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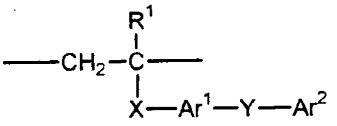
(54) Lithographic printing plate precursor

(57) The present invention provides an infrared-sensitive positive-working photosensitive lithographic printing plate precursor that exhibits both an excellent chemical resistance in the image area and an excellent developability. This positive-working photosensitive lithographic printing plate precursor comprises a support having a hydrophilic surface, and a recording layer disposed on the support and comprising an alkali-soluble or alkali-swellable polymer having a structural unit represented by general formula (1) below, a novolac resin, an infrared absorber, and at least one member selected from aromatic group-containing sulfonium salts and iodonium salts



$$-CH_2-\overset{\overset{\large R^1}{|}}{\underset{\underset{\large X-Ar^1-Y-Ar^2}{|}}{C}}- \qquad (1)$$

wherein R^1 represents a hydrogen atom or methyl group, X represents a single bond, -COO-, or -CONH-, Ar^1 and Ar^2 each represent an optionally substituted aromatic group or heteroaromatic group, and Y represents -SO_2NH- or -$NHSO_2$-.

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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to a photosensitive lithographic printing plate precursor and more specifically relates to a positive-working photosensitive lithographic printing plate precursor. The present invention in particular relates to an infrared laser-adapted photosensitive lithographic printing plate precursor and more particularly relates to an infrared laser-adapted photosensitive lithographic printing plate precursor that makes possible direct platemaking by scanning with infrared laser radiation based on a digital signal from, for example, a computer.

Description of the Related Art

[0002] Lasers have undergone remarkable growth in recent years, and in particular progress has been made in boosting the output and reducing the size of solid-state lasers and semiconductor lasers that emit in the near-infrared to infrared region. As a consequence, these lasers are very useful as photoexposure light sources for direct platemaking from digital data from, for example, a computer.

[0003] A binder resin and an IR dye that generates heat by absorbing light are essential components in an infrared laser-adapted photosensitive lithographic printing plate precursor that can utilize the aforementioned infrared lasers that emit in the infrared region as photoexposure light sources. When such an infrared laser-adapted lithographic printing plate precursor is photoexposed with such an infrared laser, and assuming the presence of a positive-working photosensitive layer, the IR dye in the non-photoexposed region (image area) in such an infrared laser-adapted lithographic printing plate precursor acts through its interaction with the binder resin as a dissolution inhibitor that substantially reduces the solubility of the binder resin. In the photoexposed region (non-image area), on the other hand, the IR dye absorbs light and produces heat, causes the interaction between the IR dye and the binder resin to become weak. As a consequence, during development the photoexposed region (non-image area) is dissolved in alkali developer solution, thus forming the lithographic printing plate.

[0004] Among the various problems that still remain with such infrared laser-adapted lithographic printing plate precursors is the problem of the balance between developability and chemical resistance. Thus, in a positive-working system, where it is the photoexposed regions that undergo development, the resistance to the developer solution and various chemicals deteriorates in the non-photoexposed regions when an increase in the solubility in the developer solution is brought about, and the issue is then how to balance the two.

[0005] There have been several attempts to date to deal with these problems. For example, the use of polyvinyl acetal has been introduced (refer, for example, to US Patent Application Publication No. 2004/0020484). It has also been proposed that the structure of the resin layer of the lithographic printing plate be split into at least two layers and that, for example, a polymer compound comprising a maleimide compound as a constituent component be used in the lower layer (refer, for example, to US Patent Application Publication No. 2004/0067432). The use of a copolymer having a special functional group has also been proposed (refer, for example, to European Patent Application Publication No. 1826001). However, none of these can perform up to a satisfactory level and a better outcome has been desired.

DISCLOSURE OF THE INVENTION

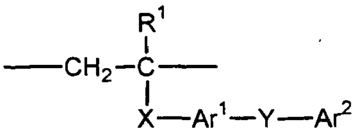
Problem to be solved by the Invention

[0006] An object of the present invention is to provide an infrared-sensitive positive-working photosensitive lithographic printing plate precursor - and particularly an infrared laser-adapted positive-working photosensitive lithographic printing plate precursor - that exhibits both an excellent chemical resistance in the image area and an excellent developability. An additional object of the present invention is to provide an infrared laser-adapted photosensitive lithographic printing plate precursor that exhibits an excellent development latitude and that can also provide a substantial improvement in printing durability when subjected to a high-temperature heat treatment after development.

Means to Solve the Problem

[0007] As a result of intensive investigations, the present inventor discovered that the preceding tasks are accomplished by the infrared laser-adapted photosensitive lithographic printing plate precursor described herebelow.

[0008] That is, the present invention is a positive-working photosensitive lithographic printing plate precursor comprising a support having a hydrophilic surface, and a recording layer disposed on the support and comprising an alkali-soluble or alkali-swellable polymer having a structural unit represented by general formula (1) below, a novolac resin, an infrared absorber, and at least one member selected from aromatic group-containing sulfonium salts and iodonium salts. The recording layer in the positive-working photosensitive lithographic printing plate precursor according to the present invention can be composed of a plurality of layers. Accordingly, the present invention is also directed to a positive-working photosensitive lithographic printing plate precursor comprising a support having a hydrophilic surface, a recording layer disposed on the support and comprising an alkali-soluble or alkali-swellable polymer having a structural unit represented by general formula (1) below, and a recording layer further disposed thereon and comprising a novolac resin, an infrared absorber, and at least one member selected from aromatic group-containing sulfonium salts and iodonium salts.



$$-\mathrm{CH_2}-\overset{\overset{\displaystyle R^1}{|}}{\underset{\underset{\displaystyle X-Ar^1-Y-Ar^2}{|}}{C}}- \qquad (1)$$

[0009] In the formula R^1 represents a hydrogen atom or methyl group.

[0010] X represents a single bond, -COO-, or -CONH-.

[0011] Ar^1 and Ar^2 each represent an optionally substituted aromatic group or an optionally substituted heteroaromatic group in which one or two of the carbon atoms participating in the aromaticity is or are replaced by the N atom, O atom, or S atom.

[0012] Y represents $-SO_2NH-$ or $-NHSO_2-$.

Effect of the Invention

[0013] The present invention can provide an infrared laser-adapted photosensitive lithographic printing plate precursor that exhibits both an excellent chemical resistance in the image area and an excellent developability. This infrared laser-adapted photosensitive lithographic printing plate precursor also exhibits an excellent development latitude and can also provide a substantial improvement in printing durability when subjected to a high-temperature heat treatment after development.

[0014] The mechanism that enables the structure of the present invention to balance an excellent chemical resistance in the image areas with an excellent developability in platemaking is believed to be as follows. The special polymer according to the present invention, the novolac resin, and the aromatic group-containing sulfonium salt or iodonium salt interact because each contains a conjugated system, such as aromaticity, and this makes it possible to raise the chemical resistance of the image areas and to increase their ability to resist the developer solution above that exhibited by the individual compounds. In addition, the sulfonium salt or iodonium salt is decomposed by heat and its interaction is thereby extinguished, which is believed to raise the developability of the photoexposed areas as a whole and to thereby result in an increase in the development latitude.

Mode for Carrying Out the Invention

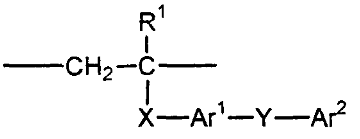
[0015] The structural elements of the lithographic printing plate precursor of the present invention will be consecutively described herebelow.

The recording layer

[0016] The recording layer of the lithographic printing plate precursor of the present invention may be executed as a single layer (monolayer) or as a plurality of layers (multilayer). The recording layer is preferably executed as two layers when it is executed as a plurality of layers. The alkali-soluble or alkali-swellable polymer having a structural unit represented by general formula (1) is also referred to in the following as the special polymer.

<The special polymer>

[0017] The special polymer is a polymer that contains the structural unit represented by the following general formula (1). More particularly, the special polymer is a polymer that contains the structural unit represented by the following general formula (1) as a copolymerized component.



$$-CH_2-\overset{\displaystyle R^1}{\underset{\displaystyle X-Ar^1-Y-Ar^2}{C}}- \qquad (1)$$

[0018] R^1 in general formula (1) represents a hydrogen atom or methyl group. X represents a single bond, -COO-, or -CONH- wherein -COO- and -CONH- are preferred. Ar^1 and Ar^2 each represent an optionally substituted aromatic group or an optionally substituted heteroaromatic group in which one or two of the carbon atoms participating in the aromaticity is or are replaced by the N atom, O atom, or S atom. Ar^1 is preferably a five- or six-membered ring and more preferably is a six-membered ring. Ar^2 is preferably a five- or six-membered ring. Preferably at least one of Ar^1 and Ar^2 is a heteroaromatic ring.

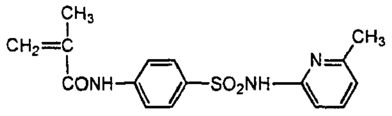
[0019] A specific example of this structural unit is a structural unit in which Ar^1 represents an aromatic ring and Ar^2 is a heteroaromatic ring in which one or two of the carbon atoms participating in the aromaticity is or are replaced by the N atom, O atom, or S atom.

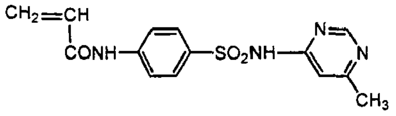
[0020] C_{1-4} alkyl and C_{1-4} alkoxyl are preferred substituents on the aromatic group or heteroaromatic group Ar^1 and Ar^2.

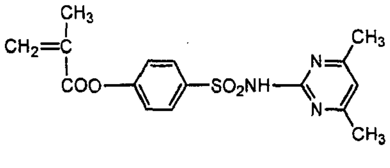
[0021] The aromatic groups and heteroaromatic groups represented by Ar^1 and Ar^2 may be selected from hydrocarbon aromatic rings, for example, benzene, naphthalene, anthracene, and so forth, and from heteroaromatic rings, for example, furan, thiophene, pyrrole, imidazole, 1,2,3-triazole, 1,2,4-triazole, tetrazole, oxazole, isoxazole, thiazole, isothiazole, thiadiazole, oxadiazole, pyridine, pyridazine, pyrimidine, pyrazine, 1,3,5-triazine, 1,2,4-triazine, 1,2,3-triazine, and so forth.

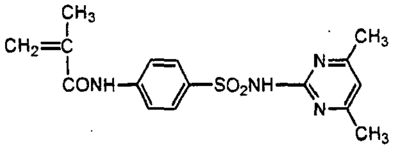
[0022] A condensed ring configuration, provided by the condensation of a plurality of the previously described rings, may also be employed, for example, benzofuran, benzothiophene, indole, indazole, benzoxazole, quinoline, quinazoline, benzimidazole, and benzotriazole.

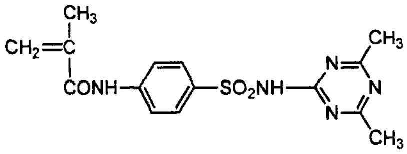
[0023] Examples of monomers that can form the structural unit represented by general formula (1) are shown below, but the present invention is not limited to these.

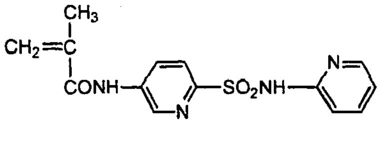


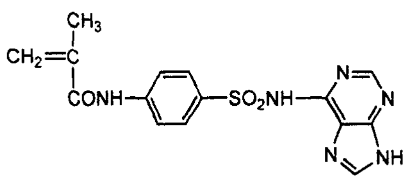


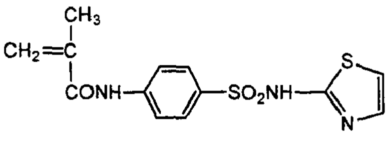


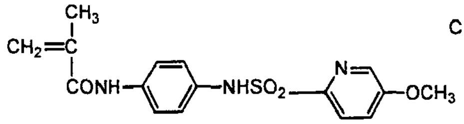


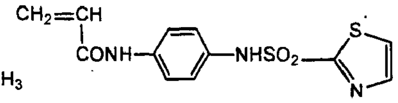


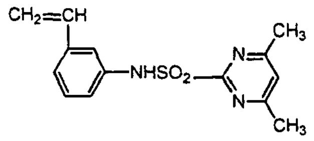


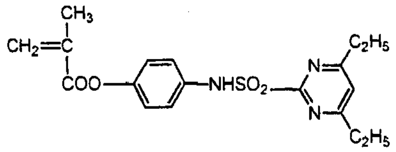












[0024] The special polymer is an alkali-soluble or alkali-swellable polymer that contains the structural unit with general formula (1) as a copolymerization component. The special polymer may contain only one species of structural unit with general formula (1) or may contain two or more species.

[0025] The content of the structural unit with general formula (1) in the special polymer is suitably 20 to 90 mol%, preferably 30 to 80 mol%, and more preferably 30 to 70 mol%.

[0026] The other structural units in the special polymer can be exemplified by hydrophobic monomers that have a substituent such as alkyl or aryl in the side chain structure of the monomer, and by hydrophilic monomers that have, for example, an acidic group, amide group, hydroxy group, or ethylene oxide group in the side chain structure of the monomer, and are selected as appropriate from such monomers in accordance with the particular goal. The selection of the monomer that copolymerizes with the monomer that provides the aforementioned structural unit with general formula (1) must be made within a range that does not impair the alkali solubility of the special polymer.

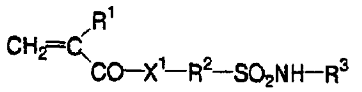
[0027] Polymerizable compounds that contain an acidic group are examples of the other comonomer in the special polymer used by the present invention in addition to the monomer that provides the structural unit with general formula (1). This acidic group can be exemplified by the following (1) to (6).

(1) the phenol group (-Ar-OH)
(2) the sulfonamide group ($-SO_2NH-R$)
(3) substituted sulfonamide-type acid groups (referred to below as "active imide groups") ($-SO_2NHCOR$, $-SO(_2NHSO_2R$, $-CONHSO_2R$)
(4) the carboxylic acid group ($-CO_2H$)
(5) the sulfonic acid group ($-SO_3H$)
(6) the phosphoric acid group ($-OPO_3H_2$)

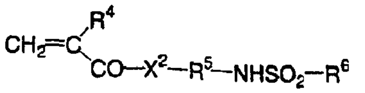
[0028] Ar in the preceding (1) to (6) represents an optionally substituted divalent aryl linking group, while R represents an optionally substituted hydrocarbyl group.

[0029] The following are examples of acidic group-containing polymerizable compounds selected from (1) to (6).

(1) Compounds containing the phenol group in side chain position, for example, phenol group-containing acrylamide, methacrylamide, acrylate esters, and methacrylate esters; also, hydroxystyrene.
(2) Sulfonamide group-containing compounds, for example, compounds that contain in the molecule at least one polymerizable unsaturated group and at least one sulfonamide group in which at least one hydrogen atom is bonded to the nitrogen atom. Preferred thereamong are low molecular weight compounds that contain in the molecule the acryloyl group, allyl group, or vinyloxy group as well as a unsubstituted or monosubstituted aminosulfonyl group or substituted sulfonylimino group; these compounds can be exemplified by the compounds represented by the following formulas (i) to (v).

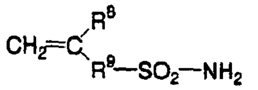


$$CH_2{=}C(R^1)-CO-X^1-R^2-SO_2NH-R^3 \qquad (\text{i})$$



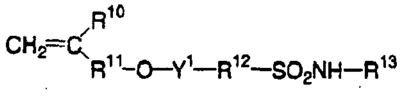
$$CH_2=\overset{R^4}{C}-CO-X^2-R^5-NHSO_2-R^6$$

(ii)



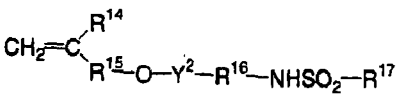
$$CH_2=\overset{R^8}{C}-R^9-SO_2-NH_2$$

(iii)



$$CH_2=\overset{R^{10}}{C}-R^{11}-O-Y^1-R^{12}-SO_2NH-R^{13}$$

(iv)



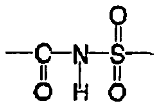
$$CH_2=\overset{R^{14}}{C}-R^{15}-O-Y^2-R^{16}-NHSO_2-R^{17}$$

(v)

(In the formulas, X^1 and X^2 each independently represent -O- or $-NR^7$. R^1 and R^4 each independently represent the hydrogen atom or $-CH_3$. R^2, R^5, R^9, R^{12}, and R^{16} each independently represent C_{1-12} alkylene, cycloalkylene, arylene, or aralkylene. R^3, R^7, and R^{13} each independently represent the hydrogen atom or C_{1-12} alkyl, cycloalkyl, aryl, or aralkyl. R^6 and R^{17} each independently represent C_{1-12} alkyl, cycloalkyl, aryl, or aralkyl. R^8, R^{10}, and R^{14} each independently represent the hydrogen atom or $-CH_3$. R^{11} and R^{15} each independently represent a single bond or C_{1-12} alkylene, cycloalkylene, arylene, or aralkylene. Y^1 and Y^2 each independently represent a single bond or CO. The aforementioned alkylene, cycloalkylene, arylene, aralkylene, alkyl, cycloalkyl, aryl, and aralkyl may be substituted, and alkyl is the preferred substituent.)

[0030] Among the compounds represented by formulas (i) to (v), m-aminosulfonylphenyl methacrylate, N-(p-aminosulfonylphenyl)methacrylamide, N-(p-aminosulfonylphenyl)acrylamide, and so forth, are particularly suitable for use with the lithographic printing plate precursor of the present invention.

(3) The active imide group-containing compounds can be exemplified by compounds that contain in the molecule at least one polymerizable unsaturated group and at least one active imide group as represented by the structural formula given below.



$$-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-$$

Specific examples that can be suitably used are N-(p-toluenesulfonyl)methacrylamide, N-(p-toluenesulfonyl)acrylamide, and so forth.

(4) Carboxyl acid group-containing compounds can be exemplified by compounds that contain in the molecule at least one polymerizable unsaturated group and at least one carboxyl acid group, wherein acrylic acid, methacrylic acid, maleic acid, and itaconic acid are particularly suitable for use.

(5) The sulfonic acid group-containing compounds can be exemplified by compounds that contain in the molecule at least one polymerizable unsaturated group and at least one sulfonic acid group.

(6) Phosphoric acid group-containing polymer compounds can be exemplified by compounds that contain in the molecule at least one polymerizable unsaturated group and at least one phosphoric acid group.

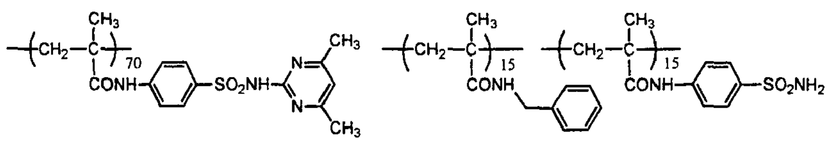
[0031] Other examples in addition to the preceding are polymerizable unsaturated compounds that contain an acidic group from (1) to (6) in side chain position and that have a urea bond as the linking group. Among polymerizable compounds that contain an acidic group according to (1) to (6), compounds that contain an acidic group according to (1), (2), or (4) are preferred, and compounds containing an acidic group according to (2) that contain the sulfonamide in terminal position are particularly preferred.

[0032] Any polymerizable monomer may also be copolymerized in the special polymer. There are no particular limitations on this other constituent component as long as it is monomer capable of copolymerizing with the monomer component already described above, and this other constituent component can be exemplified by (meth)acrylate esters, N-substituted (meth)acrylamides, acrylonitrile, styrenic compounds, maleimides, (meth)acrylamide, glycidyl (meth)acrylate, N-substituted maleimides, (meth)acrylate esters that have a polyoxyethylene chain, 2-hydroxyethyl (meth)acrylate, vinylpyridine, N-vinylcaprolactam, and N-vinylpyrrolidine.

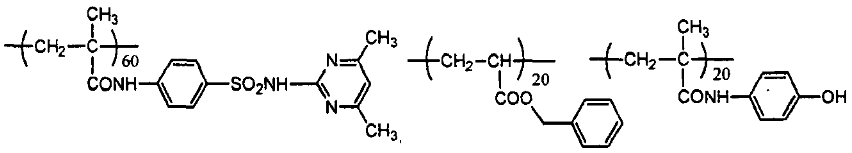
[0033] The weight-average molecular weight (Mw) of the special polymer is 5,000 to 1,000,000 and preferably is 7,000 to 500,000 and most preferably is in the range from 10,000 to 300,000. This molecular weight can be measured by gel permeation chromatography using N-methylpyrrolidone as the developing solvent. Monodisperse polystyrene can be used here as the molecular weight standard material.

[0034] Structural examples of special polymers that are preferably used by the present invention are shown below as combinations of their structural units. The numerical values are molar ratios.

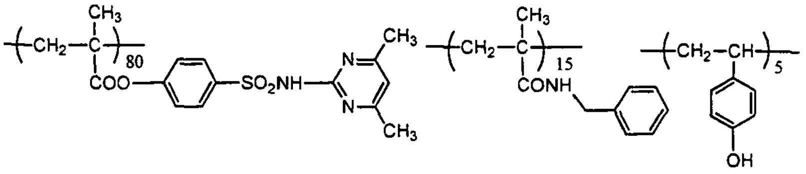
(1) weight-average molecular weight = 50,000



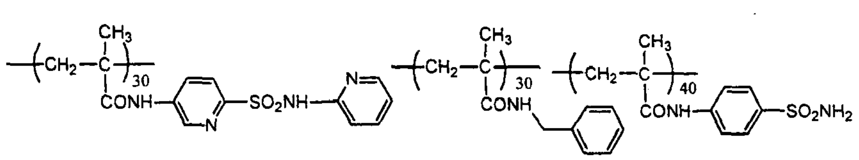
(2) weight-average molecular weight = 100,000



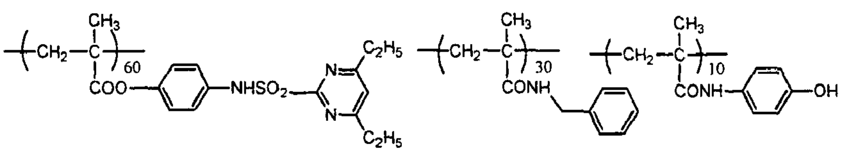
(3) weight-average molecular weight = 70,000



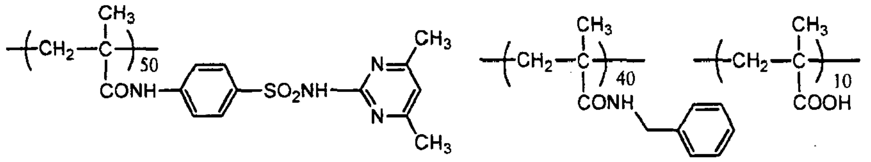
(4) weight-average molecular weight = 80,000



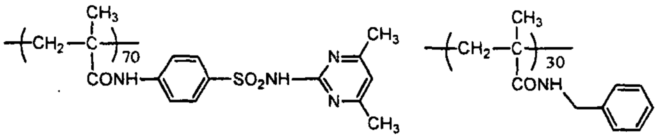
(5) weight-average molecular weight = 60,000



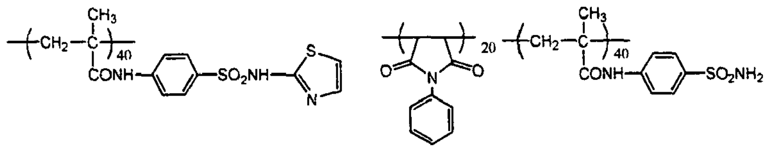
(6) weight-average molecular weight = 30,000



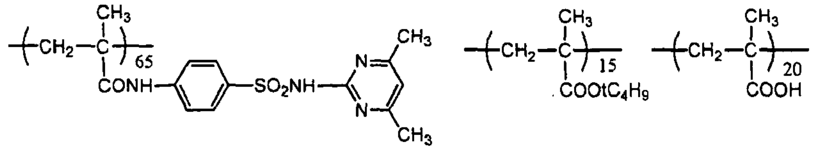
(7) weight-average molecular weight = 150,000



(8) weight-average molecular weight = 20,000



(9) weight-average molecular weight = 200,000



[0035] The content of the special polymer in the recording layer, expressed with reference to the total solids in the recording layer, is preferably 5 mass% to 95 mass% and more preferably is 10 mass% to 90 mass%.

[0036] In those instances in which the recording layer in the lithographic printing plate precursor of the present invention is a recording layer with a multilayer structure, the special polymer is preferably contained in the lower recording layer that is located adjacent to the support, and the content of the special polymer in this lower recording layer in this embodiment, expressed with reference to the total solids in the lower recording layer, is preferably 40 mass% to 95 mass% and is more preferably 50 mass% to 95 mass%. The novolac resin is preferably not present in the lower layer.

<The novolac resin>

[0037] In a broad sense, a novolac resin is a resin obtained by the reaction of a phenol with formaldehyde. The phenol can be exemplified by phenol, o-cresol, m-cresol, p-cresol, 2,3-xylenol, 2,5-xylenol, 3,5-xylenol, resorcinol, pyrogallol, and bisphenol. These may be used individually or a mixture of a plurality of these may be used. Among the preceding, the use is preferred of phenol, o-cresol, m-cresol, p-cresol, and 2,3-xylenol, either individually or as the mixture of a plurality of these.

[0038] The novolac resin used by the present invention preferably has a weight-average molecular weight of 500 to 20,000 and a number-average molecular weight of 200 to 10,000, as measured by GPC.

[0039] Specific examples are given below.

(i) novolac resin comprising phenol/m-cresol/p-cresol = 50/30/20 (molar ratio), with a weight-average molecular weight of 8,000

(ii) novolac resin comprising m-cresol/p-cresol = 60/40 (molar ratio), with a weight-average molecular weight of 6,000

(iii) novolac resin comprising 2,3-xylenol/m-cresol/p-cresol = 10/40/50 (molar ratio), with a weight-average molecular weight of 5,000

(iv) novolac resin comprising 2,5-xylenol/phenol/m-cresol = 20/40/40 (molar ratio), with a weight-average molecular weight of 8,000

[0040] For the case of a monolayer recording layer, the content of the novolac resin in the recording layer is preferably 3 mass% to 50 mass% and more preferably 5 mass% to 40 mass%, in each case expressed with reference to the total solids in the recording layer.

[0041] For the case of a recording layer that is a recording layer with a multilayer structure, the novolac resin is preferably contained in the upper recording layer that is positioned in proximity to the surface (side exposed to light), and the content of the novolac resin in this upper recording layer in this embodiment, expressed with reference to the total solids in the upper recording layer, is preferably 10 mass% to 95 mass% and is more preferably 20 mass% to 90 mass%.

<The infrared absorber>

[0042] The positive-working recording layer in the present invention contains an infrared absorber, which is a constituent component that has a photothermal conversion capacity. This infrared absorber has the capacity to convert absorbed infrared radiation into heat, and as a result laser scanning causes, for example, an extinction of interactions, degradation of a development inhibitor, the generation of acid, and so forth, which brings about a significant increase in the solubility in the developer solution. In addition, in some cases this infrared absorber itself may also interact with the alkali-soluble resin and thereby restrain the alkali solubility.

[0043] When the recording layer has a multilayer structure, the infrared absorber may be present in the upper recording layer and/or the lower recording layer, but viewed from the standpoint of sensitivity it is preferably contained in the upper recording layer.

[0044] In addition, when contained in the lower recording layer, and when the special polymer is used in combination with an alkali-soluble polymer that is incompatible with the special polymer, the infrared absorber is contained in the other alkali-soluble polymer that forms a dispersed phase. The infrared absorber then becomes localized in the dispersed phase, and this is thought to increase the interaction-extinguishing capacity and to improve the degradability of an acid generator when an acid generator is present.

[0045] The infrared absorber used in the present invention is a dye or pigment that effectively absorbs infrared radiation at a wavelength from 760 nm to 1200 nm. It is preferably a dye or pigment that has an absorption maximum at a wavelength from 760 nm to 1200 nm.

[0046] Infrared absorbers that can be suitably used in the lithographic printing plate precursor of the present invention are described herebelow.

[0047] Usable dyes can be exemplified by commercially available dyes and by known dyes described in the literature, for example, Dye Handbook (edited by The Society of Synthetic Organic Chemistry, Japan, 1970). Specific examples are dyes such as azo dyes, metal complex salt azo dyes, pyrazolone azo dyes, naphthoquinone dyes, anthraquinone dyes, phthalocyanine dyes, carbonium dyes, quinoneimine dyes, methine dyes, cyanine dyes, squarylium dyes, pyrylium salts, metal thiolate complexes, and so forth.

[0048] Preferred dyes can be exemplified by the cyanine dyes described in Japanese Patent Application Publication Nos. S58-125246, S59-84356, S59-202829, and S60-78787; the methine dyes described in Japanese Patent Application Publication Nos. S58-173696, S58-181690, and S58-194595; the naphthoquinone dyes described in Japanese Patent Application Publication Nos. S58-112793, S58-224793, S59-48187, S59-73996, S60-52940, and S60-63744; the squarylium dyes described in Japanese Patent Application Publication No. S58-112792; and the cyanine dyes described in British Patent No. 434,875.

[0049] The use is also preferred of the near infrared absorbers/sensitizers described in US Patent No. 5,156,938; the substituted arylbenzo(thio)pyrylium salts described in US Patent No. 3,881,924; the trimethine thiapyrylium salts described in Japanese Patent Application Publication No. S57-142645 (US Patent No. 4,327,169); the pyrylium compounds described in Japanese Patent Application Publication Nos. S58-181051, S58-220143, S59-41363, S59-84248, S59-84249, S59-146063, and S59-146061; the cyanine dyes described in Japanese Patent Application Publication No. S59-216146; the pentamethine thiopyrylium salts described in US Patent No. 4,283,475; and the pyrylium compounds disclosed in Japanese Examined Patent Publication Nos. H5-13514 and H5-19702.

[0050] Other preferred dye examples are the near infrared-absorbing dyes represented by formulas (I) and (II) in US Patent No. 4,756,993.

[0051] The following are particularly preferred among the dyes cited above: cyanine dyes, squarylium dyes, pyrylium dyes, and nickel thiolate complexes.

[0052] The pigment used in the present invention may be a commercially available pigment or a pigment as described in the Colour Index (C. I.) database, The Handbook of Modern Pigments (Edited by the Japan Association of Pigment Technology, 1977), Modern Pigment Applications Technology (CMC, 1986), or Printing Ink Technology (CMC, 1984).

[0053] With regard to type, the pigment can be, for example, a black pigment, yellow pigment, orange pigment, brown pigment, red pigment, purple pigment, blue pigment, green pigment, fluorescent pigment, metal powder pigment, or polymer-bonded dye. Specific examples are insoluble azo pigments, azo lake pigments, condensed azo pigments, chelate azo pigments, phthalocyanine-based pigments, anthraquinone-based pigments, perylene-based pigments, perinone-based pigments, thioindigo-based pigments, quinacridone-based pigments, dioxazine-based pigments, isoindolinone-based pigments, quinophthalone-based pigments, dyed lake pigments, azine pigments, nitroso pigments, nitro pigments, natural pigments, fluorescent pigments, inorganic pigments, carbon black, and so forth.

[0054] These pigments may be used without a surface treatment or may be used after a surface treatment. Examples of the surface treatment method include coating the surface with a resin or wax, attaching a surfactant, and bonding a reactive material (e.g., silane coupling agent, epoxy compound, polyisocyanate, and so forth) to the surface of the pigment. These surface treatment methods are described in Properties and Applications of Metal Soaps (Saiwai Shobo), Printing Ink Technology (CMC, 1984), and Modern Pigment Applications Technology (CMC, 1986).

[0055] Viewed from the perspective of the stability of the coating fluid used for the recording layer and the uniformity of the recording layer that is formed, the particle diameter of the pigment is preferably from 0.01 μm to 10 μm, more preferably from 0.05 μm to 1 μm, and particularly preferably from 0.1 μm to 1 μm.

[0056] The known dispersion technologies used, for example, for ink production or toner production, can be used as the method of dispersing the pigment. The dispersing apparatus can be exemplified by ultrasonic dispersers, sand mills, attritors, pearl mills, super mills, ball mills, impellers, dispersers, KD mills, colloid mills, dynatrons, three-roll mills, and pressure kneaders. The details are described in Modern Pigment Applications Technology (CMC, 1986).

[0057] Since the lithographic printing plate precursor of the present invention has a positive-working recording layer, the use is preferred of an infrared absorber that produces a positive action (dissolution of non-photoexposed areas in the alkali developer solution is inhibited, while this dissolution-inhibiting action is extinguished in the photoexposed regions) by interaction with a binder polymer that has a specific functional group; from this standpoint an infrared absorber having an onium salt structure is particularly preferred. In specific terms, cyanine dyes and pyrylium salts are particularly preferred among the previously described infrared absorbers. The details for these cyanine dyes and pyrylium salts are as previously provided.

[0058] The anionic infrared absorber described in Japanese Patent Application Publication No. H11-338131 can also be suitably used. This anionic infrared absorber indicates that the dye's parent nucleus that substantially absorbs the infrared radiation has an anionic structure and lacks a cationic structure.

[0059] Examples are (a-1) anionic metal complexes and (a-2) anionic phthalocyanines.

[0060] Here, the (a-1) anionic metal complex denotes an anionic metal complex in which the central metal and ligands of the complex moiety that substantially absorbs the light form an anion as a whole.

[0061] The (a-2) anionic phthalocyanine denotes a phthalocyanine in which an anionic group, e.g., a sulfonic acid group, carboxylic acid group, phosphonic acid group, and so forth, is bonded as a substituent on the phthalocyanine skeleton with the formation of an anion as a whole.

[0062] An example is the anionic infrared absorber represented by $[\text{Ga-M-Gb}]_m X^{m+}$ (Ga- represents an anionic substituent; Gb represents a neutral substituent; X^{m+} represents a cation with a valence of 1 to m, including the proton; and m is an integer from 1 to 6) described in [0014] to [0105] in Japanese Patent Application Publication No. H11-338131.

[0063] The infrared absorber is preferably a dye, and the infrared absorbers having an onium salt structure described in paragraph numbers [0018] to [0034] of Japanese Patent Application Publication No. H11-291652 are preferred examples.

[0064] An infrared absorber that exhibits a dissolution-inhibiting behavior, e.g., the previously described cyanine dyes, pyrylium salts, anionic dyes, and so forth, can also be used in the recording layer in combination with other dyes or pigments with the goal of obtaining additional improvements in the sensitivity and development latitude.

[0065] In the case of a monolayer recording layer, the infrared absorber content in the present invention is preferably 2 mass% to 20 mass% and more preferably is 3 mass% to 15 mass%, in each case expressed with reference to the total solids in the monolayer recording layer. In the case of a recording layer with a multilayer structure, and based on a consideration of the image formability and the inhibition of scumming in non-image areas, the addition of 0.01 to 50 mass%, expressed with reference to the total solids in the particular recording layer, in the lower recording layer and other recording layer(s) is preferred, while 0.1 to 20 mass% is preferred and 0.5 to 15 mass% is more preferred.

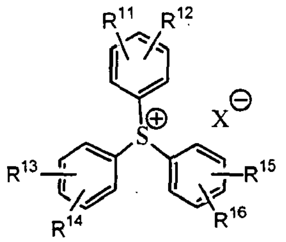
[0066] When the infrared absorber is present in a recording layer in which a dispersed phase is formed due to the combined use of two or more types of polymers, the infrared absorber may be present in either the matrix phase or dispersed phase or may be present in both phases. When desired components, e.g., initiator, infrared absorber, and so forth, are present in a latex constituting a dispersed phase as described above, these may be added with the starting materials when the latex particles are formed or may be introduced after latex formation.

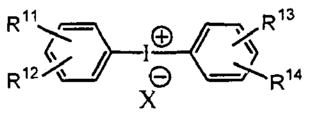
[0067] As an example of the method of introduction after latex formation, the desired components that are to be introduced into the latex dispersed in an aqueous system, e.g., initiator, dye, crosslinker, and so forth, are dissolved in an organic solvent and this is added to the dispersion medium.

<The aromatic group-containing sulfonium salt/iodonium salt>

[0068] When the recording layer has a multilayer structure, the aromatic group-containing sulfonium salt and/or iodonium salt may be contained in the upper recording layer and/or the lower recording, but is preferably contained in the upper recording layer from the standpoint of the sensitivity.

[0069] The compounds described in, for example, Japanese Patent Application Publication Nos. 2001-133969 and 2002-268217, can be used as the aromatic group-containing sulfonium salt and iodonium salt. The aromatic group-containing sulfonium salt and iodonium salt can be respectively exemplified by compounds with the structures given by the following general formulas.

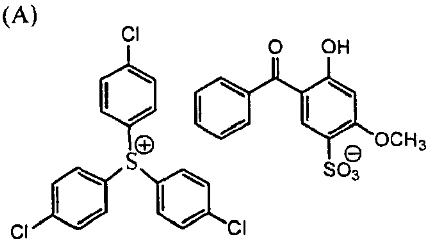




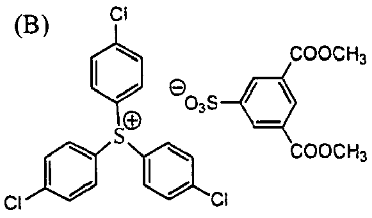
[0070] R^{11} to R^{16} in the preceding formulas each represent a freely selectable substituent and preferably represent the hydrogen atom, a halogen atom, C_{1-6} straight-chain alkyl, C_{1-6} branched alkyl, or C_{1-6} alkoxy. They particularly preferably represent the hydrogen atom, C_{1-3} alkyl, C_{1-3} alkoxyl, the chlorine atom, or the bromine atom. X represents an organic or inorganic counteranion. Sulfonium salts are particularly preferred.

[0071] Specific examples of the aromatic group-containing sulfonium salt and iodonium salt are shown below.

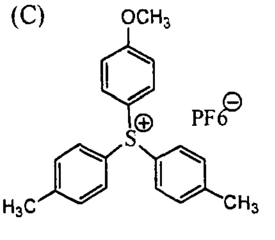
(A)



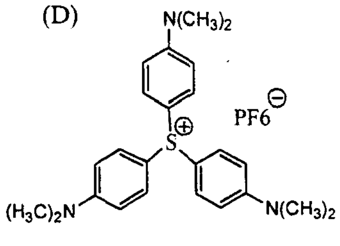
(B)



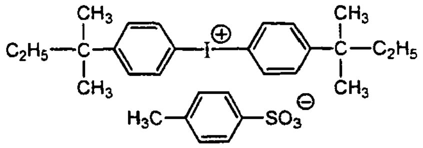
(C)



(D)



(E)



[0072] In the case of a monolayer recording layer, at least one member selected from these aromatic group-containing sulfonium salts and iodonium salts is suitably present in this invention at from 0.01 to 50 mass%, expressed with reference to the total solids in the monolayer recording layer, from the standpoint of image formability and preventing scumming in the non-image areas, while 0.1 to 25 mass% is preferred and 0.5 to 20 mass% is more preferred. In the case of a recording layer with a multilayer structure, 0.01 to 50 mass%, expressed with reference to the total solids in the particular layer, is suitable while 0.1 to 25 mass% is preferred and 0.5 to 20 mass% is more preferred.

[0073] In addition to the previously described special polymer and novolac resin, other known alkali-soluble polymers can be used on a purpose-adapted basis in the recording layer of the lithographic printing plate precursor of the present invention. Other polymer compounds may also be incorporated. The polymer compounds described in [0027] to [0044] of Japanese Patent Application Publication No. 2008-64959 are examples of polymer compounds that may be incorporated.

[0074] A fluoropolymer is preferably added to each recording layer for the purpose of improving the development resistance of the image regions. The fluoropolymers used in image-recording layers are exemplified by the copolymers of fluorine-containing monomers as described in Japanese Patent Application Publication Nos. H11-288093 and 2000-187318.

[0075] Preferred specific examples of fluoropolymers are the P-1 to P-13 acrylic-type fluoropolymers described in Japanese Patent Application Publication No. H11-288093 and fluoropolymers obtained by the copolymerization of a freely selected acrylic monomer with fluorine-containing acrylic monomers A-1 to A-33 as described in Japanese Patent Application Publication No. 2000-187318.

[0076] With regard to the molecular weight of these fluoropolymers, the weight-average molecular weight is preferably at least 2,000 and the number-average molecular weight is preferably at least 1,000. More preferably, the weight-average molecular weight is 5,000 to 300,000 and the number-average molecular weight is 2,000 to 250,000.

[0077] In addition, commercial fluorosurfactants that are compounds having the preferred molecular weight cited above can also be used as the fluoropolymer. Specific examples in this regard are MEGAFACE F-171, F-173, F-176, F-183, F-184, F-780, and F-781 (all trade names) from DIC Corporation.

[0078] A single one of these fluoropolymers may be used or two or more may be used in combination. A suitable quantity of addition is at least 1.4 mass% with reference to the solids in the image-recording layer. A preferred quantity of addition is 1.4 to 5.0 mass%. At less than 1.4 mass%, a satisfactory improvement in the development latitude of the image-recording layer - which is the goal of fluoropolymer addition - may not be obtained. The improvement in the development latitude does not increase when the addition exceeds 5.0 mass%, while the fluoropolymer-induced resistance to solubilization by the surface of the image-recording layer continues to increase, creating the risk of a lower sensitivity.

[0079] An underlying recording layer or other recording layer may also optionally contain a dissolution inhibitor in the present invention; this is a substance that is thermally degradable and that when undegraded has the ability to substantially lower the solubility of aqueous alkali-soluble polymer compounds. Examples are diazonium salts, ammonium salts, phosphonium salts, o-quinonediazide compounds, aromatic sulfone compounds, and aromatic sulfonate ester compounds. The addition of a dissolution inhibitor can improve the ability of image areas to resist dissolution in the developer solution and can also make it possible to use an infrared absorber that does not interact with alkali-soluble resins.

[0080] Suitable examples are the diazonium salts described by S. I. Schlesinger, Photogr. Sci. Eng., 18, 387 (1974), T. S. Bal et al., Polymer, 21, 423 (1980), and Japanese Patent Application Publication No. H5-158230; the ammonium salts described in US Patent Nos. 4,069,055 and 4,069,056 and in the Specification of Japanese Patent Application Publication No. H3-140140; and the phosphonium salts described in D. C. Necker et al., Macromolecules, 17, 2468 (1984), C. S. Wen et al., "The Proc. Conf. Rad. Curing ASIA", p. 478, Tokyo, October (1988), and US Patent Nos. 4,069,055 and 4,069,056.

[0081] Diazonium salts are particularly preferred for the dissolution inhibitors that can be used by the present invention. The diazonium salts described in Japanese Patent Application Publication No. H5-158230 are particularly preferred.

[0082] The counterion for the onium salt can be exemplified by tetrafluoroboric acid, hexafluorophosphoric acid, triisopropylnaphthalenesulfonic acid, 5-nitro-o-toluenesulfonic acid, 5-sulfosalicylic acid, 2,5-dimethylbenzenesulfonic acid, 2,4,6-trimethylbenzenesulfonic acid, 2-nitrobenzenesulfonic acid, 3-chlorobenzenesulfonic acid, 3-bromobenzenesulfonic acid, 2-fluorocaprylnaphthalenesulfonic acid, dodecylbenzenesulfonic acid, 1-naphthol-5-sulfonic acid, 2-methoxy-4-hydroxy-5-benzoylbenzenesulfonic acid, and para-toluenesulfonic acid. Particularly suitable among the preceding are hexafluorophosphoric acid and alkyl aromatic sulfonic acids such as triisopropylnaphthalenesulfonic acid and 2,5-dimethylbenzenesulfonic acid.

[0083] Suitable quinonediazides can be exemplified by o-quinonediazide compounds. The o-quinonediazide compounds used in the present invention are compounds that have at least one o-quinonediazide group and that upon thermal degradation undergo an increase in alkali solubility, and compounds with various structures can be used. Thus, the o-quinonediazides assist the solubility of the photosensitive material system through the following two effects: upon thermal degradation, the solubility-inhibiting action on the binder is abolished and the o-quinonediazide itself is converted into an alkali-soluble substance.

[0084] For example, the compounds described in J. Kosar (author), "Light-Sensitive Systems", pages 339 to 352 (John Wiley & Sons, Inc.) can be used as the o-quinonediazide compounds employed in the present invention, wherein the o-quinonediazide sulfonate esters or sulfonamides provided by reaction with various aromatic polyhydroxy compounds or aromatic amino compounds are particularly suitable. Also suitable for use are the esters between a pyrogallol acetone resin and benzoquinone-(1,2)-diazide sulfonyl chloride or naphthoquinone-(1,2)-diazide-5-sulfonyl chloride, as described in Japanese Examined Patent Publication No. S43-28403, and the esters between a phenol-formaldehyde resin and benzoquinone-(1,2)-diazide sulfonyl chloride or naphthoquinone-(1,2)-diazide-5-sulfonyl chloride, as described in US Patent Nos. 3,046,120 and 3,188,210.

[0085] Similarly, the esters between a phenol-formaldehyde resin or cresolformaldehyde resin and naphthoquinone-(1,2)-diazide-4-sulfonyl chloride and the esters between a pyrogallol acetone resin and naphthoquinone-(1,2)-diazide-4-sulfonyl chloride are also suitable for use. Other useful o-quinonediazide compounds are reported in and known from a large number of patents. Examples in this regard are the o-quinonediazide compounds described in the Specifications of Japanese Patent Application Publication Nos. S47-5303, S48-63802, S48-63803, S48-96575, S49-38701, and S48-13354; Japanese Examined Patent Publication Nos. S41-11222, S45-9610, and S49-17481; US Patent Nos. 2,797,213, 3,454,400, 3,544,323, 3,573,917, 3,674,495, and 3,785,825; British Patent Nos. 1,227,602, 1,251,345, 1,267,005, 1,329,888, and 1,330,932; and German Patent No. 854,890.

[0086] The quantity of addition of the o-quinonediazide compounds, expressed with reference to the total solids in the particular recording layer, is preferably in the range from 1 to 50 mass%, more preferably in the range from 5 to 30 mass%, and particularly preferably in the range from 10 to 30 mass%. A single one of these compounds can be used or a mixture of a plurality of these compounds may be used.

[0087] The quantity of addition of additives other than the o-quinonediazide compounds is preferably 1 to 50 mass%, more preferably 5 to 30 mass%, and particularly preferably 10 to 30 mass%.

[0088] A polymer having as a polymerization component a (meth)acrylate monomer that contains two or three C_{3-20} perfluoroalkyl groups in the molecule, as described in the Specification of Japanese Patent Application Publication No. 2000-87318, can also be incorporated with the goals of strengthening image discrimination and strengthening the capacity to resist surface marring.

[0089] Cyclic acid anhydrides, phenols, and organic acids can also be used with the goal of obtaining additional improvements in the sensitivity. For example, the phthalic acid anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, 3,6-endooxy-Δ4-tetrahydrophthalic anhydride, trichlorophthalic anhydride, maleic anhydride, chloromaleic anhydride, α-phenylmaleic anhydride, succinic anhydride, pyromellitic anhydride, and so forth, described in US Patent Specification No. 4,115,128 can be used as the cyclic acid anhydride. The phenols can be exemplified by bisphenol A, p-nitrophenol, p-ethoxyphenol, 2,4,4'-trihydroxybenzophenone, 2,3,4,-trihydroxybenzophenone, 4-hydroxybenzophenone, 4,4',4"-trihydroxytriphenylmethane, and 4,4',3",4"-tetrahydroxy-3,5,3',5'-tetramethyltriphenylmethane. The organic acid can be the sulfonic acids, sulfinic acids, alkyl sulfates, phosphonic acids, phosphate esters, and carboxylic acids described in, for example, Japanese Patent Application Publication Nos. S60-88942 and H2-96755, and can be specifically exemplified by p-toluenesulfonic acid, dodecylbenzenesulfonic acid, p-toluenesulfinic acid, ethyl sulfate, phenylphosphonic acid, phenylphosphinic acid, phenyl phosphate, diphenyl phosphate, benzoic acid, isophthalic acid, adipic acid, p-toluyl acid, 3,4-methoxybenzoic acid, phthalic acid, terephthalic acid, 4-cyclohexene-1,2-dicarboxylic acid, erucic acid, lauric acid, n-undecanoic acid, ascorbic acid, and so forth. The proportion of the aforementioned cyclic acid anhydrides, phenols, and organic acids in the recording layer solids is preferably 0.05 to 20 mass%, more preferably 0.1 to 5 mass%, and particularly preferably 0.1 to 10 mass%.

[0090] For example, a dye that exhibits substantial absorption in the visible light region can be added to the recording layer in the present invention as an image colorant. Specific examples are Oil Yellow #101, Oil Yellow #103, Oil Pink #312, Oil Green BG, Oil Blue BOS, Oil Blue #603, Oil Black BY, Oil Black BS, and Oil Black T-505 (the preceding are products of Orient Chemical Industries Co., Ltd.); Victoria Pure Blue, Crystal Violet (CI 42555), Methyl Violet (CI 42535), Ethyl Violet, Rhodamine B (CI 145170B), Malachite Green (CI 42000), Methylene Blue (CI 52015), Eisen Spiron Blue C-RH (Hodogaya Chemical Co., Ltd.) and so forth; and the dyes described in Japanese Patent Application Publication

No. S62-293247.

[0091] The addition of these dyes provides a sharp delineation between the image areas and non-image areas after image formation, and for this reason the addition of these dyes is preferred. The quantity of addition is preferably in the range of 0.01 to 10 mass% with reference to the total solids in the recording layer.

[0092] In order to broaden the processing stability with respect to the developing conditions, the recording layer of the present invention can also incorporate a nonionic surfactant as described in Japanese Patent Application Publication Nos. S62-251740 and H3-208514; an amphoteric surfactant as described in Japanese Patent Application Publication Nos. S59-121044 and H4-13149; a siloxane-type compound as described in EP 950,517; or a fluoromonomer-containing copolymer as described in Japanese Patent Application Publication No. H11-288093.

[0093] The nonionic surfactant can be specifically exemplified by sorbitan tristearate, sorbitan monopalmitate, sorbitan trioleate, monoglyceryl stearate, polyoxyethylene nonylphenyl ether, and so forth. The amphoteric surfactant can be specifically exemplified by alkyldi(aminoethyl)glycine, alkylpolyaminoethylglycine hydrochloride, 2-alkyl-N-carboxyethyl-N-hydroxyethylimidazolinium betaine, and N-tetradecyl-N,N-betaine types (for example, Amogen K (trade name) from Dai-ichi Kogyo Seiyaku Co., Ltd.). Block copolymers of dimethylsiloxane and polyalkylene oxide are preferred for the siloxane-type compound, and specific examples are polyalkylene oxide-modified silicones such as DBE-224, DBE-621, DBE-712, DBP-732, and DBP-534 from the Chisso Corporation and Tego Glide 100 from the German firm Tego.

[0094] The proportion of the nonionic surfactant and amphoteric surfactant in the recording layer is preferably 0.05 to 15 mass% and is more preferably 0.1 to 5 mass%.

[0095] In order to obtain a visible image immediately after the photoexposure-induced heating, the lithographic printing plate precursor of the present invention can incorporate a dye or pigment as an image colorant or can incorporate a print-out agent. A typical example of the print-out agent is the combination of a salt-forming organic dye with a compound that releases acid in response to the photoexposure-induced heating (a photoacid releasing agent).

[0096] Specific examples are the salt-forming organic dye/o-naphthoquinonediazide-4-sulfonyl halide combinations described in Japanese Patent Application Publication Nos. S50-36,209 and S53-8128 and the salt-forming organic dye/trihalomethyl compound combinations described in Japanese Patent Application Publication Nos. S53-36223, S54-74728, S60-3626, S61-143748, S61-151644, and S63-58440. These trihalomethyl compounds include oxazole-type compounds and triazine-type compounds, and both types exhibit an excellent timewise stability and provide a sharp print-out image. Other photoacid releasing agents can be exemplified by the various o-naphthoquinonediazide compounds described in Japanese Patent Application Publication No. S55-62444; the 2-trihalomethyl-5-aryl-1,3,4-oxacliazole compounds described in Japanese Patent Application Publication No. S55-77742; and diazonium salts.

The coating solvent and coating method

[0097] In the case of a monolayer structure, the lithographic printing plate precursor of the present invention can be produced and formed by preparing a coating fluid in which the components, such as polymer compounds, infrared absorber, and so forth, are dissolved in a solvent and applying this coating fluid on a support that has a hydrophilic surface.

[0098] In the case of a multilayer structure, a coating fluid is prepared in which the components in the previously described lower layer, such as polymer compounds, infrared absorber, and so forth, are dissolved in a solvent; a coating fluid is similarly prepared for the previously described upper layer; and lower and upper layers are then produced and formed on a support having a hydrophilic surface by consecutive application of the lower layer coating fluid and the upper layer coating fluid on the support.

[0099] A protective layer, intermediate resin layer, backcoat layer, and so forth, vide infra, may also be similarly formed depending on the particular goal.

[0100] The solvent used here can be exemplified by ethylene dichloride, cyclohexanone, methyl ethyl ketone, methanol, ethanol, propanol, ethylene glycol monomethyl ether, 1-methoxy-2-propanol, 2-methoxyethyl acetate, 1-methoxy-2-propyl acetate, dimethoxyethane, methyl lactate, ethyl lactate, N,N-dimethylacetamide, N,N-dimethylformamide, tetramethylurea, N-methylpyrrolidone, dimethyl sulfoxide, sulfolane, γ-butyrolactone, toluene, and so forth, but the solvent is not limited to these examples. A single one of these solvents or a mixture of these solvents may be used.

[0101] The concentration of the components (total solids including additives) in the coating fluid is preferably 1 to 50 mass%.

[0102] In the case of a monolayer, the quantity of applied solids on the support after coating and drying is preferably 0.5 to 3.0 g/m^2 and is particularly preferably 0.8 to 2.0 g/m^2.

[0103] In the case of a multilayer structure, 0.05 to 2.0 g/m^2 is preferred for the upper layer and 0.3 to 5.0 g/m^2 is preferred for the lower layer, while 0.1 to 1.0 g/m^2 is more preferred for the upper layer and 0.5 to 3.0 g/m^2 is more preferred for the lower layer. The ratio between the quantity of application for the upper layer and the quantity of application for the lower layer (upper layer/lower layer) is preferably 0.05 to 1 and more preferably is 0.1 to 0.8.

[0104] Various methods can be used to apply the individual coating fluids, for example, bar coater application, spin coating, spray coating, curtain coating, dip coating, air knife coating, blade coating, roll coating, and so forth. The apparent sensitivity increases as the quantity of application declines, but the film properties of the photosensitive film also decline with a declining quantity of application.

The support

[0105] A support that has a hydrophilic surface is employed as the support used for the lithographic printing plate precursor of the present invention.

[0106] The support is a dimensionally stable sheet or plate that has satisfactory properties in terms of, for example, the required strength and flexibility, but is not otherwise particularly limited. The support can be exemplified by paper, plastic-laminated paper (the plastic can be exemplified by polyethylene, polypropylene, polystyrene, and so forth), metal plate or sheet (e.g., aluminum, zinc, copper, and so forth), plastic film (e.g., cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose butyrate, cellulose acetate butyrate, cellulose nitrate, polyethylene terephthalate, polyethylene, polystyrene, polypropylene, polycarbonate, polyvinyl acetal, and so forth), and paper or plastic film on which any of the aforementioned metals has been laminated or vapor-deposited.

[0107] A polyester film or an aluminum plate is preferred for the support used for the lithographic printing plate precursor. Aluminum plate is particularly preferred therebetween for its excellent dimensional stability and relatively low cost.

[0108] The aluminum plate is preferably a pure aluminum plate, an alloy plate containing aluminum as its main component along with trace amounts of heteroelements, or a plastic film on which aluminum has been laminated or vapor deposited.

[0109] Heteroelements that may be present in the aluminum alloy can be exemplified by silicon, iron, manganese, copper, magnesium, chromium, zinc, bismuth, nickel, titanium, and so forth. The heteroelement content in the alloy is preferably no more than 10 mass%.

[0110] Although pure aluminum is a particularly suitable aluminum for the present invention, the production of absolutely pure aluminum is problematic from the standpoint of refining technology, and the aluminum plate may therefore contain trace amounts of heteroelements.

[0111] The aluminum plate that can be used in the present invention is not limited with regard to composition, and any aluminum plate of material in the public domain can be used as appropriate. The thickness of the aluminum plate used in the present invention is preferably from about 0.1 mm to 0.6 mm and more preferably from about 0.12 mm to 0.4 mm.

[0112] Prior to its use, the aluminum plate is subjected to a roughening treatment and its surface is subjected to a hydrophilicizing treatment. Prior to executing the roughening treatment, the aluminum plate may as desired be submitted to a degreasing treatment with, for example, surfactant, organic solvent, aqueous alkali solution, and so forth, in order to remove rolling oil from the surface.

[0113] Various methods can be employed to roughen the surface of the aluminum plate, for example, mechanical surface roughening, electrochemical dissolution roughening of the surface, and selective chemical dissolution of the surface.

[0114] Known methods, such as ball grinding, brush grinding, blast grinding, and buff grinding, can be used for the mechanical method. Electrochemical roughening can be carried out, for example, using alternating current or direct current in a hydrochloric acid or nitric acid electrolytic bath. Also usable is a method that combines both as described in Japanese Patent Application Publication No. S54-63902.

[0115] Among the preceding, at least a step of roughening in a hydrochloric acid electrolyte is preferably employed.

[0116] The surface-roughened aluminum plate may optionally be subjected to an alkali etching treatment and neutralization treatment and then as desired an anodic oxidation treatment in order to improve the abrasion resistance and water retentivity of the surface.

[0117] The various electrolytes that can bring about the formation of a porous oxide film can be used as the electrolyte employed for anodic oxidation of the aluminum plate, and sulfuric acid, phosphoric acid, oxalic acid, chromic acid, or a mixed acid of the preceding is typically used.

[0118] The concentration of these electrolytes is determined as appropriate in accordance with the type of electrolyte.

[0119] The anodic oxidation conditions vary as a function of the electrolyte used and thus cannot be unconditionally specified; however, the following are generally suitable: electrolyte concentration = 1 to 80 mass% solution, bath temperature = 5 to 70°C, current density = 5 to 60 A/dm^2, voltage = 1 to 100 V, electrolysis time = 10 seconds to 5 minutes.

[0120] When the quantity of anodic oxidation film formation is smaller than 1.0 g/m^2, the printing durability is unsatisfactory and the non-image areas of the lithographic printing plate precursor are susceptible to damage, which causes ink uptake in damaged regions - or so-called "scratch scumming" - to readily occur during printing.

[0121] As necessary, the aluminum surface may be subjected to a hydrophilization treatment after the anodic oxidation treatment has been performed. The hydrophilization treatment used by the present invention can employ, for example, the alkali metal silicate method (for example, an aqueous sodium silicate solution) described in US Patent Nos. 2,714,066, 3,181,461, 3,280,734, and 3,902,734. In this method, the support is treated, by immersion or electrolysis, in an aqueous solution of sodium silicate. Examples of other methods are treatment with potassium fluozirconate as described in Japanese Examined Patent Publication No. S36-22063 and treatment with polyvinylphosphonic acid as described in US Patent Nos. 3,276,868, 4,153,461, and 4,689,272.

The undercoat layer

[0122] The lithographic printing plate precursor of the present invention has a lower layer disposed as described above on a support, but may as necessary be provided with an undercoat layer between the lower layer and the support.

[0123] When this undercoat layer is present, the undercoat layer, residing between the support and the lower layer, functions as a heat insulating layer, and as a consequence the heat generated by photoexposure with the infrared laser is prevented from diffusing to the support and is thereby efficiently utilized, accruing the advantage of supporting an increase in the sensitivity.

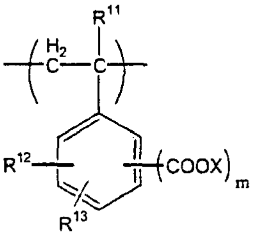
[0124] In addition, even when this undercoat layer is present, the sensitivity to the infrared laser is well maintained since the lower layer according to the present invention is positioned on the photoexposed side or in the vicinity thereof.

[0125] In the non-photoexposed areas, it is thought that the lower layer, which will not be permeable to the alkali developer solution, itself functions as a protective layer for the undercoat layer, and due to this an excellent development stability is obtained, an image is formed that exhibits an excellent discrimination, and timewise stability is also secured.

[0126] In the photoexposed regions, the components of the lower layer, in which the dissolution-inhibiting behavior had been extinguished, rapidly dissolve or disperse in the developer solution. In addition, since the undercoat layer itself, which is present adjacent to the support, comprises an alkali-soluble polymer, it exhibits an excellent solubility in the developer solution. For example, even when a reduced-activity developer solution is employed, the undercoat layer is thought to be useful because dissolution occurs rapidly without the generation of a residual film and it also contributes to an improved developability.

[0127] Various organic compounds can be used for the undercoat layer components, for example, a selection from carboxymethyl cellulose; dextrin; gum arabic; organophosphonic acids such as amino group-containing phosphonic acids (e.g., 2-aminoethylphosphonic acid and so forth) and optionally substituted phenylphosphonic acid, naphthylphosphonic acid, alkylphosphonic acid, glycerophosphonic acid, methylenediphosphonic acid, ethylenediphosphonic acid, and so forth; organophosphoric acids such as optionally substituted phenylphosphoric acid, naphthylphosphoric acid, alkylphosphoric acid, glycerophosphoric acid, and so forth; organophosphinic acids such as optionally substituted phenylphosphinic acid, naphthylphosphinic acid, alkylphosphinic acid, glycerophosphinic acid, and so forth; amino acids such as glycine, β-alanine, and so forth; and the hydrochlorides of hydroxy group-containing amines, e.g., the hydrochloride of triethanolamine and so forth. Mixtures of two or more may also be employed.

[0128] An undercoat layer is also preferred that contains at least one compound selected from the group consisting of organic polymer compounds that have a structural unit with the following formula.



[0129] In the formula, R^{11} represents the hydrogen atom, a halogen atom, or an alkyl group and R^{12} and R^{13} each independently represent the hydrogen atom, the hydroxyl group, a halogen atom, alkyl, substituted alkyl, aryl, substituted aryl, $-OR^{14}$, $-COOR^{15}$, $-CONHR^{16}$, $-COR^{17}$, or -CN. R^{12} and R^{13} may also be bonded with the formation of a ring. R^{14} to R^{17} each independently represent alkyl or aryl and X represents the hydrogen atom, a metal atom, or $NR^{18}R^{19}R^{20}R^{21}$ wherein R^{18} to R^{21} each independently represent the hydrogen atom, alkyl, substituted alkyl, aryl, or substituted aryl or R^{18} and R^{19} may be bonded with the formation of a ring. m represents an integer from 1 to 3.

[0130] The polymer compound described in Japanese Patent Application Publication No. 2000-241962, which contains an acid group-containing structural unit and an onium group-containing structural unit, is also a suitable component for the undercoat layer in the present invention.

[0131] A specific example is a copolymer from an acid group-containing monomer and an onium group-containing monomer.

[0132] Acid groups having an acid dissociation constant (pKa) of at least 7 are preferred for the acid group. -COOH,

$-SO_3H$, $-OSO_3H$, $-PO_3H_2$, $-OPO_3H_2$, $-CONHSO_2-$, and $-SO_2NHSO_2-$ are preferred and -COOH is particularly preferred.

[0133] The acid group-containing monomer can be specifically exemplified by acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, itaconic acid, maleic acid, maleic anhydride, and styrene containing an acid group as described above.

[0134] An onium group containing an atom from Group V or VI of the Periodic Table is preferred for the onium group, while an onium group containing a nitrogen atom, phosphorus atom, or sulfur atom is more preferred and a nitrogen atom-containing onium group is particularly preferred. Onium group-containing monomers can be specifically exemplified by methacrylates and methacrylamides that have the ammonium group in side chain position and by styrene having an onium group-containing substituent, e.g., a substituent containing an onium group such as the quaternary ammonium group.

[0135] Compounds as described in Japanese Patent Application Publication No. 2000-108538 and Japanese Patent Application Nos. 2002-257484 and 2003-78699 can also be used as necessary.

[0136] The undercoat layer can be put in place by methods such as the following. Thus, the previously described organic compounds can be dissolved in water or an organic solvent (e.g., methanol, ethanol, methyl ethyl ketone, and so forth) or a mixed solvent therefrom and this solution can be coated and dried on an aluminum plate to provide the undercoat layer; or, the previously described organic compounds can be dissolved in water or an organic solvent (e.g., methanol, ethanol, methyl ethyl ketone, and so forth) or a mixed solvent therefrom and an aluminum plate can be dipped in this solution in order to adsorb the organic compounds and can then be rinsed (for example, with water) and dried to provide the undercoat layer.

[0137] In the former method, the solution, which is to have an organic compound concentration of 0.005 to 10 mass%, can be applied by various procedures.

[0138] In the latter method, the concentration of the solution is 0.01 to 20 mass% and preferably 0.05 to 5 mass%; the dipping temperature is 20 to 90°C and preferably 25 to 50°C; and the dipping time is 0.1 second to 20 minutes and preferably 2 seconds to 1 minute. The solution used here may also be adjusted into the pH range of 1 to 12 using a base such as ammonia, triethanolamine, potassium hydroxide, and so forth, or an acid such as hydrochloric acid, phosphoric acid, and so forth.

[0139] A yellow dye can also be added to the undercoat layer in order to improve the tone reproducibility of the image-recording material.

[0140] The coating rate by the undercoat layer is suitably 2 to 200 mg/m^2 and preferably is 5 to 100 mg/m^2. A satisfactory printing durability performance is not obtained when this coating rate is less than 2 mg/m^2, and the same is also true for a coating rate in excess of 200 mg/m^2.

Photoexposure

[0141] Image formation with the lithographic printing plate precursor of the present invention is performed by the application of heat. In specific terms, image formation is performed by photoexposure with a high-output solid-state infrared laser that emits infrared radiation at a wavelength of 700 to 1200 nm, for example, a semiconductor laser, YAG laser, and so forth.

[0142] Also usable are infrared lamp photoexposure, high-illuminance flash photoexposure using, for example, a xenon discharge lamp, and direct imagewise recording using a thermal recording head.

[0143] The infrared laser preferably has an output of at least 100 mW, and a multibeam laser device is preferably used in order to shorten the photoexposure time. In addition, the photoexposure time per pixel is preferably not more than 20 microseconds and the energy irradiated onto the lithographic printing plate precursor is preferably from 10 to 500 mJ/cm^2.

Development

[0144] The lithographic printing plate precursor is preferably developed in the present invention with an aqueous alkali solution that has a pH of at least 12 and that substantially does not contain organic solvent. This "substantially does not contain organic solvent" means that the aqueous alkali solution does not contain organic solvent sufficient to produce problems with regard to environmental hygiene, safety, workability, and so forth. However, the developer solution in the present invention may contain not more than 0.5 mass% organic solvent, wherein not more than 0.3 mass% is preferred and the complete absence of organic solvent is most preferred. While the pH is to be at least 12.0, 12.0 to 14.0 is more preferred.

[0145] The developer solution (referred to below as the developer solution inclusive of replenishing solution) can be the heretofore known aqueous alkali solutions. Examples are inorganic alkali salts such as sodium silicate, potassium silicate, tertiary sodium phosphate, tertiary potassium phosphate, tertiary ammonium phosphate, secondary sodium phosphate, secondary potassium phosphate, secondary ammonium phosphate, sodium carbonate, potassium carbonate, ammonium carbonate, sodium bicarbonate, potassium bicarbonate, ammonium bicarbonate, sodium borate, potassium borate, ammonium borate, sodium hydroxide, ammonium hydroxide, potassium hydroxide, lithium hydroxide, and so forth. Other examples are organic bases such as monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, triisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethyleneimine, ethylenediamine, pyridine, and so forth. A single one of these aqueous alkali solutions may be used or two or more may be used in combination.

[0146] Among these aqueous alkali solutions, aqueous solutions, known as "silicate developer solutions", having a pH of at least 12 and containing alkali silicate as the base or containing a mixture of a silicon compound in base as the alkali silicate, are one type of developer solution that enables the appearance of the effects according to the present invention. So-called "nonsilicate developer solutions", which do not contain alkali silicate, but rather contain a base and a nonreducing sugar (an organic compound that has a buffering action), are another and more preferred type of developer solution that enables the appearance of the effects according to the present invention.

[0147] Considering the aforementioned silicate developer solutions, the developability with an aqueous alkali metal silicate solution can be adjusted using the concentration and the ratio between the silicon dioxide SiO_2 and alkali metal oxide M_2O (generally given by the $[SiO_2]/[M_2O]$ molar ratio) that are the components of the silicate. Suitable for use in this regard are the aqueous sodium silicate solution disclosed in Japanese Patent Application Publication No. S54-62004, which has an SiO_2/Na_2O molar ratio of 1.0 to 1.5 (i.e., $[SiO_2]/[Na_2O]$ = 1.0 to 1.5) and an SiO_2 content of 1 to 4 mass%, and the aqueous alkali metal silicate solution described in Japanese Examined Patent Publication No. S57-7427, wherein $[SiO_2]/[M]$ is 0.5 to 0.75 (i.e., $[SiO_2]/[M_2O]$ = 1.0 to 1.5), the SiO_2 concentration is 1 to 4 mass%, and the developer solution contains at least 20% potassium with reference to the total gram-atoms of alkali metal present therein.

[0148] With regard to the so-called "nonsilicate development solutions", which contain nonreducing sugar and base but lack alkali silicate, these preferably contain a nonreducing sugar that has a buffering capacity that can inhibit pH variations.

[0149] Nonreducing sugars are sugars that lack a free aldehyde or ketone group and therefore do not exhibit a reducing activity and may be classified into trehalose-type oligosaccharides, in which the reducing groups are bonded to each other; glycosides in which a nonreducing sugar is bonded to the reducing group of a sugar; and sugar alcohols, which are sugars that have been reduced by hydrogenation. The present invention can use any of these. The nonreducing sugar described in Japanese Patent Application Publication No. H8-305039 can be suitably used in the present invention.

[0150] The trehalose-type oligosaccharides can be exemplified by saccharose, trehalose, and so forth. The aforementioned glycosides can be exemplified by alkylglycosides, phenol glycosides, mustard oil glycosides, and so forth. The sugar alcohols can be exemplified by D,L-arabitol, ribitol, xylitol, D,L-sorbitol, D,L-mannitol, D,L-iditol, D,L-talitol, dulcitol, allo-dulcitol, and so forth. Other suitable examples are maltitol, obtained by the hydrogenation of the disaccharide maltose, and the reduced products (reduced starch syrup) obtained by the hydrogenation of oligosaccharides. Among these nonreducing sugars, trehalose-type oligosaccharides and sugar alcohols are preferred, while D-sorbitol, saccharose, and reduced starch syrup are preferred thereamong because they are inexpensive and have a buffering activity in a suitable pH range.

[0151] A single one of these nonreducing sugars may be used or two or more may be used in combination.

[0152] The nonreducing sugar content in the nonsilicate developer solution is preferably 0.1 to 30 mass% and more preferably is 1 to 20 mass%. A content in the range of 0.1 to 30 mass% is preferred from the standpoint of obtaining a suitable buffering capacity and a reduced unit cost and enabling the preparation of high concentrations.

[0153] The base used in combination with the nonreducing sugar can be exemplified by the heretofore known bases, for example, inorganic bases and organic bases. The inorganic bases can be exemplified by sodium hydroxide, potassium hydroxide, lithium hydroxide, trisodium phosphate, tripotassium phosphate, triammonium phosphate, disodium phosphate, dipotassium phosphate, diammonium phosphate, sodium carbonate, potassium carbonate, ammonium carbonate, sodium bicarbonate, potassium bicarbonate, ammonium bicarbonate, sodium borate, potassium borate, ammonium borate, and so forth.

[0154] The organic bases can be exemplified by monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, triisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethyleneimine, ethylenediamine, pyridine, and so forth.

[0155] A single such base may be used or two or more may be used in combination. Sodium hydroxide and potassium hydroxide are preferred among these bases. The present invention can also make use of a nonsilicate developer solution in which the main component is an alkali metal salt of a nonreducing sugar rather than the combination of a nonreducing sugar and a base.

[0156] In addition to the nonreducing sugar, the nonsilicate developer solution may also employ an alkaline buffer solution comprising a weak acid and a strong base. This weak acid preferably has a dissociation constant (pKa) of 10.0 to 13.2 and can be selected from the weak acids described in, for example, "Ionization Constants of Organic Acids In

Aqueous Solution" (Pergamon Press).

[0157] Preferred specific examples are alcohols such as 2,2,3,3-tetrafluoropropanol-1, trifluoroethanol, trichloroethanol, and so forth; aldehydes such as pyridine-2-aldehyde, pyridine-4-aldehyde, and so forth; compounds that contain a phenolic hydroxyl group, e.g., salicylic acid, 3-hydroxy-2-naphthoic acid, catechol, gallic acid, sulfosalicylic acid, 3,4-dihydroxybenzenesulfonic acid, 3,4-dihydroxybenzoic acid, hydroquinone (pKa: 11.56), pyrogallol, o-, m-, and p-cresol, resorcinol, and so forth; oximes such as acetoxime, 2-hydroxybenzaldehyde oxime, dimethylglyoxime, ethanediamide dioxime, acetophenone oxime, and so forth; nucleic acid-related substances such as adenosine, inosine, guanine, cytosine, hypoxanthine, xanthine, and so forth; and also diethylaminomethylphosphonic acid, benzimidazole, barbituric acid, and so forth.

[0158] As necessary, the aforementioned developer solutions may also incorporate various surfactants and organic solvents in order to accelerate or inhibit development, improve the dispersion of development scum, or improve the ink receptivity of the image areas on the printing plate. The surfactant is preferably an anionic, cationic, nonionic, or amphoteric surfactant. As necessary, the aforementioned developer solution may also incorporate a reducing agent, e.g., hydroquinone, resorcinol, the sodium and potassium salts of an inorganic acid such as sulfurous acid and hydrosulfurous acid, and so forth, and may also incorporate an organic carboxylic acid, defoamer, hard water softener, and so forth.

[0159] Once the lithographic printing plate precursor has been developed using the previously described developer solution, it is subjected to post-treatment with rinse water, rinse solution containing surfactant and so forth, and/or desensitizing solution containing gum arabic or a starch derivative. Various combinations of these treatments can be used for the post-treatment when the previously described image-forming materials are used for the printing plate.

[0160] Furthermore, when development is performed using automatic developing equipment, it is known that, by using a developer solution provided by the addition to the developer solution of an aqueous solution (a replenishing solution) that has a higher alkalinity than the developer solution, a large number of PS plates can be processed without having to change the developer solution in the development tank over a long period of time. This replenishment procedure is preferably also used in the present invention.

[0161] Once the lithographic printing plate has been developed using the previously described developer solution, it is submitted to post-treatment with rinse water, rinse solution containing surfactant and so forth, and/or a desensitizing solution containing gum arabic or a starch derivative. Various combinations of these treatments can be used for the post-treatment of the lithographic printing plate precursor of the present invention.

[0162] Automatic printing plate developing equipment has entered into widespread use in recent years in the platemaking and printing sectors in order to rationalize and standardize the platemaking operation. This automatic developing equipment generally comprises a development section and a post-treatment section, a printing plate transport device, a tank for each processing solution, and spraying units. While the already photoexposed printing plate is being horizontally transported, each processing solution is pumped up and sprayed through spray nozzles to perform development. A method has quite recently become known in which processing is carried out by transporting the printing plate while it is immersed in a processing solution tank filled with processing solution; transport is effected by, for example, submerged guide rolls. Processing in this automatic regime may also be performed while replenishing the processing solution with replenishing solution in accordance with the processing load, the operating time, and so-forth. A so-called disposable processing procedure may also be used in which processing is done with substantially unused processing solutions.

[0163] Erasure of the unwanted image area is performed on the lithographic printing plate precursor of the present invention in those instances in which an unwanted image area (for example, film edge traces of the original image film) is present on the lithographic printing plate precursor obtained by imagewise photoexposure, development, water rinsing, and/or rinsing and/or gumming. This erasure is preferably preformed, for example, as described in Japanese Examined Patent Publication No. H2-13293, by coating an erasing fluid on the unwanted image area following by standing in this state for a prescribed period of time and then rinsing with water. However, the method described in Japanese Patent Application Publication No. S59-174842 can also be used; in this method, development is carried out after the unwanted image area has been irradiated by actinic light guided by an optical fiber.

[0164] After the optional application of a desensitizing gum, the lithographic printing plate precursor obtained as described in the preceding is provided to the printing process; however, as desired a burning process can be performed in those instances where a lithographic printing plate precursor with an even higher printing durability is desired.

[0165] When a burning process is to be performed on the lithographic printing plate precursor, treatment with a counter-etch solution, as described in Japanese Examined Patent Publication Nos. S61-2518 and S55-28062 and Japanese Patent Application Publication Nos. S62-31859 and S61-159655, is preferably carried out prior to burning.

[0166] Methods that can be used here include application of the counter-etch solution onto the lithographic printing plate precursor using a sponge or absorbent cotton impregnated with the counter-etch solution, application of the counter-etch solution by dipping the printing plate in a vat filled with the counter-etch solution, or application of the counter-etch solution using an automatic coater. In addition, a more uniform effect is imparted by bringing about a uniform coating rate using a squeegee or squeegee roller post-application.

[0167] A suitable coating rate for the counter-etch solution is generally 0.03 to 0.8 g/m^2 (dry mass). The counter-etch solution-coated lithographic printing plate precursor is then dried when necessary and is thereafter heated to a high temperature using a burning processor (for example, a commercially available burning processor such as the "BP-1300" from FUJIFILM Corporation). The heating temperature and time here will depend on the nature of the image-forming components, but the ranges of 180 to 300°C and 1 to 20 minutes are preferred.

[0168] The burned-in lithographic printing plate precursor may as necessary and appropriate be submitted to those processes that have been carried out at this point in the past, such as a water rinse and gumming; however, a so-called desensitization treatment, such as gumming, can be omitted when a counter-etch solution has been used that contains a water-soluble polymer compound. The lithographic printing plate precursor obtained by the hereinabove described processing is mounted on, for example, an offset press and is used for long-run printing.

EXAMPLES

[0169] The present invention is described herebelow using examples, but the scope of the present invention is not limited to these examples.

Example 1

[0170] A support A was fabricated from 0.3 mm-thick JIS-A-1050 aluminum plate by processing using the steps described in the following.

[0171] An etching treatment was performed by spraying the aforementioned aluminum plate with an aqueous NaOH solution (concentration = 26 mass%, aluminum ion concentration = 6.5 mass%) having a temperature of 70°C; this resulted in the dissolution of 6 g/m^2 of the aluminum plate. The etching treatment was followed by a water rinse by spraying with well water.

[0172] A desmutting treatment was then carried out by spraying with a 1 mass% aqueous solution of nitric acid (aluminum ion content = 0.5 mass%) having a temperature of 30°C; this was followed by a water rinse by spraying.

[0173] A continuous electrochemical surface roughening treatment was carried out using 60 Hz alternating current voltage. The electrolyte used here was an aqueous solution of 7.5 g/L hydrochloric acid (aluminum ion content = 5 g/L) and had a temperature of 35°C. The electrochemical surface roughening treatment was carried out using an alternating current power source with a square waveform and using a carbon electrode as the counterelectrode. Ferrite was used for the auxiliary anode. A radial cell type electrolysis tank was used.

[0174] The current density was 25 A/dm^2 as the peak current value, while the quantity of electricity was 450 C/dm^2 as the total quantity of electricity during the time in which the aluminum plate was the anode.

[0175] This was followed by a water rinse by spraying with well water.

[0176] The aluminum plate was then subjected to an etching treatment at 32°C by spraying with 26 mass% sodium hydroxide and 6.5 mass% aluminum ion, thereby dissolving 0.10 g/m^2 of the aluminum plate. This resulted in removal of the smut component, which was composed mainly of aluminum hydroxide, that had been produced during the alternating current electrochemical surface roughening treatment in the previous step, and also resulted in a smoothing of the edge regions by dissolution of the edge regions of the pits that had been produced. This was followed by a water rinse by spraying with well water.

[0177] Desmutting was then carried out by spraying with a 25 mass% aqueous solution (aluminum ion content = 0.5 mass%) of sulfuric acid having a temperature of 60°C, followed by a water rinse by spraying with well water.

[0178] An anodic oxidation treatment was then performed. The electrolyte was nitric acid at a concentration of 170 g/L (aluminum ion content = 0.5 mass%) and the temperature was 43°C. This was followed by a water rinse by spraying using well water.

[0179] The surface roughness of the aluminum plate obtained up to this point was 0.45 μm as the Ra reading as measured using a Surfcom from Tokyo Seimitsu Co., Ltd., with a stylus tip radius of 2 μm.

[0180] The current density was approximately 30 A/dm^2. The final oxidation film weight was 2.7 g/m^2.

[0181] The anodically oxidized aluminum plate was then immersed for 5 seconds in a solution provided by heating an aqueous 0.5% polyvinylphosphonic acid solution to 60°C and was subsequently washed with water by spraying.

[0182] The procedure described above provided a support A for a photosensitive lithographic printing plate.

[0183] The support obtained as described above was coated using a wire bar with the lower layer coating solution A with the composition indicated below, after which drying was performed for 70 seconds in a drying oven set to 140°C to obtain a lower layer. The post-drying coating weight was 1.0 g/m^2.

<The lower layer coating solution A>

[0184]

- special polymer
  (structural example (1) from above) 0.80 g
- naphthalenesulfonic acid salt of Crystal Violet 0.10 g
- fluorosurfactant F-780-F
  (product of DIC Corporation) 0.01 g
- methyl ethyl ketone 5.00 g
- 1-methoxy-2-propanol 5.00 g
- N,N-dimethylformamide 10.00 g

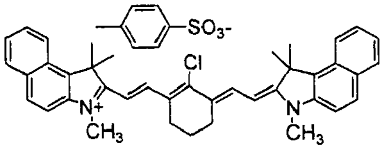
[0185] The lower layer obtained as described above was coated using a wire bar with the upper layer coating solution B with the composition indicated below, after which drying was performed for 60 seconds in a drying oven set to 130°C to obtain an upper layer. The post-drying coating weight was 0.5 g/m^2.

<The upper layer coating solution B>

[0186]

- the novolac resin (i) described above
  (novolac resin comprising phenol/m-cresol/p-cresol = 50/30/20 (molar ratio), weight-average molecular weight = 8,000) 0.80 g
- aromatic group-containing sulfonium salt
  (the previously described example (A)) 0.20 g
- cyanine dye P with the structure given below 0.10 g

P



- fluorosurfactant F-780-F
  (product of DIC Corporation) 0.02 g
- methyl ethyl ketone 10.00 g
- 1-methoxy-2-propanol 10.00 g

[0187] The preceding process yielded a photosensitive lithographic printing plate precursor in which the recording layer had a multilayer structure.

Examples 2 to 14

[0188] Photosensitive lithographic printing plate precursors were obtained as in Example 1, but changing the special polymer (1) for the lower layer, the novolac resin (i) for the upper layer, and the sulfonium salt (A) used in Example 1 to the compounds shown in Table 1.

Example 15

[0189] A photosensitive lithographic printing plate precursor was obtained as in Example 1, but in this case also adding to the lower layer 0.10 g of the cyanine dye P that was used in the upper layer in Example 1.

Example 16

[0190] A photosensitive lithographic printing plate precursor was obtained as in Example 15, but in this case omitting the cyanine dye P from the upper layer in Example 15 and changing its addition to the lower layer to 0.15 g.

Example 17

[0191] A photosensitive lithographic printing plate precursor was obtained as in Example 1, but in this changing the electrolyte used in the electrochemical surface roughening treatment in the fabrication of support A in Example 1 from the aqueous solution of 7.5 g/L hydrochloric acid (aluminum ion content = 5 g/L) to an aqueous solution of 10 g/L nitric acid (aluminum ion content = 5 g/L) and making the amount of electricity 300 C/dm^2 as the total quantity of electricity during the time in which the aluminum plate was the anode (the resulting support is referred to as support B in the following). The surface roughness of this support B was 0.25 μm as the Ra reading when measured using a Surfcom from Tokyo Seimitsu Co., Ltd., with a stylus tip radius of 2 μm.

Example 18

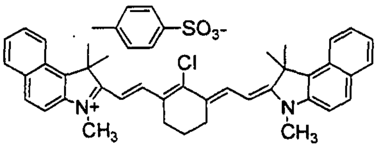
[0192] The support A obtained in Example 1 was coated using a wire bar with the coating solution C with the composition indicated below, after which drying was performed for 80 seconds in a drying oven set to 140°C to obtain a recording layer. The post-drying coating weight was 1.5 g/m^2.

<Coating solution C>

[0193]

- special polymer
  (structural example (1) from above) 0.50 g
- the novolac resin (i) described above 0.50 g
- aromatic group-containing sulfonium salt (A) 0.10 g
- cyanine dye P with the structure given below 0.10 g

P



- naphthalenesulfonic acid salt of Crystal Violet 0.10 g
- fluorosurfactant F-780-F
  (product of Dainippon Ink and Chemicals, Incorporated) 0.02 g
- methyl ethyl ketone 5.00 g
- 1-methoxy-2-propanol 5.00 g
- N,N-dimethylformamide 10.00 g

[0194] The preceding process yielded a photosensitive lithographic printing plate precursor in which the recording layer was a single layer.

Examples 19 to 31

[0195] Photosensitive lithographic printing plate precursors were obtained as in Example 18, but changing the special polymer (1), the novolac resin (i), and the sulfonium salt (A) of Example 18 to the compounds shown in Table 1.

Example 32

[0196] A photosensitive lithographic printing plate precursor was obtained as in Example 18, but using the support B described in Example 17 in place of the support A used in Example 18.

Comparative Example 1

[0197] A photosensitive lithographic printing plate precursor was obtained as in Example 1, but in this case using an N-(p-aminosulfonylphenyl)methacrylamide/methyl methacrylate/acrylonitrile = 35/35/30 (molar ratio) copolymer (weight-average molecular weight = 65,000, referred to below as polymer (X)) in place of the special polymer (1) used in the lower layer in Example 1.

Comparative Example 2

[0198] A photosensitive lithographic printing plate precursor was obtained as in Example 1, but in this case using an N-phenylmaleimide/methacrylamide/methacrylic acid = 45/35/20 (molar ratio) copolymer (weight-average molecular weight = 20,000, referred to below as polymer (Y)) in place of the special polymer (1) used in the lower layer in Example 1.

Comparative Example 3

[0199] A photosensitive lithographic printing plate precursor was obtained as in Example 1, but in this case without using the sulfonium salt (A) used in the lower layer in Example 1.

Comparative Example 4

[0200] A photosensitive lithographic printing plate precursor was obtained as in Example 18, but in this case using the polymer (X) of Comparative Example 1 in place of the special polymer (1) in Example 18.

Comparative Example 5

[0201] A photosensitive lithographic printing plate precursor was obtained as in Example 18, but in this case using the polymer (Y) of Comparative Example 2 in place of the special polymer (1) in Example 18.

Comparative Example 6

[0202] A photosensitive lithographic printing plate precursor was obtained as in Example 18, but in this case omitting the use of the novolac resin (i) in Example 18 and using 1.00 g of the special polymer (1).

Comparative Example 7

[0203] A photosensitive lithographic printing plate precursor was obtained as in Example 18, but in this case omitting the use of the sulfonium salt (A) in Example 18.

Evaluation of the developability

[0204] Using a Luxel PLATESETTER T-9800HS from FUJIFILM Corporation at a beam output of 100% and a drum rotation rate of 150 rpm, the obtained photosensitive lithographic printing plate was imaged (photoexposed) in accordance with a test pattern image that had a chart with a 1 to 99% halftone dot area ratio at 175 lpi/2400 dpi.

[0205] Development was then carried out for a development time of 25 seconds at a development bath temperature of 30°C using an Autolith PN85CE automatic developer from AGFA. The developer solution used here was obtained by diluting developer concentrate 1 (composition given below) with water to provide developer solutions in which the electroconductivity varied from 80 to 100 mS/cm in intervals of 2 mS/cm. A solution provided by diluting FG-1 (FUJIFILM Corporation) 1:1 with water was used as the gum solution. The developability was evaluated using these conditions.

<Composition of developer concentrate 1>

[0206]

• #3 sodium silicate (38.5% aqueous solution)	150 g
• sodium hydroxide (50% aqueous solution)	70 g
• dipotassium salt of p-methylphenoxypolyoxyethylene phosphate	10 g
• Pluronic TR704 (ADEKA)	2 g
• Eleminol MON-2 (Sanyo Chemical Industries, Ltd., 48.5% aqueous solution)	1 g
• pure water	267 g

[0207] In the case of a developer solution with a low bath sensitivity, development of the photoexposed areas is inadequate and a residual film will be produced in the non-image areas. In the case of a developer solution with a high bath sensitivity, the surface of the non-photoexposed areas undergoes development and film thinning occurs and a good quality image is not obtained. Each lithographic printing plate precursor was evaluated using as an index to the development latitude the electrical conductivity interval for the developer solutions that produced neither a residual film in the non-image areas nor film thinning in the image areas. The results are shown in Table 1.

[0208] As shown in Table 1, the lithographic printing plate precursors provided by the examples according to the present invention in all instances exhibited a broad electrical conductivity interval, i.e., exhibited a wide development latitude, and thus exhibited an excellent developability. In contrast to this, the lithographic printing plate precursors provided by the comparative examples exhibited a narrower electrical conductivity interval than the lithographic printing plate precursors of the examples.

Evaluation of the chemical resistance

[0209] A lithographic printing plate was obtained by subjecting the obtained photosensitive lithographic printing plate precursor to photoexposure and development as in the previously described evaluation of developability. The developer solution used in this case was the developer solution that had the electrical conductivity that was in the middle of the electrical conductivity interval determined in the evaluation of developability.

[0210] Printing was then performed using the lithographic printing plate obtained as described above. A Lithrone press from Komori Corporation was used as the press; Balius G black ink from Dainippon Ink and Chemicals, Incorporated was used as the ink; and a solution provided by diluting IF-102 from FUJIFILM Corporation with water to a 4% concentration was used as the fountain solution. At each 5000 impressions, the plate surface was wiped with Multicleaner (FUJIFILM Corporation). Printing was performed on high quality paper, and the printing durability was evaluated based on the number of sheets printed at the time point at which the beginning of attenuation of the black image density could be visually recognized. A larger numerical value in this instance is indicative of a better chemical resistance. The results are given in Table 1.

[0211] As shown in Table 1, all of the plates made from the lithographic printing plate precursors provided by the examples according to the present invention exhibited an excellent chemical resistance. In contrast to this, the plates made from lithographic printing plate precursors provided by the comparative examples all had a poor chemical resistance.

Burning evaluation

[0212] The photosensitive lithographic printing plate precursors of Examples 1 and 18 were selected from among the obtained photosensitive lithographic printing plate precursors and were used to obtain lithographic printing plates by photoexposure and development as in the evaluation of chemical resistance.

[0213] After rinsing the plate with water to remove the gum solution, the plate was coated with BC-5 (FUJIFILM Corporation) counter-etch solution held in a sponge and was then allowed to dry spontaneously. This was followed by a heat treatment for 5 minutes at 260°C in a burning oven from the Wisconsin Company. After cooling to room temperature, the counter-etch solution was removed by a water rinse and gumming was performed using a Gum Coater G-800 from FUJIFILM Corporation. A solution provided by diluting GU-7 (FUJIFILM Corporation) 1:1 with water was used as the gum.

[0214] Printing as in the evaluation of chemical resistance was performed with the burning-treated plate in order to evaluate the printing durability. According to the results, 380,000 and 340,000 impressions could be obtained, respectively, which showed that the chemical resistance could be further improved by burning.

Other evaluation

[0215] The photosensitive lithographic printing plate precursors of Examples 1 and 18 were selected from among the obtained photosensitive lithographic printing plate precursors and were used to obtain lithographic printing plates by photoexposure and development as in the evaluation of developability, with the exception that the developer solution was changed. The developer solution used was obtained by diluting developer concentrate 2 (composition given below) to provide an electrical conductivity of 43 mS/cm. According to the results, an excellent lithographic printing plate was obtained that was free of staining and film thinning, and an excellent printing plate could thus also be obtained with a developer solution that did not contain a silicic acid component.

<Composition of developer concentrate 2>

[0216]

• potassium hydroxide (48% aqueous solution)	200 g
• sorbitol	450 g

- tripotassium citrate 100 g
- Paionim C-158G (Takemoto Oil & Fat Co., Ltd.) v10 g
- pure water 240 g

[0217] As shown in the preceding examples, the present invention can provide a photosensitive lithographic printing plate precursor that exhibits both an excellent developability and an excellent chemical resistance. In addition, this photosensitive lithographic printing plate precursor can also provide an even higher printing durability through burning.

Table 1

	support	recording layer	special polymer	novolac resin	sulfonium salt / iodonium salt	development latitude (mS/cm)	interval (mS/cm)	chemical resistance (printing durability)
Example 1	A	multilayer	(1)	(i)	(A)	84-94	10	120,000
Example 2	A	multilayer	(2)	(i)	(A)	86-96	10	160,000
Example 3	A	multilayer	(3)	(i)	(A)	84-94	10	140,000
Example 4	A	multilayer	(4)	(i)	(A)	86-96	10	140,000
Example 5	A	multilayer	(5)	(i)	(A)	86-96	10	140,000
Example 6	A	multilayer	(6)	(i)	(A)	84-92	8	80,000
Example 7	A	multilayer	(7)	(i)	(A)	90-96	6	120,000
Example 8	A	multilayer	(1)	(ii)	(A)	84-94	10	120,000
Example 9	A	multilayer	(1)	(iii)	(A)	84-94	10	140,000
Example 10	A	multilayer	(1)	(iv)	(A)	90-96	6	120,000
Example 11	A	multilayer	(1)	(i)	(B)	84-94	10	120,000
Example 12	A	multilayer	(1)	(i)	(C)	84-94	10	120,000
Example 13	A	multilayer	(1)	(i)	(D)	84-92	8	90,000
Example 14	A	multilayer	(1)	(i)	(E)	84-90	6	80,000
Example 15	A	multilayer	(1)	(i)	(A)	84-94	10	120,000
Example 16	A	multilayer	(1)	(i)	(A)	86-96	10	120,000
Example 17	B	multilayer	(1)	(i)	(A)	84-94	10	120,000
Example 18	A	monolayer	(1)	(i)	(A)	84-94	10	110,000

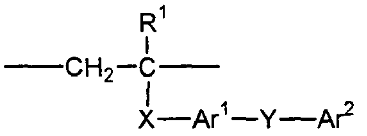
(continued)

	support	recording layer	special polymer	novolac resin	sulfonium salt / iodonium salt	development latitude (mS/cm)	interval (mS/cm)	chemical resistance (printing durability)
Example 19	A	monolayer	(2)	(i)	(A)	86-96	10	140,000
Example 20	A	monolayer	(3)	(i)	(A)	84-94	10	120,000
Example 21	A	monolayer	(4)	(i)	(A)	86-96	10	120,000
Example 22	A	monolayer	(5)	(i)	(A)	86-96	10	130,000
Example 23	A	monolayer	(6)	(i)	(A)	84-92	8	60,000
Example 24	A	monolayer	(7)	(i)	(A)	90-96	6	120,000
Example 25	A	monolayer	(1)	(ii)	(A)	84-94	10	120,000
Example 26	A	monolayer	(1)	(iii)	(A)	84-94	10	140,000
Example 27	A	monolayer	(1)	(iv)	(A)	90-96	6	120,000
Example 28	A	monolayer	(1)	(i)	(B)	84-94	10	120,000
Example 29	A	monolayer	(1)	(i)	(C)	84-94	10	120,000
Example 30	A	monolayer	(1)	(i)	(D)	84-92	8	80,000
Example 31	A	monolayer	(1)	(i)	(E)	84-90	6	70,000
Example 32	B	monolayer	(1)	(i)	(A)	84-94	10	120,000
Comp. Ex. 1	A	multilayer	(X)	(i)	(A)	82-84	2	40,000
Comp. Ex. 2	A	multilayer	(Y)	(i)	(A)	94-96	2	60,000
Comp. Ex. 3	A	multilayer	(1)	(i)	none	86	0	30,000
Comp. Ex. 4	A	monolayer	(X)	(i)	(A)	82-84	2	40,000
Comp. Ex. 5	A	monolayer	(Y)	(i)	(A)	94-96	2	60,000
Comp. Ex. 6	A	monolayer	(1)	none	(A)	86	0	60,000
Comp. Ex. 7	A	monolayer	(1)	(i)	none	86	0	30,000

[0218] Examples 15 and 16 differ with regard to the layers containing the infrared-absorbing dye.

Claims

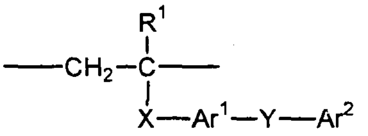
1. A positive-working photosensitive lithographic printing plate precursor, comprising a support having a hydrophilic surface; and a recording layer disposed on the support and comprising an alkali-soluble or alkali-swellable polymer having a structural unit represented by general formula (1) below, a novolac resin, an infrared absorber, and at least one member selected from aromatic group-containing sulfonium salts and iodonium salts



$$-\!\!-CH_2-\overset{\displaystyle R^1}{\underset{\displaystyle X-Ar^1-Y-Ar^2}{\overset{|}{\underset{|}{C}}}}-\!\!- \qquad (1)$$

wherein R^1 represents a hydrogen atom or methyl group, X represents a single bond, -COO-, or -CONH-, Ar^1 and Ar^2 each represent an optionally substituted aromatic group or heteroaromatic group, and Y represents - SO_2NH- or -$NHSO_2$-.

2. A positive-working photosensitive lithographic printing plate precursor, comprising: a support having a hydrophilic surface; and a recording layer disposed on the support and comprising an alkali-soluble or alkali-swellable polymer having a structural unit represented by general formula (1) below, and a recording layer further disposed thereon and comprising a novolac resin, an infrared absorber, and at least one member selected from aromatic group-containing sulfonium salts and iodonium salts



$$-\!\!-CH_2-\overset{\displaystyle R^1}{\underset{\displaystyle X-Ar^1-Y-Ar^2}{\overset{|}{\underset{|}{C}}}}-\!\!- \qquad (1)$$

wherein R^1 represents a hydrogen atom or methyl group, X represents a single bond, -COO-, or -CONH-, Ar^1 and Ar^2 each represent an optionally substituted aromatic group or heteroaromatic group, and Y represents - SO_2NH- or -$NHSO_2$-.

3. The positive-working photosensitive lithographic printing plate precursor according to claim 1 or 2, wherein, with respect to the alkali-soluble or alkali-swellable polymer having a structural unit represented by general formula (1), Ar^1 in the formula represents an aromatic group and Ar^2 in the formula represents a heteroaromatic group.

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