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(54) **Lithographic printing plate precursor**

Vorläufer einer lithographischen Druckplatte

Précurseur d'une plaque d'impression planographique

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EP-A- 0 823 327 **EP-A- 0 908 308**
EP-A- 0 943 451 **EP-A- 1 162 063**

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Description**FIELD OF THE INVENTION**

[0001] The present invention relates to a lithographic printing plate precursor and a processing method thereof. In particular, the invention is concerned with an infrared laser-responsive positive-working lithographic printing plate precursor suitable for a so-called direct plate-making wherein the plate-making is directly performed using digital signals from computer, and a processing method of such a printing plate precursor. More specifically, the invention relates to a lithographic printing plate precursor having excellent scratch resistance and sensitivity and causing no contamination in the optical system of an exposure device through inhibition of occurrence of ablation, and a processing method thereof.

BACKGROUND OF THE INVENTION

[0002] Remarkable progress of laser technologies in recent years has ensured to take easy possession of high-power, miniaturized devices of solid and semiconductor lasers, especially those emitting light in the near infrared to infrared region. These laser devices are very useful as light sources for plate-making directly using digital data from computer.

[0003] A positive-working lithographic printing plate material responsive to infrared laser contains as essential components a binder resin soluble in an aqueous alkali solution and a compound capable of generating heat by absorption of light, e.g., an IR dye. In the unexposed areas (image areas) of the plate material, the IR dye functions as a dissolution inhibitor lowering substantially the solubility of binder resin through interaction with the binder resin. In the exposed areas (non-image areas), on the other hand, the interaction of the binder resin with the IR dye is weakened by the heat generated, and as a result, the binder resin becomes soluble in an alkaline developer to form a lithographic printing plate.

[0004] However, the positive working lithographic printing plate material designed for exposure to infrared laser has a problem that difference in solubility to developer is not sufficient between the unexposed area (image area) and the exposed area (non-image area) under various conditions. As a result, over development or insufficient development tends to be caused by variations in operation conditions. In addition, the surface conditions of those materials tend to suffer variations, such as minute scratches, even by touch on the surface during the handling. The minute scratches and other variations on the surface cause the increase in solubility. Due to the dissolution of unexposed area (image area) at the time of development, the surface is scarred, resulting in deterioration of printing durability and poor inking.

[0005] Those problems are originated from substantial difference in plate-making mechanism between an infrared laser-responsive, positive-working lithographic printing plate material and a positive-working printing plate material for plate-making through UV exposure. Specifically, the positive-working lithographic printing plate material for plate-making through UV exposure contains as essential components a binder resin soluble in an aqueous alkali solution and an onium salt or quinonediazide compound. The onium salt and quinonediazide compound perform two functions, a function as dissolution inhibitor in the unexposed area (image area) by interacting with the binder resin, and a function as dissolution accelerator in the exposed area (non-image area) by generating acid through photolysis.

[0006] On the other hand, the IR dye in infrared laser-responsive, positive-working lithographic printing plate material acts only as the dissolution inhibitor in the unexposed area (image area), and does not accelerate dissolution in the exposed area (non-image area). Therefore, in order to make difference in solubility between the exposed area and the unexposed area, it cannot be helped to use a binder resin essentially having high solubility in the alkali developer. Thus, the printing plate material bears problems that its scratch resistance is low and that its states before development are unstable.

[0007] In order to solve these problems, Japanese Patent Laid-Open No. 2000-35662 discloses that the addition of an alkali-soluble novolak resin containing xylenol as a structural unit is added to a recording layer to inhibit the dissolution of the recording layer, thereby improving scratch resistance.

[0008] However, the addition of the alkali-soluble novolak resin containing xylenol as a structural unit to the recording layer causes a new problem of decreasing sensitivity, though the scratch resistance is increased thereby.

[0009] Further, ablation occurs in the recording layer to contaminate the optical system of an exposure device used.

[0010] EP 1 162 063 A, which represents prior art pursuant to Art. 54(3) and (4) EPC, discloses related positive planographic printing plate precursors.

SUMMARY OF THE INVENTION

[0011] An object of the invention is to overcome the defects in the prior art as described above.

[0012] Another object of the invention is to provide an infrared laser-responsive, positive-working lithographic printing

plate precursor that has excellent scratch resistance as well as high sensitivity, is suitable especially for the so-called direct plate-making wherein the plate-making is directly performed using digital signals from computer, and does not contaminate the optical system of an exposure device used because of preventing from the occurrence of ablation.

[0013] As a result of our intensive studies, it has been found that, when the recording layer is designed so as to have a double-layer structure, and an infrared absorbent and an alkali-soluble novolak resin containing a xylenol structural unit are incorporated in the upper layer of the double-layer structure, not only compatibility between the scratch resistance and the sensitivity but also the inhibition of ablation can be realized, thereby completing the invention.

[0014] More specifically, the invention includes the following items.

(1) A lithographic printing plate precursor of double-layer structure comprising a support, an alkali-soluble resin-containing layer, and a positive-working recording layer capable of increasing solubility in an aqueous alkali solution upon exposure to infrared laser provided on the alkali-soluble resin-containing layer, and the positive-working recording layer contains an infrared absorbing cyanine dye and an alkali-soluble novolak resin having xylenol as a structural unit.

(2) The lithographic printing plate precursor as described in item (1), wherein the positive-working recording layer contains a compound consisting of at most three monomer units in an amount of 30 weight % or less to the novolak resin.

(3) The lithographic printing plate precursor as described in item (1), wherein the alkali-soluble resin-containing layer contains an onium salt.

(4) The lithographic printing plate precursor as described in item (1), wherein the alkali-soluble resin-containing layer contains an infrared absorbent.

(5) A method of processing a lithographic printing plate precursor comprising:

subjecting a lithographic printing plate precursor to image-wise exposure and development with an alkaline developer containing a pH buffering organic compound and a base,

wherein the lithographic printing plate precursor is a lithographic printing plate precursor of double-layer structure comprising a support, an alkali-soluble resin-containing layer, and a positive-working recording layer capable of increasing solubility in an aqueous alkali solution upon exposure to infrared laser provided on the alkali-soluble resin-containing layer, and the positive-working recording layer contains an infrared absorbing cyanine dye and an alkali-soluble novolak resin having xylenol as a structural unit.

DETAILED DESCRIPTION OF THE INVENTION

[0015] In conventional recording layers of single-layer type the sensitivity is apt to decrease, although the scratch resistance is improved as described above. According to the plate material of the invention, on the contrary, the alkali-soluble resin-containing layer and the positive-working recording layer containing are provided on a support in a double-layer structure, and an infrared absorbent and an alkali-soluble novolak resin containing a xylenol structural unit are incorporated into the upper positive-working recording layer. It is believed that such a double-layer structure enables effective use of heat generated in the vicinity of the surface of plate material and as a result, decrease in sensitivity can be controlled while increasing the scratch resistance. In addition, when the content of compound consisting of at most three monomer units in the upper layer is reduced to 30 weight % or less to the novolak resin, the scratch resistance can further be improved and the occurrence of ablation can be inhibited.

[0016] The invention is described in detail below.

[0017] The lithographic printing plate precursor of the invention has on a support a double-layer structure comprising an alkali-soluble resin-containing layer (hereinafter also referred to as lower layer) and a positive-working recording layer (hereinafter also referred to as upper layer) containing an infrared absorbent and an alkali-soluble novolak resin containing a xylenol structural unit and capable of increasing its solubility in an alkaline aqueous solution upon exposure to infrared laser. Further, it is more preferable that a content of compounds consisting of at most three monomer units in the upper layer is 30 weight % or less to the novolak resin.

[0018] The alkali-soluble resin-containing layer (lower layer) and the positive-working recording layer (upper layer) of the lithographic printing plate precursor of the invention are described below.

[0019] The lithographic printing plate precursor is characterized in that the positive-working recording layer (upper layer) is arranged in a position nearer the surface (to undergo exposure) and the alkali-soluble resin-containing layer (lower layer) is arranged on the side nearer the support.

[0020] Of these layers, it is required for the positive-working recording layer (upper layer) to contain an infrared absorbent and an alkali-soluble novolak resin containing xylenol as structural units. Preferably, the proportion of compounds consisting of at most three monomer units in the upper layer is 30 weight % or less based on the novolak resin.

[0021] Each of the ingredients constituting the lithographic printing plate precursor is described below.

[0022] Into the positive-working recording layer (upper layer) positioned on the upper side of the lithographic printing plate precursor, an alkali-soluble novolak resin containing a xylene structural unit capable of inhibiting dissolution of the recording layer is incorporated for the purpose of increasing the scratch resistance.

<Alkali-Soluble Novolak Resin containing Xylene Structural Unit>

[0023] The alkali-soluble novolak resin containing xylene structural units (hereinafter also referred to as a "xylene-containing novolak resin") for use in the lithographic printing plate precursor of the invention can be synthesized according to a conventional reaction route from phenol and formaldehyde in the presence of an acid catalyst under an ordinary pressure, provided that xylene is employed as a starting monomer in addition to or in place of phenol and cresol.

[0024] The xylene unit in the novolak resin may be derived from any of six isomers. From the viewpoint of improvement in stability, however, it is preferable to use 3,5-xylene, 2,3-xylene, 2,5-xylene and 3,4-xylene, which are isomers having relatively high melting points.

[0025] Also it is preferred that a weight average molecular weight of the xylene-containing novolak resins is from 500 to 10,000. When the xylene-containing novolak resin has a weight average molecular weight lower than 500, the effect of increasing press life is insufficient. On the other hand, when the weight average molecular weight exceeds 10,000, the developability tends to decrease.

[0026] The content of xylene monomer in the resin is not particularly restricted, and the effect of increasing storage stability can be recognized even when the xylene monomer is contained in a slight proportion. The effect of increasing storage stability is enhanced with increase in the xylene content. When the proportion of xylene-containing novolak resin in the alkali-soluble resin constituting the upper layer of the lithographic printing plate precursor of the invention is taken as Y weight % and the content of xylene monomer in the novolak resin is taken as X weight %, it is preferred that the product of X and Y, namely $X \times Y$, is not smaller than 500 ($X \times Y \geq 500$). Specifically, when all those alkali-soluble resins are xylene-containing novolak resins ($Y=100$ weight %), it is preferable that the content of xylene in the novolak resin is at least 5 weight %, from the viewpoint of effects intended by the invention.

[0027] There is a tendency to decrease the developability as the xylene content is increased. In such a case, satisfactory image formation can be effected by adjusting activity of the developer. Also, there is a tendency to increase the press life with decrease in developability. Therefore, the content of xylene can be appropriately selected so as to suit the desired characteristics of the lithographic printing plate precursor of the invention.

[0028] The xylene-containing novolak resin is preferably used in an amount of 10 to 99 weight %, more preferably 15 to 95 weight %, and particularly preferably 20 to 90 weight %, based on the total solid content in the upper layer of the lithographic printing plate precursor. When the amount of alkali-soluble resin added is lower than 30 weight %, durability of the recording layer tends to deteriorate. On the other hand, the addition of alkali-soluble resin exceeding 99 weight % is undesirable from both sensitivity and durability standpoints. In case of employing a mixture of the xylene-containing novolak resin with an alkali-soluble resin other than the xylene-containing novolak resin described hereinafter, as a binder, in the upper layer, it is preferable that the amount of the binder as a whole in the upper layer is within the range defined above.

[0029] Further, in the positive-working recording layer (upper layer) of the lithographic printing plate precursor of the invention, the content of compound consisting of at most three monomer units, which causes ablation and interferes with inhibition (dissolution inhibition), is preferably not higher than 30 weight %, more preferably not higher than 20 weight %, and still more preferably not higher than 10 weight %, to the novolak resin. When the content of such compound is higher than 30 weight %, there is the fear of contamination of an optical system in an exposure device by the ablation. When the content of such compound is not lower than 20 weight %, the fear of ablation decreases, but a concern about image-forming properties still remains because such compounds accelerate development. Therefore, the more preferred content is 20 weight % or below. In order to remove the above-described fear and concern, it is still more preferred to reduce the content to 10 weight % or below. The compound consisting of at most three monomer units means a compound consisting of three or less monomer units and includes a monomer, a dimer and a trimer.

<Infrared Absorbing Dye>

[0030] The infrared absorbing dye contained in the upper layer of the lithographic printing plate precursor of the invention is not particularly restricted so far as it absorbs infrared light and generates heat, and so far as it is a cyanine dye.

[0031] As the infrared absorbing cyanine dyes according to the invention, commercially available dyes and known dyes as described in literature (e.g., Senryou Binran (Handbook of Dyes), compiled by Yuki Gosei Kagaku Kyokai (1970)) can be utilized. Of these dyes, dyes capable of absorbing infrared ray or near infrared ray are particularly

preferred from the viewpoint of suitability for use of an infrared or near infrared ray-emitting laser as an exposure light source.

[0032] Examples of the infrared or near infrared absorbing dye include the cyanine dyes as disclosed in Japanese Patent Laid-Open Nos. 125246/1983, 84356/1984, 202829/1984 and 78787/1985, and the cyanine dyes disclosed in British Patent No. 434,875.

[0033] In addition, the near infrared absorption sensitizers disclosed in U.S. Patent No. 5,156,938 can be suitably used as the dye according to the invention. Further, the cyanine dyes disclosed in 216146/1984, and commercially available dyes including Epolight III-178, Epolight III-130 and Epolight III-125 (produced by Epolin Inc.) are particularly preferably used.

[0034] Other examples of dyes particularly preferred include the near infrared absorbing dyes represented by formulae (I) and (II) in U.S. Patent No. 4,756,993.

[0035] The amount of dye added is ordinarily from 0.01 to 50 weight %, preferably from 0.1 to 10 weight %, particularly preferably from 0.5 to 10 weight %, based on the total solid content of the recording layer. When the amount of the dye added is lower than 0.01 weight %, the sensitivity decreases, while the amount higher than 50 weight % harms uniformity of the recording layer and causes deterioration in durability of the recording layer.

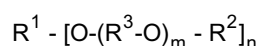
[0036] For the purpose of further enhancing the inhibition (dissolution inhibition) effect obtained by the introduction of xlenol structure in the positive-working recording layer (upper layer) of the lithographic printing plate precursor of the invention, it is preferable to add a quaternary ammonium salt capable of interacting with the novolak resin. The amount (solid basis) of ammonium salt added is preferably from 0.1 to 50 weight %, more preferably from 1 to 30 weight %, based on the total solid content of the upper layer. The amount lower than 0.1 weight % is undesirable because the increase in the interaction is small, while the amount higher than 50 weight % may apt to exert a bad influence on the film-forming property of the binder.

[0037] The quaternary ammonium salt used is not particularly restricted, and includes tetraalkylammonium salts, trialkylarylammonium salts, dialkyldiarylammonium salts, alkyltriarylammonium salts, tetraarylammonium salts, cyclic ammonium salts and bicyclic ammonium salts.

[0038] Specific examples of the ammonium salt include 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, lauryltriethylammonium bromide, phenyltrimethylammonium bromide, 3-trifluoromethylphenyltrimethylammonium bromide, benzyltrimethylammonium bromide, dibenzyltrimethylammonium bromide, distearyltrimethylammonium bromide, tristearyltrimethylammonium bromide, benzyltriethylammonium bromide, hydroxyphenyltrimethylammonium bromide and N-methylpyridinium bromide.

[0039] In addition, with the intention of further enhancing the inhibition (dissolution inhibition) effect obtained by the introduction of xlenol structure in the positive-working recording layer (upper layer) of the lithographic printing plate precursor, it is preferred to add a polyethylene glycol compound capable of interacting with the novolak resin. The amount (solid basis) of polyethylene glycol compound added is preferably from 0.1 to 50 weight %, more preferably from 1 to 30 weight %, based on the total solid content of the upper layer. The amount lower than 0.1 weight % is undesirable because the increase in the interaction is small, while the amount higher than 50 weight % may apt to exert a bad influence on an image-forming property because the polyethylene glycol compound incapable of undergoing the interaction with the binder promotes penetration of developer.

[0040] The polyethylene glycol compound used is not particularly restricted, and suitable examples thereof include compounds represented by the following formula:



wherein R^1 represents a polyhydric alcohol residue or a polyhydric phenol residue, R^2 represents a hydrogen atom, an unsubstituted or substituted C_{1-25} alkyl, alkenyl, alkynyl, alkyloyl, aryl or aryloyl group, R^3 represents an unsubstituted or substituted alkylene group, m is at least 10 on the average, and n is an integer from 1 to 4.

[0041] Examples of the polyethylene glycol compound having the structure represented by the above formula illustrated above include polyethylene glycols, polypropylene glycols, polyethylene glycol alkyl ethers, polypropylene glycol alkyl ethers, polyethylene glycol aryl ethers, polypropylene glycol aryl ethers, polyethylene glycol alkyl aryl ethers, polypropylene glycol alkyl aryl ethers, polyethylene glycol glycerine esters, polypropylene glycol glycerine esters, polyethylene glycol sorbitol esters, polypropylene glycol sorbitol esters, polyethylene glycol fatty acid esters, polypropylene glycol fatty acid esters, polyethylene glycolated ethylenediamines, polypropylene glycolated ethylenediamines, polyethylene glycolated diethylenetriamines and polypropylene glycolated diethylenetriamines.

[0042] Specific examples thereof include polyethylene glycol 1000, polyethylene glycol 2000, polyethylene glycol

4000, polyethylene glycol 10000, polyethylene glycol 20000, polyethylene glycol 5000, 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, propylene glycol dimethyl ether, propylene 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 benzoic acid ester, polyethylene glycol laurate, polyethylene glycol dilaurate, polyethylene glycol nonylic acid ester, polyethylene glycol cetylic acid ester, polyethylene glycol stearate, polyethylene glycol distearate, polyethylene glycol behenic acid ester, polyethylene glycol dibehenic acid ester, polypropylene glycol acetate, polypropylene glycol diacetate, polypropylene glycol benzoic acid ester, propylene glycol dibenzoic acid ester, polypropylene glycol lauric acid ester, polypropylene glycol dilauric acid ester, polypropylene glycol nonilic acid ester, polyethylene glycol glycerine ether, polypropylene glycol glycerine ether, polyethylene glycol sorbitol ether, polypropylene glycol sorbitol ether, polyethylene glycolated ethylenediamine, polypropylene glycolated ethylenediamine, polyethylene glycolated diethylenetriamine, polypropylene glycolated diethylenetriamine and polyethylene glycolated pentamethylenhexamine.

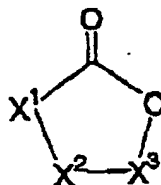
[0043] When the inhibition (dissolution inhibition) improving measure is undertaken by the introduction of the xylenol structure, the sensitivity may decrease. In such a case, the addition of lactone compound is effective. The lactone compound reacts with a developer, when the developer penetrates into the exposed areas, to newly generate a carboxylic acid compound, thereby increasing the sensitivity.

[0044] The amount (solid basis) of lactone compound added is from 0.1 to 50 weight %, preferably from 1 to 30 weight %, based on the total solid content of the upper layer. The amount of less than 0.1 weight % produces little effect, while, when the lactone compound is added in an amount higher than 50 weight %, the image-forming property deteriorates because the lactone compound has a structure incapable of undergoing interaction.

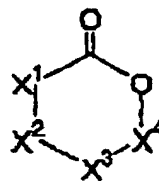
[0045] The lactone compound reacts with a developer, and it is desired to bring it into selective contact with the developer.

[0046] The lactone compound used is not particularly restricted, and includes compounds represented by the following formula (I) or (II):

Formula (I)



Formula (II)



[0047] In the above formulae, X¹, X², X³ and X⁴ are each an atom or an atomic group constituting a ring, they may be the same or different, and they each may have their respective substituent groups, provided that at least one of X¹, X² and X³ in formula (I) and at least one of X¹, X², X³ and X⁴ in formula (II) each have an electron-attracting substituent or a group containing electron-attracting substituent.

[0048] The atom or atomic group constituting a ring is a non-metallic atom having two single bonds for forming a

ring or an atomic group containing such non-metallic atom.

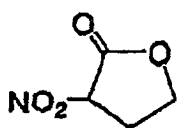
[0049] The non-metallic atom or non-metallic atom-containing group is preferably an atom or a group selected from a methylene group, a sulfinyl group, a carbonyl group, a thiocarbonyl group, a sulfonyl group, a sulfur atom, an oxygen atom and a selenium atom, more preferably a methylene group, a carbonyl group or a sulfonyl group.

[0050] At least one of X^1 , X^2 and X^3 in formula (I) and at least one of X^1 , X^2 , X^3 and X^4 in formula (II) each have an electron-attracting substituent. The term "electron-attracting substituent" used herein means a group whose Hammett's substituent constant σ_p is a positive value. Regarding the Hammett's substituent constant, *Journal of Medicinal Chemistry*, 1973, Vol. 16, No. 11, 1207-1216 can be referred to. Examples of the electron-attracting substituent whose Hammett's substituent constant σ_p is a positive value include a halogen atom (specifically including a fluorine atom having the σ_p value of 0.06, a chlorine atom having the σ_p value of 0.23, a bromine atom having the σ_p value of 0.23, and an iodine atom having the σ_p value of 0.18), a trihaloalkyl group (specifically including a tribromomethyl group having the σ_p value of 0.29, a trichloromethyl group having the σ_p value of 0.33 and a trifluoromethyl group having the σ_p value of 0.54), a cyano group (σ_p value: 0.66), a nitro group (σ_p value: 0.78), an aliphatic, aryl or heterocyclic sulfonyl group (e.g., a methanesulfonyl group having the σ_p value of 0.72), an aliphatic, aryl or heterocyclic acyl group (e.g., an acetyl group having the σ_p value of 0.50), a benzoyl group (σ_p value: 0.43), an alkynyl group (e.g., an ethynyl group having the σ_p value of 0.23), an aliphatic, aryl or heterocyclic oxycarbonyl group (e.g., a methoxycarbonyl group having the σ_p value of 0.45 and a phenoxycarbonyl group having the σ_p value of 0.44), a carbamoyl group (σ_p value: 0.36), a sulfamoyl group (σ_p value: 0.57), a sulfoxide group, a heterocyclic group, an oxo group and a phosphoryl group.

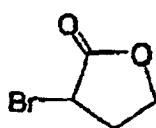
[0051] Preferred examples of the electron-attracting group include an amido group, an azo group, a nitro group, a C_{1-5} fluoroalkyl group, a nitrile group, a C_{1-5} alkoxy carbonyl group, a C_{1-5} acyl group, a C_{1-9} alkylsulfonyl group, a C_{6-9} arylsulfonyl group, a C_{1-9} alkylsulfinyl group, a C_{6-9} arylsulfinyl group, a C_{6-9} arylcarbonyl group, a thiocarbonyl group, a C_{1-9} fluorinated alkyl group, a C_{6-9} fluorinated aryl group, a C_{3-9} fluorinated allyl group, an oxo group and a halogen atom.

[0052] Of those groups, a nitro group, a C_{1-5} fluoroalkyl group, a nitrile group, a C_{1-5} alkoxy carbonyl group, a C_{1-5} acyl group, a C_{6-9} arylsulfonyl group, a C_{6-9} arylcarbonyl group, an oxo group and a halogen atom are more preferred.

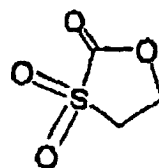
[0053] Examples of the lactone compound represented by formula (I) or (II) are illustrated below, but the invention should not be construed as being limited to these compounds.



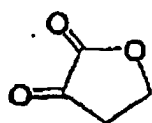
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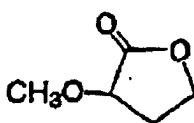
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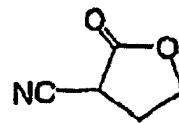
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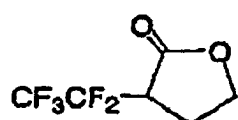
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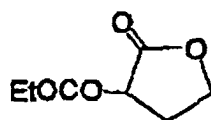
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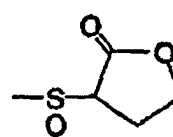
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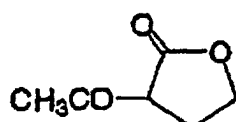
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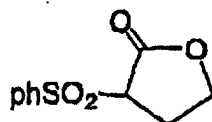
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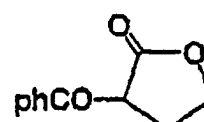
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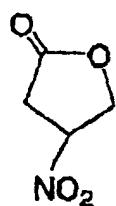
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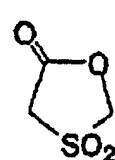
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(I-13)



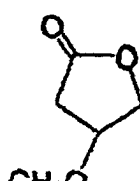
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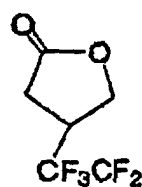
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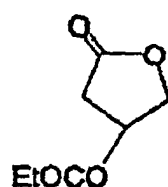
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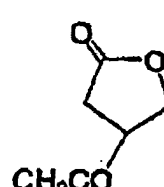
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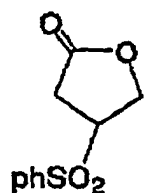
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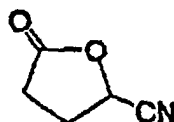
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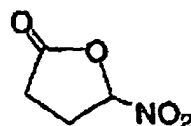
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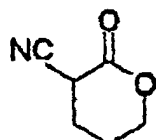
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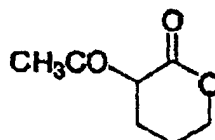
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(II-1)



(II-2)

[0054] Either or both of compounds represented by formulae (I) and (II) respectively may be used. At least two of compounds represented by formula (I) or at least two of compounds represented by formula (II) may be used in an appropriate proportion as far as the total amount thereof is within the range described above.

[0055] Furthermore, an alkali-soluble high molecular compound similar to one contained in the lower layer may be added to the upper layer of the lithographic printing plate precursor of the invention unless the addition thereof adversely affects the functions of the invention. The alkali-soluble high molecular compound is described below.

[0056] The alkali-soluble resin-containing layer (lower layer) of the lithographic printing plate precursor of the invention is described below.

<Alkali-Soluble High Molecular Compound>

[0057] In the lower layer of the lithographic printing plate precursor of the invention, a water-insoluble and alkali-soluble high molecular compound (hereinafter also referred to as an alkali-soluble polymer or an alkali-soluble resin) is contained. The term "alkali-soluble polymer" as used herein includes a homopolymer or copolymer containing an acidic group in its main chain and/or side chain, and a mixture thereof. Accordingly, the lower layer according to the invention has the property of dissolving when brought into contact with an alkaline developer.

[0058] The alkali-soluble polymer used in the lower layer is not particularly restricted so far as it is conventionally known one, but a high molecular compound having in its molecule a functional group selected from (1) a phenolic hydroxy group, (2) a sulfonamido group and (3) an active imido group is preferred. Examples of the high molecular compound include the following compounds, but the alkali-soluble polymer should not be construed as being limited to these compounds.

(1) Examples of the high molecular compound having phenolic hydroxy groups include novolak resins, for example, phenol-formaldehyde resin, m-cresol-formaldehyde resin, p-cresol-formaldehyde resin, mixed m-/p-cresol-formaldehyde resin and mixed phenol/cresol (any of m-cresol, p-cresol and mixture thereof)-formaldehyde resin, and pyrogallolacetone resins. In addition to these high molecular compounds, high molecular compounds containing phenolic hydroxy groups in their side chains are also used suitably. These high molecular compounds include homopolymers prepared by polymerizing polymerizable monomers of low molecular compounds, which each have at least one phenolic hydroxy group and at least one polymerable unsaturated bond, and copolymers prepared by copolymerizing such low molecular compounds and other polymerizable monomers.

Examples of the polymerizable monomer having a phenolic hydroxy group include phenolic hydroxy group-containing acrylamides, methacrylamides, acrylic acid esters and methacrylic acid esters, and hydroxystyrenes. Specifically, N-(2-hydroxyphenyl)acrylamide, N-(3-hydroxyphenyl)acrylamide, N-(4-hydroxyphenyl)acrylamide, N-(2-hydroxyphenyl)methacrylamide, N-(3-hydroxyphenyl)methacrylamide, N-(4-hydroxyphenyl)methacryla-

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amide, 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 can be suitably used.

Those resins containing phenolic hydroxy groups may be used as combinations of two or more thereof. In addition, as disclosed in U.S. Patent 4,123,279, a polycondensation product prepared from formaldehyde and a phenol having a C₃₋₈ alkyl group as a substituent, for example, tert-butylphenol-formaldehyde resin or octylphenol-formaldehyde resin, may be used in combination with the resin as described above.

(2) Examples of the alkali-soluble high molecular compound having sulfonamido groups include high molecular compounds prepared by homopolymerization of sulfonamido group-containing polymerizable monomers or by copolymerization of such monomers and other polymerizable monomers. Examples of the sulfonamido group-containing monomer include polymerizable monomers of low molecular compounds, which each contain at least one sulfonamido group having at least one hydrogen atom attached to the nitrogen atom, -NH-SO₂-, and at least one polymerizable unsaturated bond. Of these compounds, low molecular compounds having a combination of an acryloyl, allyl or vinyloxy group with an unsubstituted or mono-substituted aminosulfonyl group or a substituted sulfonylimino group are preferred.

(3) The alkali-soluble high molecular compounds having active imido groups are preferably high molecular compounds having active imido groups in their molecules. Examples of the high molecular compounds include homopolymers prepared by polymerizing polymerizable monomers of low molecular compounds, which each have at least one active imido group and at least one polymerizable unsaturated bond, and copolymers prepared by copolymerizing such monomers and other polymerizable monomers.

[0059] Specifically, N-(p-toluenesulfonyl)methacrylamide and N-(p-toluenesulfonyl) acrylamide can be preferably used as such monomers.

[0060] Further, it is preferable that high molecular compounds prepared by polymerizing at least two types of polymerizable monomers selected from the above-recited phenolic hydroxy group-containing monomers, sulfonamido group-containing monomers and active imido group-containing monomers, or high molecular compounds prepared by copolymerizing at least those two types of polymerizable monomers and other polymerizable monomers are used as the alkali-soluble high molecular compounds of the invention. In the case of copolymerizing the phenolic hydroxy group-containing monomer with the sulfonamido group-containing monomer and/or active imido group-containing monomer, a mixing weight ratio of the former monomer to the latter monomer(s) is preferably from 50:50 to 5:95, particularly preferably from 40:60 to 10:90.

[0061] In the case where the alkali-soluble polymer used in the invention is a copolymer of the phenolic hydroxy group, sulfonamido group or active imido group-containing polymerizable monomer and other polymerizable monomer(s), the content of alkali solubility-imparting monomer is preferably at least 10 mole %, more preferably at least 20 mole %. When the content of the alkali solubility-imparting monomer is lower than 10 mole %, the resulting copolymer is apt to have insufficient solubility in alkali and thus, the development latitude-improving effect may not be sufficiently achieved.

[0062] Examples of the monomer copolymerized with the phenolic hydroxy group-containing polymerizable monomer, sulfonamido group-containing polymerizable monomer or active imido group-containing polymerizable monomer as described above include compounds of the following groups (m1) to (m12). However, the comonomers usable in the invention should not be construed as being limited to these compounds.

(m1) Aliphatic hydroxy group-containing acrylates and methacrylates, inclusive of 2-hydroxyethyl acrylate and 2-hydroxyethyl methacrylate.

(m2) Alkyl acrylates, inclusive of methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, amyl acrylate, hexyl acrylate, octyl acrylate, benzyl acrylate, 2-chloroethyl acrylate and glycidyl acrylate.

(m3) Alkyl methacrylates, inclusive of methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, 2-chloroethyl methacrylate and glycidyl methacrylate.

(m4) Acrylamides and methacrylamides, inclusive of acrylamide, methacrylamide, N-methylolacrylamide, N-ethylacrylamide, N-hexylmethacrylamide, N-cyclohexylacrylamide, N-hydroxyethylacrylamide, N-phenylacrylamide, N-nitrophenylacrylamide and N-ethyl-N-phenylacrylamide.

(m5) Vinyl ethers, inclusive of 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, inclusive of vinyl acetate, vinyl chloroacetate, vinyl butyrate and vinyl benzoate.

(m7) Styrenes, inclusive of styrene, α -methylstyrene, methylstyrene and chloromethylstyrene.

- (m8) Vinyl ketones, inclusive of methyl vinyl ketone, ethyl vinyl ketone, propyl vinyl ketone and phenyl vinyl ketone.
 (m9) Olefins, inclusive of ethylene, propylene, isobutylene, butadiene and isoprene.
 (m10) N-Vinylpyrrolidone, acrylonitrile and methacrylonitrile.
 (m11) Unsaturated imides, inclusive of maleimide, N-acryloylacrylamide, N-acetylmethacrylamide, N-propionylmethacrylamide and N-(p-chlorobenzoyl)methacrylamide.
 (m12) Unsaturated carboxylic acids, inclusive of acrylic acid, methacrylic acid, maleic anhydride and itaconic acid.

[0063] The alkali-soluble high molecular compound preferably contains phenolic hydroxy groups. Preferred examples of the compounds include novolak resins, for example, phenol-formaldehyde resin, m-cresol-formaldehyde resin, p-cresol-formaldehyde resin, mixed m-/p-cresol-formaldehyde resin and mixed phenol/cresol (any of m-cresol, p-cresol and mixture thereof)-formaldehyde resin, and pyrogallolacetone resin.

[0064] Other examples of the alkali-soluble high molecular compound containing phenolic hydroxyl groups include a polycondensation product prepared from formaldehyde and a phenol having a C₃₋₈ alkyl group as a substituent, for example, tert-butylphenol-formaldehyde resin and octylphenol-formaldehyde resin as disclosed in U.S. Patent 4,123,279,

[0065] As copolymerization methods for the alkali-soluble high molecular compound, conventionally known graft, block and random copolymerization methods can be adopted.

[0066] When the alkali-soluble polymer for use in the invention is a homopolymer of the monomer containing a phenolic hydroxy group, a sulfonamido group or an active imido group, or a copolymer of any two of these monomers, it is preferred that the polymer has a weight average molecular weight of at least 2,000 and a number average molecular weight of at least 500. The polymer having the weight average molecular weight of from 5,000 to 300,000, the number average molecular weight of from 800 to 250,000, and a dispersion degree (weight average molecular weight/number average molecular weight) of from 1.1 to 10 are more preferred.

[0067] When the alkali-soluble polymer for use in the invention is a resin such as phenol-formaldehyde resin or cresol-formaldehyde resin, it is preferred that the resin has a weight average molecular weight of 500 to 20,000 and a number average molecular weight of 200 to 10,000.

[0068] As the alkali-soluble polymer for use in the lower layer, an acrylic resin is preferred from the viewpoint of image formation at the time of development, because the acrylic resin can ensure good solubility of the lower layer in an alkali developer containing an organic compound having a buffering action and a base as the main components. In particular, an acrylic resin having sulfonamido groups is preferably used.

[0069] The alkali-soluble high molecular compounds described above may be used individually or as a combination of two or more thereof. They are incorporated in the lower layer in an amount of 30 to 99 weight %, preferably 40 to 95 weight %, particularly preferably 50 to 90 weight %, based on the total solid content of the lower layer. When the amount of the alkali-soluble polymer added is lower than 30 weight %, the lower layer undergoes deterioration in durability, while the amount exceeding 99 weight % is undesirable from the viewpoints of both sensitivity and durability.

<Other Ingredients>

[0070] In the formation of upper layer and lower layer, various additives can be added, if desired, in addition to the above described essential components unless the effects of the invention are damaged. The additives may be added to the lower layer alone or the upper layer alone. Also, they may be added to both layers. Examples of additives for use in the invention are illustrated below.

[0071] For the purpose of improving the dissolution inhibition of image areas in a developer, it is preferable to add a material which is thermally decomposable and can substantially decrease solubility of the alkali-soluble high molecular compound before it is thermally decomposed, for example, onium salts, o-quinonediazide compounds, aromatic sulfone compounds and aromatic sulfonic acid ester compounds. Examples of the onium salt include diazonium salts, ammonium salts, phosphonium salts, iodonium salts, sulfonium salts, selenonium salts and arsonium salts.

[0072] Examples of the onium salt suitably used in the invention include the diazonium salts as described in S.I. Schlesinger, Photogr. Sci. Eng., 18, 387 (1974), T.S. Bal et al., Polymer, 21, 423 (1980), and Japanese Patent Laid-Open No. 158230/1993; the ammonium salts as disclosed in U.S. Patents 4,069,055 and 4,069,056, and Japanese Patent Laid-Open No. 140140; the phosphonium salts as described in D.C. Necker et al., Macromolecules, 17, 2468 (1984), C.S. Wen et al., Tech. Proc. Conf. Rad. Curing ASIA, p478, Tokyo, Oct (1988), and U.S. Patents 4,069,055 and 4,069,056; the iodonium salts as described in J.V. Crivello et al., Macromolecules, 10(6), 1307 (1977), Chem. & Eng. News, Nov. 28, p31 (1988), European Patent 104,143, U.S. Patents 339,049 and 410,201, and Japanese Patent Laid-Open Nos. 150848/1990 and 296514/1990; the sulfonium salts as 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), European Patents 370,693, 233,567, 297,443

and 297,442, U.S. Patents 4,933,377, 3,902,114, 410,201, 339,049, 4,760,013, 4,734,444 and 2,833,827, and German Patents 2,904,626, 3,604,580 and 3,604,581; the selenonium salts as 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 the arsonium salts as described in C.S. Wen et al., Teh. Proc. Conf. Rad. Curing ASIA, p478, Tokyo, Oct. (1988).

[0073] Of the onium salts, the diazonium salts are particularly preferred. Moreover, the diazonium salts disclosed in Japanese Patent Laid-Open No. 158230/1993 are especially preferred.

[0074] Examples of counter ion of the onium salt include tetrafluoroborate, hexafluorophosphate, triisopropyl-naphthalenesulfonate, 5-nitro-o-toluenesulfonate, 5-sulfosalicylic acid, 2,5-dimethylbenzenesulfonate, 2,4,6-trimethylbenzenesulfonate, 2-nitrobenzenesulfonate, 3-chlorobenzenesulfonate, 3-bromobenzenesulfonate, 2-fluorocaprylnaphthalenesulfonate, dodecylbenzenesulfonate, 1-naphthol-5-sulfonate, 2-methoxy-4-hydroxy-5-benzoylbenzenesulfonate and p-toluenesulfonate ions. Of these ions, hexafluorophosphate ion and an alkyl aromatic sulfonate ion, e.g., triisopropyl-naphthalenesulfonate or 2,5-dimethylbenzenesulfonate ion, are preferred.

[0075] The onium salts may be added to either the upper layer or the lower layer. However, the addition to the lower layer is preferable from the viewpoint of image-forming property.

[0076] As to the quinonediazides, o-quinonediazide compounds are preferred. The o-quinonediazide compound for use in the invention has at least one o-quinonediazido group and can increase alkali solubility upon thermal decomposition. The compounds may have various structures. More specifically, o-quinonediazide compound assists the dissolution of sensitive system by both losing the dissolution-inhibiting effect to the binder through thermal decomposition and changing to an alkali-soluble substance. In the invention, the o-quinonediazide compounds described, e.g., in J. Kosar, Light-Sensitive Systems, pp. 339-352 (John Wiley & Sons, Inc.) are usable. In particular, sulfonic acid esters or sulfonic acid amides of o-quinonediazide obtained by reaction with various aromatic polyhydroxy compounds or aromatic amino compounds respectively are preferably used. In addition, the esters of benzoquinone(1,2)-diazido-sulfonic acid chloride or naphthoquinone-(1,2)-diazido-5-sulfonic acid chloride with pyrogallol-acetone resin as disclosed in Japanese Patent Laid-Open No. 28403/1968, and the esters of benzoquinone-(1,2)-diazidosulfonic acid chloride or naphthoquinone-(1,2)-diazido-5-sulfonic acid chloride with phenol-formaldehyde resin as disclosed in U.S. Patents 3,046,120 and 3,188,210 are also preferably used.

[0077] Furthermore, the ester of naphthoquinone-(1,2)-diazido-4-sulfonic acid chloride with phenol-formaldehyde resin or cresol-formaldehyde resin, and the ester of naphthoquinone-(1,2)-diazido-4-sulfonic acid chloride with pyrogallol-acetone resin are preferably used. Other useful o-quinonediazide compounds are disclosed in many patents and known. For instance, those disclosed in Japanese Patent Laid-Open Nos. 5303/1972, 63802/1973, 63803/1973, 96575/1973, 38701/1974, 13354/1973, 11222/1966, 9610/1970 and 17481/1974, U.S. Patents 2,797,213, 3,454,400, 3,544,323, 3,573,917, 3,674,495 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 are useful.

[0078] The amount of o-quinonediazide compound added is preferably from 1 to 50 weight %, more preferably from 5 to 30 weight %, particularly preferably from 10 to 30 weight %, based on the total solid content of the layer. These compounds can be used singly or as a mixture of two or more thereof.

[0079] The amount of additives other than o-quinonediazide compound is preferably from 1 to 50 weight %, more preferably from 5 to 30 weight %, particularly preferably from 10 to 30 weight %. In the invention, it is preferred that the additives and the alkali-soluble polymer is contained in the same layer.

[0080] For the purpose of intensifying discrimination of images and strengthening resistance to surface scratches, it is preferable to use a polymer containing as a polymerization component, (meth)acrylate unit having two or three C₃₋₂₀ perfluoroalkyl groups as disclosed in Japanese Patent Laid-Open No. 2000-187318. Though such a polymer may be added to either the upper layer or the lower layer, it is more effective to contain the polymer in the upper layer.

[0081] The amount of the polymer added is preferably from 0.1 to 10 weight %, more preferably from 0.5 to 5 weight %, based on the total solid content of the upper layer.

[0082] For the purpose of imparting resistance to scratches, a compound capable of lowering a static friction constant of the surface may also be added to the printing plate material of the invention. Examples of the compound include long-chain alkyl carboxylic acid esters as described in U.S. Patent 6,117,913. Such a compound may be added to either the lower layer or the upper layer, but it is more effective to add it to the upper layer.

[0083] The amount of compound added is preferably from 0.1 to 10 weight %, more preferably from 0.5 to 5 weight %, based on the total solid content of the layer.

[0084] In the lower or upper layer, a low molecular compound containing an acid group may be contained, if desired. Examples of the acid group include sulfonic, carboxylic and phosphoric acid groups. Sulfonic acid group-containing compound is preferred. Specific examples thereof include an aromatic sulfonic acid, e.g., p-toluenesulfonic acid or naphthalenesulfonic acid and an aliphatic sulfonic acid.

[0085] Such a compound may be contained in either the lower layer or the upper layer. The amount of compound is preferably from 0.05 to 5 weight %, more preferably from 0.1 to 3 weight %, based on the total solid content of the layer. The amount greater than 5 weight % is not preferred, since the layer in which the compound is contained increases

solubility in a developer.

[0086] In addition, various dissolution inhibitors may be contained in the lower layer or the upper layer according to the invention for the purpose of adjusting the solubility of the lower or upper layer. As the dissolution inhibitor, the disulfone compound or sulfone compound as disclosed in Japanese Patent Laid-Open No. 119418/1999 is preferably used. Specifically, it is preferred to use 4,4'-bisdihydroxyphenylsulfone as the dissolution inhibitor.

[0087] Such a compound may be contained in either the lower layer or the upper layer. The amount of the compound is preferably from 0.05 to 20 weight %, preferably from 0.5 to 10 weight %, based on the total solid content of the layer.

[0088] In addition, cyclic acid anhydrides, phenols or organic acids may further be contained for the purpose of further increasing the sensitivity. Examples of the cyclic acid anhydride used include phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, 3,6-endoxy- Δ^4 -tetrahydrophthalic anhydride, tetrachloro-phthalic anhydride, maleic anhydride, chloromaleic anhydride, α -phenylmaleic anhydride, succinic anhydride and pyromellitic anhydride as disclosed in U.S. Patent No. 4,115,128. Examples of the phenol used 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. Examples of the organic acid used include sulfonic acids, sulfinic acids, alkylsulfuric acids, phosphonic acids, phosphoric acid esters and carboxylic acids as disclosed in Japanese Patent Laid-Open Nos. 88942/1985 and 96755/1990. Specific examples thereof include p-toluenesulfonic acid, dodecylbenzenesulfonic acid, p-toluenesulfinic acid, ethyl sulfuric acid, phenyl phosphonic acid, phenyl phosphinic acid, phenyl phosphate, diphenyl phosphate, benzoic acid, isophthalic acid, adipic acid, p-toluic acid, 3,4-dimethoxybenzoic acid, phthalic acid, terephthalic acid, 4-cyclohexene-1,2-dicarboxylic acid, erucic acid, lauric acid, n-undecanoic acid and ascorbic acid. The content of the cyclic anhydride, phenol and organic acid is preferably from 0.05 to 20 weight %, more preferably from 0.1 to 15 weight %, particularly preferably from 0.1 to 10 weight %, based on the total solid content of the layer.

[0089] Furthermore, for the purpose of increasing the processing suitability in development under varying conditions, nonionic surfactants as disclosed in Japanese Patent Laid-Open Nos. 251740/1987 and 208514/1991, amphoteric surfactants as disclosed in Japanese Patent Laid-Open Nos. 121044/1984 and 13149/1992, siloxane compounds as disclosed in European Patent 950,517 and fluorinated monomer-containing copolymers as disclosed in Japanese Patent Laid-Open No. 288093/1999 may be added to a coating solution for the upper or lower layer.

[0090] Examples of the nonionic surfactant include sorbitan tristearate, sorbitan monopalmitate, sorbitan trioleate, stearic acid monoglyceride, and polyoxyethylene nonyl phenyl ether. Examples of the amphoteric surfactant include alkyl di(amonoethyl)glycine, alkylpolyaminoethylglycine hydrochloride, 2-alkyl-N-carboxyethyl-N-hydroxyethylimidazoliniumbetaine, and an N-tetradecyl-N, N-betaine type surfactant (e.g., Amorgen K, trade name, produced by Dai-ichi Kogyo Seiyaku Co., Ltd.).

[0091] As the siloxane compound, a block copolymer of dimethylsiloxane and polyalkylene oxide is preferred. Specific examples thereof include polyalkylene oxide-modified silicone, e.g., DBE-224, DBE-621, DBE-712, DBP-732 and DBP-534 produced by Chisso Corp., and Tego Glide 100 produced by Tego A.G.

[0092] The content of the nonionic and amphoteric surfactants is preferably from 0.05 to 15 weight %, more preferably from 0.1 to 5 weight %, based on the whole ingredients in a coating solution for the layer.

[0093] To the lower layer or the upper layer in the invention, dyes or/and pigments may be added as a printing-out agent or an image-coloring agent for obtaining visible images immediately after heating upon exposure.

[0094] The representative examples of the printing-out agent include a combination of a compound capable of releasing an acid when heated by exposure (photo-acid releasing agent) with an organic dye capable of forming a salt. Specific examples thereof include the combination of o-naphthoquinonediazido-4-sulfonic acid halogenide with a salt-forming organic dye as disclosed in Japanese Patent Laid-Open Nos. 36209/1975 and 8128/1978, and the combination of trihalomethyl compound with a salt-forming organic dye as disclosed in Japanese Patent Laid-Open Nos. 36223/1978, 74728/1979, 3626/1985, 143748/1986, 151644/1986 and 58440/1988. The trihalomethyl compound includes oxazole type compounds and triazine type compounds. The compounds of both types have excellent storage stability, and enable the formation of clear print-out images.

[0095] In addition to the salt-forming organic dyes as described above, other dyes can also be used as the image-coloring agents. The suitable dyes include oil-soluble dyes and basic dyes as well as the salt-forming organic dyes. Specific examples of such dyes include Oil Yellow #101, Oil Yellow #103, Oil Pink #312, Oil Green BG, Oil Blue BOS, Oil Blue #603, Oil Black BY, Oil Black BS, Oil Black T-505 (produced by Orient Chemical Industry Co., Ltd.), Victoria Pure Blue, Crystal Violet (CI42555), Methyl Violet (CI42535), Ethyl Violet, Rhodamine B (CI145170B), Malachite Green (CI42000) and Methylene Blue (CI52015). In particular, the dyes disclosed in Japanese Patent Laid-Open No. 293247/1987 are preferable. The dyes can be added to a printing plate material in an amount of 0.01 to 10 weight %, preferably 0.1 to 3 weight %, based on the total solid content of the printing plate material.

[0096] Furthermore, a plasticizer is added to the printing plate material of the invention, if desired, for imparting flexibility to coating. Examples of the plasticizer used include butyl phthalyl, polyethylene glycol, tributyl citrate, diethyl phthalate, dibutyl phthalate, dihexyl phthalate, dioctyl phthalate, tricresyl phosphate, tributyl phosphate, trioctyl phos-

phate, tetrahydrofurfuryl oleate, and an oligomer and polymer of acrylic acid or methacrylic acid.

[0097] Each of the upper layer and lower layer of the lithographic printing plate precursor of the invention can be ordinarily formed by dissolving the ingredients as described above in a solvent and coating on an appropriate support.

[0098] Examples of the solvent used include ethylene dichloride, cyclohexanone, methyl ethyl ketone, methanol, ethanol, propanol, ethylene glycol monomethyl ether, 1-methoxy-2-propanol, 2-methoxyethyl acetate, 1-methoxy-2-propyl acetate, dimethoxyethane, methyl lactate, ethyl lactate, N,N-dimethylacetamide, N,N-dimethylformamide, tetramethylurea, N-methylpyrrolidone, dimethyl sulfoxide, sulfolane, γ -butyrolactone and toluene. However, the solvent should not be construed as being limited thereto. The solvents may be used alone or as a mixture of two or more thereof.

[0099] It is preferable that solvents used for forming the upper layer and the lower layer are selected individually from those having a solubility difference between the alkali-soluble polymer used in the upper layer and that used in the lower layer. More specifically, in the case of coating the lower layer and then coating the upper layer adjacent thereto, the use of a solvent capable of dissolving the alkali-soluble polymer of the lower layer as the coating solvent for the upper layer causes considerable mixing at the interface between these two layers and, at the extreme, the formation of a single layer and not a double layer. When the mixing occurs at the interface between the adjacent two layers or the adjacent two layers mingle with each other to behave as a uniform layer, there is a fear of impairing the effects produced by two-layer structure according to the invention. Therefore, it is desirable that the solvent used for coating the upper layer be a poor solvent of the alkali-soluble polymer contained in the lower layer.

[0100] The concentration of the foregoing ingredients (the total solid content including additives) in the solvent used for coating each layer is preferably from 1 to 50 weight %.

[0101] The coverage (solid basis) of the upper layer and that of the lower layer on a support after drying may be varied depend on the use, but are preferably from 0.05 to 1.0 g/m² and from 0.3 to 3.0 g/m², respectively. When the coverage of the upper layer is smaller than 0.05 g/m², the image-forming property is lowered. When the coverage is increased beyond 1.0 g/m², on the other hand, there is a possibility of decreasing the sensitivity. When the coverage of the lower layer is outside the foregoing range, greater or smaller, the image-forming property is apt to be lowered. It is preferable that the total coverage of two layers is from 0.5 to 3.0 g/m². When the total coverage is smaller than 0.5 g/m², the coating characteristics deteriorate, while, when the total coverage is greater than 3.0 g/m², the sensitivity tends to be decreased. Although the apparent sensitivity is increased with a decrease in the coverage, the coating characteristics of the upper and lower layer are degraded.

[0102] The formation of coating can be effected using various methods, for example, bar coater coating, spin coating, spray coating, curtain coating, dip coating, air knife coating, blade coating and roll coating methods.

[0103] To the upper and lower layers in the invention, a surfactant, e.g., the fluorine-containing surfactant disclosed in Japanese Patent Laid-Open No. 170950/1987, can be added for improving the coatability. The amount of surfactant added is preferably from 0.01 to 1 weight %, more preferably from 0.05 to 0.5 weight %, based on the total solid content of the lower or upper layer.

<Support>

[0104] The support for use in the lithographic printing plate precursor of the invention is a dimensionally stable sheet material having the required strength and durability. Examples of such a sheet material include paper, plastic-laminated paper (e.g., polyethylene-, polypropylene- or polystyrene-laminated paper), metal sheets (e.g., aluminum, zinc and copper sheets), plastic films (e.g., cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose butyrate, cellulose acetate butyrate, cellulose nitrate, polyethylene terephthalate, polyethylene, polystyrene, polypropylene, polycarbonate and polyvinyl acetal films), and paper or plastic film on which any of the metals as recited above is laminated or vacuum-deposited.

[0105] Of these materials, a polyester film or an aluminum sheet is preferred for the support in the invention. In particular, an aluminum sheet is preferably used because it has satisfactory dimensional stability and is relatively inexpensive. The suitable aluminum sheet includes a pure aluminum sheet and an alloy sheet containing aluminum as a major component and trace amounts of foreign elements. Further, the aluminum sheet may be an aluminum-laminated or aluminum-evaporated plastic film. Examples of the foreign metal contained in aluminum alloy include silicon, iron, manganese, copper, magnesium, chromium, zinc, bismuth, nickel and titanium. The content of those foreign metals in the aluminum alloy is up to 10 weight %. Although it is preferable to use a pure aluminum sheet in the invention, sheets of aluminum containing trace amounts of foreign elements may be employed because absolutely pure aluminum is difficult to produce due to limitations of smelting technology.

[0106] In other words, the aluminum sheet for use in the invention is not particularly restricted as to its composition, and any of hitherto known and widely used aluminum materials can be appropriately utilized. The aluminum sheet used in the invention has a thickness of approximately 0.1 to 0.6 mm, preferably 0.15 to 0.4 mm, particularly preferably 0.2 to 0.3 mm.

[0107] Prior to a surface-roughening treatment, the aluminum sheet is subjected to degreasing treatment with, e.g.,

a surfactant, an organic solvent or an aqueous alkali solution, if desired, in order to remove rolling oil from the sheet surface. The surface-roughening treatment of an aluminum sheet can be effected using various methods. For instance, a method of roughening mechanically the aluminum sheet surface, a method of electrochemically dissolving and roughening the surface, and a method of selectively dissolving the surface through chemical action can be adopted. Examples of the mechanical method include previously known methods including a ball graining method, a blush graining method, a blast graining method and a buff graining method. As to the electrochemical method, there is a method of roughening the aluminum sheet surface in an electrolytic solution of hydrochloric acid or nitric acid by passing AC or DC current therethrough. In addition, as disclosed in Japanese Patent Laid-Open No. 63902/1979, the combination of those two methods can also be utilized. The thus surface-roughened aluminum sheet is subjected to an alkali etching treatment and neutralizing treatment, if desired, and then to an anodic oxidation treatment, if desired, for enhancing water-retaining capability and abrasion resistance of the surface. For the anodic oxidation treatment of an aluminum sheet, various electrolytes can be used as far as they can form porous film of oxide. In general, sulfuric acid, phosphoric acid, oxalic acid, chromic acid and a mixture of two or more thereof can be used. The electrolyte concentration can be appropriately determined depending on the kind of an electrolyte used.

[0108] Conditions for the anodic oxidation treatment may vary depending on the electrolyte used, and they cannot be specified generally. However, it is appropriate that the concentration of an electrolytic solution is from 1 to 80 weight %, the electrolytic solution temperature is from 5 to 70°C, the current density is from 5 to 60 amperes/dm², the voltage is from 1 to 100 V, and the electrolysis time is from 10 sec. to 5 min. When the amount of anodically oxidized film is smaller than 1.0 g/m², the lithographic printing plate obtained cannot have a sufficiently long press life, or tends to receive scratches on the non-image areas. At the time of printing, therefore, the so-called scratch toning, namely adhesion of ink to the scratch is apt to occur. After the anodic oxidation treatment, the aluminum sheet surface receives a treatment for imparting hydrophilicity thereto, if desired. As the hydrophilicity imparting treatment, the method of using an alkali metal silicate (e.g., an aqueous solution of sodium silicate) as disclosed in U.S. Patents 2,714,066, 3,181,461, 3,280,734 and 3,902,732 can be adopted in the invention. In this method, the support undergoes immersion treatment or electrolysis treatment with an aqueous solution of sodium silicate. In addition to such a method, the method of treating the aluminum sheet surface with potassium fluorozirconate as disclosed in Japanese Patent laid-Open No. 22063/1961 and the method of treating the aluminum sheet surface with polyvinyl phosphonic acid as disclosed in U.S. Patents 3,276, 868, 4,153,461 and 4,689,272 can be adopted.

[0109] The lithographic printing plate precursor according to the invention has on a support a layer structure consisting of at least two layers, a positive-working recording layer and a lower layer. A subbing layer may be provided between the support and the lower layer.

[0110] As subbing layer constituents, various organic compounds can be used. For instance, they can be selected from carboxymethyl cellulose, dextrin, gum arabic, amino group-containing phosphonic acids (e.g., 2-aminoethylphosphonic acid), organic phosphonic acids (e.g., phenylphosphonic acid, naphthylphosphonic acid, alkylphosphonic acid, glycerophosphonic acid, methylenediphosphonic acid and ethylenediphosphonic acid, which each may have a substituent), organic phosphoric acids (e.g., phenylphosphoric acid, naphthylphosphoric acid, alkylphosphoric acid and glycerophosphoric acid, which each may have a substituent), organic phosphinic acids (e.g., phenylphosphinic acid, naphthylphosphinic acid, alkylphosphinic acid and glycerophosphinic acid, which each may have a substituent), amino acids (e.g., glycine and β -alanine), or hydroxyl group-containing amine hydrochlorides (e.g., ethanolamine hydrochloride). These compounds may be used as a mixture of two or more thereof.

[0111] The organic subbing layer can be provided in the following manner. Specifically, the subbing layer is formed by coating on an aluminum sheet a solution prepared by dissolving the organic compound described above in water, an organic solvent, e.g., methanol, ethanol or methyl ethyl ketone, or a mixture thereof is coated on an aluminum sheet, and drying the coated solution. In another manner, the organic subbing layer is formed by immersing an aluminum sheet in a solution prepared by dissolving organic compound in water, an organic solvent, e.g., methanol, ethanol or methyl ethyl ketone, or a mixture thereof, thereby making the organic compound adsorb to the sheet surface, washing with water or the like, and then drying. In the former manner, the solution having an organic compound concentration of 0.005 to 10 weight % can be coated using various methods. In the latter manner, on the other hand, the concentration of the solution is from 0.01 to 20 weight %, preferably from 0.05 to 5 weight %. The immersion temperature is from 20 to 90°C, preferably from 25 to 50°, and the immersion time is from 0.1 sec. to 20 min., preferably from 2 sec. to 1 min. The solution used can be adjusted to pH of 1 to 12 using a basic material, e.g., ammonia, triethylamine or potassium hydroxide, or an acidic material, e.g., hydrochloric acid or phosphoric acid. Also, yellow dye may be added to the solution for improving tone reproducibility of the image-recording material.

[0112] The coverage of organic subbing layer is ordinarily from 2 to 200 mg/m², preferably from 5 to 100 mg/m². When the coverage is less than 2 mg/m², sufficient printing durability may not be obtained. Likewise, the coverage greater than 200 mg/m² may not ensure sufficient printing durability.

[0113] The positive-working lithographic printing plate precursor prepared as described above is subjected to image-wise exposure, and then to development processing.

[0114] Examples of a light source of actinic ray used for the imagewise exposure include a mercury lamp, a metal halide lamp, a xenon lamp, a chemical lamp and carbon arc lamp. Examples of radiation used include electron beams, X-rays, ion beams and far infrared rays. In addition, g-ray, i-ray, deep UV light, high-density energy beams (laser beams) can also be used. Examples of the laser beam include helium-neon laser, argon laser, krypton laser, helium-cadmium-laser and KrF excimer laser. In the invention, light sources having light emission wavelengths in the region of near infrared to infrared are preferred. In particular, solid lasers and semiconductor lasers are preferably used.

[0115] The developer and its replenisher used for the development of the lithographic printing plate precursor according to the invention are heretofore known aqueous alkali solutions.

[0116] Examples of the alkali agent include inorganic alkali salts, for example, 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 hydrogen carbonate, potassium hydrogen carbonate, ammonium hydrogen carbonate, sodium borate, potassium borate, ammonium borate, sodium hydroxide, ammonium hydroxide, potassium hydroxide and lithium hydroxide. Also, organic alkali agents, for example, monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, triisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethyleneimine, ethylenediamine and pyridine can be used. The alkali agents can be used alone or as a combination of two or more thereof.

[0117] Of developers containing the alkali agent, an aqueous solution of silicate, e.g., sodium silicate or potassium silicate are particularly preferred. This is because the developability can be controlled by appropriately adjusting a ratio between silicon oxide SiO_2 and alkali metal oxide M_2O as constituents of the silicate and concentration. For instance, the alkali metal silicates as disclosed in Japanese Patent Laid-Open No. 62004/1979 and Japanese Patent Publication No. 7427/1982 can be used effectively.

[0118] The so-called non-silicate developer, which does not contain an alkali silicate but contains a pH buffering organic compound, for example, a non-reducing sugar and a base, is more preferably used for the development of the lithographic printing plate precursor according to the present invention. By using such a non-silicate developer, degradation of the surface of image-recording layer is prevented and inking of the image-recording layer is maintained in good condition. In general, a lithographic printing plate precursor has a narrow development latitude and severe change in a line width of image occurs depending on variation in pH of the developer used. However, since the non-silicate developer contains a non-reducing sugar having a buffering function capable of restraining the variation in pH, it is advantageous in comparison with a developer containing a silicate. Further, the non-reducing sugar has a property of less contaminating a conductivity sensor or a pH sensor for controlling the activity of developer compared with the silicate, and from this viewpoint the non-silicate developer is also advantageous. Moreover, the non-silicate developer exhibits remarkable improvement in discrimination between the image areas and the non-image areas. It is believed that contact (penetration) of the developer to the lithographic printing plate precursor, which is important for the discrimination and maintenance of film properties in the invention, becomes mild and as a result, the difference between the image areas and the non-image areas is easily obtained.

[0119] The non-reducing sugar means a saccharide that does not contain a free aldehyde group or ketone group and is not reducing, and includes trehalose-type oligosaccharides wherein the reducing groups are connected each other, glycosides wherein the reducing group of saccharide is connected to aglycone, and sugar alcohols obtained by reducing saccharides with hydrogenation. Any of these compounds can be preferably used in the invention. Non-reducing sugars disclosed in Japanese Patent Laid-Open No. 305039/1996 is also preferably used in the invention.

[0120] Examples of the trehalose-type oligosaccharide include saccharose and trehalose. Examples of the glycoside include alkyl glycoside, phenol glycoside and mustered oil glycoside. Examples of the sugar alcohol include D- or L-arabitol, ribitol, xylitol, D- or L-sorbitol, D- or L-mannitol, D or L-iditol, D or L-talitol, dulcitol and allodulcitol. Also, maltitol obtained by hydrogenation of maltose that is a disaccharide and a reduction product (reduced starch sirup) obtained by hydrogenation of oligosaccharide are preferably used. Of the non-reducing sugars, trehalose-type oligosaccharides and sugar alcohols are preferred, and D-sorbitol, saccharose and reduced starch sirup are particularly preferred since they each have a buffering function in an appropriate pH range and they are cheaply available.

[0121] The non-reducing sugars may be used alone or as a combination of two or more thereof. The content of non-reducing sugar in the non-silicate developer is preferably from 0.1 to 30 weight %, more preferably from 1 to 20 weight %. When the content is less than 0.1 weight %, there is a tendency that a sufficient buffering function is difficult to obtain. On the other hand, it exceeds 30 weight %, it is difficult to highly concentrate the developer and disadvantageous in view of cost.

[0122] The base used together with the non-reducing sugar in the developer includes conventionally known alkali agents, for example, inorganic alkali agents and organic alkali agents. Examples of the inorganic alkali agent include sodium hydroxide, potassium hydroxide, lithium hydroxide, 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 hydrogen carbonate, potassium

hydrogen carbonate, ammonium hydrogen carbonate, sodium borate, potassium borate and ammonium borate.

[0123] Examples of the organic alkali agent include monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, triisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethyleneimine, ethylenediamine and pyridine.

[0124] The bases may be used alone or as a combination of two or more thereof. Of the bases, sodium hydroxide and potassium hydroxide are preferred.

[0125] In the invention, a non-silicate developer containing, as the main component, an alkali metal salt of non-reducing sugar in place of the combination of non-reducing sugar and base may also be employed.

[0126] Further, an alkaline buffer containing a weak acid other than the non-reducing sugar described above and a strong base is used as the non-silicate developer. The weak acid is preferably a compound having a dissociation constant (pKa) of 10.0 to 13.2, and selected from the compounds described, for example, in Ionization Constants of Organic Acids in Aqueous Solution, published by Pergmon Press.

[0127] Specifically, preferred examples thereof include an alcohol, e.g., 2,2,3,3-tetrafluoropropanol-1, trifluoroethanol or trichloroethanol; an aldehyde, e.g., pyridine-2-aldehyde or pyridine-4-aldehyde; a compound having a phenolic hydroxy group, e.g., salicylic acid, 3-hydroxy-2-naphthoic acid, catechol, gallic acid, sulfosalicylic acid, 3,4-dihydroxybenzenesulfonic acid, 3,4-dihydroxybenzoic acid, hydroquinone, pyrogallol, o-, m- or p-cresol or resorcinol; an oxime, e.g., acetoxime, 2-hydroxybenzaldehydoxime, dimethylglyoxime, ethanediamidoxime or acetophenonoxime; a nucleic acid-related compound, e.g., adenine, inosine, guanine, cytosine, hypoxanthine or xanthine; and others, e.g., diethylaminomethylphosphonic acid, benzimidazole or barbituric acid.

[0128] It is known that, when the development is carried out with an automatic developing machine, a replenisher, namely an aqueous solution having higher alkalinity than a developer, is added to the developer and thereby enables a large number of lithographic printing plate precursors to be processed without replacing the developer in a developing tank for a long time. Such a replenishing system can be preferably applied to the invention. Various surfactants and organic solvents can be added to the developer and replenisher used, if desired, for the purposes of accelerating or retarding development, dispersing development residue and enhancing ink receptivity in the image areas of printing plate.

[0129] Preferable surfactants include anionic, cationic, nonionic and amphoteric surfactants. To the developer and replenisher, reducing agents, such as hydroquinone, resorcinol and sodium or potassium salt of inorganic acids, e.g., sodium or potassium sulfite or sodium or potassium hydrogen sulfite, organic carboxylic acids, anti-foaming agents and water softening agents can be further added, if desired.

[0130] Printing plates development-processed with the developer and replenisher are subjected to after-treatment with washing water, a rinsing solution containing a surfactant and a desensitizing solution containing gum arabic or a starch derivative. Such after-treatments may be used in combination thereof for the after-treatment of the lithographic printing plate precursor of the invention.

[0131] In recent years, automatic developing machines for making printing plates have been used widely for rationalizing and standardizing plate-making operations in the plate-making and printing industries. In general, the automatic developing machine are comprised of a development section and an after-treatment section, and equipped with a plate conveying device, tanks for various processing solutions and a spraying device. In the developing machine, exposed printing plate precursor is development-processed by spraying each processing solution drawn with a pump on the plate surface via a spray nozzle while conveying it in a horizontal direction. There has been also known the method of processing exposed printing plate precursor by immersing in a processing tank filled with a processing solution and conveying with the aid of submerged guide rolls. In such automatic processing, the processing can be performed while adding a replenisher to a processing solution in an amount depending on the amount of processing and the operation-time. In addition, a so-called single-use processing method, in which the processing is conducted using a substantially virgin processing solution, is applicable.

[0132] When a lithographic printing plate made by subjecting the lithographic printing plate precursor according to the invention to imagewise exposure, development, washing and/or rinsing and/or gumming has unnecessary image areas (e.g., film edge mark of an original film), the unnecessary image areas are removed. It is preferable that the removal is effected by coating on the unnecessary image areas an image remover as disclosed in Japanese Patent Publication No. 13293/1990, allowing to stand for a specified time, and then washing with water. However, it is also possible to use the method as disclosed in Japanese Patent Laid-Open No. 174842/1984, wherein the unnecessary image areas are exposed to actinic rays guided by optical fibers and then developed.

[0133] The thus prepared lithographic printing plate is coated with desensitizing gum, if desired, and subjected to printing operations. When it is desired to impart higher press life to the lithographic printing plate, a burning treatment is carried out in advance of printing operations. Prior to the burning treatment, it is preferred that the lithographic printing plate is treated with a burning conditioner as disclosed in Japanese Patent Publication Nos. 2518/1986 and 28062/1980, and Japanese Patent Laid-Open Nos. 31859/1987 and 159655/1986.

[0134] Such a pretreatment can be effected in various manners. For instance, a method wherein the burning conditioner is applied to the lithographic printing plate using sponge or cotton wool impregnated with the burning conditioner, a method wherein the printing plate is dipped in a vat filled with the burning conditioner to coat, or a method of coating the burning conditioner by an automatic coater is adopted. In addition, more preferred results are obtained by making the amount of burning conditioner coated uniform with a squeegee or a squeegee roller.

[0135] An amount of the burning conditioner coated is ordinarily from 0.03 to 0.8 g/m² (solid basis). The lithographic printing plate coated with the burning conditioner is heated to a high temperature by a burning processor (Burning Processor BP-1300, sold by Fuji Photo Film, Co., Ltd.) after drying, if desired. The heating temperature and time for the burning treatment, which may be varied depending on the kinds of image-forming ingredients, are preferably in the ranges of 180 to 300°C and 1 to 20 minutes, respectively.

[0136] The lithographic printing plate having undergone the burning treatment may be subjected to a conventional treatment, for example, washing or gumming, if desired. However, in the case of using a burning conditioner containing a water-soluble high molecular compound, a so-called desensitizing treatment such as gumming, can be omitted. The thus treated lithographic printing plate is mounted in an offset printing machine, and used for printing of a great number of sheets.

[0137] Now, the invention will be illustrated in more detail with reference to the following examples, but these examples should not be construed as limiting the scope of the invention in any way.

[Production of Lithographic Printing Plate Precursors 1 to 17]

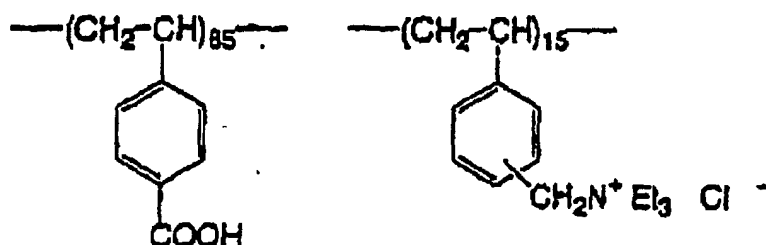
<Preparation of Substrate>

[0138] A 0.3 mm-thick aluminum sheet (JIS 1050) was degreased by washing with trichloroethylene, and then surface-grained using a nylon brush and an aqueous suspension of 400-mesh pumice stone, and further washed thoroughly with water. The grained sheet was etched by 9-second immersion in a 25 % aqueous solution of sodium hydroxide kept at 45°C, washed with water, further immersed in 20 % nitric acid for 20 seconds, and then washed with water. At that time, the etched quantity of the grained surface was about 3 g/m². Then, a 3 g/m² of anodic coating was formed on the thus etched sheet by performing direct-current electrolysis in a 7 % sulfuric acid as electrolyte under the condition of a current density of 15 A/dm², and then washed and dried. Further, the thus treated aluminum sheet was treated with a 2.5 weight % aqueous solution of sodium silicate for 10 seconds at 30°C, and then coated with the following subbing solution, and further dried for 15 seconds at 80°C, thereby preparing a substrate. The coverage of the coating after drying was 15 mg/m².

Subbing Solution:

[0139]

High molecular compound illustrated below	0.3 g
Methanol	100 g
Water	1 g



Molecular weight: 2.8×10^4

<Formation of Recording Layer>

[0140] On the substrate prepared, the following coating solution for a lower layer was coated so as to have a coverage

EP 1 262 318 B1

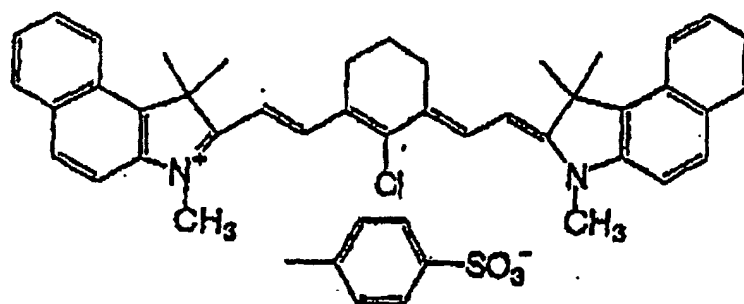
of 0.85 g/m², and then dried for 50 seconds at 140°C by use of PERFECT OVEN PH 200, produced by TABAI CO., setting of Wind Control to 7. Thereafter, the following coating solution for an upper layer was coated so as to have a coverage of 0.15 g/m², and then dried for 1 minute at 120°C. Thus, lithographic printing plate precursors 1 to 17 were produced.

Coating Solution for Lower layer:

[0141]

N-(4-Aminosulfonylphenyl)methacrylamide/ acrylonitrile/methyl methacrylate (36/34/30) copolymer (weight average molecular weight: 50,000)	2.133 g
3-Methoxy-4-diazodiphenylamine hexafluorophosphate	0.030 g
Cyanine Dye A (having the structure illustrated below)	0.109 g
4,4'-Bishydroxyphenylsulfone	0.063 g
Tetrahydrophthalic anhydride	0.190 g
p-Toluenesulfonic acid	0.008 g
Dye obtained by replacing the counter ion of Ethyl Violet with 6-hydroxynaphthalenesulfone	0.05 g
Fluorine-containing surfactant (Megafac F176, produced by 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

Cyanine Dye A



Coating Solution for Upper Layer:

[0142]

Novolak resin set forth in Table 1	0.237 g
Cyanine Dye A (illustrated above)	0.047 g
Dodecyl stearate	0.060 g
3-Methoxy-4-diazodiphenylaminehexafluorophosphate	0.030 g
Fluorine-containing surfactant (Megafac F176, produced by Dainippon Ink & Chemicals, Inc.)	0.110 g
Fluorine-containing surfactant (Megafac MCF-312 (30 %), produced by Dainippon Ink & Chemicals, Inc.)	0.120 g
Methyl ethyl ketone	15.1 g
1-Methoxy-2-propanol	7.7 g
Additive set forth in Table 1	X g

[Evaluation of Lithographic Printing Plate Precursor]

[0143] Development of the lithographic printing plate precursor was conducted using Developer DT-1 and DT-1R, each produced by Fuji Photo Film Co., Ltd., in an ordinary manner. Scratch resistance test and evaluation of sensitivity and ablation were performed in the following manner.

<Scratch Resistance Test>

[0144] Each of the lithographic printing plate precursors obtained was rubbed 20 times with abramer felt CS5 under a load of 250 g by using a rotary abrasion tester (Toyoseiki CO., LTD.). Thereafter, the precursor was developed by a PS Processor 900H made by Fuji Photo Film Co., Ltd. furnished with the alkali developer described above under conditions that the developer temperature was 30°C and the development time was 12 seconds. Optical density change caused in the rubbed areas of the recording layer was visually observed.

[0145] The following are evaluation criteria for the scratch resistance, and the evaluation results are shown in Table 1.

- : No change was observed at all in optical density.
- Δ: Scratch marks were visually recognized.
- Δ: Slight exposure of the substrate was observed.
- Δ×: The optical density was dropped about on-half.

<Evaluation of Sensitivity>

[0146] Each of the lithographic printing plate precursors was installed in a Trendsetter made by CREO Co. and subjected to imagewise drawing of test patterns while changing the exposure energy. Then, it was developed with a solution prepared by diluting Developer DT-1 produced by Fuji Photo Film Co., Ltd. so as to have electric conductivity of 45 mS/cm, and the exposure energy capable of developing non-image areas with the developer was determined. The energy value thus determined was defined as sensitivity. The smaller the energy value determined, the higher the sensitivity. The results obtained are set forth in Table 1.

<Evaluation of Ablation>

[0147] A polyethylene terephthalate film (0.10 mm in thickness, produced by Fuji Photo Film Co., Ltd.) was brought into contact with each of the printing plate precursors, and exposed using a Trendsetter made by CREO Co. at the drum rotation speed of 100 rpm and the beam intensity of 8.0 W. Then, the polyethylene terephthalate film was removed, and the amount of an ablation residue transferred thereto was visually evaluated.

[0148] The following are evaluation criteria for the ablation, and the evaluation results are shown in Table 1.

- : No ablation residue was observed at all on the polyethylene terephthalate film.
- Δ: Ablation residue was slightly observed on the polyethylene terephthalate film.
- ×: Ablation residue was fairly observed on the polyethylene terephthalate film.

Table 1

	Precursor	Novolak Resin	Additive	Amount added (g)	Scratch Resistance	Sensitivity (mJ/cm)	Ablation
Example 1	1	1	-	-	OΔ	95	OΔ
Example 2	2	2	-	-	OΔ	100	OΔ
Example 3	3	3	-	-	OΔ	105	O
Example 4	4	4	-	-	O	100	O
Example 5	5	5	-	-	OΔ	95	OΔ
Example 6	6	6	-	-	OΔ	110	OΔ
Example 7	7	7	-	-	OΔ	100	Δ
Example 8	8	8	-	-	Δ	100	Δx
Comparative Example 1	9	9	-	-	Δx	100	x
Example 9	10	1	Tetraoctylammonium bromide	0.020	O	100	OΔ
Example 10	11	2	Tetrabutylammonium bromide	0.030	O	105	OΔ
Example 11	12	3	Stearyltrimethylammonium bromide	0.080	O	110	O
Example 12	13	4	PEG1000	0.020	O	100	O
Example 13	14	5	PEG1000 distearoyl ester	0.060	O	100	OΔ
Example 14	15	6	Lactone compound I-4	0.040	OΔ	90	OΔ
Example 15	16	7	Lactone compound I-10	0.080	OΔ	95	Δ
Example 16	17	10	-	-	Δ	90	Δx

Structure of Novolak Resin

[0149]

- 5 Novolak 1: 2,3-xyleneol/m-cresol/p-cresol/phenol = 35/30/30/5 (Mw: 6,800; total content of compounds consisting of at most three monomers: 14 %)
- Novolak 2: 2,5-xyleneol/m-cresol/p-cresol/phenol = 35/30/30/5 (Mw: 5,200; total content of compounds consisting of at most three monomers: 16 %)
- 10 Novolak 3: 3,5-xyleneol/m-cresol/p-cresol/phenol = 35/30/30/5 (Mw: 7,500; total content of compounds consisting of at most three monomers: 10 %)
- Novolak 4: 2,3-xyleneol/m-cresol/p-cresol/phenol = 45/5/5/45 (Mw: 8,000; total content of compounds consisting of at most three monomers: 9 %)
- Novolak 5: 2, 5-xyleneol/phenol = 40/60 (Mw: 5,500; total content of compounds consisting of at most three monomers: 19 %)
- 15 Novolak 6: 3,5-xyleneol/m-cresol/p-cresol = 30/35/35 (Mw: 6,300; total content of compounds consisting of at most three monomers: 11 %)
- Novolak 7: 2,3-xyleneol/m-cresol/p-cresol/phenol = 35/50/10/5 (Mw: 4,500; total content of compounds consisting of at most three monomers: 22 %)
- 20 Novolak 8: 2,3-xyleneol/m-cresol/phenol = 35/55/10 (Mw: 2,800; total content of compounds consisting of at most three monomers: 25 %)
- Novolak 9: m-cresol/p-cresol = 60/40 (Mw: 6,000; total content of compounds consisting of at most three monomers: 32 %)
- Novolak 10: 2,3-xyleneol/m-cresol/p-cresol/phenol = 35/30/30/5 (Mw: 3,500; total content of compounds consisting of at most three monomers: 35 %)

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[0150] The total content of compounds consisting of at most three monomers in each novolak resin was determined by gel permeation chromatography (GPC), HLC-8020, made by Tosoh Corporation using 2 columns having length of 30 cm, TSKgel GMHXL-N, made by Tosoh Corporation, an UV-utilized detector and tetrahydrofuran (reagent grade) as a mobile phase under conditions that the injection amount and the flow velocity were set at 100 μ l and 1.0 ml/min, respectively. Calibration was performed with standard polystyrene. A content of the fraction having molecular weight of 300 or below was regarded as the content of compounds consisting of at most three monomers.

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[0151] As can be seen from Table 1, the lithographic printing plate precursors according to the invention have high scratch resistance and satisfactory sensitivity, and are resistant to ablation.

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[0152] On the other hand, the printing plate precursor (Precursor 9) having the recording layer free from the novolak resin containing xyleneol structural units was inferior in the scratch resistance.

[0153] The lithographic printing plate precursor according to the invention has a lower layer containing an alkali-soluble resin and an upper layer containing an infrared absorbent and an alkali-soluble novolak resin having xyleneol as a structural unit, thereby enabling improvements in the scratch resistance, sensitivity and ablation resistance. When the content of compound consisting of at most three monomer units in the upper layer is controlled to at most 30 % by weight to the novolak resin, more preferred results are obtained.

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[0154] While the invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the scope thereof, as defined in the appended claims.

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Claims

1. A lithographic printing plate precursor of double-layer structure comprising a support, an alkali-soluble resin-containing layer, and a positive-working recording layer capable of increasing solubility in an aqueous alkali solution upon exposure to infrared laser provided on the alkali-soluble resin-containing layer, and the positive-working recording layer contains an infrared absorbing cyanine dye and an alkali-soluble novolak resin having xyleneol as a structural unit.
- 50 2. The lithographic printing plate precursor as claimed in Claim 1, wherein the positive-working recording layer contains a compound consisting of at most three monomer units in an amount of 30 weight % or less to the novolak resin.
- 55 3. The lithographic printing plate precursor as claimed in Claim 1, wherein the alkali-soluble resin-containing layer

contains an onium salt.

4. The lithographic printing plate precursor as claimed in Claim 1, wherein the alkali-soluble resin-containing layer contains an infrared absorbent.

5. A method of processing a lithographic printing plate precursor comprising:

subjecting a lithographic printing plate precursor to image-wise exposure and development with an alkaline developer containing a pH buffering organic compound and a base, wherein the lithographic printing plate precursor is a lithographic printing plate precursor of double-layer structure comprising a support, an alkali-soluble resin-containing layer, and a positive-working recording layer capable of increasing solubility in an aqueous alkali solution upon exposure to infrared laser provided on the alkali-soluble resin-containing layer, and the positive-working recording layer contains an infrared absorbing cyanine dye and an alkali-soluble novolak resin having xylenol as a structural unit.

Patentansprüche

1. Lithografiedruckplattenvorläufer mit einer Doppelschichtstruktur, umfassend einen Träger, eine ein basenlösliches Harz enthaltende Schicht und eine positiv arbeitende Aufzeichnungsschicht, die geeignet ist zur Erhöhung der Löslichkeit in einer wässrigen basischen Lösung nach Einwirkung eines Infrarotlasers, die auf der das basenlösliche Harz enthaltenden Schicht vorliegt und wobei die positiv arbeitende Aufzeichnungsschicht einen Infrarotabsorbierenden Cyaninfarbstoff und ein basenlösliches Novolakharz mit Xylenol als Struktureinheit enthält.

2. Lithografiedruckplattenvorläufer nach Anspruch 1, worin die positiv arbeitende Aufzeichnungsschicht eine Verbindung, bestehend aus höchstens drei Monomereinheiten in einer Menge von 30 Gew.% oder weniger, bezogen auf das Novolakharz, enthält.

3. Lithografiedruckplattenvorläufer nach Anspruch 1, worin die das basenlösliche Harz enthaltende Schicht ein Oniumsalz enthält.

4. Lithografiedruckplattenvorläufer nach Anspruch 1, worin die das basenlösliche Harz enthaltende Schicht ein Infrarot-Absorptionsmittel enthält.

5. Verfahren zur Behandlung eines Lithografiedruckplattenvorläufers, umfassend:

Unterwerfen eines Lithografiedruckplattenvorläufers der bildseitigen Bestrahlung und Entwicklung mit einem basischen Entwickler, enthaltend eine den pH puffernde organische Verbindung und eine Base, worin der Lithografiedruckplattenvorläufer ein Lithografiedruckplattenvorläufer mit Doppelschichtstruktur ist, umfassend einen Träger, eine ein basenlösliches Harz enthaltende Schicht und eine positiv arbeitende Aufzeichnungsschicht, die geeignet ist zur Erhöhung der Löslichkeit in einer wässrigen basischen Lösung nach Einwirkung eines Infrarotlasers, die auf der das basenlösliche Harz enthaltenden Schicht vorliegt, und wobei die positiv arbeitende Aufzeichnungsschicht einen Infrarotabsorbierenden Cyaninfarbstoff und ein basenlösliches Novolakharz mit Xylenol als Struktureinheit enthält.

Revendications

1. Précurseur de planche d'impression lithographique à structure à double couche comprenant un support, une couche contenant une résine soluble dans un produit alcalin, et une couche d'enregistrement à action positive permettant d'augmenter la solubilité dans une solution aqueuse alcaline lors d'une exposition à un laser infrarouge appliquée sur la couche contenant une résine soluble dans un produit alcalin, et la couche d'enregistrement à action positive contient un colorant cyanine absorbant l'infrarouge et une résine de novolaque soluble dans un produit alcalin comportant un xylénol comme motif structurel.

2. Précurseur de planche d'impression lithographique selon la revendication 1, dans lequel la couche d'enregistrement à action positive contient un composé constitué d'au plus trois motifs monomères dans une quantité de 30 % en poids ou moins de la résine de novolaque.

3. Précurseur de planche d'impression lithographique selon la revendication 1, dans lequel la couche contenant une résine soluble dans un produit alcalin contient un sel d'onium.

5 4. Précurseur de planche d'impression lithographique selon la revendication 1, dans lequel la couche contenant une résine soluble dans un produit alcalin contient un absorbant d'infrarouge.

5. Procédé de traitement d'un précurseur de planche d'impression lithographique comprenant :

10 la soumission d'un précurseur de planche d'impression lithographique à une exposition conforme à une image et à un développement avec un révélateur alcalin contenant un composé organique tampon de pH et une base,

15 dans lequel le précurseur de planche d'impression lithographique est un précurseur de planche d'impression lithographique à structure à double couche comprenant un support, une couche contenant une résine soluble dans un produit alcalin et une couche d'enregistrement à action positive capable d'augmenter la solubilité dans une solution aqueuse alcaline lors d'une exposition à un laser infrarouge appliquée sur la couche contenant une résine soluble dans un produit alcalin, et la couche d'enregistrement à action positive contient un colorant cyanine absorbant l'infrarouge et une résine de novolaque soluble dans un produit alcalin comportant un xylénol comme motif structurel.