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(54) Lithographic printing plate precursor

Lithographischer Druckplattenvorläufer

Précurseur d'une plaque d'impression lithographique

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Description

FIELD OF THE INVENTION

[0001] This invention relates to a lithographic printing plate precursor particularly suited to direct-to-plate (DTP) or computer-to-plate (CTP) technology in which an image is formed in direct response to digital signals from a computer.

BACKGROUND OF THE INVENTION

[0002] Recent years have seen marked development of lasers. In particular, high-output and yet compact solid state lasers and semiconductor lasers operating in the near infrared to infrared region have come to be available easily. These lasers are very useful as an exposure light source for DTP technology.

[0003] A lithographic printing plate precursor for infrared laser DTP imaging has a photosensitive layer essentially comprising an alkali-soluble binder resin and an infrared absorber which absorbs light to generate heat (hereinafter sometimes referred to as an "IR dye"). The IR dye and the alkali-soluble binder resin mutually act on each other, and the IR dye serves as a dissolution inhibitor which substantially reduces the alkali-solubility of the resin. Upon imagewise exposure, the IR dye in an exposed area (non-image area) absorbs light to generate heat, whereby the mutual action between the IR dye and the binder resin is lessened. As a result, the binder resin in the exposed area becomes alkali-soluble and removable with an alkali developer to provide a lithographic printing plate having image and non-image areas.

[0004] Where a grained and anodized aluminum plate is used as a support, because the support is much more heat conductive than the photosensitive layer, part of the heat generated in the interface with the support is diffused inside the support before the imaging reaction, i.e., alkali solubilization, proceeds sufficiently. It would follow that the part of the exposed photosensitive layer near the interface with the support fails to gain sufficient solubility in a developer and tends to remain where it should be removed to become a non-image area. The film remaining is noticeable where the photosensitive layer has a large thickness, i.e., a large coating weight. In order to avert the film remaining problem it is necessary to use a highly active developer or reduce the coating weight. However, such an approach is liable to result in image missing from the image area. That is, a slight variation of developer activity, being represented by the electrical conductivity of a developer, can easily result in development failure, such as film remaining or image missing. It is a problem essentially associated with the IR-sensitive lithographic printing plate precursors that the development latitude is considerably narrower than with conventional presensitized plates. To address this problem, various improvements on lithographic printing plate precursor materials sensitive to IR lasers have been proposed, including methods for improving developability of a photosensitive layer in the vicinities of the interface with a support and methods for suppressing developer solubility of an unexposed photosensitive layer, but satisfactory results have not yet been accomplished.

[0005] Furthermore, if the part of a photosensitive layer which should remain to form an image area is damaged by some cause, the part would become susceptible to development with a developer. That is, the printing plate precursor of this type is very susceptible to damage by scratching in practical use. For instance, scratchy image missing would occur on slight contact with other objects due to, for example, shocks on handling, sliding contact with an interleaf or finger touch. Therefore, the state-of-the-art printing plate precursors of this type are very difficult to handle.

[0006] In order to settle the above-mentioned problems, JP-A-2002-72458 proposes a lithographic printing plate precursor in which the amount of aluminum etched out by alkali etching of an aluminum plate is 0.5 to 4 g/m^2, and the average thickness of thinnest 10% of a photosensitive layer formed on projections of the aluminum support is 0.2 to 2 μm as observed under an SEM. This plate precursor still cannot be seen as sufficient in scratch resistance and development latitude.

SUMMARY OF THE INVENTION

[0007] An object of the present invention is to provide a lithographic printing plate precursor which has a broad development latitude and hardly suffers from scratchy image missing.

[0008] As a result of extensive investigation, the present inventors have found that the above object is accomplished by a lithographic printing plate precursor comprising an aluminum support preferably prepared by subjecting an aluminum plate to at least graining and alkali etching and a photosensitive layer comprising a water-insoluble and alkali-soluble resin and an infrared absorber, wherein the photosensitive layer has a coating weight of 0.5 to 3 g/m^2 and a thickness distribution with a relative standard deviation of 20% or less. The coating weight of the photosensitive layer is preferably 0.7 to 1.5 g/m^2, still preferably 0.7 to 1.2 g/m^2. Too small a coating weight results in poor press life, and too large a coatingweight results in increased load in development.

[0009] It is assumed that the specific coating weight (i.e., film thickness) and film thickness distribution of a photosensitive layer bring about improved development latitude for the following reason. Since an aluminum support of a lithographic printing plate precursor generally has surface roughness produced by graining and other surface treatments, the photosensitive layer formed thereon usually has a non-uniform thickness. Image missing tends to occur in areas with a small thickness, whilst film remaining tends to occur in areas with a large thickness. Therefore, it is believed that providing a photosensitive layer with a uniform thickness will eliminate the image missing and film remaining problems.

[0010] It is considered that the specific coating weight (i.e., film thickness) and film thickness distribution of a photosensitive layer bring about improved scratch resistance for the following reasons. Scratchy image missing is liable to occur in areas with a small film thickness. Therefore, providing a photosensitive layer with a uniform thickness will eliminate areas with an extremely small thickness and solve the scratchy image missing problem.

[0011] The present inventors prepared a number of samples and accurately measured the thickness of the photosensitive layer provided on a grained support to obtain a relative standard deviation. They have found as a result that a lithographic printing plate precursor having a specific film thickness and a specific film thickness distribution accomplished the object of the invention and reached the present invention.

BRIEF DESCRIPTION OF THE DRAWING

[0012]

Fig. 1 schematically illustrates an apparatus configuration used to carry out continuous application and drying of a coating film.

DETAILED DESCRIPTION OF THE INVENTION

[0013] The lithographic printing plate precursor of the invention comprises an aluminum support prepared by subjecting an aluminum plate to at least graining and alkali etching and a photosensitive layer comprising a water-insoluble and alkali-soluble resin and an infrared absorber, wherein the photosensitive layer has a coating weight of 0.5 to 3 g/m^2, preferably 0.7 to 1.5 g/m^2, still preferably 0.7 to 1.2 g/m^2, and a thickness distribution with a relative standard deviation of 20% or less.

[0014] The relative standard deviation of the film thickness distribution is preferably 15% or less, still preferably 10% or less.

[0015] Methods for controlling the relative standard deviation of the film thickness distribution to 20% or less include, but are not limited to, a method comprising rapidly drying the coating layer by blowing high pressure air or by bringing the coating layer with a hot roll, a method comprising adjusting the concentration of the photosensitive layer coating composition, and a method comprising adjusting the viscosity or surface tension of the coating composition by proper selection of a solvent or various additives to be used therein.

[0016] Fig. 1 shows a configuration of an apparatus for continuously applying a coating composition on a grained aluminum web as a support and continuously drying the coating layer.

[0017] The apparatus shown in Fig. 1 has a coating head 2 for applying a photosensitive coating composition to a grained aluminum web 1, a first drying zone 3 wherein the coating film is subjected to hot air drying and rapid drying by blowing high pressure air, and a second drying zone 4 wherein the coating film subjected to hot air drying. The first drying zone 3 is equipped with a feed port 5 through which hot air is introduced, a high pressure air generator 9 for achieving rapid drying, a heat exchanger 10, a pressure gauge 11, high pressure air nozzles 12, air flow regulating dampers 18 and 19, and an exhaust vent 6 for discharging hot air. The second drying zone 4 has a hot air feed port 7 and a hot air exhaust vent 8. Guide rolls 13 to 17 are placed at appropriate positions in the apparatus 1 for carrying the aluminum web 1.

[0018] In the apparatus 1, the grained aluminum web 1 continuously runs at a speed of 5 to 150 m/min, coated with 5 to 40 ml/m^2 of a photosensitive coating composition with the coating head 2 , and guided into the first drying zone 3. In the first drying zone 3, hot air typically at a temperature of 50 to 150°C is fed through the feed port 5 to dry the coated web 1. Solvent vapor from the coating composition is expelled through the exhaust vent 6 together with the hot air. The coating film having received the hot air near the inlet of the first drying zone 3 is usually still wet.

[0019] The high pressure air nozzles 12 are each disposed above the running web 1 with their slots at substantially right angles with the web running direction. The still wet coating film of the web 1 is extremely rapidly dried by the high speed air flow from the nozzles 12.

[0020] High pressure air is generated in the high pressure air generator 9 having a compressor or a highpressure blower, heated to 50 to 200°C by the heat exchanger 10, regulated to a desired air flow by the dampers 18 and 19, and fed to the first drying zone 3 through the slit nozzles 12. The high pressure air having thus regulated desired temperature and flowing speed is made to strike vigorously against the wet coating film, whereby the solvent of the coating film is rapidly evaporated in an extremely short time to form a photosensitive layer. The air pressure in the nozzles 12 is usually about 300 mmAq (H_2O) to 3 kg/cm^2, preferably about 1000 mmAq to 1 kg/cm^2. The velocity of air from the nozzles 12 is about 20 m to 300 m/s. The slit width of the nozzles 12 is about 0.1 to 5 mm, preferably 0.3 to 1 mm. The blowing angle of the high pressure air against the aluminum web 1 is 0 to 90°, preferably 10 to 60°. The number of the nozzles, which is two in the example shown in Fig. 1, can be from 1 to about 8.

[0021] The drying with high pressure air is preferably combined with drying with a hot roll. For example, the guide roll 14 can be replaced with a hot roll. In this case, the surface temperature of the hot roll can be kept at 80 to 200°C by circulating a heating medium, such as steam, inside the roll. The hot roll gives heat energy through heat conduction from the lower side of the aluminum web. A combined use of such a hot roll achieves rapider evaporation of the solvent than in drying with the high pressure air alone and brings about a more uniform distribution of the film thickness.

[0022] Thus the coating film is rapidly dried in the first drying zone 3 to form a dry film with a decided thickness distribution. The web 1 is then guided into the second drying zone 4, where it is heated with hot air at 100° to 150°C fed from the feed port 7. By this second drying the solvent content remaining in a trace amount in the film is reduced to 30 to 200 mg/m^2. The solvent vapor is driven out of the system through the exhaust bent 8.

[0023] A desired film thickness distribution is thus achieved through these drying operations.

[0024] While, in the above-described embodiment, the coating layer is dried first with hot air and then with high pressure air, the hot air drying may be omitted. That is, it is possible that the web may be dried with high pressure air immediately after coated.

[0025] The present invention is preferably carried out by continuous application followed by continuous drying by use of such an apparatus as shown in Fig. 1. It is preferred for productivity that graining of an aluminum plate be also carried out in a continuous manner by, for example, arranging means for graining in the upstream of the coating head 2.

[0026] The relative standard deviation of the photosensitive layer thickness distribution is determined as follows. A 1 cm square specimen cut out of a printing plate precursor is analyzed with no deposition on an electron probe microanalyzer (EPMA) JXA8000 from JEOL to measure the characteristic X-ray intensity of carbon by a stage scan method under conditions of an accelerating voltage of 20 kV, a probe current of about 5 x 10^{-7} A, a probe diameter of 2 μm, a measuring interval of 2 μm in the x direction and 2 μm in the y direction, a measurement point number of 512 x 256, a dwell time of 50 ms, and a diffraction angle θ of 46.4°. LDE1H is selected as an LDE (layered dispersive element) analyzing crystal. A relative standard deviation RSD is calculated from an average characteristic X-ray intensity I of the 512 x 256 measurement points and the standard deviation σ according to equation: $RSD=\sigma/I \times 100$ (%).

[0027] The elements composing the lithographic printing plate precursor of the invention will be described hereunder.

[1] Alkali-soluble resin

[0028] The photosensitive layer comprises a water-insoluble and alkali-soluble resin (hereinafter simply referred to as an alkali-soluble resin or polymer). The alkali-soluble polymer includes a homopolymer containing an acidic group in the main chain and/or the side chain thereof, a copolymer comprising the unit of the homopolymer, and a mixture of such a homopolymer and/or a copolymer. Therefore, the photosensitive layer is removable with an alkaline developer.

[0029] While any polymer known to be alkali-soluble can be used, preferred is one having a functional group selected from a phenolic hydroxyl group, a sulfonamido group, and an active imido group. Non-limiting examples of such alkali-soluble polymers are listed below.

[0030] Polymers having a phenolic hydroxyl group include novolak resins, such as phenol formaldehyde resins, m-cresol formaldehyde resins, p-cresol formaldehyde resins, xylenol formaldehyde resins, m-/p-mixed cresol formaldehyde resins, and phenol/cresol (m-, p- or m-/p-mixed) mixed formaldehyde resins; pyrogallol acetone resins; and polymers having a phenolic hydroxyl group in the side chain thereof. The polymers having a phenolic hydroxyl group in the side chain include those produced by polymerizing a low-molecular monomer having a phenolic hydroxyl group and a polymerizable unsaturated bond either alone or with a comonomer.

[0031] The monomer having a phenolic hydroxyl group includes acrylamides, methacrylamides, acrylic esters, and methacrylic esters each having a phenolic hydroxyl group, and, hydroxystyrenes. Suitable examples are
N-(2-hydroxyphenyl)acrylamide,
N-(3-hydroxyphenyl)acrylamide,
N-(4-hydroxyphenyl)acrylamide,
N-(2-hydroxyphenyl)methacrylamide,
N-(3-hydroxyphenyl)methacrylamide,
N- (4-hydroxyphenyl)methacrylamide, o-hydroxyphenyl acrylate, m-hydroxyphenyl acrylate, p-hydroxyphenyl acrylate, o-hydroxyphenyl methacrylate, m-hydroxyphenyl methacrylate, p-hydroxyphenyl methacrylate, o-hydroxystyrene, m-hydroxystyrene, p-hydroxystyrene,
2-(2-hydroxyphenyl) ethyl acrylate, 2-(3-hydroxyphenyl) ethyl acrylate, 2-(4-hydroxyphenyl)ethyl acrylate,
2-(2-hydroxyphenyl)ethyl methacrylate,
2-(3-hydroxyphenyl)ethyl methacrylate, and
2-(4-hydroxyphenyl)ethyl methacrylate. These resins having a phenolic hydroxyl group can be used either individually

or as a combination of two or more thereof. Polycondensates between phenol substituted with an alkyl group having 3 to 8 carbon atoms and formaldehyde, such as a t-butylphenol formaldehyde resin and an octylphenol formaldehyde resin, may be used in combination as taught in U.S. Patent 4,123,279.

[0032] Alkali-soluble polymers having a sulfonamido group include those produced by polymerizing a monomer having a sulfonamido group either alone or with a comonomer. Monomers having a sulfonamido group include low-molecular compounds having a sulfonamido group carrying at least one hydrogen atom on the nitrogen atom ($-NH-SO_2-$) and a polymerizable unsaturated bond in the molecule. Preferred are those having an acryloyl group, an allyl group or a vinyloxy group and a monosubstituted or unsubstituted aminosulfonyl group or a substituted sulfonylimino group in the molecule.

[0033] Alkali-soluble polymers having an active imido group include those produced by polymerizing a low-molecular monomer having an active imido group and a polymerizable unsaturated bond in the molecule thereof either alone or with a comonomer. Examples of such a monomer are
N-(p-toluenesulfonyl)methacrylamide and
N-(p-toluenesulfonyl)acrylamide.

[0034] Also included under preferred alkali-soluble resins are copolymers produced by copolymerizing at least two monomers selected from (1) the monomer having a phenolic hydroxyl group, (2) the monomer having a sulfonamido group, and (3) the monomer having an active imido group and copolymers produced by copolymerizing at least two of the monomers (1), (2), and (3) and (4) other comonomer(s). In copolymerizing the monomer (1) with the monomer (2) and/or the monomer (3), a preferred copolymerization ratio of (1) to (2) and/or (3) is 50:50 to 5:95, particularly 40:60 to 10:90.

[0035] The copolymer prepared from the monomers selected from (1), (2) and (3), and the comonomer (4) preferably contains at least 10 mol%, particularly 20 mol% or more, of the units derived from those monomers contributory to alkali solubility. With less than 10 mol% of the content of the units contributory to alkali solubility, the copolymer tends to have insufficient alkali solubility and can fail to exhibit improved development latitude.

[0036] The comonomers (4) which are copolymerizable with the monomers (1), (2), and (3) include, but are not limited to, the following compound groups (m1) to (m12).

[0037] The alkali-soluble copolymers can be produced by known techniques including graft copolymerization, block copolymerization, and random copolymerization.

(m1) Acrylic esters and methacrylic esters having an aliphatic hydroxyl group, such as 2-hydroxyethyl acrylate and 2-hydroxyethyl methacrylate.
(m2) Alkyl acrylates, such as methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, amyl acrylate, hexyl acrylate, octyl acrylate, benzyl acrylate, 2-chloroethyl acrylate, and glycidyl acrylate.
(m3) Alkyl methacrylate, such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, 2-chloroethyl methacrylate, and glycidyl methacrylate.
(m4) Acrylamide, methacrylamide, and their derivatives, such as N-methylolacrylamide, N-ethylacrylamide, N-hexylmethacrylamide, N-cyclohexylacrylamide, N-hydroxyethylacrylamide, N-phenylacrylamide, N-nitrophenylacrylamide, and N-ethyl-N-phenylacrylamide.
(m5) Vinyl ethers, such as ethyl vinyl ether, 2-chloroethyl vinyl ether, hydroxyethyl vinyl ether, Propyl vinyl ether, butyl vinyl ether, octyl vinyl ether, and phenyl vinyl ether.
(m6) Vinyl esters, such as vinyl acetate, vinyl chloroacetate, vinyl butyrate, and vinyl benzoate.
(m7) Styrene and its derivatives, such as α-methylstyrene, methylstyrene, and chloromethylstyrene.
(m8) Vinyl ketones, such as methyl vinyl ketone, ethyl vinyl ketone, propyl vinyl ketone, and phenyl vinyl ketone.
(m9) Olefins, such as ethylene, propylene, isobutylene, butadiene, and isoprene.
(m10) N-vinylpyrrolidone, acrylonitrile, and methacrylonitrile.
(m11) Unsaturated imides, such as maleimide, N-acryloylacrylamide, N-acetylmethacrylamide, N-propionylmethacrylamide, and N-(p-chlorobenzoyl)methacrylamide.
(m12) Unsaturated carboxylic acids, such as acrylic acid, methacrylic acid, maleic anhydride, and itaconic acid.

[0038] The homo- or copolymers comprising at least one of the monomers (1) to (3) preferably have a weight average molecular weight (Mw) more than 2,000 and a number average molecular weight (Mn) more than 500, particularly an Mw of 5,000 to 300,000 and an Mn of 800 to 250,000, and a molecular weight distribution (Mw/Mn) of 1.1 to 10.

[0039] The phenol formaldehyde resins, the cresol aldehyde resins, and the like preferably have an Mw of 500 to 20,000 and an Mn of 200 to 10,000.

[0040] The above-recited alkali-soluble polymers can be used either individually or as a combination of two or more thereof. The alkali-soluble polymers are used in an amount of 30 to 99% by weight, preferably 40 to 95% by weight, still preferably 50 to 90% by weight, based on the total solids content of the photosensitive layer. With less than 30% by weight of the alkali-soluble polymer content, the photosensitive layer has reduced durability. Alkali-soluble polymer contents exceeding 99% by weight result in reduction of both sensitivity and durability.

[2] Infrared absorber

[0041] The infrared absorber used in the photosensitive layer (hereinafter sometimes referred to as an "IR dye") is not particularly limited as long as it absorbs infrared light rays to generate heat. Various known IR dyes can be used.
[0042] Commercially available IR dyes and IR dyes known in literature (e.g., *Senryo Binran,* The Society of Synthetic Organic Chemistry, Japan (ed.), 1970) can be used. Useful dyes include azo dyes, metal complex azo dyes, pyrazolone azo dyes, anthraquinone dyes, phthalocyanine dyes, carbonium dyes, quinoneimine dyes, methine dyes, and cyanine dyes. Preferred of them are those absorbing infrared light or near infrared light in view of suitability to lasers emitting infrared light or near infrared light.
[0043] Infrared- or near infrared absorbing dyes include cyanine dyes described in JP-A-58-125246, JP-A-59-84356, JP-A-59-202829, and JP-A-60-78787; methine dyes described in JP-A-58-173696, JP-A-58-181690, and JP-A-58-194595; naphthoquinone dyes described in JP-A-58-112793, JP-A-58-224793, JP-A-59-48187, JP-A-59-73996, JP-A-60-52940, and JP-A-60-63744; squarylium dyes described in JP-A-58-112792; and cyanine dyes described in British Patent 434,875.
[0044] Near infrared sensitizers disclosed in U.S. Patent 5,156,938 are also suitable as dyes. Particularly preferred dyes include arylbenzo(thio)pyrylium salts described in U.S. Patent 3,881,924; trimethinethiapyrylium salts described in U.S. Patent 4,327,169 (corresponding to JP-A-57-142645); pyrylium compounds described in JP-A-58-181051, JP-A-58-220143, JP-A-59-41363, JP-A-59-84248, JP-A-59-84249, JP-A-59-146063, and JP-A-59-146061; cyanine dyes described in JP-A-59-216146; pentamethinethiopyrylium salts described in U. S. Patent 4,283,475; pyrylium compounds described in JP-B-5-13514 and JP-B-5-19702; and Epolight III-178, III-130 and III-125 (trade names, available from Epolin, Inc.). The near infrared absorbing dyes represented by formulae (I) and (II) which are described in U.S. Patent 4,756,993 are also particularly preferred.
[0045] The infrared absorber is used in an amount of 0.01 to 50% by weight, preferably 0.1 to 50% by weight, still preferably 0.1 to 30% by weight, based on the total solids content of the photosensitive layer. Infrared absorber contents less than 0.01% tend to result in insufficient sensitivity. More than 50% infrared absorber contents can damage uniformity and durability of the photosensitive layer.

[3] Dissolution inhibitor

[0046] The photosensitive layer can contain a dissolution inhibitor which enhances the resistance of an unexposed area against dissolution in an alkali developer. The dissolution inhibitors include, but are not limited to, quaternary ammonium salts and polyethylene glycol compounds.
[0047] The quaternary ammonium salts include tetraalkylammonium salts, trialkylarylammonium salts, dialkyldiarylammonium salts, alkyltriarylammonium salts, tetraarylammonium salts, cyclic ammonium salts, and bicyclic ammonium salts. Specific examples are tetrabutylammonium bromide, tetrapentylammonium bromide, tetrahexylammonium bromide, tetraoctylammonium bromide, tetralaurylammonium bromide, tetraphenylammonium bromide, tetranaphthylammonium bromide, tetrabutylammonium chloride, tetrabutylammonium iodide, tetrastearylammonium bromide, lauryltrimethylammonium bromide, stearyltrimethylammonium bromide, behenyltrimethylammonium bromide, lauryltriethylamnmonium bromide, phenyltrimethylammonium bromide, 3-trifluoromethylphenyltrimethylammonium bromide, benzyltrimethylammonium bromide, dibenzyldimethylammonium bromide, distearyldimethylammonium bromide, tristearylmethylammonium bromide, benzyltriethylammonium bromide, hydroxyphenyltrimethylammonium bromide, and N-methylpyridinium bromide.
[0048] An advisable amount of the quaternary ammonium salt to be added is 0.1 to 50% by weight, particularly 1 to 30% by weight, on a solid basis based on the total solids content of the photosensitive layer. Addition of less than 0.1% is little effective. Addition of more than 50% can adversely affect the film forming capability of the binder resin.
[0049] The polyethylene glycol compounds as a dissolution inhibitor include compounds represented by formula:

$$R^1\text{-}[\text{-O-}(R^3\text{-O-})_m\text{-}R^2]_n$$

wherein R^1 represents a polyhydric alcohol residue or a polyhydric phenol residue; R^2 represents a hydrogen atom, a substituted or unsubstituted alkyl, alkenyl, alkynyl or alkyloyl group having 1 to 25 carbon atoms or a substituted or unsubstituted aryl or aryloyl group having 6 to 25 carbon atoms; R^3 represents a substituted or unsubstituted alkylene group; m is an integer of 10 or greater in average; and n is an integer of 1 to 4.
[0050] The polyethylene glycol compounds of the above formula include polyethylene glycols, polypropylene glycols, polyethylene glycol alkyl ethers, polypropylene glycol alkyl ethers, polyethylene glycol aryl ethers, polypropylene glycol aryl ethers, polyethylene glycol alkylaryl ethers, polypropylene glycol alkylaryl ethers, polyethylene glycol glyceryl ether,

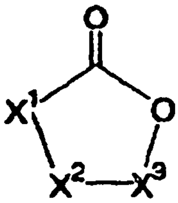
polypropylene glycol glyceryl ether, polyethylene glycol sorbitol ether, polypropylene glycol sorbitol ether, polyethylene glycol fatty acid esters, polypropylene glycol fatty acid esters, polyethylene glycolated ethylenediamines, polypropylene glycolated ethylenediamines, polyethylene glycolated diethylenetriamines, and polypropylene glycolated diethylenetriamines.

[0051] Specific examples of the polyethylene glycol compounds are polyethylene glycol 1000, polyethylene glycol 2000, polyethylene glycol 4000, polyethylene glycol 10000, polyethylene glycol 20000, polyethylene glycol 50000, polyethylene glycol 100000, polyethylene glycol 200000, polyethylene glycol 500000, polypropylene glycol 1500, polypropylene glycol 3000, polypropylene glycol 4000, polyethylene glycol methyl ether, polyethylene glycol ethyl ether, polyethylene glycol phenyl ether, polyethylene glycol dimethyl ether, polyethylene glycol diethyl ether, polyethylene glycol diphenyl ether, polyethylene glycol lauryl ether, polyethylene glycol dilauryl ether, polyethylene glycol nonyl ether, polyethylene glycol cetyl ether, polyethylene glycol stearyl ether, polyethylene glycol distearyl ether, polyethylene glycol behenyl ether, polyethylene glycol dibehenyl ether, polypropylene glycol methyl ether, polypropylene glycol ethyl ether, polypropylene glycol phenyl ether, polypropylene glycol dimethyl ether, polypropylene glycol diethyl ether, polypropylene glycol diphenyl ether, polypropylene glycol lauryl ether, polypropylene glycol dilauryl ether, polypropylene glycol nonyl ether, polyethylene glycol acetate, polyethylene glycol diacetate, polyethylene glycol benzoate, polyethylene glycol laurate, polyethylene glycol dilaurate, polyethylene glycol nonylate, polyethylene glycol cetylate, polyethylene glycol stearate, polyethylene glycol distearate, polyethylene glycol behenate, polyethylene glycol dibehenate, polypropylene glycol acetate, polypropylene glycol diacetate, polypropyleneglycolbenzoate, polypropylene glycol dibenzoate, polypropylene glycol laurate, polypropylene glycol dilaurate, polypropylene glycol nonylate, polyethylene glycol glyceryl ether, polypropylene glycol glyceryl ether, polyethylene glycol sorbitol ether, polypropylene glycol sorbitol ether, polyethylene glycolated ethylenediamine, polypropylene glycolated ethylenediamine, polypropylene glycolated ethylenediamine, polyethylene glycolated diethylenetriamine, polypropylene glycolated diethylenetriamine, and polyethylene glycolated pentamethylenehexamine.

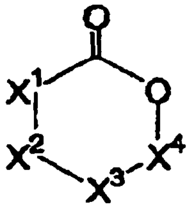
[0052] A recommended amount of the polyethylene glycol compound to be added is 0.1 to 50% by weight, particularly 1 to 30% by weight, on a solid basis based on the total solids content of the photosensitive layer. Addition of less than 0.1% produces little dissolution inhibitory effect. Where the polyethylene glycol compound is added in amounts exceeding 50%, the excess incapable of mutually acting on a binder resin can accelerate penetration of a developer, resulting in adverse influences on image formation.

[0053] Addition of the dissolution inhibitor results in reduction of sensitivity, which is averted effectively by addition of a lactone compound. When a developer penetrates into an exposed area, the lactone compound reacts with the developer to produce a corresponding carboxylic acid compound, which contributes to dissolution of the exposed area, i.e., brings about improved sensitivity.

[0054] Lactone compounds useful for this purpose include, but are not limited to, compounds represented by formulae (L-I) and (L-II):



(L-I)



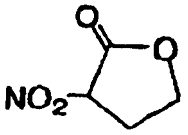
(L-II)

wherein X^1, X^2, X^3, and X^4, which may be the same or different, each represent a substituted or unsubstituted atom or atomic group completing the ring; at least one of X^1, X^2, and X^3 in formula (L-I) and at least one of X^1, X^2, X^3, and X^4 in formula (L-II) each have an electron attractive group or an electron attractive group-substituted group.

[0055] The atom or atomic group represented by X^1, X^2, X^3 or X^4 is a non-metal atom having two single bonds or an atomic group containing such a non-metal atom. Preferred non-metal atoms or atomic groups are selected from a methylene group, a sulfinyl group, a carbonyl group, a thiocarbonyl group, a sulfonyl group, a sulfur atom, an oxygen atom, and a selenium atom. A methylene group, a carbonyl group, and a sulfonyl group are more preferred.

[0056] At least one of X^1, X^2, and X^3 in formula (L-I) and at least one of X^1, X^2, X^3, and X^4 in formula (L-II) each have an electron attractive group. The terminology "electron attractive group" as used herein denotes a group having a positive Hammet's substituent constant σp. Journal of *Medicinal Chemistry*, (1973), vol. 16, No. 11, 1207-1216 can be referred to as for Hammet' s substituent constant. Examples of such electron attracting groups include halogen atoms (e.g., fluorine (σp: 0.06), chlorine (σp: 0.23), bromine (σp: 0.23), and iodine (σp: 0.18)); trihaloalkyl groups (e.g., tribromomethyl (σp: 0.29), trichloromethyl (σp: 0.33), and trifluoromethyl (σp: 0.54)); a cyano group (σp: 0.66), a nitro group (σp: 0.78); aliphatic aryl or heterocyclic sulfonyl groups (e.g., methanesulfonyl (σp: 0.72)); aliphatic aryl or heterocyclic acyl groups (e.g., acetyl (σp: 0.50) and benzoyl (σ: 0.43)); alkynyl groups (e.g., ethynyl (σp: 0.23)); aliphatic aryl or heterocyclic oxycarbonyl groups (e.g., methoxycarbonyl (σp: 0.45) and phenoxycarbonyl (σp: 0.44)); a carbamoyl group (op: 0.36); a sulfamoyl group (σp: 0.57), a sulfoxide group, heterocyclic groups, an oxo group, and a phosphoryl group. Preferred electron attracting groups are amido, azo, nitro, fluoroalkyl having 1 to 5 carbon atoms, nitrile, alkoxycarbonyl having 1 to 5 carbon atoms in the alkyl moiety, acyl having 1 to 5 carbon atoms, alkylsulfonyl having 1 to 9 carbon atoms, arylsulfonyl having 6 to 9 carbon atoms, alkylsulfinyl having 1 to 9 carbon atoms, arylsulfinyl having 6 to 9 carbon atoms, arylcarbonyl having 6 to 9 carbon atoms in the aryl moiety, thiocarbonyl, fluoroalkyl having 1 to 9 carbon atoms, fluoroaryl having 6 to 9 carbon atoms, fluoroallyl having 3 to 9 carbon atoms, oxo, and halogen. Still preferred are nitro, fluoroalkyl having 1 to 5 carbon atoms, nitrile, alkoxycarbonyl having 1 to 5 carbon atoms in the alkyl moiety, acyl having 1 to 5 carbon atoms, arylsulfonyl having 6 to 9 carbon atoms, arylcarbonyl having 6 to 9 carbon atoms in the aryl moiety, oxo, and halogen.

[0057] Specific examples of the lactone compounds represented by formula (L-1) or (L-2) are shown below for illustrative purposes only but not for limitation.



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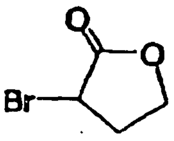

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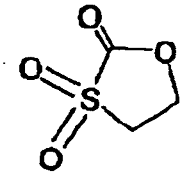

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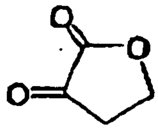

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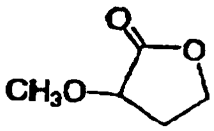

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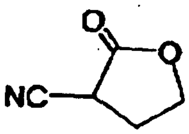

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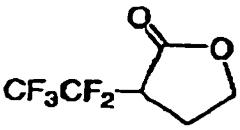

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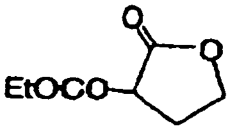

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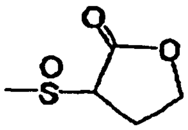

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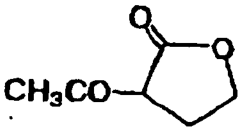
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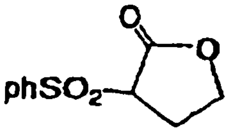
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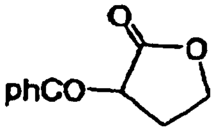
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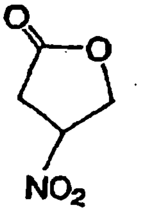
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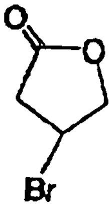
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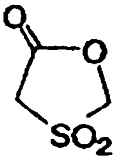
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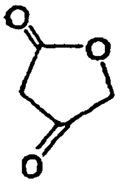
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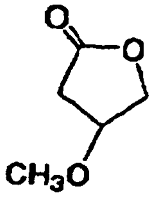
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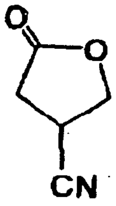
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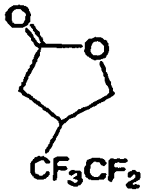
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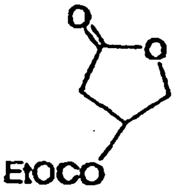
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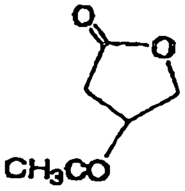
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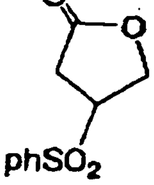
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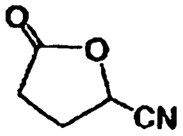
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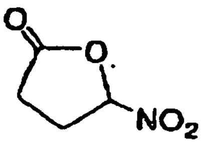
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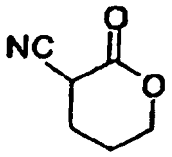

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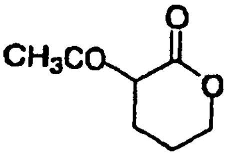


(LII-2)

[0058] An advisable amount of the lactone compound of formula (L-1) or (L-2) to be added is 0.1 to 50% by weight, particularly 1 to 30% by weight, based on the total solids content of the photosensitive layer. Addition of less than 0.1% is little effective. Addition of more than 50% results in poor imaging performance. Since the lactone compounds of formula (L-1) and (L-2) are reactive with a developer as stated above, it is desirable that contact of the photosensitive layer with a developer be selective.

[0059] The lactone compounds of formula (L-1) or (L-2) can be used either individually or as a mixture of two or more thereof in an arbitrary mixing ratio as long as the total amount falls within the above-recited range.

[0060] The photosensitive layer preferably contains a thermally decomposable substance which substantially reduces alkali solubility of the alkali-soluble resin before thermal decomposition. Such a substance sharpens the solubility contrast between exposed and unexposed areas. Various onium salts and quinone diazide compounds are useful as such a thermally decomposable substance. Onium salts are preferred for their thermal decomposability.

[0061] Useful onium salts include diazonium salts, ammonium salts, phosphonium salts, iodonium salts, sulfonium salts, selenonium salts, and arsonium salts. Suitable onium salts include diazonium salts described in S. I. Schelsinger, *Photogra. Sci. Eng.*, 18, 387 (1974), T.S. Bal *et al.*, *Polymer*, 21, 423 (1980), and JP-A-5-158230; ammonium salts described in U.S. Patents 4,069,055, 4,069,056, and RE 27,992, and Japanese Patent Application No. 2001-140140; phosphonium salts described in D.C. Necker *et al.* , *Macromolecules,* 17, 2468 (1984), C.S. Wen *et al.*, *Tech. Proc. Conf. Rad. Curing ASIA,* p 478 Tokyo (Oct., 1988), and U.S. Patents 4,069,055 and 4,069,056; iodonium salts described in J.V. Crivello *et al.*, *Macromolecules*, 10(6), 1307 (1977), *Chem. & Eng. News.*, Nov. 28, p. 31 (1988), EP 104,143, U.S. Patents 339,049 and 410,201, JP-A-2-150848 and JP-A-2-296514; sulfonium salts described in J.V. Crivello *et al., Polymer J.,* 17, 73 (1985), J.V. Crivello *et al., J. Org. Chem.,* 43, 3055 (1978), W.R. Watt *et al.*, *J. Polymer Sci., Polymer Chem. Ed.,* 22, 1789 (1984), J.V. Crivello *et al., Polymer Bull.,* 14, 279 (1985), J.V. Crivello *et al., Macromolecules,* 14 (5), 1141 (1981), J.V. Crivello *et al., J. Polymer Sci., Polymer Chem. Ed.,* 17, 2877 (1979), EP 370,693, EP 3,902,114, EP 233,567, EP 297,443, 297,442, U.S. Patents 4,933,377, 161,811, 410,201, 339,049, 4,760,013, 4,734,444, and 2,833,827, German Patents 2,904,626, 3,604,580, and 3,604,581; selenonium salts described in J.V. Crivello *et al.*, *Macromolecules,* 10(6), 1307 (1977), and J.V. Crivello *et al.*, *J. Polymer Sci., Polymer Chem. Ed.*, 17, 1047 (1979) ; and arsonium salts described in C.S. Wen *et al., Proc. Conf. Rad. Curing ASIA,* p478 Tokyo (Oct., 1988).

[0062] Of the onium salts preferred for use in the invention are diazonium salts. The diazonium salts described in JP-A-5-158230 are particularly preferred.

[0063] Counter ions of the onium salts include a tetrafluoroborate ion, a hexafluorophosphate ion, a triisopropylnaphthalenesulfonate ion, a 5-nitro-o-toluenesulfonate ion, a 5-sulfosalicylate ion, a 2,5-dimethylbenzenesulfonate ion, a 2,4,6-trimethylbenzenesulfonate, a 2-nitrobenzenesulfonate, a 3-chlorobenzenesulfonate ion, a 3-bromobenzenesulfonate ion, a 2-fluorocaprylnaphthalenesulfonate ion, a dodecylbenzenesulfonate ion, a 1-naphthol-5-sulfonate ion, a 2-methoxy-4-hydroxy-5-benzoylbenzenesulfonate ion, and a p-toluenesulfonate ion. Preferred of them are a hexafluorophosphate ion and alkyl aromatic sulfonate ions, e.g., a triisopropylnaphthalenesulfonate ion and a 2,5-dimethylbenzenesulfonate ion. A recommended amount of the onium salt is 0.1 to 50% by weight, preferably 0.1 to 30% by weight, still preferably 0.3 to 30% by weight, based on the total solids content of the photosensitive layer.

[0064] The quinone diazide compounds are preferably o-quinone diazide compounds. Orthoquinone diazide compounds suitable for use in the invention may have various structures as long as they have at least one o-quinone diazido group and thermally decompose to increase alkali solubility of the photosensitive layer. On thermally decomposing, o-quinone diazide compounds not only lose their inhibitory effect on dissolution of the alkali-soluble resin but become alkali-soluble *per se*, thereby helping the exposed photosensitive layer be dissolved in an alkali developer. The o-quinone diazide compounds which can be used in the invention include those described, e.g., in J. Kosar, *Light-Sensitive Systems,* John Wiley & Sons, Inc., pp. 339-352. In particular, sulfonates or sulfonamides of o-quinone diazide obtained by reacting with various aromatic polyhydroxy compounds or aromatic amino compounds are preferred. Also preferred are esters between benzoquinone (1,2)-diazidosulfonyl chloride or naphthoquinone (1,2)-diazido-5-sulfonyl chloride and a pyrogallol-acetone resin described in JP-B-43-2840) and esters between benzoquinone(1,2)-diazidosulfonyl chloride or naphthoquinone (1,2)-diazido-5-sulfonyl chloride and a phenol-formaldehyde resin described in U.S. Patents 3,046,120 and 3,188 ,210. Esters between naphthoquinone(1,2)-diazido-4-sulfonyl chloride and a phenol-formaldehyde resin or a cresol-formaldehyde resin and esters between naphthoquinone(1,2)-diazido-4-sulfonyl chloride and a pyrogallol-acetone resin are preferred as well. Additional examples of useful o-quinone diazide compounds are reported in JP-A-47-5303, JP-A-48-63802, JP-A-48-63803, JP-A-48-96575, JP-A-49-38701, JP-A-48-13354, JP-B-41-11222, JP-B-45-9610, JP-B-49-17481, U.S. Patents 2,797,213, 3,454,400, 3,544,323, 3,573,917, 3,674,459, and 3,785,825, British Patents 1,227,602, 1,251,345, 1,267,005, 1,329,888, and 1,330,932, and German Patent 854,890.

[0065] A recommended amount of the o-quinone diazide compound to be added is 1 to 50% by weight, preferably 5 to 30% by weight, still preferably 10 to 30% by weight, based on the total solids content of the photosensitive layer. The above-recited o-quinone diazide compounds can be used either individually or as a mixture of two or more thereof. Addition of less than 1% of the o-quinone diazide compound is ineffective on improvement of imaging performance. Addition of more than 50% of the o-quinone diazide compound can result in reduction of durability of the image area or reduction of sensitivity.

[0066] From the standpoint of thermal decomposability, onium salts are preferred to the quinone diazide compounds. The onium salt having higher thermal decomposability is considered more effective to increase the discrimination (contrast) between exposed and unexposed areas of the photosensitive layer.

[0067] The photosensitive layer provided on the aluminum support may have either a single layer structure or a multilayer structure composed of two or more layers. The multilayer structure will be described taking for instance a double layer structure composed of an upper layer and a lower layer.

[0068] In designing a double layer structure, it is preferred to select alkali-soluble resins for making up the upper and lower layers so that the alkali-soluble resin of the upper layer be less soluble in an alkali developer than that of the lower layer.

[0069] The infrared absorbers can be added to either one of or both of the upper and lower layers. The infrared absorbers used in different layers may be the same or different. Each layer may contain a plurality of infrared absorbers. In whichever layer the infrared absorber may be used, the amount of the infrared absorber is in a range of 0.01 to 50% by weight, preferably 0.1 to 50% by weight, still preferably 0.1 to 30% by weight, based on the solids content of the layer in which it is added. Where the infrared absorber is incorporated in two or more layers, it is preferred that the total amount of the infrared absorbers present in the multilayered photosensitive layer be within the above-recited range.

[0070] Where the photosensitive layer has a multilayer structure, the above-described thermally decomposable substance which substantially reduces alkali solubility of the alkali-soluble resin before thermal decomposition may be added to either of, or both of the upper and lower layers. Because the thermally decomposable substance can partially decompose with time, it is preferably added to the lower layer, though. Where the thermally decomposable substance is added to two or more layers, the amount to be added to each layer is preferably selected so as to give a total content falling within the above-recited range.

[0071] The lactone compound can be added to either of or both of the upper and lower layers. It is more effective that the lactone compound is added to the upper layer.

[4] Other components

[0072] If desired, the photosensitive layer can further contain various additives as described below as long as the effects of the present invention are not impaired.

[0073] For the purpose of enhancing discrimination between image and non-image areas or improving scratch resistance, it is preferred to add a polymer of a (meth) acrylate monomer having, in the molecule thereof, two or three perfluoroalkyl groups having 3 to 20 carbon atoms, such as the polymer described in JP-A-2000-187318. Where the photosensitive layer has a double layer structure, the polymer can be added to either the upper layer or the lower layer, but addition to the upper layer is more effective. The amount of the polymer to be added is typically 0.1 to 10% by weight, preferably 0.5 to 5% by weight, based on the layer-forming materials.

[0074] For the purpose of improving scratch resistance, a compound which reduces the coefficient of static friction can be added to the photosensitive layer. For example, long-chain alkylcarboxylic acid esters, such as those described in U.S. Patent 6,117,913, can be used. While such a compound may be added to either the upper layer or the lower layer, addition to the upper layer is more effective. The amount of the compound to be added is typically 0.1 to 10% by weight, preferably 0.5 to 5% by weight, based on the layer-forming materials.

[0075] If necessary, the photosensitive layer may contain a low-molecular compound having an acidic group, such as a sulfonic acid group, a carboxyl group or a phosphoric acid group. Compounds having a sulfonic acid group including aromatic sulfonic acids (e.g., p-toluenesulfonic acid and naphthalenesulfonic acid) and aliphatic sulfonic acids are preferred. The compound may be added to either layer. The amount of the compound to be added is typically 0.05 to 5% by weight, preferably 0.1 to 3% by weight, based on the layer-forming materials. Addition of more than 5% results in unfavorably increased solubility of the layer in a developer.

[0076] The photosensitive layer may contain various dissolution suppressors for solubility control. Suitable dissolution suppressors include disulfone compounds and sulfone compounds, such as 4,4'-bishydroxyphenylsulfone, as disclosed in JP-A-11-119418. The dissolution suppressor may be added to either layer. The amount to be added is typically 0.05 to 20% by weight, preferably 0.5 to 10% by weight, based on the layer to which it is added.

[0077] In order to improve sensitivity, a cyclic acid anhydride, a phenol compound or an organic acid can be used in combination. Useful cyclic acid anhydrides include those described in U.S. Patent 4,115,128, such as phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, cis-1,2,3,6-endoxy-tetrahydrophthalic anhydride, tetrachlorophthalic anhydride, maleic anhydride, chloromaleic anhydride, α-phenylmaleic anhydride, succinic anhydride, and pyromellitic anhydride. Useful phenol compounds include 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. Useful organic acids include those described in JP-A-60-88942 and JP-A-2-96755, such as sulfonic acids, sulfinic acids, alkylsulfuric acids, phosphonic acids, phosphoric esters, and carboxylic acids. Examples are p-toluenesulfonic acid, dodecylbenzenesulfonic acid, p-toluenesulfinic acid, ethylsulfuric acid, phenylphosphonic acid, phenylphosphinic acid, phenyl phosphate, diphenyl phosphate, benzoic acid, isophthalic acid, adipic acid, p-toluylic acid, 3,4-diemthoixybenzoic acid, phthalic acid, terephthalic acid, 4-cyclohexene-1,2-dicarboxylic acid, erucic acid, lauric acid, n-undecanoic acid, and ascorbic acid. The amount of the cyclic acid anhydride, phenol or organic acid to be added is usually 0.05 to 20% by weight, preferably 0.1 to 15% by weight, still preferably 0.1 to 10% by weight, based on the layer-forming materials.

[0078] For the purpose of enhancing stability of the photosensitive layer under development conditions, the photosensitive layer can contain nonionic surface active agents (such as those described in JP-A-62-251740 and JP-A-3-208514), amphoteric surface active agents (such as those described in JP-A-59-121049 and JP-A-4-13149), siloxane compounds (such as those described in EP950517) or fluorine-containing compound copolymers (such as those described in JP-A-11-288093). These compounds can be added to either one or both of upper and lower layers.

[0079] Examples of the nonionic surface active agents include sorbitan tristearate, sorbitan monopalmitate, sorbitan trioleate, glycerol monostearate, and polyoxyethylene nonylphenyl ether. Examples of the amphoteric surface active agents include alkyldi(aminoethyl)glycines, alkylpolyaminoethylglycine hydrochlorides, 2-alkyl-N-carboxyethyl-N-hydroxyethylimidazolinium betaines, and N-tetradecyl-N,N-betaines (e.g., Amogen K from Dai-ichi Kogyo Seiyaku Co., Ltd.).

[0080] Examples of preferred siloxane compounds include dimethylsiloxane/alkylene oxide block copolymers, such as DBE-224, DBE-621, DBE-712, DBP-732 and DBP-534 (all available from Chisso Corp.) and Tego Glide 100 (polyether siloxane copolymer available from Tego Chemie Service GmbH).

[0081] The nonionic or amphoteric surface active agent can be used in an amount usually of 0.05 to 15% by weight, preferably 0.1 to 5% by weight, based on the coating composition.

[0082] The photosensitive layer can contain a printing-out agent for providing a visible image upon heating or a colorant inclusive of a dye and a pigment for providing a colored image area.

[0083] The printing-out agent typically includes a combination of a compound capable of generating an acid on heating by exposure, namely, a photo-acid generator and a salt-forming organic dye. For example, a combination of an o-naphthoquinonediazido-4-sulfonyl halide and a salt-forming organic dye disclosed in JP-A-50-36209 and JP-A-53-8128 and a combination of a trihalomethyl compound and a salt-forming organic dye described in JP-A-53-36223, JP-A-54-74728, JP-A-60-3626, JP-A-61-143748, JP-A-61-151644, and JP-A-63-58440 can be used. The trihalomethyl compound includes an oxazole compound and a triazine compound, both of which provide a clear printed-out image having high stability with time.

[0084] The colorant for image coloring includes the above-described salt-forming organic dyes and other dyes. Suitable dyes, inclusive of the salt-forming organic dyes, include oil-soluble dyes and basic dyes. Specific examples are Oil Yellow #101, Oil Yellow #103, Oil Pink #312, Oily Green BG, Oil Blue BOS, Oil Blue #603, Oil Black BY, Oil Black BS, and Oil Black T-505 (all available from Orient Chemical Industries, Ltd.); Victoria Pure Blue, Crystal Violet (C.I. 42555), Methyl Violet (C.I. 42535), Ethyl Violet, Rhodamine B (C.I. 145170B), Malachite Green (C.I. 42000), and Methylene Blue (C.I. 52015). The dyes recited in JP-A-62-293247 are particularly preferred. The colorant is added in an amount usually of 0.01 to 10% by weight, preferably of 0-1 to 3% by weight, based on the total solids content of the photosensitive layer.

[0085] Where the photosensitive layer has a double layer structure, the printing-out agent or the colorant can be added to either one or both of the upper and lower layers.

[0086] If desired, a plasticizer can be added to the photosensitive layer for improving flexibility and the like of the layer. Suitable plasticizers include butyl phthalyl, polyethylene glycol, tributyl citrate, diethyl phthalate, dibutyl phthalate, dihexyl phthalate, dioctyl phthalate, tricresyl phosphate, tributyl phosphate, trioctyl phosphate, tetrahydrofurfuryl oleate, and oligomers or polymers of (meth)acrylic acid.

[0087] The term "lower layer" as used herein means the layer closer to the support out of a plurality of layers provided on the support. According to this definition, where a photosensitive layer formed on the support is composed of two layers, the term "lower layer" indicates the lower photosensitive layer. Where a layer having no imaging function is provided between the photosensitive layer and the support, such a non-imaging layer can be called a "lower layer". In the former case, unless there is a fear of confusion, the upper photosensitive layer is sometimes simply called a "'photosensitive layer" while the lower photosensitive layer is sometimes called a "lower layer". The lower layer having no imaging function as referred to in the latter case can be made up of the same components as used in the photosensitive layer except an infrared absorber. The proportions of the components except an infrared absorber in the lower layer are selected from the respective ranges recited above. In order to make the lower layer more soluble than the upper layer, the amounts of a dissolution inhibitor, a dissolution accelerator, and a development sensitivity improving compound to be added in that lower layer should be adjusted appropriately, or additional additives could be used in that lower layer.

[0088] The lithographic printing plate precursor of the present invention is produced by coating an aluminum support with a coating composition prepared by dissolving the above-recited components in an appropriate solvent. The photosensitive layer and the lower layer can be formed by successively applying to the support the respective coating compositions separately prepared by dissolving the respective components in a solvent.

[0089] The solvents to be used include, but are not limited to, 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-diemthylacetamide, N,N-dimethylformamide, tetramethylurea, N-methylpyrrolidone, dimethyl sulfoxide, sulfolane, γ-butyrolactone, and toluene. These solvents can be used either individually or as a mixture thereof.

[0090] When a photosensitive coating composition is applied to a previously formed lower layer, if the solvent used in the coating composition is capable of dissolving the alkali-soluble resin contained in the lower layer, layer mixing can occur in the interface to an unignorable degree. In an extreme case, the two layers can be mixed up into one. If such interfacial mixing of adjacent layers happens, or if adjacent layers are so compatible with each other as to behave like a uniform single layer, the effects that should have been exerted by providing two independent layers maybe ruined. Therefore it is desirable that the solvent to be used for forming the photosensitive layer be a poor solvent for the alkali-soluble resin contained in the lower layer.

[0091] Each coating composition preferably has a total solids content of 1 to 50% by weight.

[0092] Where the photosensitive layer is composed of an upper layer and a lower layer, a preferred coating weight of the upper layer is 0.05 to 1.0 g/m^2, and that of the lower layer is 0.3 to 3.0 g/m^2, both on a solid basis, while varying according to use. With the upper layer having a coating weight less than 0.05 g/m^2, the imaging performance can reduce. With the upper layerhavingacoatingweightmore than 1.0 g/m^2, the sensitivity can reduce. The total coating weight of the upper and lower layers is preferably 0.5 to 3.0 g/m^2. A total coating weight less than 0.5 g/m^2 results in deteriorated film properties, and a total coating weight exceeding 3.0 g/m^2 tends to result in reduced sensitivity. As the coating weight decreases, the apparent sensitivity increases, but the film properties of the upper and lower layers will deteriorate.

[0093] The lower layer and the photosensitive layer can be applied by various techniques, such as bar coating, spin coating, spray coating, curtain coating, dip coating, air knife coating, blade coating, and roll coating.

[0094] The photosensitive coating composition can contain surface active agents for improving coating properties, such as the fluorine-containing surface active agents disclosed in JP-A-62-170950. A suitable amount of such a surface active agent is 0.01 to 1% by weight, particularly 0.05 to 0.5% by weight, based on the total solids content of the layer to which it is added.

[0095] Each of the coating composition for lower layer and that for photosensitive layer is dried after application. Drying is carried out in a conventional manner known per se. For instance, the coating film is dried by a convection heating method in which hot air is blown to the coating film applied to the support, a radiation heating method in which the coating film is dried by heat radiated from hot plates set above and below the coated support (see JP-A-60-149871), or a conduction heating method in which a coated support is brought into contact with a roller having a heating medium circulated therein (see JP-A-60-21334 and JP-A-60-62778).

[0096] The convection heating method is preferred of these drying methods. For controlling the water content of the photosensitive layer, the water content of the hot air to be blown is preferably 0.007 kg/kg or smaller, still preferably 0.05 kg/kg or smaller.

[0097] With respect to developability of the printing plate precursor, a photosensitive layer having been dried under severer conditions tends to demand a developer having a higher electrical conductivity for sufficient development. That is, the severer the drying conditions, the lower the developability of the photosensitive layer. Conversely, a photosensitive layer having been dried under milder conditions tends to be developable with a developer having a lower electrical conductivity. In other words, the milder the drying conditions, the higher the developability. Drying conditions as designed are realized by adjusting the air temperature, the amount of air, the direction of air flow, the temperature and material of a contact heating medium, and the like.

[0098] It is preferred for the lower layer immediately before being coated with a photosensitive coating composition to have as small a residual solvent content as possible, preferably a residual solvent content of not more than 80 mg/m^2, particularly not more than 60 mg/m^2.

[5] Aluminum support

[0099] The aluminum plate which can be used in the invention is made of dimensionally stable aluminum-based metal, i.e., aluminum or an aluminum alloy. Not only a pure aluminum plate but a plate of an aluminum-based alloy containing a trace amount of other elements and a plastic film or paper laminated or deposited with aluminum or an aluminum alloy can be employed. A composite sheet composed of a polyethylene terephthalate film and an aluminum sheet is also employable.

[0100] In what follows, various types of the above-mentioned substrates comprising aluminum or an aluminum alloy will be inclusively referred to as an aluminum plate. The other elements making up the aluminum-based alloy include silicon, iron, manganese, copper, magnesium, chromium, zinc, bismuth, nickel, and titanium. The total content of the other elements in the aluminum alloy is 10% by weight at the most.

[0101] A pure aluminumplate is preferred in the present invention. In view of refining technological difficulty in obtaining completely pure aluminum, aluminum containing a trace amount of impurity elements will do. The aluminum plate to be used in the invention can be chosen appropriately from those of materials known in the art and widely available, such as JIS A1050, JIS A1100, JIS A3005, JIS A3004, and International Registration Record (AA) 3103A. The aluminum plate may be from an ingot produced either by continuous casting or DC casting. An aluminum plate prepared by DC casting with no process annealing nor soaking pit treatment is also employable. An aluminum plate textured by laminate rolling, transfer, and the like in the final rolling processing is also useful. The aluminum plate to be used in the invention is about 0.1 to 0.6 mm thick. This thickness is subject to variation according to the size of a printing machine, the size of a printing plate, and users' demand.

[0102] The aluminum support used in the lithographic printing plate precursor is prepared by subjecting the aluminum plate to (1) graining, (2) alkali etching, and (3) anodizing. The process of preparing the aluminum support from the aluminum plate may further comprise additional steps.

(1) Graining

[0103] The aluminum plate is grained to have a desired surface profile. Graining includes the mechanical graining, chemical graining, and electrolytic graining disclosed in JP-A-56-28893; electrochemical graining in an electrolytic solution containing hydrochloric acid or nitric acid; and other mechanical graining techniques such as wire brush graining (the aluminum surface is scratched with metal wire), ball graining with abrasive balls and a polishing agent, and brush graining with a nylon brush and a polishing agent. These graining techniques can be used either individually or as a combination thereof.

[0104] Electrochemical graining in a hydrochloric acid electrolytic solution or a nitric acid electrolytic solution is preferred to prepare the aluminum support for use in the invention. A suitable current density is 50 to 400 C/dm^2 at the anode. In more detail, electrochemical graining is carried out in, for example, an electrolytic solution having a hydrochloric acid or nitric acid concentration of 0.1 to 50% by weigh at a temperature of 20 to 100°C for 1 second to 30 minutes using a direct current or an alternating current at a current density of 100 to 400 C/dm^2. The electrochemical graining is preferred in view of ease of finely texturing the aluminum surface and thereby improving adhesion between the support and the photosensitive layer.

[0105] As a result of electrochemical graining, crater-like or honeycomb pits of about 0.5 to 20 μm in diameter are formed on the aluminum plate in an area ratio of 30 to 100%. The formed pits are contributory to improvements in stain resistance of non-image areas and press life of the resulting printing plate. For conducting electrochemical graining, the electricity quantity, i.e., the product of the current and the time, necessary to form sufficient pits is an important condition. To form sufficient pits with a less electricity quantity is desirable from the standpoint of energy saving. The surface roughness after graining is preferably 0.2 to 0.5 μm in terms of an arithmetic mean roughness (Ra) measured at a cut-off of 0.8 mm over an assessment length of 3.0 mm in accordance with JIS B0601-1994.

(2) Alkali etching

[0106] The grained aluminum plate is then chemically etched with an alkali etchant. The alkali includes, but is not limited to, sodium hydroxide, sodium carbonate, sodium aluminate, sodium metasilicate, sodium phosphate, potassium hydroxide, and lithium hydroxide.

[0107] Alkali etching conditions are notparticularly restricted as long as 0.5 to 4 g/m^2 of aluminum is etched out. In general, the etchant preferably has an alkali concentration of 1 to 50% by weight, particularly 5 to 30% by weight, and a temperature of 20 to 100°C, particularly 30 to 50°C.

[0108] After alkali etching, the aluminum plate is desmutted with an acid, such as nitric acid, sulfuric acid, phosphoric acid, chromic acid, hydrofluoric acid or fluoroboric acid. Desmutting after electrochemical graining is preferably effected with 15 to 65 wt% sulfuric acid at 50 to 90°C as taught in JP-53-12739.

(3) Anodizing

[0109] The resulting aluminum plate is preferably subjected to anodizing in a conventional manner to form an anodized film on the aluminum surface. Anodizing is carried out by applying a direct current or an alternating current to the aluminum plate in an aqueous or nonaqueous solution of sulfuric acid, phosphoric acid, chromic acid, oxalic acid, sulfamic acid, benzenesulfonic acid, etc. or a mixture of two or more of these acids.

[0110] The electrolytic solution is allowed to contain impurity components usually originated in an aluminum alloy plate, electrodes, tap water, well water, etc. and/or additional components. Additional components that may be present include ions of Na, K, Mg, Li, Ca, Ti, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn or like metals; cations, e.g., an ammonium ion; and anions, e.g., a nitrate ion, a carbonate ion, a chloride ion, a phosphate ion, a fluoride ion, a sulfite ion, a titanate ion, a silicate ion, and a borate ion. The additional components may be present in a total concentration of up to about 10,000 ppm.

[0111] Anodizing conditions vary depending on the kind of the electrolyte used. Generally speaking, the electrolyte concentration is 1 to 80% by weight, the liquid temperature is -5 to 70°C, the current density is 0. 5 to 60 A/dm^2, the voltage is 1 to 100 V, and the electrolysis time is 10 to 200 seconds. The anodizing method disclosed in British Patent 1,412,768, in which a high current density is applied in a sulfuric acid electrolytic solution, is particularly preferred.

[0112] A suitable thickness of the anodized film is 1 to 10 g/m^2, preferably 1.5 to 7 g/m^2, still preferably 2 to 5 g/m^2. With an anodized film thickness less than 1 g/m^2 the aluminum support is liable to scratches. Formation of an anodized film of more than 10 g/m^2 requires large electric energy, which is economically disadvantageous.

(4) Alkali metal silicate treatment

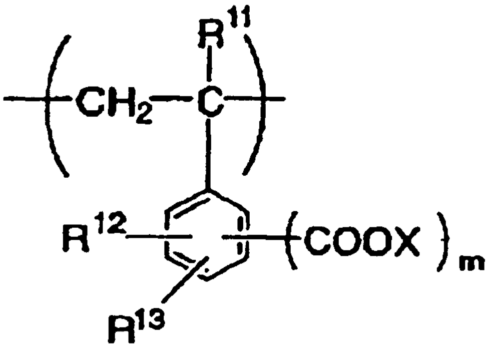
[0113] If necessary, the anodized aluminum plate is soaked in an aqueous solution of an alkali metal silicate. In an illustrative example of the treatment, the aluminum plate is soaked in a 0.01 to 5.0 wt% alkali metal silicate aqueous solution at 5 to 40°C, preferably 10 to 40°C, for 1 to 60 seconds, preferably 2 to 20 seconds, followed by washing with running water.

[0114] The alkali metal silicate includes sodium silicate, potassium silicate, and lithium silicate. The alkali metal silicate aqueous solution may contain an appropriate amount of sodium hydroxide, potassium hydroxide, lithium hydroxide, etc. The solution may further contain an alkaline earth metal salt or a salt of a group 4 (group IVB) metal salt. The alkaline earth metal salt includes nitrates, e.g., calcium nitrate, strontium nitrate, magnesium nitrate, and barium nitrate, sulfates, hydrochlorides, phosphates, acetates, oxalates, and borates. The group 4 (group IVB) metal salts include titanium tetrachloride, titanium trichloride, potassium titanium fluoride, potassium titanium oxalate, titanium sulfate, titanium tetraiodide, zirconium dioxide, zirconium oxychloride, and zirconium tetrachloride. These alkaline earth metal salts and group 4 (group IVB) metal salts can be used either individually or as a combination of two or more thereof.

[0115] The amount of silicon adsorbed by the soaking treatment, which is measured by X-ray fluorescence analysis, is preferably about 1.0 to 15.0 mg/m^2. The alkali metal silicate treatment is effective to increase resistance of the aluminum support against an alkali developer. As a result, leaching of aluminum into an alkali developer is suppressed, and scum generation in a developer due to exhaustion can be reduced.

[0116] The lithographic printing plate precursor according to the present invention essentially comprises the above-described aluminum support and the photosensitive layer provided thereon. If desired, a primer coat may be provided between the support and the photosensitive layer. Various organic compounds are used to form a primer coat, including carboxymethyl cellulose, dextrin, gum arabic, organic phosphonic acids such as amino-containing phosphonic acids (e.g., 2-aminoethylphosphonic acid), substituted or unsubstitutedphenylphosphonic acid, naphthylphosphonic acid, alkylphosphonic acids, glycerophosphonic acid, methylenediphosphonic acid, and ethylenediphosphonic acid; organic phosphoric acids, such as substituted or unsubstituted phenylphosphoric acid, naphthylphosphoric acid, alkylphosphoric acids, and glycerophosphoric acid; organic phosphinic acids, such as substituted or unsubstituted phenylphosphinic acid, naphthylphosphinic acid, alkylphosphinic acids, and glycerophosphinic acid; amino acids, such as glycine and β-alanine; and hydroxyl-containing amine hydrochlorides, such as triethanolamine hydrochloride. These organic compounds can be used either individually or as a mixture of two or more thereof.

[0117] A primer coat containing at least one of organic polymers having a repeating unit shown below is also preferred.



wherein R^{11} represents a hydrogen atom, a halogen atom or an alkyl group; R^{12} and R^{13} each represent a hydrogen atom, a hydroxyl group, a halogen atom, an alkyl group, a substituted alkyl group, an aryl group, a substituted aryl group, $-OR^{14}$, $-COOR^{15}$, $-CONHR^{16}$, $-COR^{17}$ or -CN, or R^{12} and R^{13} are taken together to form a ring; R^{14}, R^{15}, R^{16}, and R^{17} each represent an alkyl group or an aryl group; X represents a hydrogen atom, a metal atom or $NR^{18}R^{19}R^{20}R^{21}$; R^{18}, R^{19}, R^{20}, and R^{21} each represent a hydrogen atom, an alkyl group, a substituted alkyl group, an aryl group or a substituted aryl group, or R^{18} and R^{19} are taken together to form a ring; and m represents an integer of 1 to 3.

[0118] The primer coat can be provided by applying a solution of the above-described organic compound in water, an organic solvent (e.g., methanol, ethanol or methyl ethyl ketone) or a mixture thereof to the aluminum support. The solution can be applied with various application means and dried to form a primer coat. Alternatively, the aluminum support is dipped in the solution to make the compound be adsorbed, followed by washing with water, etc. and dried. The solution to be used in the former method has a concentration of 0.005 to 10% by weight. The solution to be used in the latter method has a concentration of 0.01 to 20% by weight, preferably 0.05 to 5% by weight. The latter method is carried out by dipping the aluminum support in the solution at 20 to 90°C, preferably 25 to 50°C, for 0.1 second to 20 minutes, preferably 2 seconds to 1 minute. The solution to be used in the latter method may be adjusted to a pH of 1 to 12 with a basic substance, e.g., ammonia, triethylamine or potassium hydroxide, or an acidic substance, e.g., hydrochloric acid or phosphoric acid. The solution may contain a yellow dye for improving tone reproducibility of the imaging materials.

[0119] The coating weight of the primer coat is suitably 2 to 200 mg/m^2, preferably 5 to 100 mg/m^2. A primer coat less than 2 mg/m^2 or more than 200 mg/m^2 will fail to assure a sufficient press life.

[0120] The thus produced lithographic printing plate precursors are generally packaged in a stack with an interleaf between every adjacent precursors, shipped, transported, and stored. In a typical site of platemaking and printing, a printing plate precursor with an interleaf on is held on an autoloader, carried, and mounted on a place where platemaking is conducted. Thereafter, the interleaf is removed. Where a DTP system is adopted, the place of platemaking is on a press.

[0121] After the interleaf is removed, the printing plate precursor is imagewise exposed and developed.

[0122] A light source used for imagewise exposure is preferably one having a light emission wavelength in the near infrared to infrared region. The exposure may be either scanning exposure or planar exposure. Scanning exposure using a solid state laser or a semiconductor laser is preferred. A preferred light emission wavelength is 760 to 1080 nm.

[0123] A developer which can be used to develop the exposed printing plate precursor of the present invention is an alkaline solution having a pH ranging from 9.0 to 14.0, preferably 12.0 to 13.5. The term "developer" as used herein is intended to include a replenisher. Known alkali aqueous solutions can be used as a developer. The alkali includes inorganic alkali metal salts, e.g., sodium silicate, potassium silicate, sodium tertiary phosphate, potassium tertiary phosphate, ammonium tertiary phosphate, sodium secondary phosphate, potassium secondary phosphate, ammonium secondary phosphate, sodium carbonate, potassium carbonate, ammonium carbonate, sodium hydrogencarbonate, potassium hydrogencarbonate, ammonium hydrogencarbonate, sodium borate, potassium borate, ammonium borate, sodium hydroxide, ammonium hydroxide, potassium hydroxide, and lithium hydroxide; and organic alkalis, e.g., monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, triisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethyleneimine, ethylenediamine, and pyridine. The alkali aqueous solutions can be used either individually or as a mixture thereof.

[0124] Out of the above-recited alkali aqueous solutions, a preferred one is a so-called silicate developer, which contains an alkali metal silicate as a base or a mixture of a base and a silicon compound (capable of forming an alkali silicate in situ) and has a pH of 12 or higher. Another preferred one is a so-called non-silicate developer, which contains no alkali silicate but a non-reducing sugar (an organic compound having a buffering action) and a base.

[0125] Developing performance of the silicate developer is adjustable by controlling a concentration of the alkali metal silicate and a ratio of silicon oxide (SiO_2) to an alkali metal oxide (M_2O), generally expressed in an $[SiO_2]/[M_2O]$ molar ratio. Examples of suitable silicate developers are an aqueous sodium silicate solution having 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% by weight (disclosed in JP-A-54-62004) and an aqueous alkali metal silicate solution having an $[SiO_2]/[M]$ molar ratio of 0.5 to 0.75 (i.e., $[SiO_2]/[M_2O]$=1.0 to 1.5) and an SiO_2 content of 1 to 4% by weight and further containing potassium in an amount of at least 20% based on the gram atomic weight of the total alkali metal content of the developer.

[0126] The non-silicate developer is more advantageous than the silicate developer for developing the lithographic printing plate precursor of the present invention for the following reasons. The non-silicate developer does no harm to the surface of the photosensitive layer and is effective to maintain satisfactory ink receptivity on the image area. Considering that a lithographic printing plate material generally has a narrow development latitude and tends to undergo large variation of line width with variation of a developer's pH, the non-silicate developer containing a non-reducing sugar, which exhibits buffering performance on pH variation, is advantageous over a silicate-containing developer. Compared with a silicate, a non-reducing sugar is less apt to contaminate a conductivity sensor, a pH sensor, etc. used to control the developer activity. Furthermore, the non-silicate developer is more effective in improving discrimination between image and non-image areas. This is assumed tobebecause the non-silicate developer exhibits mild behavior in penetrating into the photosensitive layer, which is important for achieving discrimination and maintenance of film properties. As a result, a difference between image and non-image areas can be obtained more easily.

[0127] The non-reducing sugar is a saccharide that has no free aldehyde or ketone reducing group and therefore exhibits no reducing properties. Non-reducing sugars are classified into trehalose type oligosaccharides having reducing groups bonded to each other, glycosides having a non-sugar moiety bonded to the reducing group of a saccharide, and sugar alcohols produced by hydrogenation of corresponding reducing sugars. Any of these groups of non-reducing sugars can be used suitably. The non-reducing sugars described in JP-A-8-305039 are preferably used in the invention.

[0128] The trehalose type oligosaccharides include saccharose and trehalose. The glycosides include alkyl glycosides, phenol glycosides, and mustard oil glycosides. The sugar alcohols include D,L-arabinitol, ribitol, xylitol, D,L-glucitol, D, L-mannitol, D,L-iditol, D,L-altritol, galactitol, and allitol. Additionally, maltitol obtained by hydrogenation of dissacharide maltose, reduced sugar syrup obtained by hydrogenation of oligosaccharides, and the like are also suitable. Preferred of these non-reducing sugars are trehalose type oligosaccharides and sugar alcohols. D-Glucitol, saccharose, reduced sugar syrup, etc. are particularly preferred for their buffering action in a proper pH region and low price.

[0129] The non-reducing sugars can be used either individually or as a mixture of two or more thereof. A preferred content of the non-reducing sugar in the non-silicate developer is 0.1 to 30% by weight, particularly 1 to 20%byweight. Anon-reducing sugar content of less than 0.1% by weight tends to fail to exhibit a substantial buffering effect. It is difficult to prepare such a high concentration solution that can be diluted on use to give a non-reducing sugar concentration of higher than 30% by weight. Besides, use of more than 30% of the non-reducing sugar results in increased cost.

[0130] The base to be used in combination with the non-reducing sugar is selected from known alkalis including inorganic alkalis and organic alkalis. The inorganic alkalis include 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 hydrogencarbonate, potassium hydrogencarbonate, ammonium hydrogencarbonate, sodiumborate, potassium borate, and ammonium borate.

[0131] The organic alkalis include monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, triisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethyleneimine, ethylenediamine, and pyridine.

[0132] The above-recited bases can be used either individually or as a mixture of two or more thereof. Sodium hydroxide and potassium hydroxide are preferred of them.

[0133] A non-silicate developer containing an alkali metal salt of a non-reducing sugar in place of a combination of a non-reducing sugar and a base is also useful. The non-silicate developer can contain an alkaline buffer solution comprising a weak acid and a strong base in combination with the non-reducing sugar. The weak acid is preferably one having a dissociation constant pKa of 10.0 to 13.2, which is selected from, for example, those described in Ionization Constants of Organic Acids in Aqueous Solution, Pergman Press. Specific examples of useful weak acids are alcohols, such as 2,2,3,3-tetrafluoropropanol-1, trifluoroethanol, and trichloroethanol; aldehydes, such as pyridine-2-aldehyde and pyridine-4-aldehyde; compounds having a phenolic hydroxyl group, such as salicylic acid, 3-hydroxy-2-naphthoic acid, catechol, gallic acid, sulfosalicylic acid, 3,4-dihydroxysulfonic acid, 3,4-dihydroxybenzoic acid, hydroquinone (pKa: 11.56), pyrogallol, o-, m- or p-cresol, and resorcinol; oximes, such as acetoxime, 2-hydroxybenzaldehyde oxime, dimethyl glyoxime, ethanediamide dioxime, and acetophenone oxime; nucleic acid-related substances, such as adenosine, inosine, guanine, cytosine, hypoxanthine, and xanthine; diethylaminomethylphosphonic acid, benzimidazole, and barbituric acid.

[0134] If desired, various surface active agents or organic solvents may be added to the developer and the replenisher for the purpose of accelerating or suppressing the developing activity, facilitating dispersion of development scum, or improving ink receptivity of the image area. Anionic, cationic, nonionic or amphoteric surface active agents are preferred. If necessary, the developer and the replenisher may contain a reducing agent, such as hydroquinone, resorcin, and sodium or potassium salts of inorganic acids, such as sulfites and hydrogensulfites; an organic carboxylic acid, a defoaming agent, a water softener, and so forth.

[0135] The lithographic printing plate precursor having been developed with the developer and the replenisher is subjected to an after-treatment with washing water, a rinsing solution containing a surface active agent or a desensitizing solution containing gum arabic or a starch derivative, or a combination of such after-treatments.

[0136] In the field of platemaking and printing, an automatic developing machine (plate processor) has recently been spreading for rationalization and standardization. A plate processor is generally sectioned into a developing part and an after-treatment part and composed of a conveyer, processing solution tanks, and spraying units. An exposed plate is development processed while being transferred horizontally on the conveyer by receiving successive sprays of each pumped processing solution through a spray nozzle. An immersion development process is recently proposed, in which the plate precursor is dipped in a holding tank containing a processing solution as guided by submerged guide rolls. In these automatic processing systems, each tank is replenished with a replenisher as scheduled based on the throughput, the operating time, and the like. A so-called "one-shot processing system" using a substantially unused processing solution is also applicable.

[0137] Where a lithographic printing plate obtained by exposure, development, washing and/or rinsing, and/or gumming has an unnecessary image area (e.g., a portion corresponding to original film edges), the unnecessary image area is deleted. Deletion is preferably carried out by applying an image remover to the unnecessary image area and allowing the plate to stand for a prescribed period of time, followed by washing with water as taught in JP-B-2-13293. A deletion method comprising irradiating the unnecessary image area with active light rays led through an optical fiber and then developing as disclosed in JP-A-59-174842.

[0138] If desired, the printing plate thus obtained is coated with desensitizing gum prior to printing. Where higher impression capacity is desired, the plate is subjected to a burning-in treatment. Prior to burning-in, it is preferred to treat the printing plate with a burning conditioner as described in JP-B-61-2518, JP-B-55-28062, JP-A-62-31859, and JP-A-61-159655. The treatment with a burning conditioner is carried out by applying sponge or absorbent wadding impregnated with a burning conditioner to the plate or dipping the plate in a vat filled with a burning conditioner or by use of an automated coating device. For better results, the burning conditioner applied is leveled with a squeegee or a squeegee roller.

[0139] The burning conditioner is usually applied in an amount of 0.03 to 0.8 g/m^2 on a dry basis. The applied burning conditioner is then heated as such or after drying to a high temperature in a burning processor (e.g., BP-1300 supplied by Fuji Photo Film Co., Ltd.). The heating is preferably conducted at 180 to 300°C for 1 to 20 minutes, while varying according to the imaging material.

[0140] The burnt-in printing plate may be subjected to conventional treatments, such as washing with water and gumming, according to necessity. Where a burning conditioner containing a water-soluble polymer, etc. has been applied, a desensitizing treatment such as gumming can be omitted. The resulting lithographic printing plate is mounted on an offset printing press and used to produce a large number of impressions.

EXAMPLES

[0141] The present invention will now be illustrated in greater detail with reference to Examples, but it should be understood that the invention is not deemed to be limited thereto. Unless otherwise noted, all the percents are by weight.

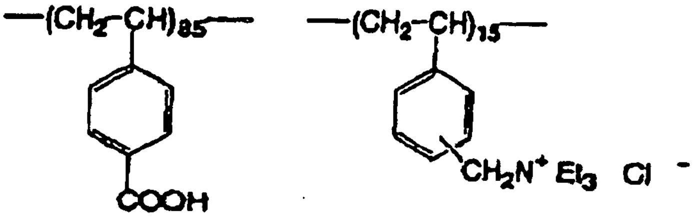
[0142] An aluminum support used in Examples and Comparative Examples was prepared as follows.

[0143] A 0.3mm thick aluminum plate (JIS A1050) was degreased with trichloroethylene and grained with a nylon brush and an aqueous slurry of pumice stone (400 mesh). After thoroughly washing with water, the aluminum plate was immersed in a 25% sodium hydroxide aqueous solution at 45°C for 9 seconds to etch out about 3 g/m^2 of aluminum, followed by washing with water. After neutralizing by immersion in 20% nitric acid for 20 seconds and washing with water, the aluminum plate was anodized in 7% sulfuric acid using a direct current at a current density of 15 A/dm^2 to form 3 g/m^2 of an anodized film. After washing with water and drying, the anodized aluminum plate was treated with a 2.5% sodium silicate aqueous solution at 30°C for 10 seconds to prepare an aluminum support. A primer having the following composition was applied to a dry coating thickness of 15 mg/m^2 and dried at 80°C for 15 seconds to form a primer coat.

Composition of primer:

[0144]

Polymer of formula:	**0.3 g**



(molecular weight: 28,000)

Methanol	**100 g**
Water	**1 g**

EXAMPLES 1 AND 2 AND COMPARATIVE EXAMPLE 1

[0145] A coating composition for photosensitive layer having formulation A shown below was applied to the primer coat of the aluminum support and dried in the apparatus shown in Fig. 1 under the following conditions to prepare a lithographic printing plate precursor of Example 1. About 10 seconds after the application, high pressure air of 3000 mmAq was blown from slit nozzles to the wet coating film. The total drying time in the first drying zone 3 was 15 seconds. The temperature of hot air fed to the first drying zone 3 was 80°C (velocity: 5 m/s), and the high pressure air temperature was 60°C (velocity: 200 m/s). In the second drying zone 4, the total drying time was 20 seconds, and the hot air temperature was 120°C. The dry coating weight of the photosensitive layer thus formed was 1 g/m^2. The film thickness distribution of the photosensitive layer was measured according to the aforementioned method. As a result, the relative standard deviation was found to be 15%.

[0146] A lithographic printing plate precursor of Example 2 was produced in the same manner as in Example 1, except for replacing the guide roll 14 with a hot roll heated to 100°C to carry out hot roll drying for 1.2 second. The photosensitive layer thus formedhadacoatingweightof 1 g/m^2 and a thickness distribution with a relative standard deviation of 10%.

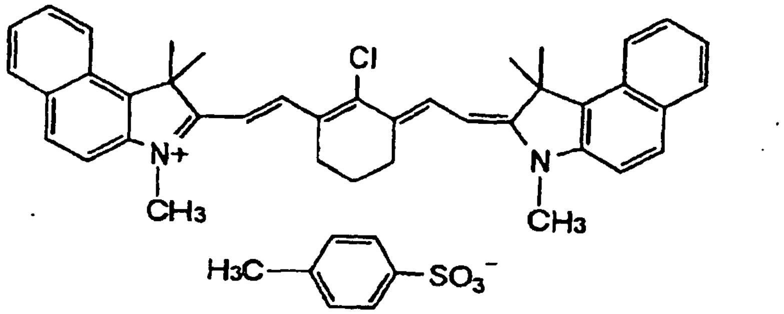
[0147] For comparison, a lithographic printing plate precursor of Comparative Example 1 was produced in the same manner as in Example 1, except that the coating film was dried by hot air drying at 100°C for 2 minutes (hot air velocity: 2 m/s). The photosensitive layer had a coating weight of 1 g/m^2 and a thickness distribution with a relative standard deviation of 30%.

Formulation A of photosensitive layer:

[0148]

N-(4-Aminosulfonylphenyl)methacrylamide/

acrylonitrile/methyl methacrylate (35/30/35) copolymer (Mw: 50,000)	2.370 g
m-/p-Cresol novolak (PR54046, from Sumitomo Dulles Co., Ltd.)	0.474 g
Cyanine dye A of formula:	0.109 g



4,4'-Bis(hydroxyphenyl)sulfone	0.126 g
Tetrahydrophthalic anhydride	0.190 g
p-Toluenesulfonic acid	0.008 g
Ethyl Violet with its counter anion replaced with 6-hydroxynaphthalenesulfonate	0.100 g
Dimyristyl 3,3'-thiodipropionate	0.030 g
Di-n-dodecyl 3,3'-thiodipropionate	0.030 g
Fluorine-containing surface active agent (Megafac F-176, From Dainippon Ink & Chemicals, Inc.)	0.035 g
Fluorine-containing surface active agent (Defensa MCF-312, from Dainippon Ink & Chemicals, Inc.)	0.035 g
Methyl ethyl ketone	26.6 g
1-Methoxy-2-propanol	13.6 g

γ-Butyrolactone	13.8 g

EXAMPLE 3 AND COMPARATIVE EXAMPLE 2

[0149] A lithographic printing plate precursor of Example 3 was produced in the same manner as in Example 2, except that a coating composition for photosensitive layer having formulation B shown below was applied with a wire bar to give a wet coating weight of 1.8 g/m^2. The resulting photosensitive layer had a coating weight of 1.3 g/m^2 and a thickness distribution with a relative standard deviation of 9%.

[0150] For comparison, a lithographic printing plate precursor of Comparative Example 2 was produced in the same manner as in Example 3, except that drying was carried out in hot air (velocity: 2 m/s) at 100°C for 2 minutes. The photosensitive layer thus formed had a coating weight of 1.3 g/m^2 and a thickness distribution with a relative standard deviation of 25%.

Formulation B of photosensitive layer:

[0151]

m-/p-Cresol novolak (PR54046, from Sumitomo Dulles Co. , Ltd.)	1.000 g
Copolymer 1 synthesized as described below	0.100 g
Cyanine dye A	0.100 g
4,4'-Bis(hydroxyphenyl)sulfone	0.050 g
Tetrahydrophthalic anhydride	0.050 g
p-Toluenesulfonic acid Ethyl Violet with its counter anion replaced with	0.002 g
6-hydroxynaphthalenesulfonate	0.020 g
Dimyristyl 3,3'-thiodipropionate	0.010 g
Di-n-dodecyl 3,3'-thiodipropionate	0.010 g
Fluorine-containing surface active agent (Megafac F-176, From Dainippon Ink & Chemicals, Inc.)	0.015 g
Fluorine-containing surface active agent (Defensa MCF-312, from Dainippon Ink & Chemicals, Inc.)	0.035g
Methyl ethyl ketone	12.0 g

Synthesis of copolymer 1:

[0152] A 20 ml three-necked flask equipped with a stirrer, a cooling tube, and a dropping funnel were put 6.39 g (0.045 mol) of n-propyl methacrylate, 1.29 g (0.015 mol) of methacrylic acid, and 20 g of 1-methoxy-2-propanol, and the mixture was stirred while heating at 65°C on a hot water bath. To the mixture was added 0.15 g of a radical polymerization initiator V-601 (from Wako Pure Chemical Industries, Ltd.), and the mixture was kept at 70°C for 2 hours while stirring in a nitrogen stream. To the reaction mixture was further added dropwise a mixture of 6.39 g (0.045 mol) of n-propyl methacrylate, 1.29 g (0.015 mol) of methacrylic acid, 20 g of 1-methoxy-2-propanol, and 0.15 g of V-601 through the dropping funnel over a period of 2 hours, followed by stirring at 90°C for 2 hours. After completion of the reaction, 40 g of methanol was added to the reaction mixture, followed by cooling. The resulting mixture was poured into 2 liters of water while stirring. After pouring, the stirring was continued for an addition 30 minutes. The precipitate was collected by filtration and dried to give 15 g of copolymer 1 as a white solid. The polystyrene equivalent Mw of copolymer 1 was 53,000 as measured by gel-permeation chromatography.

EXAMPLE 4 AND COMPARATIVE EXAMPLE 3

[0153] A coating composition for lower layer having the formulation shown below was applied and dried in the same manner as in Example 2. A coating composition for photosensitive layer having formulation C shown below was then applied and dried in the same manner as in Example 2 to obtain a lithographic printing plate precursor of Example 4. The double-layered photosensitive layer had a coating weight of 1.2 g/m^2 and a thickness distribution with a relative standard deviation of 10%.

[0154] For comparison, a lithographic printing plate precursor of Comparative Example 3 was produced in the same manner as in Example 4, except that the two coating films were each dried by hot air drying at 100°C for 2 minutes (hot air velocity: 2 m/s). The double-layered photosensitive layer had a coating weight of 1.2 g/m^2 and a thickness distribution with a relative standard deviation of 25%.

Coating composition for lower layer:

[0155]

N-(4-Aminosulfonylphenyl) methacrylamide/ acrylonitrile/methyl methacrylate (36/34/30) copolymer (Mw: 50,000)	2.133 g
Cyanine dye A	0.109 g
4,4'-Bis(hydroxyphenyl)sulfone	0.126 g
Tetrahydrophthalic anhydride	0.190 g
p-Toluenesulfonic acid	0.008 g
Ethyl Violet with its counter anion replaced with 6-hydroxynaphthalenesulfonate	0.100 g
3-Methoxy-4-diazophenylamine hexafluorophosphate (thermally decomposable compound)	0.03 g
Fluorine-containing surface active agent (Megafac F-176, From Dainippon Ink & Chemicals, Inc.)	0.035 g
Methyl ethyl ketone	26.6 g
1-Methoxy-2-propanol	13.6 g
γ-Butyrolactone	13.8 g

Formulation C of photosensitive layer:

[0156]

m-/p-Cresol novolak (PR54046, from Sumitomo Dulles Co., Ltd.)	0.348 g
Cyanine dye A	0.0192 g
Tetraethylammonium bromide	0.030 g
Fluorine-containing surface active agent (Megafac F176, from Dainippon Ink & Chemicals, Inc.)	0.035 g
Methyl ethyl ketone	26.6 g
1-Methoxy-2-propanol	13.6 g

Evaluation of lithographic printing plate precursors:

[0157] The lithographic printing plate precursors obtained in Examples and Comparative Examples was evaluated for scratch resistance and development latitude in accordance with the test methods described below. The results obtained are shown in Table 1. In testing, a developer DT-1 available from Fuji Photo Film was used for the photosensitive layers having the formulation A or C, and an alkali developer A having the following formulation was used for the photosensitive layers having the formulation B.

Formulation of alkali developer A:

[0158]

$SiO_2 \cdot K_2O$ (K_2O/SiO_2=1/1 by mole)	4.0%
Citric acid	0.5%
Polyethylene glycol lauryl ether (Mw: 1,000)	0.6%
Water	50.0%

(a) Scratch resistance

[0159] The printing plate precursor was mounted on a Heidon scratch resistance tester, and the photosensitive layer was scratched with a sapphire stylus (1.0 mm) under an increasing load. The plate precursor was then developed with DT-1 diluted to an electrical conductivity of 45 mS/cm or developer A diluted to an electrical conductivity of 75 mS/cm. The stylus load which caused a visible scratch after the development was taken as a measure of scratch resistance. A larger value means higher scratch resistance.

(b) Development latitude

[0160] The printing plate precursor was imaged with Trendsetter available from Creo using a test pattern with an exposure energy of 90 mJ/cm^2.

[0161] Prior to development, the initial electrical conductivity of each developer was measured. The exposedplate was developed with the prescribed developer. The image density of the unexposed area (image area) was measured with a reflection densitometer D196 available from GretagMacbeth. When the image density reduced from the initial one by 0.06 or more, the conductivity of the developer (conductivity after use) was again measured. A greater difference between the initial conductivity and the conductivity after use means a broader tolerance of developer exhaustion, indicating that the printing plate precursor has broad development latitude against variation of the developer activity. The figures given in Table 1 in the column "development latitude", for example 37-55 show that the initial conductivity was 37 mS/cm and the conductivity after use was 55 mS/cm.

TABLE 1

	Photo-sens itive Layer	Drying		RSD* %	Scratch Resis-ta nce (g)	Development Latitude (mS/cm)
		Method	Hot Roll			
Ex. 1	A	high pressure air	no	15	5	37-55
Ex. 2	A	high pressure air	100°C	10	8	37-57
Comp. Ex. 1	A	hot air	no	30	1	41-47
Ex. 3	B	high pressure air	100°C	9	10	40-58
Comp. Ex. 2	B	hot air	no	25	2	45-50
Ex. 4	C	high pressure air	100°C	10	10	37-58
Comp. Ex. 3	C	hot air	no	25	3	40-47

* Relative standard deviation of photosensitive layer thickness distribution

[0162] It is seen from the results in Table 1 that the lithographic printing plate precursors having a narrow distribution of the photosensitive layer thickness (Examples 1 to 4) are excellent in scratch resistance and development latitude.

[0163] The infrared sensitive lithographic printing plate precursor according to the present invention has a uniform film thickness and exhibits high scratch resistance and excellent development latitude.

Claims

1. A lithographic printing plate precursor comprising:

   an aluminum support; and
   a photosensitive layer comprising a water-insoluble and alkali-soluble resin and an infrared absorber,
   wherein the photosensitive layer has a coating weight of 0.5 to 3 g/m^2 and a thickness distribution with a relative standard deviation of 20% or less, said relative standard deviation being determined as described in the description.

2. The lithographic printing plate precursor according to claim 1, wherein the photosensitive layer has a coating weight of 0.7 to 1.5 g/m^2.

3. The lithographic printing plate precursor according to claim 1, wherein the photosensitive layer has a coating weight of 0.7 to 1.2 g/m^2.

4. The lithographic printing plate precursor according to any one of claims 1 to 3, wherein the photosensitive layer has a thickness distribution with a relative standard deviation of 15% or less.

5. The lithographic printing plate precursor according to any one of claims 1 to 3, wherein the photosensitive layer has a thickness distribution with a relative standard deviation of 10% or less.

6. The lithographic printing plate precursor according to any one of claims 1 to 5, wherein the resin is a polymer comprising a functional group selected from a phenolic hydroxyl group, a sulfonamido group and an active imido group.

7. The lithographic printing plate precursor according to any one of claims 1 to 6, wherein the photosensitive layer further comprises a dissolution inhibitor.

8. The lithographic printing plate precursor according to claim 7, wherein the dissolution inhibitor is a quaternary ammonium salt or a polyethylene glycol compound.

9. The lithographic printing plate precursor according to any one of claims 1 to 8, wherein the photosensitive layer has a multilayer structure composed of two or more layers.

10. The lithographic printing plate precursor according to claim 9, wherein the photosensitive layer having the multilayer structure comprises an upper layer and a lower layer so that the aluminum support, the lower layer and the upper layer are in this order, and the resin contained in the upper layer is less soluble in an alkali developer than that contained in the lower layer.

11. A method for producing a lithographic printing plate precursor comprising:

applying a photosensitive coating solution comprising a water-insoluble and alkali-soluble resin and an infrared absorber to an aluminum support so as to form a wet coating film; and
subjecting the wet coating film to at least one of high pressure air and hot air so as to form the lithographic printing plate precursor according to any one of claims 1 to 10.

12. The method according to claim 11, wherein the subjecting of the wet coating film to at least one of high pressure air and hot air is conducted in combination with drying of the wet coating film with a hot roll.

Patentansprüche

1. Lithografischer Druckplattenvorläufer, der folgendes umfaßt:

einen Aluminiumträger; und
eine lichtempfindliche Schicht, die ein wasserunlösliches und alkalilösliches Harz und einen Infrarotabsorber umfaßt,
worin die lichtempfindliche Schicht ein Flächengewicht von 0,5 bis 3 g/m^2 und eine Dickenverteilung mit einer relativen Standardabweichung von 20 % oder weniger hat, wobei die relative Standardabweichung wie in der Beschreibung beschrieben bestimmt wird.

2. Lithografischer Druckplattenvorläufer gemäß Anspruch 1, worin die lichtempfindliche Schicht ein Flächengewicht von 0,7 bis 1,5 g/m^2 hat.

3. Lithografischer Druckplattenvorläufer gemäß Anspruch 1, worin die lichtempfindliche Schicht ein Flächengewicht von 0,7 bis 1,2 g/m^2 hat.

4. Lithografischer Druckplattenvorläufer gemäß einem der Ansprüche 1 bis 3, worin die lichtempfindliche Schicht eine Dickenverteilung mit einer relativen Standardabweichung von 15 % oder weniger hat.

5. Lithografischer Druckplattenvorläufer gemäß einem der Ansprüche 1 bis 3, worin die lichtempfindliche Schicht eine Dickenverteilung mit einer relativen Standardabweichung von 10 % oder weniger hat.

6. Lithografischer Druckplattenvorläufer gemäß einem der Ansprüche 1 bis 5, worin das Harz ein Polymer ist, das eine funktionelle Gruppe umfaßt, die aus einer phenolischen Hydroxylgruppe, einer Sulfonamidogruppe und einer aktiven Imidogruppe ausgewählt ist.

7. Lithografischer Druckplattenvorläufer gemäß einem der Ansprüche 1 bis 6, worin die lichtempfindliche Schicht ferner einen Auflösungsinhibitor umfaßt.

8. Lithografischer Druckplattenvorläufer gemäß Anspruch 7, worin der Auflösungsinhibitor ein quaternäres Ammoniumsalz oder eine Polyethylenglycolverbindung ist.

9. Lithografischer Druckplattenvorläufer gemäß einem der Ansprüche 1 bis 8, worin die lichtempfindliche Schicht eine aus zwei oder mehr Schichten zusammengesetzte Mehrschichtstruktur hat.

10. Lithografischer Druckplattenvorläufer gemäß Anspruch 9, worin die lichtempfindliche Schicht mit der Mehrschichtstruktur eine obere Schicht und eine untere Schicht umfaßt, so daß der Aluminiumträger, die untere Schicht und die obere Schicht in dieser Reihenfolge sind und das in der oberen Schicht enthaltene Harz weniger löslich in einem alkalischen Entwickler als dasjenige ist, das in der unteren Schicht enthalten ist.

11. Verfahren zur Herstellung eines lithografischen Druckplattenvorläufers, das folgendes umfaßt:

Auftragen einer lichtempfindlichen Beschichtungslösung, die ein wasserunlösliches und alkalilösliches Harz und einen Infrarotabsorber umfaßt, auf einen Aluminiumträger, um einen nassen Beschichtungsfilm zu bilden; und
Unterwerfen des nassen Beschichtungsfilm wenigstens einem aus Hochdruckluft und Heißluft, um den lithografischen Druckplattenvorläufer gemäß einem der Ansprüche 1 bis 10 zu bilden.

12. Verfahren gemäß Anspruch 11, worin das Unterwerfen des nassen Beschichtungsfilms wenigstens einem aus Hochdruckluft und Heißluft in Kombination mit Trocknen des nassen Beschichtungsfilms mit einer Heizwalze durchgeführt wird.

Revendications

1. Précurseur de plaque d'impression lithographique comprenant :

un support d'aluminium; et
un couche photosensible comprenant une résine insoluble dans l'eau et soluble dans les alcalis et un absorbeur de rayonnement infrarouge,
dans lequel la couche photosensible a un poids de la couche de 0,5 à 3 g/m^2 et une répartition de l'épaisseur avec un coefficient de variation de 20 % ou moins, ledit coefficient de variation étant déterminé comme décrit dans la description.

2. Précurseur de plaque d'impression lithographique selon la revendication 1, dans lequel la couche photosensible a un poids de la couche de 0,7 à 1,5 g/m^2.

3. Précurseur de plaque d'impression lithographique selon la revendication 1, dans lequel la couche photosensible a un poids de la couche de 0,7 to 1,2 g/m^2.

4. Précurseur de plaque d'impression lithographique selon l'une quelconque des revendications 1 à 3, dans lequel la couche photosensible a une répartition de l'épaisseur avec un coefficient de variation de 15 % ou moins.

5. Précurseur de plaque d'impression lithographique selon l'une quelconque des revendications 1 à 3, dans lequel la couche photosensible a une répartition de l'épaisseur avec un coefficient de variation de 10 % ou moins.

6. Précurseur de plaque d'impression lithographique selon l'une quelconque des revendications 1 à 5, dans lequel la résine est un polymère comprenant un groupe fonctionnel choisi parmi un groupe hydroxyle phénolique, un groupe sulfonamido et un groupe imido actif.

7. Précurseur de plaque d'impression lithographique selon l'une quelconque des revendications 1 à 6, dans lequel la couche photosensible comprend en outre un inhibiteur de dissolution.

8. Précurseur de plaque d'impression lithographique selon la revendication 7, dans lequel l'inhibiteur de dissolution est un sel d'ammonium quaternaire ou un composé de polyéthylène glycol.

9. Précurseur de plaque d'impression lithographique selon l'une quelconque des revendications 1 à 8, dans lequel la couche photosensible a une structure multicouche composée de deux ou plus de deux couches.

10. Précurseur de plaque d'impression lithographique selon la revendication 9, dans lequel la couche photosensible ayant la structure multicouche comprend une couche supérieure et une couche inférieure de sorte que le support d'aluminium, la couche inférieure et la couche supérieure soient dans cet ordre, et la résine contenue dans la couche supérieure est moins soluble dans un révélateur alcalin que celle contenue dans la couche inférieure.

11. Procédé pour la production d'un précurseur de plaque d'impression lithographique comprenant :

l'application d'une solution de revêtement photosensible comprenant une résine insoluble dans l'eau et soluble dans les alcalis et un absorbeur de rayonnement infrarouge sur un support d'aluminium de manière à former un film de revêtement humide; et
la soumission du film de revêtement humide à au moins l'un parmi de l'air à haute pression et de l'air chaud de manière à former le précurseur de plaque d'impression lithographique selon l'une quelconque des revendications 1 à 10.

12. Procédé selon la revendication 11, dans lequel la soumission du film de revêtement humide à au moins l'un parmi de l'air à haute pression et de l'air chaud est effectuée en combinaison avec un séchage du film de revêtement humide avec un cylindre chaud.

FIG. 1