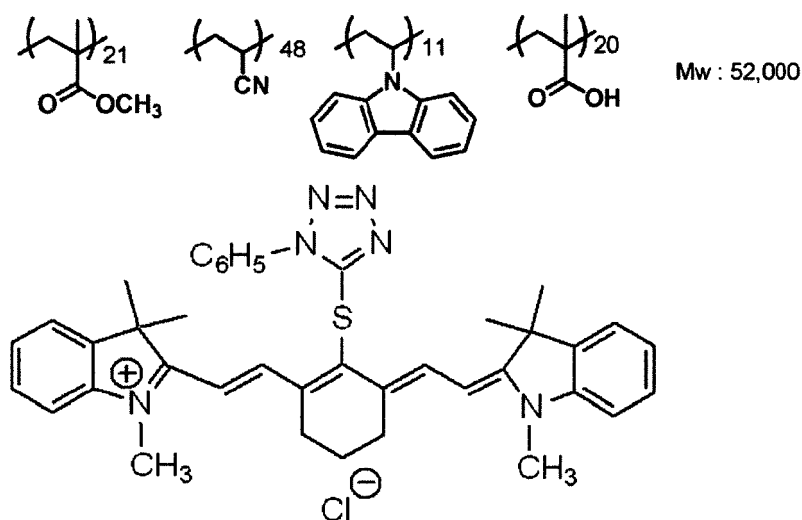
1-Methoxy-2-propanol: 48.18 parts

2-Butyrolactone: 13.77 parts

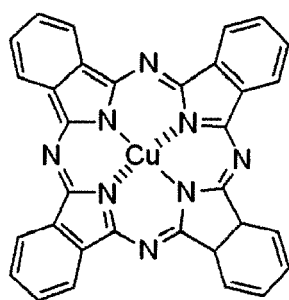
2-Butanone: 1.94 parts

Binder polymer

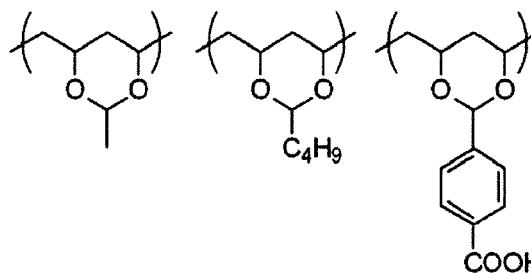
[0244]



IR absorbing agent (2)



Irgalith Blue GLVO
(C.I. Pigment Blue 15:4) 76.9 mass%



Disperbyk 167 15.4 mass%

7.7 mass%

Pigment 1

[0245] DisperByk 167 is a dispersant available from Byk Chemie.

<Formation of protective layer 1>

[0246] Protective layer coating solution 1 having the formulation below was applied using a bar at a dry coat weight of 0.75 g/m² and then dried at 125°C for 70 seconds, thus forming protective layer 1.

<Protective layer coating solution 1>

[0247]

Polyvinyl alcohol (degree of saponification: 98 mole%, degree of polymerization: 500): 40 parts

Polyvinylpyrrolidone (weight-average molecular weight: 50,000): 5 parts

Poly[vinylpyrrolidone/vinyl acetate (1/1)] (weight-average molecular weight: 70,000): 0.5 parts

Surfactant (Emalex 710, Nihon Emulsion Co., Ltd.): 0.5 parts

Water: 950 parts

<Formation of protective layer 2>

[0248] Protective layer coating solution 2 having the formulation below was applied using a bar at a dry coat weight of 0.75 g/m² and then dried at 125°C for 70 seconds, thus forming protective layer 2.

<Protective layer coating solution 2>

Inorganic lamellar compound dispersion (1) below: 1.5 parts

[0249]

6 mass% aqueous solution of sulfonic acid-modified polyvinyl alcohol (CKS50, degree of saponification at least 99 mole%, degree of polymerization 300, The Nippon Synthetic Chemical Industry Co., Ltd.): 0.55 parts

6 mass% aqueous solution of polyvinyl alcohol (PVA-405, degree of saponification 81.5 mole%, degree of polymerization 500, 6 mass% aqueous solution, Kuraray Co., Ltd.): 0.03 parts

1 mass% aqueous solution of surfactant (Emalex 710, Nihon Emulsion Co., Ltd.): 0.86 parts

Ion-exchanged water: 6.0 parts

<Preparation of inorganic lamellar compound dispersion (1)>

[0250] 6.4 g of the synthetic mica Somasif ME-100 (Co-op Chemical Co., Ltd.) was added to 193.6 g of ion-exchanged water, and the mixture was dispersed using a homogenizer to give an average particle size (laser scattering) of 3 μm, thus preparing inorganic lamellar compound dispersion (1). The aspect ratio of the scattered particles thus obtained was at least 100.

[0251] The aluminum support, the type of Component A and the type of Component B added to the intermediate layer,

the image recording layer coating solution, and the protective layer coating solution were combined as shown in Table 1 below, thus producing lithographic printing plate precursors P-1 to P-28 and P'-1 to P'-13.

(Table 1-1)

	Printing plate precursor	Support	Intermediate layer (A)	Intermediate layer (B)	Mass Ratio of (B) relative to (A)	Image recording layer coating solution	Protective layer coating solution
Example 1	P-1	1	A-1	B-1	1	1-1	2
Example 2	P-2	1	A-2	B-1	1	1-1	2
Example 3	P-3	1	A-3	B-1	1	1-1	2
Example 4	P-4	1	A-4	B-1	1	1-1	2
Example 5	P-5	1	A-5	B-1	1	1-1	2
Example 6	P-6	1	A-1	B-1	0.5	1-1	2
Example 7	P-7	1	A-1	B-1	5	1-1	2
Example 8	P-8	1	A-1	B-1	1	1-1	1
Example 9	P-9	1	A-1	B-1	1.44	2	1
Example 10	P-10	2	A-1	B-1	1.44	2	2
Example 11	P-11	2	A-1	B-1	1.91	3	1
Example 12	P-12	2	A-1	B-1	1.91	3	2
Example 13	P-13	1	A-1	B-2	1	1-1	2
Example 14	P-14	1	A-1	B-3	1	1-1	2
Example 15	P-15	1	A-1	B-4	1	1-1	2
Example 16	P-16	1	A-1	B-5	1	1-1	2
Example 17	P-17	1	A-6	B-1	1	1-1	2
Example 18	P-18	1	A-7	B-1	1	1-1	2
Example 19	P-19	3	A-1	B-1	1	4	1
Example 20	P-20	1	A-1	None	1	1-2	1

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(continued)

	Printing plate precursor	Support	Intermediate layer (A)	Intermediate layer (B)	Mass Ratio of (B) relative to (A)	Image recording layer coating solution	Protective layer coating solution
Example 21	P-21	1	A-1	None	1	1-2	2
Example 22	P-22	1	A-1	B-6	1	1-1	2
Example 23	P-23	1	A-1	B-1	1	5	2
Example 24	P-24	1	A-1	B-2	1	5	2
Example 25	P-25	1	A-1	B-3	1	5	2
Example 26	P-26	1	A-1	B-4	1	5	2

(Table 1-2)

	Printing plate precursor	Support	Intermediate layer (A)	Intermediate layer (B)	Mass Ratio of (B) relative to (A)	Image recording layer coating solution	Protective layer coating solution
Example 27	P-27	1	A-1	B-5	1	5	2
Example 28	P-28	1	A-1	B-6	1	5	2
Comparative Example 1	P'-1	1	A-1	None	0	1-1	2
Comparative Example 2	P'-2	1	None	B-1	-	1-1	2
Comparative Example 3	P'-3	1	None	None	0	1-1	2
Comparative Example 4	P'-4	1	A-1	B-1	0.3	1-1	2
Comparative Example 5	P'-5	1	A-1	B-1	7	1-1	2
Comparative Example 6	P'-6	1	R-1	None	0	1-1	2
Comparative Example 7	P'-7	1	R-2	None	0	1-1	2
Comparative Example 8	P'-8	1	R-1	R-2	1	1-1	2
Comparative Example 9	P'-9	1	R-1	R-3	1	1-1	2
Comparative Example 10	P'-10	1	R-1	R-4	1	1-1	2

(continued)

	Printing plate precursor	Support	Intermediate layer (A)	Intermediate layer (B)	Mass Ratio of (B) relative to (A)	Image recording layer coating solution	Protective layer coating solution
Comparative Example 11	P'-11	1	R-1	None	0	5	2
Comparative Example 12	P'-12	1	R-2	None	0	5	2
Comparative Example 13	P'-13	1	R-1	R-2	1	5	2

B-1 poly(ethylene glycol) methyl ether (732621, number-average molecular weight (Mn): 10,000, SIGMA-ALDRICH)

B-2 polyethylene glycol (92897, molecular weight range (Mr): 8,500 to 11,500, SIGMA-ALDRICH)

B-3 polyvinyl alcohol (341584, weight-average molecular weight (Mw): 89,000 to 98,000, SIGMA-ALDRICH)

B-4 polyacrylic acid (181293, Mn: 130,000, SIGMA-ALDRICH)

B-5 polyvinylpyrrolidone (PVP40, average molecular weight 40,000, SIGMA-ALDRICH)

B-6 polyoxyethylene-polyoxypropylene condensation product (Pluronic L44, average molecular weight 2,200, ADE-KA)

(Evaluation of lithographic printing plate precursors (P-1 to P-22, P'-1 to P'-10))

(1) On-machine developability

[0252] The lithographic printing plate precursor thus obtained was exposed using an infrared semiconductor laser-equipped T-6000 III Luxel PLATESETTER manufactured by Fujifilm Corporation under conditions of a drum outer face rotational speed of 1,000rpm, a laser output of 70%, and a resolution of 2,400 dpi. The exposed image contained a solid image and a 50% halftone chart of a 20 μ m dot FM screen.

[0253] The exposed plate precursor thus obtained was mounted on a plate cylinder of a LITHRONE 26 printer manufactured by Komori Corporation without processing. While a dampening roller was reduced in speed by 5% with respect to a plate cylinder, dampening water and ink were supplied by the LITHRONE 26 standard automated print start method using Ecolity-2 (Fujifilm Corporation)/tap water = 2/98 (volume ratio) dampening water and Space Color Fusion G black ink (DIC GRAPHICS CORPORATION) so as to carry out on-machine development, and 500 sheets of Tokubishi Art (76.5 kg) paper were then printed at a printing speed of 10,000 sheets per hour.

[0254] The number of sheets of printing paper required to attain a state in which on-machine development of an unexposed portion of the image recording layer on the printer was completed and there was no ink transfer to a non-image area was measured and defined as the on-machine developability. The results are shown in Table 2.

[0255] With regard to on-machine developability after aging, the same experiment as above was carried out using a lithographic printing plate precursor that had been subjected to forced aging at a temperature of 60°C and a humidity of 70% for 2 days, and the on-machine developability was measured. The results are shown in Table 2.

(2) Printing durability

[0256] After the evaluation of on-machine developability prior to aging described above was carried out, printing was further carried out. As the number of prints was increased, since the image recording layer was gradually abraded, the ink density on the printed material decreased. The number of prints when the value obtained from the percentage halftone area of the FM screen 50% halftone in the printed material measured using a Gretag densitometer decreased by 5% compared with the 100th print was defined as the number of sheets to the end of printing, and the printing durability was thus evaluated. The results are shown in Table 2.

[0257] A lithographic printing plate obtained as above was mounted on a plate cylinder of a printer having an Alcolor dampener.

[0258] The printer was equipped with the above dampening water and as inks a sheetfed ink and an S type Fusion-G process red ink manufactured by DIC GRAPHICS CORPORATION. As printing paper, Geiou Matt C2S was used.

[0259] Subsequently, while reducing the speed of the dampening roller by 12% with respect to the plate cylinder, the printer was operated at 3,000 rotations per hour, 10 rotations (number of rotations of plate cylinder) of water application to the plate face by means of the dampening form roller and 3 rotations (as above) of ink application to the plate face by the ink-application roller were carried out, printing was then started by carrying out impression, and printing was carried out up to 5,000 sheets by increasing the print speed. With regard to printing, the amount of dampening water (minimum amount of water lift) that did not cause staining or decrease the ink density was determined, and printing was carried out with this minimum amount of water lift.

<Evaluation>

[0260] The 5,000th sheet of printed material was evaluated in terms of the items below. The results obtained are shown in Table 2.

(3) Stain resistance evaluation when dampening roller slips

[0261] Staining in a non-image area positioned beneath a solid printed area of a printed material was evaluated using the evaluation criteria below. The evaluation results are shown in Table 2. The closer to 4 the evaluation was, the more suppressed was staining of the non-image area of the printed material caused by operating the slip mechanism of the dampener.

4: not stained at all

3: could not be identified by eye, but when examined using magnifying glass, attachment of spot-shaped ink could be found

2: difficult to identify by eye, but when examined using magnifying glass, there was attachment of spot-shaped ink (some problem in practice)

1: colored red when examined by eye

(Table 2)

	Printing plate	On-machine developability (sheets)	On-machine developability (sheets) after 2 days at 60°C, 70%	Printing durability (10,000 sheets)	Evaluation of stain resistance when there is water supply roller slip
Example 1	P-1	10	20	4.5	4
Example 2	P-2	10	20	4.5	4
Example 3	P-3	10	30	3.0	3
Example 4	P-4	10	30	3.0	3
Example 5	P-5	10	20	3.0	4
Example 6	P-6	10	20	4.0	4
Example 7	P-7	10	15	2.5	4
Example 8	P-8	10	20	4.0	4
Example 9	P-9	10	20	4.0	4
Example 10	P-10	10	20	4.5	4
Example 11	P-11	10	20	4.0	4
Example 12	P-12	10	20	4.5	4
Example 13	P-13	10	20	3.0	4
Example 14	P-14	10	30	3.5	4

(continued)

	Printing plate	On-machine developability (sheets)	On-machine developability (sheets) after 2 days at 60°C, 70%	Printing durability (10,000 sheets)	Evaluation of stain resistance when there is water supply roller slip
Example 15	P-15	10	30	3.0	4
Example 16	P-16	10	30	3.0	4
Example 17	P-17	10	30	3.0	3
Example 18	P-18	10	20	1.5	4
Example 19	P-19	10	20	3.0	4
Example 20	P-20	10	15	4.5	4
Example 21	P-21	10	15	4.5	4
Example 22	P-22	10	25	4.0	4
Comparative Example 1	P'-1	15	≥200	4.5	4
Comparative Example 2	P'-2	18	150	3.0	4
Comparative Example 3	P'-3	20	≥200	4.0	4
Comparative Example 4	P'-4	14	80	3.5	4
Comparative Example 5	P'-5	9	16	1.5	2
Comparative Example 6	P'-6	13	150	3.8	3
Comparative Example 7	P'-7	10	150	3.0	1
Comparative Example 8	P'-8	10	150	3.5	1
Comparative Example 9	P'-9	10	≥200	3.0	1
Comparative Example 10	P'-10	10	70	1.5	1

Evaluation of lithographic printing plate precursors (P-23 to P-28, P'-11 to P'-13)

<Exposure, development, and printing>

[0262] Each lithographic printing plate precursor shown in Table 3 was imagewise exposed with a 50% screen tint in a Trendsetter 3244VX manufactured by Creo (equipped with a water cooled type 40 W infrared semiconductor laser (830 nm)) under conditions of an output of 9 W, a drum outer face rotational speed of 210 rpm, and a resolution 2,400 dpi. Subsequently, processing was carried out using a developer in an automated processor having the structure shown in FIG. 2 by setting the heater so that the plate surface temperature was 100°C for a preheated area and the transport speed so that the immersion time (developing time) in the developer was 20 seconds. As the developer, developer 1 below was used.

<Developer 1>

[0263]

Surfactant-1 (Softazoline LPB-R, Kawaken Fine Chemicals Co., Ltd.) 15 parts
 Surfactant-2 (Softazoline LAO, Kawaken Fine Chemicals Co., Ltd.): 4 parts
 Chelating agent trisodium ethylenediamine succinate (Octaquest E30, InnoSpec Specialty Chemicals): 0.68 parts
 2-Bromo-2-nitropropane-1,3-diol: 0.025 parts
 2-Methyl-4-isothiazolin-3-one: 0.025 parts
 Silicone-based antifoaming agent (TSA739, GE TOSHIBA SILICONES): 0.15 parts
 Sodium gluconate: 1.5 parts
 Sodium carbonate: 1.06 parts
 Sodium bicarbonate: 0.52 parts
 Water: 77.04 parts

(pH: 9.8)

[0264] The lithographic printing plate thus obtained was mounted on an SOR-M printer manufactured by Heidelberg, and printing was carried out using dampening water (EU-3 (etching liquid, Fujifilm Corporation)/water/isopropyl alcohol = 1/89/10 (ratio by volume)) and TRANS-G (N) black ink (Dainippon Ink and Chemicals, Incorporated) at a printing speed of 6,000 sheets per hour.

<Evaluation>

[0265] With regard to each lithographic printing plate precursor, the printing durability and developability were evaluated as described below. The results are shown in the Table below.

<Printing durability>

[0266] As the number of prints was increased, since the image recording layer was gradually abraded, the ink density on the printed material decreased. The number of prints when the value obtained from the percentage halftone area of the FM screen 50% halftone in the printed material measured using a Gretag densitometer decreased by 5% compared with the 100th print was defined as the number of sheets to the end of printing, and the printing durability was thus evaluated. The results are shown in Table 3.

<Developability>

[0267] The above processing was carried out with the transport speed being changed to a variety of speeds, and the cyan density in a non-image area of the lithographic printing plate thus obtained was measured using a Macbeth densitometer. The transport speed at which the cyan density of the non-image area became equal to the cyan density of the aluminum support was determined and defined as the developability. The value obtained for Comparative Example 11 was used as a reference (100), and the relative developability defined as shown below was obtained. The results are shown in Table 3. The larger the relative developability, the higher the developability and the better the performance.

[0268] Relative developability = (transport speed of target lithographic printing plate precursor)/(transport speed of reference lithographic printing plate precursor)

[0269] With regard to developability after aging, the same experiment as above was carried out using a lithographic printing plate precursor that had been subjected to forced aging at a temperature of 60°C and a humidity of 70% for 2 days, and the developability was measured. The results are shown in Table 3.

[0270] Subsequently, while reducing the speed of the dampening roller by 12% with respect to the plate cylinder, the printer was operated at 3,000 rotations per hour, 10 rotations (number of rotations of plate cylinder) of water application to the plate face by means of a dampening form roller and 3 rotations (as above) of ink application to the plate face by the ink-application roller were carried out, printing was then started by carrying out impression, and printing was carried out up to the number described in Table 3 by increasing the print speed. With regard to printing, the amount of dampening water (minimum amount of water lift) that did not cause staining or decrease the ink density was determined, and printing was carried out with this minimum amount of water lift.

<Evaluation>

[0271] The 5,000th sheet of printed material was evaluated in terms of the items below. The results obtained are shown in Table 3.

(Evaluation of stain resistance when dampening roller slips)

[0272] Staining in a non-image area positioned beneath a solid printed area of a printed material was evaluated using the evaluation criteria below. The closer to 4 the evaluation was, the more suppressed was staining of the non-image area of the printed material caused by operating the slip mechanism of the dampener.

4: not stained at all

3: could not be identified by eye, but when examined using magnifying glass, attachment of spot-shaped ink could be found

2: difficult to identify by eye, but when examined using magnifying glass, there was attachment of spot-shaped ink

1: colored red when examined by eye

(Table 3)

	Printing plate	Developer	Develop-ability	Developability after 2 days at 60°C, 70%	Printing durability (10,000 sheets)	Evaluation of stain resistance when there is water supply roller slip
Example 23	P-23	1	150	250	4.5	4
Example 24	P-24	1	150	250	4.5	4
Example 25	P-25	1	100	180	4.5	4
Example 26	P-26	1	100	150	4.5	4
Example 27	P-27	1	100	190	4.5	4
Example 28	P-28	1	150	250	4.5	4
Comparative Example 11	P'-11	1	100	100	3.0	1
Comparative Example 12	P'-12	1	100	95	3.0	4
Comparative Example 13	P'-13	1	100	100	3.0	1

Claims

1. A lithographic printing plate precursor comprising, in order above a support, an intermediate layer and an image recording layer,
the intermediate layer comprising, as Component A, a copolymer comprising constituent repeating unit 1-1 comprising a phosphonic acid structure, a phosphonic acid salt structure, a phosphoric acid ester structure, or a phosphoric acid ester salt structure in a side chain and constituent repeating unit 1-2 comprising a zwitterionic structure in a side chain,
the image recording layer comprising an infrared absorbing agent,
either the intermediate layer or the image recording layer comprising, as Component B, a water-soluble polymer compound that does not have a phosphonic acid structure, a phosphonic acid salt structure, a phosphoric acid ester structure, or a phosphoric acid ester salt structure, and
the mass ratio of Component A and Component B being Component A:Component B = 1:0.5 to 1:5.

2. The lithographic printing plate precursor according to Claim 1, wherein Component B has a weight-average molecular weight of at least 1,000 but no greater than 200,000.
3. The lithographic printing plate precursor according to Claim 1 or 2, wherein Component B comprises as a constituent repeating unit at least one selected from the group consisting of a hydroxy group-containing structure, a carboxy group-containing structure, a pyrrolidone group-containing structure, and an oxyalkylene group-containing structure.
4. The lithographic printing plate precursor according to Claim 3, wherein Component B comprises an oxyalkylene group-containing structure as a constituent repeating unit.
5. The lithographic printing plate precursor according to any one of Claims 1 to 4, wherein Component A further comprises constituent repeating unit 1-3 comprising an ethylenically unsaturated double bond in a side chain.
6. The lithographic printing plate precursor according to any one of Claims 1 to 5, wherein constituent repeating unit 1-2 has a content of at least 50 mass% but no greater than 90 mass% relative to the total mass of Component A.
7. The lithographic printing plate precursor according to any one of Claims 1 to 6, wherein constituent repeating units 1-1 and 1-2 have a total content of at least 70 mass% but no greater than 95 mass% relative to the total mass of Component A.
8. The lithographic printing plate precursor according to any one of Claims 1 to 7, wherein the image recording layer further comprises a polymerizable compound as Component C, a binder as Component D, and a polymerization initiator as Component E.
9. The lithographic printing plate precursor according to any one of Claims 1 to 8, wherein the image recording layer comprises hydrophobic thermoplastic polymer particles.
10. The lithographic printing plate precursor according to any one of Claims 1 to 9, wherein the image recording layer is removable with dampening water composition and/or a printing ink.
11. A process for making a lithographic printing plate comprising
an exposure step of imagewise exposing the lithographic printing plate precursor according to any one of Claims 1 to 10, and
a development step of removing a non-exposed area of the image recording layer of the lithographic printing plate precursor in the presence of a developer having a pH of 2 to 14.
12. A process for making a lithographic printing plate comprising
an exposure step of imagewise exposing the lithographic printing plate precursor according to any one of Claims 1 to 10, and
a development step of removing a non-exposed area of the image recording layer of the lithographic printing plate precursor by supplying a printing ink and dampening water on a printer.

FIG. 1

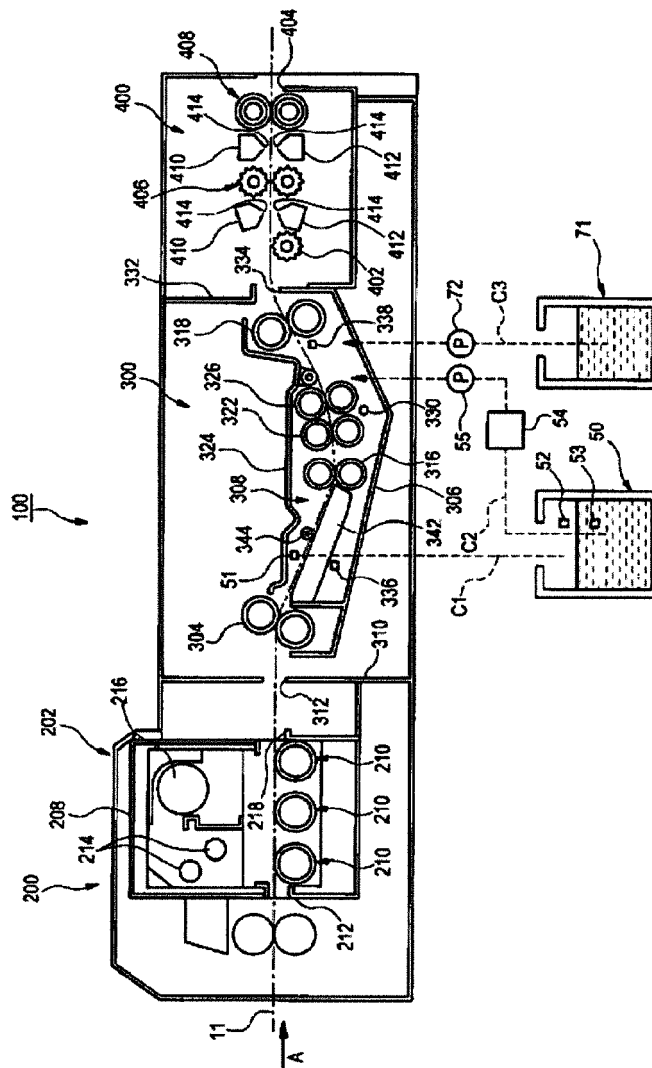
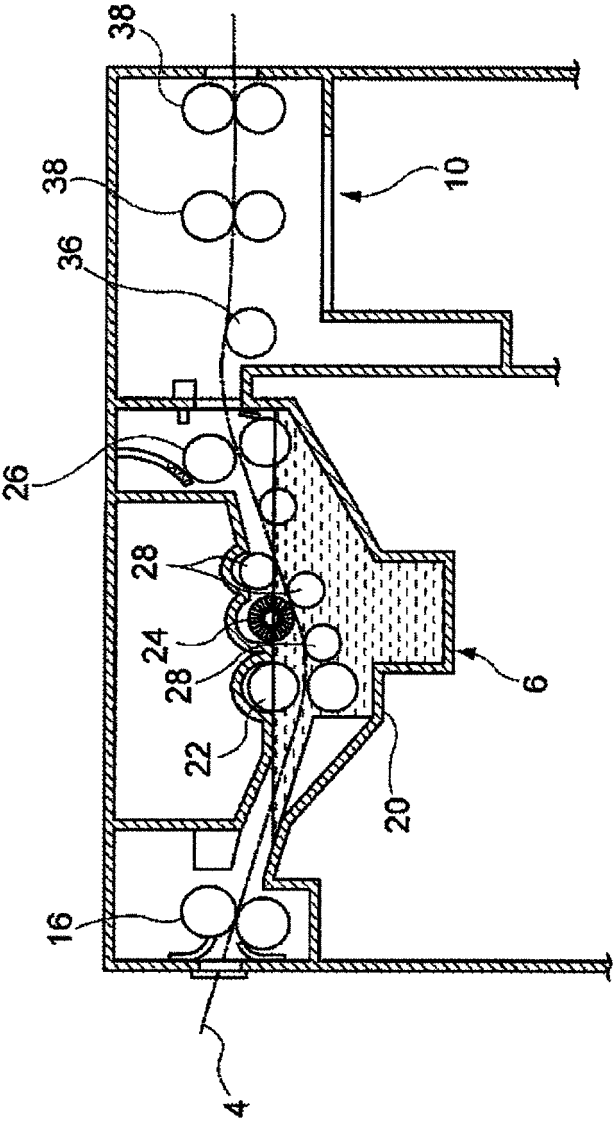


FIG. 2





EUROPEAN SEARCH REPORT

Application Number
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Place of search The Hague		Date of completion of the search 3 February 2016	Examiner Bacon, Alan
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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