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(54) **Planographic printing plate precursor**

(57) The invention provides a planographic printing plate precursor having at least: a support; and two or more positive recording layers, each of the layers having at least a resin and an infrared absorber and respectively having a solubility with respect to an aqueous alkali solution that is increased by exposure to infrared laser light, wherein: of the two or more positive recording layers, a positive recording layer that is nearest to the support

comprises two resins; the two resins each has at least a specific polymer comprising a specific structural unit; one of the two resins constitutes a dispersion phase that is dispersed in a matrix phase; and the matrix phase serves as a dispersing medium and contains at least the other of the two resins. The invention further provides a method of forming the planographic printing plate precursor.

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Description

BACKGROUND OF THE INVENTION

5 Field of the Invention

[0001] The present invention relates to a planographic printing plate precursor. More specifically, the invention relates to an infrared-laser-applicable planographic printing plate precursor from which a printing plate can be directly formed based on digital signals from a computer or the like.

10 Description of the Related Art

[0002] The development of lasers for planographic printing in recent years has been remarkable. In particular, high-power, small-sized solid lasers and semiconductor lasers that emit near-infrared and infrared rays have become easily obtainable. These lasers are very useful as exposure light sources when forming printing plates directly from digital data of computers or the like.

[0003] Materials which can be used for positive planographic printing plate precursors applicable for infrared lasers include, as essential components, a binder resin soluble in an aqueous alkaline solution (hereinafter referred to where appropriate as an "alkali-soluble resin"), and an infra red dye which absorbs light to generate heat. When an image is formed in a positive planographic printing plate precursor, the infra red dye interacts with the binder resin in its unexposed portions (image portions) so as to function as a dissolution inhibitor which can substantially reduce the solubility of the binder resin. On the other hand, in its exposed portions (non-image portions), interaction of the infra red dye with the binder resin is weakened by the heat generated. Consequently, an exposed portion can turn into a state in which it can be dissolved in an alkaline developer, so that an image is formed thereon and a planographic printing plate is produced.

[0004] However, insofar as such infrared-laser-applicable positive planographic printing plate precursor are concerned, differences in the degree of resistance against dissolution in a developer between unexposed portions (image portions) and exposed portions (non-image portions) therein, that is, differences in development latitude have not yet been sufficient under various conditions of use. Thus, problems have occurred insofar that, with changes in conditions of use of materials, materials have tended to be either excessively developed or inadequately developed.

Further, when using an infrared-laser-applicable positive planographic printing plate precursor, if the surface state of the unexposed portions of the plate precursor is slightly changed by human finger touching the surface or some other action, the affected unexposed portions (image portions) are dissolved by development to generate marks like scars. As a result, the plate precursor has problems in that the printing durability thereof deteriorates and the ink-acceptability thereof worsens.

[0005] Such problems stem from fundamental differences in plate-making mechanisms between that of infrared-laser-applicable positive planographic printing plate precursors and that of positive planographic printing plate precursor materials from which printing plates are made up by exposure to ultra violet rays. That is, the positive planographic printing plate material used for plate-making by exposure to UV light comprises a binder resin soluble in an aqueous alkali solution, an onium salt and a quinone diazide compound as essential ingredients. The onium salt and quinone diazide compound act, in light-unexposed regions (image regions), as a dissolution inhibitor by interaction with the binder resin. In light-exposed regions (non-image regions), on the other hand, they act as a dissolution accelerator by generating an acid upon decomposition by light. That is, the onium salt and quinone diazide compound play two roles, that is, the role of dissolution inhibitor and the role of acid generator.

[0006] On the other hand, in infrared-laser-applicable positive planographic printing plate precursor materials, the infra red dye functions only as a dissolution inhibitor of unexposed portions (image portions), and does not promote the dissolution of exposed portions (non-image portions). Therefore, in order to make distinctive the difference in solubility between the unexposed portion and the exposed portion in the a positive planographic printing plate precursor for infrared laser, it is inevitable to use a that a material having which already has a high solubility in an alkali developing solution is used as the binder resin. There is therefore the case that the state of the plate material before developed becomes unstable. Furthermore, an ink-receptive recording layer of such a planographic printing plate precursor is formed on a hydrophilic support, and as a result, adhesion of the recording layer at the interface of the support may become unstable, which may affect printing durability of an unexposed area (image area) of a planographic printing plate formed therefrom.

[0007] Various proposals have been offered to address the above. For example, a method has been proposed in which the distribution of an infrared absorbing agent is localized in the layer to improve the discrimination of an image (see, for example, the publication of Japanese Patent Application Laid-Open (JP-A) No. 2001-281856). Although there is something improved in discrimination by this method, the problem concerning scratching resistance on the surface of the recording layer has yet to be still unsolved.

[0008] Also, a planographic printing plate precursor has been proposed which is provided with a recording layer,

comprising a lower recording layer containing a sulfonamide acryl resin, and an upper layer, which contains a water-insoluble and alkali-soluble resin and a light-heat photo-thermo converting agent, and which is improved in solubility in an aqueous alkali solution by exposure to light (see, for example, the publication of JP-A No 11-218914). This type of planographic printing plate precursor produces the effect that, because the lower recording layer which is highly alkali-soluble is exposed when the recording layer is removed on an exposed portion, an undesired residual film and the like are removed smoothly by an alkali developing agent. In addition, the lower recording layer also functions as an insulating layer so that thermal diffusion to the support is efficiently suppressed. A planographic printing plate precursor has been proposed in which a polymer is blended in the lower recording layer to provide chemical resistance (see, for example, a leaflet of International Publication (W/O) No. 01/46318). Furthermore, a planographic printing plate precursor has been proposed which is provided with a hydrophilic support having provided thereon a lower layer containing a polymer having a specific structure and a thermosensitive layer (an upper layer) which contains a phenol resin (for example, US 2004/0003870 A1).

[0009] However, in order to form the multilayer structure, resins used in respective layers should differ in characteristics from each other. This may cause reduction in the interaction between these resins. Also, the excellent developing characteristics of the lower recording layer may cause an undesired dissolution phenomenon at both end portions of the lower recording layer during developing, which adversely affects printing durability, chemical resistance and image reproducibility. Therefore, there is ample room to sufficiently make use of the merits of a multilayer structure.

SUMMARY OF THE INVENTION

[0010] The present invention is made in view of the above circumstances and provides a positive planographic printing plate precursor excellent in image reproducibility as well as printing durability and chemical resistance.

[0011] Namely, the invention provides planographic printing plate precursor comprising:

a support; and

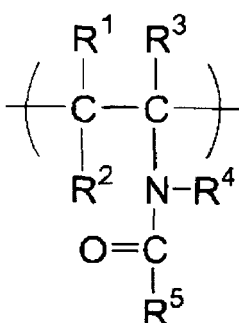
two or more positive recording layers respectively comprising a resin and an infrared absorber, each of the layers having a solubility with respect to an aqueous alkali solution that is increased by exposure to infrared laser light, wherein:

of the two or more positive recording layers, a positive recording layer that is nearest to the support comprises two resins;

the two resins each comprise a polymer comprising a structural unit represented by the following Formula (I); one of the two resins constitutes a dispersion phase that is dispersed in a matrix phase; and the matrix phase serves as a dispersing medium and comprises the other of the two resins.

[0012]

Formula (I)



[0013] In Formula (I), each of R^1 , R^2 and R^3 independently represents a hydrogen atom, a substituted or unsubstituted alkyl group; each of R^4 and R^5 independently represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted arylalkyl group; and R^4 and R^5 may be bonded together to form a ring structure.

[0014] The positive recording layer nearest to a support is hereinafter referred to as a "lower layer" or a "lower recording layer" as necessary.

[0015] Other layers such as a surface protective layer, an undercoat layer, a back coat layer and the like may be

provided to the planographic printing plate precursor of the invention in addition to the plurality of the positive recording layers as long as the effect of the invention is not hindered.

[0016] The dispersion phase formed by a resin in the recording layer can be formed by, for example, (1) using a plural kinds of resins that are incompatible with each other in combination, or (2) dispersing, in a resin constituting the matrix phase, the resin constituting the dispersion phase in granular form such as microcapsule or latex form.

[0017] The planographic printing plate precursor of the invention employs a system utilizing change of solubility of the recording layer to an alkaline water. Therefore, in a preferable embodiment, a resin used in the positive recording layer has a water-insoluble and alkaline water-soluble resin. In the invention, the method (1), which is a method including forming a dispersion phase and a matrix phase (a disperse medium) by using a plural kind of resins that are incompatible with each other in combination, is preferable from the standpoint of ease of production.

[0018] The plural kind of resins may be those which are incompatible, or may be those which can be dissolved uniformly in a coating solvent and form a dispersion phase along with the removal of the solvent when forming the recording layer.

[0019] In one preferable embodiment of the lower recording layer of the planographic printing plate of the invention, a resin which forms the matrix phase (disperse medium) is formed of a polymer compound which is insoluble in water and soluble in an aqueous alkali solution, while the dispersion phase contains a compound which generates an acid or a radical when irradiated with an infrared laser. In another preferable embodiment of the lower recording layer of the planographic printing plate of the invention, a resin which forms the matrix phase is formed of a polymer compound which is insoluble in water and soluble in an aqueous alkali solution, while the dispersion phase contains a compound having an alkali solubility that is changed by irradiation with an infrared laser.

[0020] At least one of the resins contained in the lower recording layer is a specific polymer in the present invention. The specific polymer is preferably used as a resin which forms a matrix phase (disperse medium).

[0021] The rate of dissolution of the resin constituting the dispersion phase with respect to an alkaline aqueous solution is preferably slower than that of the resin included in the matrix phase. A polymer which configures the dispersion phase in the invention can be selected from resins described hereinafter. Among those resins, a novolak resin is particularly preferable as the polymer which configures the dispersion phase.

[0022] The maximum major axis of the dispersion phase is preferably from 0.1 μm to 0.8 μm , and the average major axis of the dispersion phase is preferably from 0.05 μm to 0.6 μm . The size of the dispersion phase can be evaluated by cutting the recording layer with a microtome or the like to give sections of the photosensitive layer, then making the sections electroconductive, taking a photograph thereof with a scanning electron microscope (SEM) and evaluating the size of the circular or elliptical dispersion phase by an image analyzer.

[0023] The resin matrix phase in the lower recording layer of the planographic printing plate precursor of the invention is provided with a dispersion phase, the solubility of which to an aqueous alkali solution is increased by heat or light. In the light-exposed regions (non-image regions), this configuration results in formation of paths by which an aqueous alkali solution permeates into the matrix phase, whereby accelerates the dissolution of the alkali-soluble resin matrix phase in the lower recording layer to the aqueous alkali solution. On the other hand, in the unexposed regions (image regions), the solubility of the dispersion phase to an aqueous alkali solution is lower than that of the resin which configures the matrix phase. Therefore, the permeation of an aqueous alkali solution into the resin matrix phase in the lower recording layer, particularly the permeation from the side (in the lateral direction) of the image regions, can be efficiently suppressed so as to prevent the image regions from being damaged by the aqueous alkali solution. Further, the image regions have excellent adherence to the support.

It is expected that these conditions result in the excellent image reproducibility as well as printing durability and chemical resistance of the planographic printing plate precursor of the invention. Further, since the specific polymer, that is necessarily contained in the lower recording layer, exhibits remarkable solubilization resistance against organic solvents, the lower recording layer is expected as being able to avoid being damaged.

[0024] The properties in relation to the invention are particularly remarkable in a high definition image having a small image area. For this reason, the planographic printing plate precursor of the invention is particularly useful in formation of a high definition image using, for example, a FM screen which increases its use with recent CTP application, and can preferably be used in image formation using commercially available FM screens such as STACCATO (trade name, manufactured by CREO Co., Ltd.), FAIRDOT, RANDOT (both trade names, manufactured by Dainippon Screen Mfg. Co., Ltd.) or Co-Re SCREEN (trade name, manufactured by FUJIFILM Corporation).

BRIEF DESCRIPTION OF DRAWINGS

[0025] Figure 1 is a graph of one example of an alternating current waveform used for electrochemical surface roughening treatment applied for the preparation of a support of a planographic printing plate precursor in the following EXAMPLES.

Figure 2 is a side view of one example of a radial-type cell used for the electrochemical surface roughening treatment with the alternating current waveform used for the preparation of a support of a planographic printing plate precursor in

the following

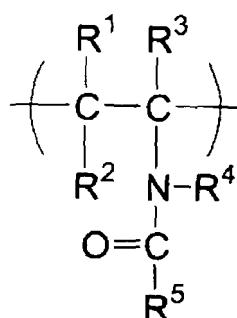
EXAMPLES.

DETAILED DESCRIPTION OF THE INVENTION

[0026] The planographic printing plate precursor of the invention has at least: a support; and two or more positive recording layers respectively containing at least a resin and an infrared absorber, each of the layers having a solubility with respect to an aqueous alkali solution that is increased by exposure to infrared laser light, wherein: of the two or more positive recording layers, a positive recording layer that is nearest to the support contains at least two resins; the two resins each has at least a polymer (hereinafter referred as a "specific polymer") having at least a structural unit represented by the following Formula (I); one of the two resins constitutes a dispersion phase that is dispersed in a matrix phase; and the matrix phase serves as a dispersing medium and contains at least the other of the two resins.

[0027]

Formula (I)



[0028] In Formula (I), each of R¹, R² and R³ independently represents a hydrogen atom, a substituted or unsubstituted alkyl group; each of R⁴ and R⁵ independently represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted arylalkyl group; and R⁴ and R⁵ may be bonded together to form a ring structure.

[0029] Examples of the method for forming the dispersion phase in the invention include the following embodiments.

Embodiment (1): a dispersion phase is formed in a matrix phase, i.e., a disperse medium, using at least two resins (polymer compounds) which are incompatible with each other. A dispersion phase formed thereby is formed of a material which is incompatible with a material which forms the disperse medium.

Embodiment (2): a dispersion phase containing given components is formed using a microcapsule or a latex, and the dispersion phase is then introduced into a polymer binder, i.e., a rein matrix phase.

A dissolution inhibitor and/or an infrared absorber can be added to the dispersion phase if necessary.

[0030] Hereinafter, a dispersion phase of an embodiment (1), which is formed by the method of the embodiment (1), will be described.

In the dispersion phase of an embodiment (1), at least one of the two or more incompatible polymer compounds is a polymer insoluble in water and soluble in an aqueous alkali solution, and this polymer is preferably the polymer compound forming the matrix phase. The polymer insoluble in water and soluble in an aqueous alkali solution is preferably a specific polymer.

[0031] The phrase "incompatible" means that a combination of the two or more polymers does not outwardly appear as a one-phase solid or liquid, this being confirmed by suitably processing of sections of the recording layer and visually observing the sections or taking photographs of the sections with a scanning electron microscope and observing them.

[0032] Examples of the polymer compound used in the combination of the at least two polymers that are incompatible with each other include a urethane polymer compound, an acrylic polymer compound, a styrene polymer compound, a novolak resin, a diazo resin, an amide polymer compound, and a polyether compound.

[0033] Examples of the preferable combination include: a combination of an acrylic polymer compound and a urethane polymer compound; a combination of an acrylic or urethane polymer compound and a diazo resin; and a combination of a novolak resin and an acylic polymer compound or a urethane polymer compound. A combination containing a urethane polymer compound is preferable from the standpoint that it is relatively free from being damaged at the time of development.

[0034] When a lower recording layer is formed from the two or more polymer compounds in the presence of the infrared

absorber, a dispersion phase is formed in the resin matrix phase, and an amount of the infrared absorber in the dispersion phase becomes large. When two or more polymer compounds incompatible are used to form a binder layer, a polymer which shows a stronger interaction due to hydrogen bonding, ionic properties etc., easily forms spheres or flat spheres in the binder. Such localization occurs because when an infrared absorber is present in a dispersion phase, the infrared absorber, which is generally ionic or a coordination complex, tends to be easily incorporated into the polymer compound showing the stronger interaction in the binder. When an acid generator or a radical generator (polymerization initiator) is made to coexist, the initiator usually has a group having high polarity such as an onium salt structure, triazine or sulfonate ester, and, similar to the infrared absorber, is easily incorporated into the dispersion phase.

[0035] Here, when two or more incompatible polymer compounds are used to form the lower recording layer, a structure in which a dispersion phase is formed in a polymer matrix phase as the disperse medium is referred to as an island structure. In the invention, the island structure can be observed and evaluated in the following manner: a section of the recording layer obtained by cutting the planographic printing plate precursor by a microtome or the like is made to have conductivity and then a photograph of an image of the section is taken by a scanning electron microscope (SEM) to analyze the size of a circular or elliptic dispersion phase by using an image analyzer. When the image on the taken photograph taken is blurred, the section of the photosensitive layer can be subjected to, for example, etching with solvent and then a photograph of the section can be taken according to the method described in, for example, "Polymer Alloy and Polymer Blend" (L. A. UTRACKI, translated by Toshio NISHII, Tokyo Kagaku Dojzin), the disclosure of which is incorporated by reference herein, to thereby obtain a highly distinct image.

[0036] In such a sea-island structure, a size of the dispersion phase present in the polymer binder phase (disperse medium) depends on a coating solvent system, drying conditions after application, and the like. A dispersion phase having the longest diameter of 0.8 μm or less, which is preferably 0.6 μm or less, and an average major diameter of 0.6 μm or less, which is preferably 0.5 μm or less, can be formed by controlling those conditions. In this case, it is preferable that the longest diameter and the average major diameter are small. The lower limit of the size of a dispersion phase is not particularly limited. In general, the longest diameter is about 0.1 μm , and the average major diameter is about 0.05 μm . The "major diameter" is obtained by subjecting a dispersion phase to image analysis as described above, and means a diameter when a particle of the dispersion phase is circle, or means a major diameter when a particle of the dispersion phase is ellipse.

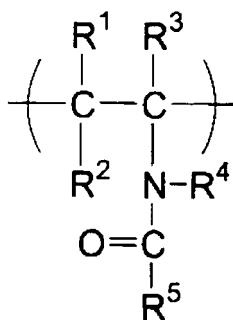
[0037] At least one resin among one or more resins contained in the lower recording layer is required to be the specific polymer in the planographic printing plate precursor of the present invention. The specific polymer is preferably contained as a resin which configures a resin matrix phase in the lower recording layer.

Specific polymer

[0038] The specific polymer used in the invention is a polymer having the following structural unit represented by the following Formula (I).

[0039]

Formula (I)



[0040] In Formula (I), each of R^1 , R^2 and R^3 independently represents a hydrogen atom, a substituted or unsubstituted alkyl group; each of R^4 and R^5 independently represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted arylalkyl group; and R^4 and R^5 may be bonded together to form a ring structure.

[0041] The ring structure formed by R^4 and R^5 is preferably a ring structure having five or more carbon atoms.

[0042] The structural unit represented by Formula (I) is preferably a structural unit derived from vinyl caprolactam.

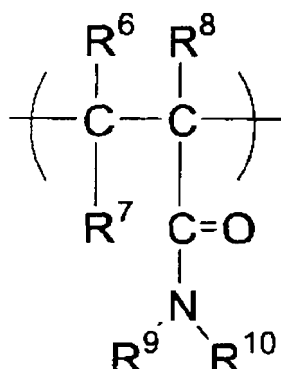
[0043] The content of the structural unit represented by Formula (I) in the specific polymer is preferably 3 mol% to 75

mol%, more preferably 4 mol% to 50 mol% and yet more preferably 5 mol% to 40 mol%.

[0044] The specific polymer preferably also additionally has a structural unit represented by the following Formula (II).

[0045]

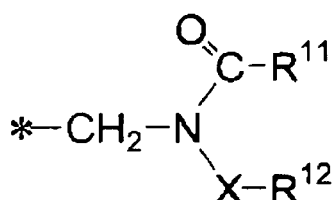
Formula (II)



[0046] In Formula (II), each of R^6 , R^7 and R^8 independently represents a hydrogen atom or a substituted or unsubstituted alkyl group. R^9 represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted arylalkyl group. R^{10} represents a group represented by the following Formula (III) or (IV).

[0047]

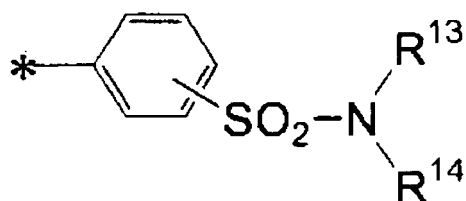
Formula (III)



[0048] In Formula (III), "*" represents the position at which R^{10} is bonded with the nitrogen atom in Formula (II). X represents $-\text{C}(=\text{O})$ or $-\text{SO}_2-$. Each of R^{11} and R^{12} independently represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted arylalkyl group, or a substituted or unsubstituted heteroaryl group, and R^{11} and R^{12} may be bonded together to form a ring structure.

[0049]

Formula (IV)

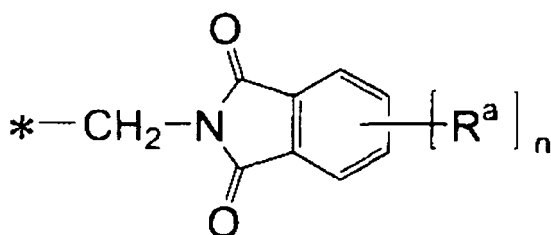


[0050] In Formula (IV), "*" represents the position at which R¹⁰ is bonded with the nitrogen atom in Formula (II). Each of R¹³ and R¹⁴ independently represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted arylalkyl group, or a substituted or unsubstituted heteroaryl group, and R¹³ and R¹⁴ may be bonded together to form a ring structure.

[0051] R¹⁰ in Formula (II) is more preferably a group represented by the following Formula (V).

[0052]

Formula (V)



[0053] In Formula (V), "*" represents the position at which R¹⁰ is bonded with the nitrogen atom in Formula (II). n represents 0, 1, 2, 3 or 4. R^a represents a hydrogen atom, a halogen atom, -CN, -NO₂, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted heterocyclic group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heteroaryl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted heteroaralkyl group, -O-R^b, -S-R^c, -SO₃-R^d, -CO-O-R^e, -O-CO-R^f, -NR^gR^h, -NRⁱ-CO-R^j, -NR^k-SO₂-R^l, -CO-R^m, -CO-NRⁿR^o, -SO₂-NR^pR^q, or -P(=O)(-O-R^r)(-O-R^s). Here, each of R^b to R^s independently represents a hydrogen atom, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl group. When there is more than one R^a, respective groups represented by R^a may be the same as or different from each other.

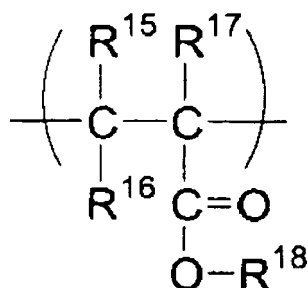
[0054] The structural unit represented by Formula (II) is more preferably a structural unit derived from N-acryloyl aminomethyl phthalimide or N-methacryloyl aminomethyl phthalimide.

[0055] The content of the structural unit represented by Formula (II) in the specific polymer is preferably in a range of 5 mol% to 95 mol%, more preferably in a range of 10 mol% to 85 mol% and yet more preferably in a range of 20 mol% to 75 mol%.

[0056] The specific polymer preferably also additionally has a structural unit represented by the following Formula (VI).

[0057]

Formula (VI)



[0058] In Formula (VI), each of R¹⁵, R¹⁶ and R¹⁷ independently represents a hydrogen atom or a substituted or unsubstituted alkyl group. R¹⁷ represents a hydrogen atom, a metal ion having a positive electric charge, an ammonium ion, a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted arylalkyl group.

[0059] The structural unit represented by Formula (VI) is more preferably a structural unit derived from a (meth)acrylic acid or a salt thereof, or alkyl esters thereof.

[0060] The content of the structural unit represented by Formula (VI) in the specific polymer is preferably in a range of 2 mol% to 70 mol%, more preferably in a range of 5 mol% to 60 mol% and yet more preferably in a range of 10 mol% to 50 mol%.

[0061] One preferable embodiment of the specific polymer is a polymer having a combination of the structural unit represented by Formula (I), the structural unit represented by Formula (II) and the structural unit represented by Formula (VI). This kind of the specific polymer is preferably a polymer that contains the three kinds of structural units as follows: the structural unit represented by Formula (I) in a range of 5 mol% to 35 mol%, the structural unit represented by Formula (II) in a range of 20 mol% to 75 mol% and the structural unit represented by Formula (VI) in a range of 3 mol% to 35 mol%.

[0062] A more preferable embodiment of the specific polymer is a polymer having a combination of structural units respectively derived from N-vinyl caprolactam, N-(meth)acryloyl aminomethyl phthalimide and (meth)acrylic acid. A polymer containing the structural unit derived from N-vinyl caprolactam in a range of 5 mol% to 35 mol% (more preferably 10 mol% to 30 mol%), the structural unit derived from N-(meth)acryloyl aminomethyl phthalimide in a range of 20 mol% to 75 mol% (more preferably 30 mol% to 65 mol%), and the structural unit derived from (meth)acrylic acid in a range of 3 mol% to 35 mol% (more preferably 10 mol% to 30 mol%) is preferable as this kind of specific polymer.

[0063] The content of the specific polymer in the lower recording layer is preferably in a range of 2 mass% to 98 mass% with respect to the total solid content of the lower recording layer, more preferably in a range of 5 mass% to 95 mass% and yet more preferably in a range of 10 mass% to 90 mass%.

[0064] When the specific polymer is used as a resin which constitutes a matrix phase in the lower recording layer, the ratio between the content of the resin constituting the matrix phase and that of the resin constituting the dispersion phase (resin for the matrix phase : resin for the dispersion phase) is preferably from 95:5 to 50:50, and more preferably from 90:10 to 60:40, in terms of mass ratio.

[0065] The positive recording layer contains at least a resin (namely, a polymer compound insoluble in water and soluble in an aqueous alkali solution) and an infrared absorber (namely, a compound which suppresses the alkali solubility of the resin). When the positive recording layer is exposed to infrared laser light, the ability of the infrared absorber to inhibit dissolution of the resin is removed so that the solubility of the exposed region to an alkali developing solution is increased, and an image is formed as a result of the removal of the exposed region with the alkali developing solution.

[0066] In the invention, the water-insoluble and aqueous alkali-soluble polymer compound (hereinafter referred to as an "alkali-soluble polymer" as required) which is used in plural positive recording layers includes homopolymers having an acidic group on a main chain and/or a side chain thereof, copolymers having an acidic group on a main chain and/or a side chain thereof, and mixtures of these polymers. The polymer layer according to the invention therefore has the characteristics that it is dissolved when being brought into contact with an alkali developing solution. The scope of the alkali-soluble polymer contained in the lower recording layer in the planographic printing plate precursor of the invention includes the specific polymer.

[0067] Any known alkali-soluble polymer may be used as the alkali-soluble polymer to be used in the lower recording layer and other recording layers (hereinafter referred to as an upper recording layer as required) in the invention without any particular limitation, while the alkali-soluble polymer is preferably a polymer compound having one functional group selected from (1) a phenolic hydroxyl group, (2) a sulfonamide group and (3) an active imide group in its molecule. The following compounds are given as examples, while these examples are not intended to be limiting of the invention.

[0068] (1) Examples of the polymer compounds having phenolic hydroxyl group include novolak resin such as condensation polymers of phenol and formaldehyde; condensation polymers of m-cresol and formaldehyde, condensation polymers of p-cresol and formaldehyde, condensation polymers of m-/p-mixed cresol and formaldehyde, and condensation polymers of phenol/cresol (m-, p-, or m-/p-mixture) and formaldehyde; and condensation copolymers of pyrogallol and acetone. As the polymer compound having a phenolic hydroxyl group, it is preferable to use polymer compounds having a phenolic hydroxyl group at their side chains besides the above compounds. Examples of the polymer compound having a phenolic hydroxyl group at its side chain include polymer compounds obtained by homopolymerizing a polymerizable monomer comprising a low-molecular compound having one or more phenolic hydroxyl groups and one or more polymerizable unsaturated bonds or copolymerizing this monomer with other polymerizable monomers.

[0069] Examples of the polymerizable monomer having a phenolic hydroxyl group include acrylamides, methacrylamides, acrylates and methacrylates each having a phenolic hydroxyl group or hydroxystyrenes. Specific examples of the polymerizable monomer which may be preferably used include N-(2-hydroxyphenyl)acrylamide, N-(3-hydroxyphenyl)acrylamide, N-(4-hydroxyphenyl)acrylamide, N-(2-hydroxyphenyl)methacrylamide, N-(3-hydroxyphenyl)methacrylamide, N-(4-hydroxyphenyl)methacrylamide, o-hydroxyphenylacrylate, m-hydroxyphenylacrylate, p-hydroxyphenylacrylate, o-hydroxyphenylmethacrylate, m-hydroxyphenylmethacrylate, p-hydroxyphenylmethacrylate, o-hydroxystyrene, m-hydroxystyrene, p-hydroxystyrene, 2-(2-hydroxyphenyl)ethylacrylate, 2-(3-hydroxyphenyl)ethylacrylate, 2-(4-hydroxyphenyl)ethylacrylate, 2-(2-hydroxyphenyl)ethylmethacrylate, 2-(3-hydroxyphenyl)ethylmethacrylate and 2-(4-hydroxyphenyl)ethylmethacrylate. Moreover, condensation polymers of phenols having an alkyl group having 3 to 8 carbon atoms as a substituent and formaldehyde, such as a t-butylphenol formaldehyde resin and octylphenol formaldehyde resin as described in the specification of U.S. Patent No. 4,123,279 may be used together.

[0070] (2) Examples of the alkali-soluble polymer compound having a sulfonamide group include polymer compounds obtained by homopolymerizing polymerizable monomers having a sulfonamide group or by copolymerizing the monomer with other polymerizable monomers. Examples of the polymerizable monomer having a sulfonamide group include polymerizable monomers comprising a low-molecular compound having, in one molecule thereof, one or more sulfonamide groups -NH-SO₂- in which at least one hydrogen atom is added to a nitrogen atom and one or more polymerizable unsaturated bonds. Among these compounds, low-molecular compounds having an acryloyl group, allyl group or vinyloxy group and a substituted or monosubstituted aminosulfonyl group or substituted sulfonylimino group are preferable.

[0071] (3) The alkali-soluble polymer compound having an active imide group is preferably those having an active imide group in its molecule. Examples of the polymer compound include polymer compounds obtained by homopolymerizing a polymerizable monomer comprising a low-molecular compound having one or more active imide groups and one or more polymerizable unsaturated bonds or copolymerizing this monomer with other polymerizable monomers. As such a compound, specifically, N-(p-toluenesulfonyl)methacrylamide, N-(p-toluenesulfonyl)acrylamide and the like are preferably used.

[0072] Moreover, as the alkali-soluble polymer compound of the invention, polymer compounds obtained by polymerizing two or more types among the polymerizable monomers having a phenolic hydroxyl group, polymerizable monomers having a sulfonamide group and polymerizable monomers having an active imide group, or polymer compounds obtained by copolymerizing these two or more polymerizable monomers with other polymerizable monomers are preferably used. When a polymerizable monomer having a sulfonamide group and/or a polymerizable monomer having an active imide group is copolymerized with a polymerizable monomer having an active imide group, the ratio by weight of these components to be compounded is preferably in a range from 50:50 to 5:95 and particularly preferably in a range from 40:60 to 10:90.

[0073] When the alkali-soluble polymer is a copolymer of the polymerizable monomer having a phenolic hydroxyl group, polymerizable monomer having a sulfonamide group or polymerizable monomer having an active imide group and other polymerizable monomers in the invention, it is preferable to contain a monomer imparting alkali-solubility in an amount of 10 mol% or more and more preferably 20 mol% or more in view of improving the solubility to an alkali solution and the development latitude of the precursor.

[0074] Examples of the monomer component to be copolymerized with the polymerizable monomer having a phenolic hydroxyl group, the polymerizable monomer having a sulfonamide group and the polymerizable monomer having an active imide group may include, though not particularly limited to, compounds represented by the following (m1) to (m12).

(m1) Acrylic acid esters and methacrylic acid esters having aliphatic hydroxyl groups such as 2-hydroxyethyl acrylate or 2-hydroxyethyl methacrylate.

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

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

(m4) Acrylamide or methacrylamide such as acrylamide, methacrylamide, N-methylol acrylamide, N-ethylacrylamide, N-hexylmethacrylamide, N-cyclohexylacrylamide, N-hydroxyethylacrylamide, N-phenylacrylamide, N-nitrophenylacrylamide, and N-ethyl-N-phenylacrylamide.

[0075] (m5) Vinyl ethers such as ethyl vinyl ether, 2-chloroethyl vinyl ether, hydroxyethyl vinyl ether, propyl vinyl ether, butyl vinyl ether, octyl vinyl ether, and phenyl vinyl ether.

(m6) Vinyl esters such as vinyl acetate, vinyl chloroacetate, vinyl butyrate, and vinyl benzoate.

(m7) Styrenes such as styrene, α -methylstyrene, methylstyrene, and chloromethylstyrene.

(m8) Vinyl ketones such as methyl vinyl ketone, ethyl vinyl ketone, propyl vinyl ketone, and phenyl vinyl ketone.

(m9) Olefins such as ethylene, propylene, isobutylene, butadiene, and isoprene.

(m10) N-vinylpyrrolidone, acrylonitrile, and methacrylonitrile.

(m11) Unsaturated imides such as maleimide, N-acryloylacrylamide, N-acetylmethacrylamide, N-propionylmethacrylamide, and N-(p-chlorobenzoyl)methacrylamide.

(m12) Unsaturated carboxylic acid such as acrylic acid, methacrylic acid, maleic anhydride, and itaconic acid.

[0076] The alkali-soluble polymer compound preferably has a phenolic hydroxyl group, in terms of the excellent image formability by exposure by infrared laser. Examples the alkali-soluble polymer compound having a phenolic hydroxyl group include condensed copolymers of phenol and formaldehyde comprising an alkyl group having 3 to 8 carbon atoms as a substitute, such as tert-butylphenol formaldehyde resin and octylphenol formaldehyde resin described in US Patent No. 4,123,279.

[0077] As a method of copolymerizing the aqueous alkali-soluble polymer compound, for example, a conventionally known graft copolymerization method, block copolymerization method or random copolymerization method may be used.

As the alkali-soluble polymer used in the upper recording layer, a resin having a phenolic hydroxyl group is desirable in the point that it develops strong hydrogen bonding characteristics in an unexposed portion whereas a part of hydrogen bonds are released with ease in an exposed portion. The alkali-soluble polymer is more preferably a novolac resin. The alkali-soluble resin preferably has a weight average molecular weight of 500 to 20,000 and a number average molecular weight of 200 to 10,000.

[0078] Hereinafter, a preferable method of forming a dispersion phase in the lower recording layer will be described. In the invention, selection of a coating solvent is an important factor in order that the dispersion phase forms a sea island structure in the lower recording layer with a maximum major axis of 0.8 μm or less and average major axis of 0.6 μm or less. By using a suitable coating solvent system, a sea island structure having the target size can be formed.

[0079] A clear mechanism has not been found out as to the reason why the size of the dispersion phase is reduced or varied by the selection of a coating solvent system. A ketone solvent such as cyclohexanone or methyl ethyl ketone, alcohol solvent such as methanol, ethanol, propanol or 1-methoxy-2-propanol, cellosolve solvent such as ethylene glycol monomethyl ether, lactone solvent such as γ -butyrolactone, sulfoxide such as dimethyl sulfoxide or sulfolane, halogen solvent such as ethylene dichloride, acetate solvent such as 2-methoxyethyl acetate or 1-methoxy-2-propyl acetate, ether solvent such as dimethoxyethane, ester solvent such as methyl lactate or ethyl lactate, amide solvent such as N, N-dimethoxyacetamide or N,N-dimethylformamide, pyrrolidone solvent such as N-methylpyrrolidone, urea solvent such as tetramethylurea or aromatic solvent such as toluene is preferably used as the coating solvent. Among these compounds, methyl ethyl ketone, 1-methoxy-2-propanol, ethylene glycol monomethyl ether, γ -butyrolactone and dimethyl sulfoxide are preferable. These solvents may be used either singly or by mixing two or more.

[0080] In addition to the coating solvent, the condition under which a coating layer that has not yet been dried (after the photosensitive coating liquid is applied) is dried is known as an important factor to make the dispersion phase constituting the island structure in the lower recording layer to have a specified size. The descriptions in JP-A No. 9-90610 may be adopted as a reference for the production of such an island structure.

[0081] The polymer compound used to form the dispersion phase in the case of forming the polymer matrix phase and the dispersion phase by using the two or more polymer compounds incompatible with each other are shown below.

[0082] Examples of the polymer compound which can be preferably used for forming the dispersion phase in the invention include copolymers having a structural unit derived from at least one of monomers corresponding to any one of the following (1) to (5), urethane polymer compounds, novolac resins, diazo resins and polyethers. Among these, novolac resin is particularly preferable as the polymer compound used for forming the dispersion phase.

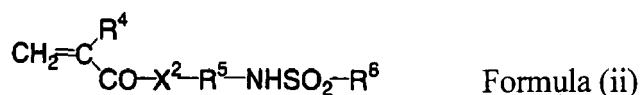
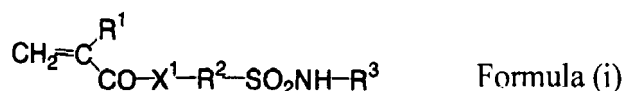
[0083]

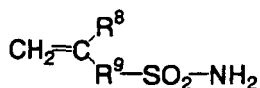
(1) Examples of the above structural unit include acrylamides, methacrylamides, acrylates and methacrylates having an aromatic hydroxyl group. Specific examples these compounds include N-(4-hydroxyphenyl)acrylamide or N-(4-hydroxyphenyl)methacrylamide, o-, p- or m-hydroxyphenylacrylate or methacrylate and 2-hydroxyethylmethacrylate.

(2) Examples of the above structural unit also include unsaturated carboxylic acids such as acrylic acid, methacrylic acid, maleic acid anhydride and itaconic acid.

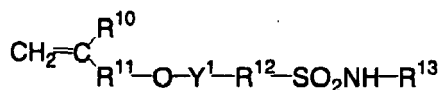
(3) Examples of the above structural unit also include low-molecular compounds having at least one sulfonamide group in which at least one hydrogen atom is bonded to a nitrogen atom and at least one polymerizable unsaturated bond, for example, compounds represented by the following Formulae (i) to (v).

[0084]

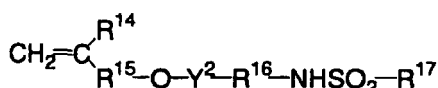




Formula (iii)



Formula (iv)



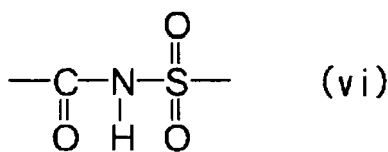
Formula (v)

[0085] In Formulae (i) to (v), X^1 and X^2 each independently represent -O-, or -NR⁷-; R¹ and R⁴ each independently represent a hydrogen atom, or -CH₃; R², R⁵, R⁹, R¹² and R¹⁶ each independently represent an alkylene group, a cycloalkylene group, an arylene group or an aralkylene group which has 1 to 12 carbon atom and may have a substituent; R³, R⁷ and R¹³ each independently represent a hydrogen atom, or an alkyl group, a cycloalkyl group, an aryl group or an aralkyl group which has 1 to 12 carbon atom and may have a substituent; R⁶ and R¹⁷ each independently represent an alkyl group, a cycloalkyl group, an aryl group or an aralkyl group which has 1 to 12 carbon atom and may have a substituent; R⁸, R¹⁰ and R¹⁴ each independently represent a hydrogen atom or -CH₃; R¹¹ and R¹⁵ each independently represent a single bond, or an alkylene group, a cycloalkylene group, an arylene group or an aralkylene group which has 1 to 12 carbon atom and may have a substituent; and Y¹ and Y² each independently represent a single bond or -CO-.

[0086] Specific examples of the compounds represented by any one of Formulae (i) to (v) include m-aminosulfonylphenyl methacrylate, N-(p-aminosulfonylphenyl)methacrylamide and N-(p-aminosulfonylphenyl)acrylamide.

[0087] (4) Examples of the above structural unit also include low-molecular compounds containing at least one active imino group represented by the following Formula (vi) and at least one polymerizable unsaturated bond, for example, N-(p-toluenesulfonyl)methacrylamide and N-(p-toluenesulfonyl)acrylamide.

[0088]



[0089] (5) Examples of the above structural unit also include styrene compounds, vinyl acetate and vinyl alcohol, for example, o-, m- or p-hydroxystyrene, styrene p-sulfonate and o-, m- or p-carboxystyrene.

[0090] The monomers corresponding to any one of the above (1) to (5) may be used either singly or in combinations of two or more. Copolymers obtained by combining any one of these monomers (1) to (5) with monomers other than these monomers are more preferable. In this case, the structural unit derived from any one of the above monomers (1) to (5) is contained in an amount 10 mol% or more, preferably 20 mol% or more and still more preferably 25 mol% or more of such a copolymer. Examples of the monomer used in combination with any one of the monomers (1) to (5) include the following compounds (6) to (16).

[0091] (6) Acrylates and methacrylates having an aliphatic hydroxyl group, for example, 2-hydroxyethylacrylate or 2-hydroxyethylmethacrylate.

[0092] (7) (Substituted) alkylacrylates such as methylacrylate, ethylacrylate, propylacrylate, butylacrylate, amylacrylate, hexylacrylate, octylacrylate, benzylacrylate, 2-chloroethylacrylate, glycidylacrylate and N-dimethylaminoethylacrylate.

[0093] (8) (Substituted) alkylmethacrylates such as methylmethacrylate, ethylmethacrylate, propylmethacrylate, butylmethacrylate, amylmethacrylate, hexylmethacrylate, cyclohexylmethacrylate, benzylmethacrylate, glycidylmethacrylate and N-dimethylaminoethylmethacrylate.

[0094] (9) Acrylamide or methacrylic acid amides such as acrylamide, methacrylamide, N-methylolacrylamide, N-ethylacrylamide, N-hexylmethacrylamide, N-cyclohexylacrylamide, N-hydroxyethylacrylamide, N-phenylacrylamide, N-nitrophenylacrylamide and N-ethyl-N-phenylacrylamide.

[0095] (10) Vinyl ethers such as ethyl vinyl ether, 2-chloroethyl vinyl ether, hydroxyethyl vinyl ether, propyl vinyl ether, butyl vinyl ether, octyl vinyl ether and phenyl vinyl ether.

[0096] (11) Vinyl esters such as vinyl acetate, vinyl chloroacetate, vinyl butyrate and vinyl benzoate.

[0097] (12) Styrenes such as styrene, α -methylstyrene, methylstyrene and chloromethylstyrene.

[0098] (13) Vinyl ketones such as methyl vinyl ketone, ethyl vinyl ketone, propyl vinyl ketone and phenyl vinyl ketone.

[0099] (14) Olefins such as ethylene, propylene, isobutylene, butadiene and isoprene.

[0100] (15) N-vinylpyrrolidone, N-vinylcarbazole, 4-vinylpyridine, acrylonitrile and methacrylonitrile.

[0101] (16) Unsaturated imides such as maleimide, N-acryloylacrylamide, N-acetylmethacrylamide, N-propionylmethacrylamide and N-(p-chlorobenzoyl)methacrylamide.

[0102] Furthermore, monomers copolymerizable with the above monomers may be copolymerized to form the polymer compound. The polymer compound preferably has a weight average molecular weight of 2,000 or more and a number average molecular weight of 1000 or more, and more preferably has a weight average molecular weight of 5,000 to 300,000, a number average molecular weight of 2,000 to 250,000 and a degree of dispersion (the weight average molecular weight/the number average molecular weight) of 1.1 to 10.

[0103] Examples of the water-insoluble and aqueous alkali solution-soluble urethane polymer compound include, though not limited to, urethane type polymer compounds described in each publication of JP-A Nos. 63-124047, 63-287946, 2-866 and 2-156241.

In the invention, the acryl polymer compound may be used together with the urethane polymer compound.

[0104] Examples of the alkali-soluble novolac resin used in the invention may include alkali-soluble novolac resins such as a phenolformaldehyde resin, m-cresolformaldehyde resin, p-cresolformaldehyde resin, m-/p- mixed cresolformaldehyde resin and phenol/cresol (any of m-, p- and m-/p- mixture) mixed formaldehyde resin. As these alkali-soluble novolac resins, those having a weight average molecular weight of 500 to 20,000 and a number average molecular weight of 200 to 10,000 are used. Further, a condensate of a phenol having an alkyl group having 3 to 8 carbon atoms as a substituent and formaldehyde such as a t-butylphenolformaldehyde resin and octylphenolformaldehyde resin as described in U.S. Patent No. 4,123,279 may be used together.

[0105] The alkali-soluble novolac resin preferably has a high content of a novolac resin, the bonding property of an ortho position thereof being high. Examples of the novolac resin include a xylenol cresol formaldehyde resin, a m-cresol formaldehyde resin or a p-cresol formaldehyde resin. Any of those specific novolac resins are preferably contained in an amount of preferably 10% by mass or more, and more preferably 30% by mass or more relative to the total amount of the whole novolac resin used in the alkali-soluble novolac resin.

[0106] The lower recording layer having a resin matrix phase containing the thus formed dispersion phase contains, in the dispersion phase, a compound which changes solubility to an alkaline solution by an infrared absorber and heat in a high content in the case that the lower recording layer is a positive recording layer, thereby efficiently improves solubility of the polymer matrix phase to an alkaline solution.

[0107] Next, a dispersion phase of an embodiment (2), which is formed by the method of the embodiment (2), will be described.

The resin constituting the dispersion phase in microcapsule form in the invention can be easily prepared by methods described in the examples of JP-A No. 1-145190 or the method described in "NEW EDITION, MICROCAPSULE-ITS PREPARATION, NATURE AND APPLICATION" published by Sankyo Shuppan. The resin constituting the dispersion phase in latex form in the invention can be produced by methods shown in JP-A Nos. 10-265710, 10-270233 or 5-2281 or "CHEMISTRY OF POLYMER LATEX" issued from Polymer Publishing Association and "POLYMER LATEX" published by New Polymer Library.

[0108] Examples of materials which can be included in the microcapsule or in the latex include an acid generator, an initiator such as a radical generator, a light-heat converting material and a crosslinking agent.

Examples of the polymer compound which can be used for the polymer matrix phase for forming the lower recording layer having the dispersion phase of an embodiment (2) include the compounds exemplified for the dispersion phase of an embodiment (1).

[0109] Next, compounds which can be contained in the dispersion phase will be respectively explained.

The dispersion phase may contain an acid generator that is decomposed by light or heat to generate an acid, to improve the solubility of the aqueous alkali-soluble polymer compound of an exposed portion in aqueous alkali.

The "acid generator" means those that are decomposed by irradiation with light having a wavelength of 200 nm to 500 nm or by heating at 100°C or more. Examples of the acid generator include a photoinitiator for photo-cationic polymer-

ization, photoinitiator for photo-radical polymerization, photo-achromatizing agent for dyes, photo-discoloring agent, known acid generator used for micro-resist, known compound which is thermally decomposed to generate an acid and a mixture of these compounds. The acid which is generated from the acid generator is preferably a strong acid having a pKa of 2 or less such as sulfonic acid and hydrochloric acid.

Preferable examples of the initiator include the triazine compounds described in JP-A No. 11-95415 and the latent Bronsted acid described in JP-A No. 7-20629. Here, the latent Bronsted acid means a precursor that is to be decomposed to generate a Bronsted acid. It is assumed that the Bronsted acid catalyzes a matrix generating reaction between a resol resin and a novolac resin. Typical examples of the Bronsted acid fitted to this purpose include trifluoromethanesulfonic acid and hexafluorophosphonic acid.

[0110] An ionic latent Bronsted acid may be preferably used in the invention. Examples of the ionic latent Bronsted acid include onium salts, particularly, iodonium, sulfonium, phosphonium, selenonium, diazonium and arsonium salts. Particularly useful and specific examples of the onium salt include diphenyliodonium hexafluorophosphate, triphenylsulfonium hexafluoroantimonate, phenylmethyl-ortho-cyanobenzylsulfoniumtrifluoromethane sulfonate and 2-methoxy-4-aminophenyldiazonium hexafluorophosphate.

[0111] Nonionic latent Bronsted acids are also appropriately used in the invention. Examples of these nonionic latent Bronsted acids include compounds represented by the following formula:

RCH_2X , $RCHX_2$, RCX_3 , $R(CH_2X)_2$ and $R(CH_2X)_3$ (wherein X represents Cl, Br, F or CF_3SO_3 and R represents an aromatic group, an aliphatic group or a combination of an aromatic group and an aliphatic group).

Useful ionic latent Bronsted acid is those represented by the following formula.

[0112]



[0113] In the formula, R^3 and R^4 respectively represent a lone electron pair and R^1 and R^2 respectively represent an aryl or substituted aryl group when X is iodine. When X is S or Se, R^4 represents a lone electron pair and R^1 , R^2 and R^3 respectively represent an aryl group, a substituted aryl group, an aliphatic group or substituted aliphatic group. When X is P or As, R^4 represents an aryl group, a substituted aryl group, an aliphatic group or a substituted aliphatic group. W represents BF_4 , CF_3SO_3 , SbF_6 , CCl_3CO_2 , ClO_4 , AsF_6 , PF_6 or may be any corresponding acid having a pH less than 3. All the onium salts described in U.S. patent No. 4,708,925 may be used as the latent Bronsted acid used in the invention. Examples of these onium salts include iodonium, sulfonium, phosphonium, bromonium, chloronium, oxysulfoxonium, oxysulfonium, sulfoxonium, selenonium, telluronium and arsonium.

[0114] It is particularly preferable to use a diazonium salt as the latent Bronsted acid. These diazonium salts provide a sensitivity equivalent to that of other latent Bronsted acids in the infrared region and a higher sensitivity than other latent Bronsted acid in the ultraviolet region.

[0115] The acid generator can be added in a proportion of 0.01 to 50% by weight, preferably 0.1 to 25% by weight and more preferably 0.5 to 20% by weight with respect to the total solid content of the lower recording layer from the viewpoint of image forming characteristics and from the viewpoint of preventing a non-image portion from being contaminated.

[0116] The positive recording layer in the invention contains an infrared absorbing agent that is a structural component which develops a light-to-heat converting function. This infrared absorbing agent has the ability to convert absorbed infrared rays into heat. Laser scanning causes the infrared absorbing agent to lose the interaction, a developing inhibitor to decompose and generates an acid, which significantly improves the solubility of the infrared absorbing agent. Also, there is also the case where the infrared absorbing agent itself interacts with the alkali-soluble resin to suppress alkali-solubility.

It is considered that the inclusion of such an infrared absorbing agent within the dispersion phase of the lower recording layer results in the localization of the infrared absorbing agent in the dispersion phase, and resultantly promotes interaction releasability, and improves the ability to decompose an acid generator when the acid generator is contained.

The infrared absorbing agent used in the invention is dyes or pigments which efficiently absorb infrared rays having a wavelength from 760 nm to 1,200 nm and is preferably dyes or pigments having an absorption maximum in a wavelength range from 760 nm to 1,200 nm.

[0117] The infrared absorbing agent which can be used preferably for the planographic printing plate precursor of the invention will be hereinafter explained in detail.

The dyes may be commercially available ones and known ones described in publications such as "Dye Handbook" (edited by the Society of Synthesis Organic Chemistry, Japan, and published in 1970). Specific examples thereof include azo dyes, metal complex azo dyes, pyrazolone azo dyes, naphthoquinone dyes, anthraquinone dyes, phthalocyanine dyes, carbonium dyes, quinoneimine dyes, methine dyes, cyanine dyes, squarylium dyes, pyrylium dyes, metal thiolate complexes, and the like.

[0118] Preferable examples of the dye include cyanine dyes described in JP-A Nos. 58-125246, 59-84356, 59-202829,

and 60-78787; methine dyes described in JP-ANos. 58-173696, 58-181690, and 58-194595; naphthoquinone dyes described in JP-A Nos. 58-112793, 58-224793, 59-48187, 59-73996, 60-52940, and 60-63744; squarylium dyes described in JP-A No. 58-112792; and cyanine dyes described in GB Patent No. 434,875.

[0119] Other preferable examples of the dye include near infrared absorbing sensitizers described in U.S. Patent No. 5,156,938; substituted arylbenzo(thio)pyrylium salts described in U.S. Patent No. 3,881,924; trimethinethiapyrylium salts described in JP-A No. 57-142645 (U.S. Patent No. 4,327,169); pyrylium type compounds described in JP-ANos. 58-181051, 58-220143, 59-41363, 59-84248, 59-84249, 59-146063, and 59-146061; cyanine dyes described in JP-A No. 59-216146; pentamethinethiopyrylium salts described in U.S. Patent No. 4,283,475; and pyrylium compounds described in Japanese Patent Application Publication (JP-B) Nos. 5-13514 and 5-19702.

[0120] Preferable examples of the dye further include near infrared absorbing dyes represented by formulae (I) or (II) described in U.S. Patent No. 4,756,993.

[0121] Among these dyes, particularly preferable are cyanine dyes, squarylium dyes, pyrylium salts, and nickel thiolate complexes.

[0122] The pigment which can be used as the infrared absorbent in the invention may be a commercially available pigment or a pigment described in publications such as Color Index (C.I.) Handbook, "Latest Pigment Handbook" (edited by Japan Pigment Technique Association, and published in 1977), "Latest Pigment Applied Technique" (by CMC Publishing Co., Ltd. in 1986), and "Printing Ink Technique" (by CMC Publishing Co., Ltd. in 1984).

[0123] Examples of the pigment include black pigments, yellow pigments, orange pigments, brown pigments, red pigments, purple pigments, blue pigments, green pigments, fluorescent pigments, metal powder pigments, and polymer-bonded dyes. Specifically, the following can be used: insoluble azo pigments, azo lake pigments, condensed azo pigments, chelate azo pigments, phthalocyanine pigments, anthraquinone pigments, perylene and perynone pigments, thioindigo pigments, quinacridone pigments, dioxazine pigments, isoindolinone pigments, quinophthalone pigments, dyeing lake pigments, azine pigments, nitroso pigments, nitro pigments, natural pigments, fluorescent pigments, inorganic pigments, and carbon black.

[0124] These pigments may be used with or without surface treatment. Examples of a method of the surface treatment include a method of coating the surface of the pigments with resin or wax; a method of adhering a surfactant onto the surface; and a method of bonding a reactive material (such as a silane coupling agent, an epoxy compound, or a polyisocyanate) to the pigment surface. The surface treatment methods are described in "Nature and Application of Metal Soap" (Saiwai Shobo), "Printing Ink Technique" (by CMC Publishing Co., Ltd. in 1984). And "Latest Pigment Applied Technique" (by CMC Publishing Co., Ltd. in 1986).

[0125] The particle size of the pigment is preferably from 0.01 μm to 10 μm , more preferably from 0.05 μm to 1 μm , and even more preferably from 0.1 μm to 1 μm .

[0126] Any known methods for dispersing technique used to produce ink or toner can be used for dispersing the pigment in the invention. Examples of a machine which can be used for the dispersing include an ultrasonic disperser, a sand mill, an attriter, a pearl mill, a super mill, a ball mill, an impeller, a disperser, a KD mill, a colloid mill, a dynatron, a three-roll mill, and a pressing kneader. Details are described in "Latest Pigment Applied Technique" (by CMC Publishing Co., Ltd. in 1986).

[0127] The planographic printing plate precursor of the invention has a positive recording layer. The positive recording layer utilizes a positive action, in which solubility of an unexposed portion in an alkali developer is suppressed while the suppression of the solubility is cancelled in an exposed portion. It is preferable to use an infrared absorbing agent which causes the cancellation by interacting with a binder polymer having a specific functional group. In this regard, it is particularly preferable that the infrared absorbing agent has an onium salt structure. Specifically, among the aforementioned absorbers, cyanine dyes and pyrylium salts are particularly preferable. The details of these cyanine dyes and pyrylium salts are as described above.

[0128] Moreover, an anionic infrared absorbing agent as described in JP-A No. 11-338131 is also preferably used. This anionic infrared absorbing agent represents those having no cationic structure but an anionic structure on the mother nucleus of a dye which substantially absorbs infrared rays.

Examples of the anionic infrared absorbing agent include (a-1) an anionic metal complex and (a-2) an anionic phthalocyanine.

Here, the anionic metal complex (a-1) denotes a compound in which the core metal and the ligands in the complex part that substantially absorbs light are an anion as a whole.

The anionic phthalocyanine (a-2) denotes a compound in which an anionic group such as a sulfonic acid, carboxylic acid or phosphonic acid group is bonded as a substituent with a phthalocyanine skeleton to form an anion as a whole.

Examples of the anionic phthalocyanine further include anionic infrared absorbing agents represented by the formula $[\text{Ga-M-Gb}]_m\text{X}^{m+}$ (Ga represents an anionic substituent, Gb⁻ represents a neutral substituent, and X^{m+} represents a cation having a valency of 1 to m (where m denotes an integer from 1 to 6) including a proton) as described in JP-A No. 11-338131.

[0129] The infrared absorbing agent used in the positive recording layer is preferably a dye. Preferable examples of

the dye include that having an onium salt structure as described in JP-A No. 11-291652, paragraphs [0018] to [0034].

[0130] Besides the infrared absorbing agent such as the cyanine dye, pyrylium salt dye or anionic dye, which exhibit dissolution inhibitive ability, other dyes or pigments may be used together in the recording layer of the planographic printing plate precursor of the invention in view of further improving sensitivity and developing latitude.

[0131] The infrared absorbing agent is preferably added in an amount of 0.01 % to 50% by weight, more preferably 0.1% to 20% by weight and more preferably 0.5% to 15% by weight based on the total solid content in each of the lower recording layer and other layers from the viewpoint of image formation characteristics and from the viewpoint of suppressing generation of contamination to a non-image portion.

[0132] The infrared absorbing agent may be contained in either or both of the matrix phase and the dispersion phase. When desired components such as the initiator or the infrared absorbing agent are contained in the latex which forms the dispersion phase, the infrared absorbing agent may be added together with the raw materials when the latex particles are formed or may be introduced after the latex is formed.

[0133] Examples of the method of introducing the infrared absorbing agent into the latex after the latex is formed include a method in which a water system, in which desired components such as the initiator, a coloring material or a crosslinking agent to be introduced in the latex are dissolved in an organic solvent, is added to the disperse medium.

[0134] It is necessary that the recording layer of the planographic printing plate precursor of the invention is resistant to abrasion in relation to an infrared laser irradiation system. While any polymer material may be used as a binder which forms the recording layer as long as its solubility to an aqueous alkali, namely, an alkali developing solution, is changed by imparting thermal energy, it is preferable to use a polymer insoluble in water and soluble in aqueous alkali solution from the viewpoint of availability and resistance to abrasion.

[0135] The ceiling temperature of the polymer is given as an example of an index of the abrasion resistance. This ceiling temperature is a temperature at which the rate of a polymerization reaction is equal to the rate of a depolymerization reaction. It is preferable to select polymers having a high ceiling temperature to obtain high abrasion resistance. As a simple method, a proper polymer may be selected using the decomposition temperature thereof as an index.

In the invention, the polymer constituting the recording layer is a polymer having a decomposition temperature of preferably 150°C or more and more preferably 200°C or more. When the decomposition temperature is less than 150°C, this may not be preferable because the possibility of abrasion can be increased. Each component other than the polymer compound contained in the recording layer preferably has a decomposition temperature of 150°C or more, while a small amount of a component having a decomposition temperature less than 150°C may also be contained as long as it gives substantially no problem.

[0136] Not only the components described above but also a wide variety of known additives can be used in combination in the positive recording layer of the planographic printing plate precursor of the invention depending on the purpose of applications. Among plural recording layers, the lower recording layer should have a configuration to achieve the dispersion phase. Additives which can be used in the other recording layers may basically be used in the lower recording layer as long as the requirement of the lower recording layer is satisfied.

[0137] Each recording layer of the invention is preferably compounded of a fluorine-containing polymer for the purpose of improving the resistance to development in an image region. Examples of the fluorine-containing polymer used in an image recording layer include copolymers formed from fluorine-containing monomers as described in each of JP-A Nos. 11-288093 and 2000-187318.

[0138] Preferable and specific examples of the fluorine-containing polymer include fluorine-containing acryl polymers P-1 to P-13 as described in JP-A No. 11-288093 and fluorine-containing polymers obtained by copolymerizing fluorine-containing acryl monomers A-1 to A-33 with arbitrary acryl monomers.

[0139] The fluorine-containing polymer exemplified above preferably has a weight average molecular weight of 2,000 or more and a number average molecular weight of 1,000 or more.

It is more preferable that the weight average molecular weight is 5,000 to 300,000 and the number average molecular weight is 2,000 to 250,000.

[0140] Commercially available fluorine surfactants having the preferable molecular weight may be used as the fluorine-containing polymer. Specific examples of such surfactants include MEGAFAC F-171, F-173, F-176, F-183, F-184, F-780 and F-781 (all are trade names, manufactured by DIC Corporation).

[0141] These fluorine-containing polymers may be used either singly or combinations of two or more.

It is necessary that the amount of the fluorine-containing polymer is 1.4 mass% or more based on the solid content of the image recording layer to meet the requirements in the invention. The amount is preferably 1.4 to 5.0 mass%. When the amount is below 1.4 mass%, the purpose of the addition of the fluorine-containing polymer, namely, the effect of improving the developing latitude of the image recording layer may become insufficient. Even if the fluorine-containing polymer is added in an amount exceeding 5.0 mass%, the effect of bettering the developing latitude may not be improved; on the contrary, the solubility of the surface of the image recording layer may be made more sparing by the influence of the fluorine-containing polymer and there is a possibility of decreasing sensitivity.

[0142] A dissolution inhibitor, which is a thermally decomposable material and substantially reduces the solubility of

the aqueous alkali-soluble polymer compound in an decomposed state, may be additionally used in the lower recording layer or other layers of the precursor of the invention according to the need. Examples of the dissolution inhibitor include an onium salt, an o-quinonediazide compound, an aromatic sulfone compound and an aromatic sulfonate compound. The addition of the dissolution inhibitor makes it possible not only to improve the dissolution resistance of the image portion in a developing solution but also to use, as the infrared absorbing agent, a compound which does not interact with the alkali-soluble resin. Examples of the onium salt include diazonium salts, ammonium salts, phosphonium salts, iodonium salts, sulfonium salts, selenonium salts and arsonium salts.

[0143] Preferable examples of the onium salt used in the invention include diazonium salts described in S. I. Schlesinger, *Photogr. Sci. Eng.*, 18, 387 (1974), T. S. Bal et al., *Polymer*, 21, 423 (1980), and JP-A No. 5-158230; ammonium salts described in U.S. Patent Nos. 4,069,055 and 4,069,056, and JP-A No. 3-140140; phosphonium salts described in D. C. Necker et al., *Macromolecules*, 17, 2468 (1984), C. S. Wen et al., *Tech. Proc. Conf. Rad. Curing ASIA*, p478 Tokyo, Oct (1988), and U.S. Patent Nos. 4,069,055 and 4,069,056; iodonium salts described in J. V. Crivello et al., *Macromolecules*, 10 (6), 1307 (1977), *Chem. & Eng. News*, Nov. 28, p31 (1988), EPNo. 104,143, U.S. Patent Nos. 5,041,358 and 4,491,628, and JP-A Nos. 2-150848 and 2-296514;

[0144] sulfonium salts described in J. V. Crivello et al., *Polymer J.* 17, 73 (1985), J. V. Crivello et al., *J. Org. Chem.*, 43, 3055 (1978), W. R. Watt et al., *J. Polymer Sci., Polymer Chem. Ed.*, 22, 1789 (1984), J. V. Crivello et al., *Polymer Bull.*, 14, 279 (1985), J. V. Crivello et al., *Macromolecules*, 14 (5), 1141 (1981), J. V. Crivello et al., *J. Polymer Sci., Polymer Chem. Ed.*, 17, 2877 (1979), EP Nos. 370,693, 233,567, 297,443 and 297,442, U.S. Patent Nos. 4,933,377, 3,902,114, 5,041,358, 4,491,628, 4,760,013, 4,734,444 and 2,833,827, and DE Patent Nos. 2,904,626, 3,604,580 and 3,604,581; selenonium salts described in J. V. Crivello et al., *Macromolecules*, 10 (6), 1307 (1977), J. V. Crivello et al., *J. Polymer Sci., Polymer Chem. Ed.*, 17, 1047 (1979); and arsonium salts described in C. S. Wen et al., and *The Proc. Conf. Rad. Curing ASIA*, p478, Tokyo, Oct (1988).

[0145] A diazonium salt is particularly preferably used as the dissolution inhibitor. Particularly preferable examples of the diazonium salt include those described in JP-A No. 5-158230.

Examples of the counter ion of the onium salt include tetrafluoroboric acid, hexafluorophosphoric acid, triisopropyl-naphthalenesulfonic acid, 5-nitro-o-toluenesulfonic acid, 5-sulfosalicylic acid, 2,5-dimethylbenzenesulfonic acid, 2,4,6-trimethylbenzenesulfonic acid, 2-nitrobenzenesulfonic acid, 3-chlorobenzenesulfonic acid, 3-bromobenzenesulfonic acid, 2-fluorocaprylnaphthalenesulfonic acid, dodecylbenzenesulfonic acid, 1-naphthol-5-sulfonic acid, 2-methoxy-4-hydroxy-5-benzoyl-benzenesulfonic acid, and p-toluenesulfonic acid. Among these examples, hexafluorophosphoric acid, and alkylaromatic sulfonic acids such as triisopropyl-naphthalenesulfonic acid and 2,5-dimethylbenzenesulfonic acid are particularly preferable.

[0146] Preferable examples of the quinonediazide include an o-quinonediazide compound. The o-quinonediazide compound used in the invention is a compound having at least one o-quinonediazide group and having an alkali-solubility increased by being thermally decomposed. The compound may be any one of compounds having various structures. In other words, the o-quinonediazide compound assists the solubilization property of the photosensitive material from the effects of losing the function of suppressing the dissolution of the binder by being thermally decomposed as well as the effect that the o-quinonediazide itself is changed into an alkali-soluble material.

Preferable examples of the o-quinonediazide compound used in the invention include compounds described in J. Coser, "Light-Sensitive Systems" (John Wiley & Sons. Inc.), pp. 339-352. Particularly preferable are sulfonic acid esters or sulfonamides of o-quinonediazide made to react with various aromatic polyhydroxy compounds or with aromatic amino compounds. Preferable examples of the o-quinonediazide compound further include an ester made from benzoquinone-(1,2)-diazidesulfonic acid chloride or naphthoquinone-(1,2)-diazide-5-sulfonic acid chloride and pyrogallol-acetone resin, as described in JP-B No. 43-28403; and an ester made from benzoquinone-(1,2)-diazidesulfonic acid chloride or naphthoquinone-(1,2)-diazide-5-sulfonic acid chloride and phenol-formaldehyde resin.

[0147] Preferable examples of the o-quinonediazide compound further include an ester made from naphthoquinone-(1,2)-diazide-4-sulfonic acid chloride and phenol-formaldehyde resin or cresol-formaldehyde resin; and an ester made from naphthoquinone-(1,2)-diazide-4-sulfonic acid chloride and pyrogallol-acetone resin. Other useful o-quinonediazide compounds are reported in unexamined or examined patent documents, examples of which include JP-A Nos. 47-5303, 48-63802, 48-63803, 48-96575, 49-38701 and 48-13354, JP-B No. 41-11222, 45-9610 and 49-17481, U.S. Patent Nos. 2,797,213, 3,454,400, 3,544,323, 3,573,917, 3,674,495 and 3,785,825, GB Patent Nos. 1,227,602, 1,251,345, 1,267,005, 1,329,888 and 1,330,932, and DE Patent No. 854,890.

[0148] The amount of the o-quinonediazide compound is preferably in a range from 1 mass% to 50 mass%, more preferably in a range from 5 mass% to 30 mass%, and particularly preferably in a range from 10 mass% to 30 mass% based on the total solid content of each recording layer. These compounds may be used singly or as a mixture of plural kinds thereof.

The amount of the additives except for the o-quinonediazide compound is preferably 1 mass% to 50 mass%, more preferably 5 mass% to 30 mass%, and particularly preferably 10 mass% to 30 mass%. The additives and binder used in the invention are preferably compounded in the same layer.

[0149] A polymer having, as a polymerization component, a (meth)acrylate monomer having two or three perfluoroalkyl group having 3 to 20 carbon atoms in its molecule as described in the specification of JP-A No. 2000-87318 may be used together for the purpose of intensifying the discrimination of an image to be formed and increasing resistance to surface damages of the precursor of the invention.

[0150] In order to enhance sensitivity, the recording layer may further contain a cyclic acid anhydride, a phenolic compound, an organic acid or the like.

Examples of the cyclic acid anhydride include phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, 3,6-endooxy- Δ 4-tetrahydrophthalic anhydride, tetrachlorophthalic anhydride, maleic anhydride, chloromaleic anhydride, α -phenylmaleic anhydride, succinic anhydride, and pyromellitic anhydride which are described in U.S. Patent No. 4,115,128.

Examples of phenolic compound include bisphenol A, p-nitrophenol, p-ethoxyphenol, 2,4,4'-trihydroxybenzophenone, 2,3,4-trihydroxybenzophenone, 4-hydroxybenzophenone, 4,4',4"-trihydroxytriphenylmethane, 4,4',3",4"-tetrahydroxy-3,5,3', 5' -tetramethyltriphenylmethane.

Examples of the organic acid include sulfonic acids, sulfonic acids, alkylsulfuric acids, phosphonic acids, phosphates, and carboxylic acids, which are described in JP-A No. 60-88942 or 2-96755. Specific examples thereof include p-toluenesulfonic acid, dodecylbenzenesulfonic acid, p-toluenesulfonic acid, ethylsulfuric acid, phenylphosphonic acid, phenylphosphinic 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.

When the cyclic acid anhydride, the phenol or the organic acid is added to the recording layer of a planographic printing plate precursor, the content thereof is preferably from 0.05 to 20%, more preferably from 0.1 to 15%, and even more preferably from 0.1 to 10% by mass in terms to the total solid content of the recording layer.

[0151] A dye having an absorption in the visible light region may be added to each recording layer according to the invention as a colorant for an image to be formed. Examples of the dye 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 and Oil Black T-505 (these products are manufactured by Orient Chemical Industries, Ltd.), Victoria Pure Blue, Crystal Violet (CI42555), Methyl Violet (CI42535), Ethyl Violet, Rhodamine B (CI145170B), Malachite Green (CI42000), Methylene Blue (CI52015), AIZEN SPIROL BLUE C-RH (manufactured by Hodogaya Chemical Co., Ltd.), and dyes as described in JP-A No. 62-293247.

[0152] The addition of these dyes is preferable because discrimination between an image portion and a non-image portion can be intensified after an image is formed. The amount of these dyes to be added is preferably in a range from 0.01 to 10 mass % based on the total solid content of the recording layer.

[0153] Nonionic surfactants as described in JP-A Nos. 62-251740 and 3-208514, amphoteric surfactants as described in JP-A Nos. 59-121044 and 4-13149, siloxane compounds as described in EP No. 950517, and/or copolymers made from a fluorine-containing monomer as described in JP-A No. 11-288093 can be added to the image recording layer of the planographic printing plate precursor of the invention in order to make processes more stable upon development conditions in processes.

[0154] Specific examples of nonionic surfactants include sorbitan tristearate, sorbitan monopalmitate, sorbitan trioleate, monoglyceride stearate, and polyoxyethylene nonyl phenyl ether. Specific examples of amphoteric surfactants include alkyl di(aminoethyl)glycine, alkylpolyaminoethylglycine hydrochloride, 2-alkyl-N-carboxyethyl-N-hydroxyethylimidazolium betaine and N-tetradecyl-N,N'-betaine type surfactants (trade name: "AMOGEN K", manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.). The siloxane compounds are preferably block copolymers made from dimethylsiloxane and polyalkylene oxide. Specific examples thereof include polyalkylene oxide modified silicones such as DBE-224, DBE-621, DBE-712, DBE-732, and DBE-534 (all trade names: manufactured by Chisso Corporation) or TEGO® GLIDE 100 (trade name, manufactured by Tego Chemie, Essen, Germany).

The content of the nonionic surfactant and/or the amphoteric surfactant is preferably from 0.05% to 15% by mass, and more preferably from 0.1% to 5% by mass with respect to the total solid content of the photosensitive composition.

[0155] A printing-out agent, which is a material for obtaining a visible image immediately after the photosensitive composition of the invention has been heated by exposure to light, or a dye or pigment as an image coloring agent, may be added to the photosensitive composition of the invention.

A typical example of the printing-out agent is a combination of a photo acid-generating agent (a compound which is heated by exposure to light, thereby generating an acid), and an organic dye which can form salts.

[0156] Specific examples the combination include combinations of an o-naphthoquinonediazide-4-sulfonic acid halogenide with a salt-formable organic dye, described in JP-A Nos. 50-36209 and 53-8128; and combinations of a trihalomethyl compound with a salt-formable organic dye, described in each of JP-A Nos. 53-36223, 54-74728, 60-3626, 61-143748, 61-151644 and 63-58440. The trihalomethyl compound is classified into an oxazol compound or a triazine compound. Both of the compounds provide excellent stability over the passage of time and produce a clear printed-out image. Examples of the photo-acid releasing agent further include various o-naphthoquinonediazide compounds as described in JP-A No. 55-62444; 2-trihalomethyl-5-aryl-1,3,4-oxadiazole compound as described in JP-A No. 55-77742;

and diazonium salts.

[0157] Whenever necessary, a plasticizer may be added to a coating liquid for forming the recording layer of the precursor of the invention to give flexibility to a coating film made from the coating liquid. Examples of the plasticizer include oligomers and polymers of butyl phthalyl, polyethylene glycol, tributyl citrate, diethyl phthalate, dibutyl phthalate, dihexyl phthalate, dioctyl phthalate, tricresyl phosphate, tributyl phosphate, trioctyl phosphate, tetrahydrofurfuryl oleate, and acrylic acid and/or methacrylic acid.

[0158] The planographic printing plate precursor of the invention may be usually produced by sequentially applying, to an appropriate support, coating liquids for forming respective recording layers which contain the components.

[0159] Examples of a solvent appropriate for applying the recording layer include, though not limited to, ethylene dichloride, cyclohexanone, methyl ethyl ketone, methanol, ethanol, propanol, ethylene glycol monomethyl ether, 1-methoxy-2-propanol, 2-methoxyethyl acetate, 1-methoxy-2-propyl acetate, dimethoxyethane, methyl lactate, ethyl lactate, N,N-dimethylacetamide, N,N-dimethylformamide, tetramethylurea, N-methylpyrrolidone, dimethylsulfoxide, sulfolane, γ -butyrolactone and toluene. These solvents may be used either singly or as a mixture of two or more of them. The concentration of the above components (total solid content including additives) in the solvent is preferably 1 mass% to 50 mass%.

[0160] The lower recording layer and upper recording layers (other recording layers) are preferably formed so as to form two layers separate from each other in principle.

[0161] Examples of the method of forming the separate two layers include, though not limited to: a method utilizing a difference between the solubility of the components contained in the lower recording layer to a solvent and that of the components contained in the upper layer; and a method in which a solvent is vaporized and removed quickly by drying after the upper layer is applied.

[0162] Examples of the method utilizing the difference between the solubility of the components contained in the lower recording layer to a solvent and that of the components contained in the upper layer include a method which uses a solvent which does not dissolve the alkali-soluble resin contained in the lower recording layer when an upper layer coating liquid is applied. This makes it possible to separate each layer clearly to form coating films even if two-layer coating is carried out. For example, components insoluble in solvents such as methyl ethyl ketone and 1-methoxy-2-propanol, which dissolve the alkali-soluble resin which is the upper layer component, are selected as the lower recording layer components; the lower recording layer is applied by using a solvent which contains the lower recording layer components dissolved therein and dried; the upper layer components, which have the alkali-soluble resins as a primary component, are dissolved in methyl ethyl ketone, 1-methoxy-2-propanol or the like; and the upper layer coating liquid is applied and dried, whereby the formation of two layers can be attained.

[0163] When a method is adopted in which a solvent which does not dissolve the alkali-soluble resin contained in the lower recording layer is used when applying the upper layer coating liquid, a solvent which dissolves the alkali-soluble resin contained in the lower recording layer may be mixed with a solvent which does not dissolve this alkali-soluble resin.

Mixing of components which causes between the upper layer and the lower recording layer can be arbitrarily controlled by changing the mixing ratio of both solvents. If the ratio of the solvent that dissolves the alkali-soluble resin contained in the lower recording layer is increased, a part of the lower recording layer is dissolved when applying the upper layer and the dissolved component becomes to be contained in the upper layer as a particle-shape component after the upper layer is dried. The particle-shape component forms projections provided on the surface of the upper layer, which increases damage resistance. The dissolution of the lower recording layer components, on the other hand, tends to deteriorate the quality of the lower recording layer and hence tends to deteriorate resistance of the lower recording layer against chemicals. As described above, controlling of the mixing ratio with taking the characteristics of each solvent into account enables exhibition of various characteristics as well as making layers being partially compatible therebetween, which is explained below.

[0164] When a mixed solvent as mentioned above is used as a solvent for the coating liquid of the upper layer, the amount of a solvent which can dissolve the alkali-soluble resin in the lower recording layer is preferably 80 mass% or less relative to the amount of the solvent used to the upper layer coating liquid from the viewpoint of resistance to chemicals, and taking resistance to damage into account, it is more preferably in a range from 10 mass% to 60 mass%.

[0165] Examples of a method of drying a solvent very quickly after the second layer (upper recording layer) is applied include a method including spraying high pressure air from a slit nozzle located at almost a right angle with respect to the running direction of a web, a method including supplying, to a web, thermal energy as conductive heat from the underside of the web through a roll (heating roll) to which a heating medium such as steam is supplied, and a combination of these methods.

Various methods may be used as a method of applying each of the layers such as the image recording layer. Examples of the coating method may include bar coater coating, rotation coating, spray coating, curtain coating, dip coating, air knife coating, blade coating and roll coating.

The coating method used to form the upper recording layer is preferably carried out in a non-contact system to prevent damages to the lower recording layer when applying the upper recording layer. While bar coater coating, though it is a

contact system, may be used as the method generally used in a solvent system coating, it is desirable to carry out the coating in forward driving to prevent damages to the lower recording layer.

[0166] The coating amount of the lower recording layer after the layer is dried in the planographic printing plate precursor of the invention is preferably in a range from 0.5 g/m² to 1.5 g/m² and more preferably in a range from 0.7 g/m² to 1.0 g/m² from the viewpoint of suppressing generation of a residual film during developing of the precursor and ensuring printing durability of a printing plate formed from the precursor.

[0167] The amount of other recording layer (upper recording layer) after drying (or if there are two or more recording layers as the upper recording layers, the total amount thereof) is preferably in the range of 0.05 g/m² to 1.0 g/m², more preferably in the range of 0.07 g/m² to 0.7 g/m².

[0168] A surfactant such as a fluorine surfactant as described in JP-A No. 62-170950 may be added to the coating liquid for the lower recording layer or the coating liquids of other recording layers to improve coating characteristics. The amount of the surfactant is preferably 0.01 mass% to 1 mass% and more preferably 0.05 mass% to 0.5 mass% based on the total solid content of the coating liquid.

[0169] There is no limitation to the support used in the planographic printing plate precursor of the invention as long as it is a plate-shape material having dimensional stability. Examples thereof include paper, papers laminated with plastic (such as polyethylene, polypropylene or polystyrene), metal plates (such as aluminum plates, zinc plates or copper plates), plastic films (such as cellulose biacetate films, cellulose triacetate films, cellulose propionate films, cellulose lactate films, cellulose acetate lactate films, cellulose nitrate films, polyethylene terephthalate films, polyethylene films, polystyrene films, polypropylene films, polycarbonate films, or polyvinyl acetate films), and papers or plastic films on which a metal such as aluminum, zinc or copper is laminated or vapor-deposited.

[0170] The support is preferably a polyester film or an aluminum plate, and more preferably an aluminum plate, since an aluminum plate is excellent in terms of dimensional stability and is also relatively inexpensive.

Preferable examples of the aluminum plate include a pure aluminum plate and alloy plates made of aluminum as a main component with a very small amount of other elements. A plastic film on which aluminum is laminated or vapor-deposited may also be used. Examples of other elements which may be contained in the aluminum alloys include silicon, iron, manganese, copper, magnesium, chromium, zinc, bismuth, nickel, and titanium. The content by percentage of different elements in the alloy is at most 10% by mass. A particularly preferable aluminum plate in the invention is a pure aluminum plate; however, since from the viewpoint of refining a completely pure aluminum cannot be easily produced, a very small amount of other elements may also be contained in the plate.

The aluminum plate used as the support is not specified in terms of the composition thereof. Thus, aluminum plates which are conventionally known can be appropriately used. The thickness of the aluminum plate used in the invention is from about 0.1 mm to 0.6 mm, preferably from 0.15 mm to 0.4 mm, and more preferably from 0.2 mm to 0.3 mm.

[0171] If necessary, the aluminum plate may be arbitrarily subjected to degreasing treatment prior to the surface-roughening treatment, in order to remove rolling oil or the like on the surface, with a surfactant, an organic solvent, an aqueous alkaline solution or the like.

The surface-roughening treatment of the aluminum surface can be performed by various methods such as a mechanical surface-roughening method, a method of dissolving and roughening the surface electrochemically, or a method of dissolving the surface selectively in a chemical manner.

Mechanical surface-roughening methods which can be used may be known methods, such as a ball polishing method, a brush polishing method, a blast polishing method or a buff polishing method. An electrochemical surface-roughening method may be a method of performing surface-roughening in an electrolyte of hydrochloric acid or nitric acid, by use of an alternating current or a direct current. As disclosed in JP-A No. 54-63902, a combination of the two kinds of methods may be used.

An aluminum plate whose surface is roughened as described above is if necessary subjected to alkali-etching treatment and neutralizing treatment. Thereafter, an anodizing treatment is arbitrarily applied in order to improve the water holding capacity and wear resistance of the surface.

The electrolyte used in the anodizing treatment of the aluminum plate is any one selected from various electrolytes which can form a porous oxide film. Among which in general use are electrolytes of sulfuric acid, phosphoric acid, oxalic acid, chromic acid, or a mixed acid thereof. The concentration of the electrolyte may be appropriately decided depending on the kind of electrolyte selected.

[0172] Treatment conditions for anodization cannot be specified as a general rule since conditions vary depending on the electrolyte used; however, the following range of conditions are generally suitable: an electrolyte concentration of 1% to 80% by mass, a solution temperature of 5°C to 70°C, a current density of 5 A/dm² to 60 A/dm², a voltage of 1 V to 100 V, and an electrolyzing time of 10 seconds to 5 minutes. If the amount of anodic oxide film is less than 1.0 g/m², printing durability is inadequate or non-image portions of the planographic printing plate tend to become easily damaged and the so-called "blemish stains", resulting from ink adhering to damaged portions at the time of printing, are easily generated.

[0173] After the anodizing treatment, the surface of the aluminum is subjected to treatment for obtaining hydrophilicity

if necessary. Example of the hydrophilization treatment include a method using an alkali metal silicate (for example, an aqueous sodium silicate solution) as disclosed in U.S. Patent Nos. 2,714,066, 3,181,461, 3,280,734, and 3,902,734. In this method, the support is subjected to an immersing treatment or an electrolyzing treatment with an aqueous sodium silicate solution.

In addition, the following methods may also be used: a method of treating the support with potassium fluorozirconate, as disclosed in JP-B No. 36-22063, or with polyvinyl phosphonic acid, as disclosed in U.S. Patent Nos. 3,276,868, 4,153,461, and 4,689,272.

[0174] While the planographic printing plate precursor of the invention has at least two layers including the lower recording layer and other layer(s) (upper recording layer(s)) which are provided on the support, the planographic printing plate precursor may further have an undercoat layer provided between the support and the lower recording layer according to the need.

[0175] Various organic compounds can be used as components of the undercoat layer. Examples thereof include carboxymethylcellulose, dextrin, gum arabic, phosphonic acids having an amino group, such as 2-aminoethylphosphonic acid, organic phosphonic acids which may have a substituent, such as phenyl phosphonic acid, naphthylphosphonic acid, alkylphosphonic acid, glycerophosphonic acid, methylenediphosphonic acid and ethylenediphosphonic acid, organic phosphoric acids which may have a substituent, such as phenylphosphoric acid, naphthylphosphoric acid, alkylphosphoric acid and glycerophosphoric acid, organic phosphinic acids which may have a substituent, such as phenylphosphinic acid, naphthylphosphinic acid, alkylphosphinic acid and glycerophosphinic acid, amino acids such as glycine and β -alanine, and hydrochlorides of amines having a hydroxyl group, such as a hydrochloride of triethanolamine. These organic compounds may be used alone or in the form of a mixture of two or more thereof.

[0176] Examples of the method for forming the organic undercoat layer include: a method including applying, onto the aluminum plate, a solution in which the above-mentioned organic compound is dissolved in water, or an organic solvent such as methanol, ethanol or methyl ethyl ketone, or a mixed solvent thereof and then drying the resultant aluminum plate; and a method including immersing the aluminum plate into a solution in which the above-mentioned organic compound is dissolved in water or an organic solvent such as methanol, ethanol, methyl ethyl ketone or a mixed solvent thereof so as to adsorb the compound, washing the aluminum plate with water or the like, and then drying the resultant aluminum plate. In the former method, the solution of the organic compound having a concentration of 0.05 to 10% by mass may be applied in various ways. In the latter method, the concentration of the organic compound in the solution is from 0.01 to 20%, preferably from 0.05 to 5%, the temperature for the immersion is from 20 to 90°C, preferably from 25 to 50°C, and the time taken for immersion is from 0.1 second to 20 minutes, preferably from 2 seconds to 1 minute. The pH of the solution used in the above-mentioned methods can be adjusted into a range of 1 to 12 with a basic material such as ammonia, triethylamine or potassium hydroxide, or an acidic material such as hydrochloric acid or phosphoric acid. Moreover, a yellow dye may be added to the solution, in order to improve the tone reproducibility of the recording layer.

[0177] The amount of the organic undercoat layer applied is suitably from 2 mg/m² to 200 mg/m², and is preferably from 5 mg/m² to 100 mg/m².

[0178] The positive planographic printing plate precursor produced as described above is usually subjected to image exposure and developing treatment.

In the invention, the planographic printing plate precursor is exposed to light from a light source which preferably has an emitting wavelength in the near-infrared region to the infrared region. Specifically, the planographic printing plate precursor is preferably exposed imagewise to light from a solid laser or a semiconductor laser radiating infrared rays having a wavelength of 760 nm to 1,200 nm.

[0179] The planographic printing plate precursor of the invention is developed using water or an alkali developing solution after exposure. Although the developing treatment may be carried out immediately after exposure, heating treatment may be carried out between an exposure step and a developing step. When the heat treatment is carried out, the heating is preferably carried out at a temperature range from 60°C to 150°C for 5 seconds to 5 minutes. As the heating method, conventionally known various methods may be used. Examples of the heating method include a method in which a recording material is heated with bringing it into contact with a panel heater or ceramic heater and a non-contact method using a lamp or hot air. This heat treatment enables to reduce the energy required for recording when a laser is applied.

[0180] Any conventionally known aqueous alkali solution may be used as a developing solution and replenishing solution to be used for plate-making of the planographic printing plate of the invention.

The developing solution which may be applied to the developing treatment of the planographic printing plate precursor of the invention is a developing solution having a pH range from 9.0 to 14.0 and preferably a pH range from 12.0 to 13.5.

A conventionally known aqueous alkali solution may be used as the developing solution (hereinafter referred to as a developing solution including a replenishing solution).

Examples of the alkali agent for the aqueous alkali solution include inorganic alkali salts such as sodium silicate, potassium silicate, trisodium phosphate, tripotassium phosphate, triammonium phosphate, disodium hydrogenphosphate, dipotas-

sium hydrogenphosphate, diammonium hydrogenphosphate, sodium carbonate, potassium carbonate, ammonium carbonate, sodium hydrogencarbonate, potassium hydrogencarbonate, ammonium hydrogen carbonate, sodium borate, potassium borate, ammonium borate, sodium hydroxide, ammonium hydroxide, potassium hydroxide or lithium hydroxide; and organic alkali agents such as monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, triisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethyleneimine, ethylenediamine, or pyridine. These alkali agents may be used alone or in combinations of two or more thereof.

[0181] Moreover, an aqueous alkali solution having a non-reducing sugar and a base may also be used. The non-reducing sugar denotes a sugar having no reducing ability due to lack of a free aldehyde group, a ketone group and the like, and is classified into trehalose oligosaccharides in which reducing groups are combined with other, glycosides in which reducing groups of sugars are combined with non-sugars, or sugar alcohols in which sugars are reduced by hydrogenation. Any of these non-reducing sugars may be preferably used.

Examples of the trehalose oligosaccharides include saccharose and trehalose. Examples of the glycosides include alkylglucosides, phenolglucosides, and mustard seed oil glucoside. Examples of the sugar alcohols include D, L-arabite, ribitol, xylitol, D, L-sorbitol, D, L-mannitol, D, L-iditol, D, L-talitol, dulcitol, and allodulcitol. Furthermore, maltitol, obtained by hydrogenating a disaccharide, and a reductant obtained by hydrogenating an oligosaccharide (i.e., reduced starch syrup) are preferable. Of these examples, sugar alcohol and saccharose are more preferable. D-sorbitol, saccharose, and reduced starch syrup are even more preferable since they have buffer effect within an appropriate pH range and are inexpensive.

[0182] These nonreducing sugars may be used alone or in combination of two or more thereof. The content of the nonreducing sugar in the developer is preferably from 0.1% to 30% by mass, more preferably from 1% to 20% by mass with respect to the total amount of the developer.

The base combined with the nonreducing sugar(s) may be an alkali agent that has been conventionally known. Examples thereof include inorganic alkali agents such as sodium hydroxide, potassium hydroxide, lithium hydroxide, trisodium phosphate, tripotassium phosphate, triammonium phosphate, disodium phosphate, dipotassium phosphate, diammonium phosphate, sodium carbonate, potassium carbonate, ammonium carbonate, sodium hydrogencarbonate, potassium hydrogencarbonate, ammonium hydrogencarbonate, sodium borate, potassium borate or ammonium borate; and organic alkali agents such as monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, triisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethyleneimine, ethylenediamine, or pyridine.

[0183] The bases may be used singly or in combination of two or more. Among the bases, sodium hydroxide and potassium hydroxide are preferable. The reason is that pH adjustment can be made in a wide pH range by regulating the amount of the alkali agent to be added to the non-reducing sugar. Also, trisodium phosphate, sodium carbonate, potassium carbonate or the like itself have a buffer action and are hence preferable.

[0184] In a case where an automatic developing machine is used to perform development, an aqueous solution having a higher alkali intensity than that of the developer (or, replenisher) can be added to the developer. It is known that this enables to treat a great number of photosensitive plates without recourse to replacing the developer in the developing tank over a long period of time. This replenishing manner is also preferably used in the invention.

If necessary, various surfactants or organic solvents can be incorporated into the developer and the replenisher in order to promote and suppress development capacity, disperse scum generated during development, and enhance the ink-affinity of image portions of the printing plate.

Preferable examples of the surfactant include anionic surfactants, cationic surfactants, nonionic surfactants and amphoteric surfactants. If necessary, the following may be added to the developer and the replenisher: a reducing agent (such as hydroquinone, resorcin, a sodium or potassium salt of an inorganic acid such as sulfurous acid or hydrogen sulfite acid), an organic carboxylic acid, an antifoaming agent, and/or a water softener.

The printing plate developed with the developer and replenisher described above is subsequently subjected to treatments with washing water, a rinse solution containing a surfactant and other components, and a desensitizing solution containing gum arabic and a starch derivative. Various combinations of these treatments may be employed for after treatment when the photosensitive composition precursor of the invention is to be used for forming a planographic printing plate.

[0185] In recent years, automatic developing machines for printing plate precursors have been widely used in order to rationalize and standardize plate-making processes in the plate-making and printing industries. These automatic developing machines are generally made up of a developing section and a post-processing section, and include a device for carrying printing plate precursors, various treating solution tanks, and spray devices. These machines are machines for spraying respective treating solutions, which are pumped up, onto an exposed printing plate through spray nozzles, for development, while the printing plate is transported horizontally.

Recently, a method has also attracted attention in which a printing plate precursor is immersed in treating solution tanks filled with treating solutions and conveyed by means of in-liquid guide rolls. Such automatic processing can be performed while replenishers are being replenished into the respective treating solutions in accordance with the amounts to be

treated, operating times, and other factors.

A so-called use-and-dispose processing manner can also be used, in which treatments are conducted with treating solutions which in practice have yet been used.

[0186] A method of treating the heat-sensitive planographic printing plate precursor of the invention will be explained. In cases where unnecessary image portions (for example, a film edge mark of an original picture film) are present on a planographic printing plate obtained by exposing imagewise to light a planographic printing plate precursor to which the invention is applied, developing the exposed precursor, and subjecting the developed precursor to water-washing and/or rinsing and/or desensitizing treatment(s), unnecessary image portions can be erased. The erasing is preferably performed by applying an erasing solution to unnecessary image portions, leaving the printing plate as it is for a given time, and washing the plate with water, as described in, for example, JP-B No. 2-13293. This erasing may also be performed by a method of radiating active rays introduced through an optical fiber onto the unnecessary image portions, and then developing the plate, as described in JP-A No. 59-174842.

[0187] The planographic printing plate obtained as described above is, if desired, coated with a desensitizing gum, and subsequently the plate can be made available for printing. When it is desired to make a planographic printing plate with a higher degree of printing durability, burning treatment can be applied to the planographic printing plate.

In a case where the planographic printing plate is subjected to the burning treatment, it is preferable that the plate is treated with a surface-adjusting solution before the burning treatment takes place as described in JP-B No. 61-2518, or JP-A Nos. 55-28062, 62-31859 or 61-159655.

Examples of the method of the surface-adjusting treatment include: a method of applying the surface-adjusting solution onto the planographic printing plate with a sponge or absorbent cotton infiltrated with the solution; a method of immersing the planographic printing plate in a vat filled with the surface-adjusting solution; and a method of applying the surface-adjusting solution to the planographic printing plate with an automatic coater. In a case where when the amount of solution applied is made uniform with a squeegee or a squeegee roller after application, a better result may be obtained.

[0188] In general, the amount of surface-adjusting solution applied is suitably from 0.03 g/m² to 0.8 g/m² (dry mass). If necessary the planographic printing plate onto which the surface-adjusting solution is applied can be dried, and then the plate is heated to a high temperature by means of a burning processor (for example, a burning processor BP-1300 (trade name, available from FUJIFILM Corporation)) or the like. In this case the heating temperature and the heating time, which depend on the kind of components forming the image, are preferably from 180°C to 300°C and from 1 minute to 20 minutes, respectively.

If necessary, a planographic printing plate subjected to burning treatment can be further subjected to treatments which have been conventionally conducted, such as a water-washing treatment and gum coating. However, in a case where a surface-adjusting solution containing a water soluble polymer compound or the like is used, the so-called desensitizing treatment (for example, gum coating) can be omitted. The planographic printing plate obtained as a result of such treatments can be applied to an offset printing machine or to some other printing machine, and can be used for printing on a great number of sheets.

EXAMPLES

[0189] The invention will be explained by way of examples, which, however, are not intended to limit the scope of the invention.

Synthesis of Specific polymer

[0190] In the present Examples, polymers 1-3, synthesized as per the following, were used as the specific polymer.

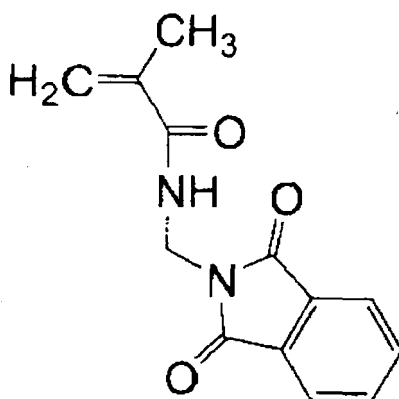
Synthesis of Polymer 1

[0191] Polymer 1 was synthesized by the method indicated below.

Polymer 1 is a copolymer of (a) N-vinyl caprolactam, (b) monomer 1 having the following structure, and (c) acrylic acid (copolymerization molar ratio (a/b/c) of 23/25/20).

[0192]

Monomer 1



[0193] 6.90 g (0.050 mol) of N-vinyl caprolactam, 30.0 g (0.123 mol) of monomer 1 and 3.11 g (0.043 mol) of acrylic acid were added to a sealed reaction container equipped with a water-cooled cooling tube, a temperature gauge, a nitrogen-inlet tube and a mechanical stirrer and into which 129.6 g of γ -butyrolactone had already been added. The resultant mixture was heated at 90°C and stirred until it became a transparent solution.

1.52 g of dimethyl-2,2'-azobisisobutyrate (trade name: V-601, an azo initiator available from Wako Pure Chemical Industries Co., Ltd.) were dissolved in 28.9 g of γ -butyrolactone. The resultant solution was dripped into the reaction mixture obtained above over a period of 30 minutes. Then, the reaction was continued at 90°C for 7 hours. After completion of the reaction, the temperature was adjusted to room temperature. The resultant polymer solution had a concentration of approximately 20%.

Synthesis of Polymer 2

[0194] Polymer 2 was synthesized by the method indicated below.

Polymer 2 is a copolymer of (a) N-vinyl caprolactam, (b) monomer 1 having the following structure, and (c) methacrylic acid (copolymerization molar ratio (a/b/c) of 23/57/20).

[0195] 6.80 g (0.0488 mol) of N-vinyl caprolactam, 29.55 g (0.121 mol) of monomer 1 and 3.65 g (0.0424 mol) of methacrylic acid were added to a sealed reaction container equipped with a water-cooled cooling tube, a temperature gauge, a nitrogen-inlet tube and a mechanical stirrer and into which 129.6 g of γ -butyrolactone had already been added. The resultant mixture was heated at 90°C and stirred until it became a transparent solution.

1.52 g of dimethyl-2,2'-azobisisobutyrate (trade name: V-601, an azo initiator available from Wako Pure Chemical Industries Co., Ltd.) were dissolved in 28.9 g of γ -butyrolactone. The resultant solution was dripped into the reaction mixture obtained above over a period of 30 minutes. Then, the reaction was continued at 90°C for 7 hours. After completion of the reaction, the temperature was adjusted to room temperature. The resultant polymer solution had a concentration of approximately 20%.

Synthesis of Polymer 3

[0196] Polymer 2 was synthesized by the method indicated below.

Polymer 2 is a copolymer of (a) N-vinyl caprolactam, (b) monomer 1 having the following structure, and (c) methacrylic acid (copolymerization molar ratio (a/b/c) of 11/69/20).

[0197] 3.05 g (0.0219 mol) of N-vinyl caprolactam, 33.57 g (0.137 mol) of monomer 1 and 3.43 g (0.0398 mol) of methacrylic acid were added to a sealed reaction container equipped with a water-cooled cooling tube, a temperature gauge, a nitrogen-inlet tube and a mechanical stirrer and into which 129.6 g of γ -butyrolactone had already been added. The resultant mixture was heated at 90°C and stirred until it became a transparent solution.

1.52 g of dimethyl-2,2'-azobisisobutyrate (trade name: V-601, an azo initiator available from Wako Pure Chemical Industries Co., Ltd.) were dissolved in 28.9 g of γ -butyrolactone. The resultant solution was dripped into the reaction mixture obtained above over a period of 30 minutes. Then, the reaction was continued at 90°C for 7 hours. After completion of the reaction, the temperature was adjusted to room temperature. The resultant polymer solution had a concentration of approximately 20%.

Examples 1 to 5 and Comparative examples 1 to 4

Preparation of Support

5 **[0198]** An aluminum alloy, which contains 0.06 wt% Si, 0.30 wt% Fe, 0.025 wt% Cu, 0.001 wt% Mn, 0.001 wt% Mg, 0.001 wt% Zn and 0.03 wt% Ti, the balance being Al and inevitable impurities, was used to prepare a molten metal. The molten metal was then subjected to molten metal treatment, filtered and formed into an ingot of 500 mm in thickness and 1,200 mm in width by a DC casting method. After scalping its surface layer at 10 mm average thickness with a scalping machine, the ingot was soaked at 550°C for about 5 hours, and when the temperature decreased to 400°C, 10 the ingot was formed into a rolled plate of 2.7 mm in thickness with a hot rolling mill. Then, the plate was subjected to heat treatment at 500°C with a continuous annealing device and finished with cold rolling to give a plate of 0.24 mm in thickness as an aluminum plate. This aluminum plate was formed into a plate of 1030 mm in width and then subjected to the following surface treatment.

15 Surface treatment

[0199] The following treatments (a) to (h) were successively conducted in the surface treatment. After each treatment and water washing, remaining liquid was removed with nip rollers.

20 (a) Mechanical surface roughening treatment

[0200] The surface of the aluminum plate was subjected to mechanical surface roughening treatment with a rotating roller-shaped nylon brush while it was supplied with an aqueous suspension of an abrasive (Pumice) having a specific gravity of 1.12 as an abrasive slurry. The average particle diameter of the abrasive was 8 μm , and the maximum particle 25 diameter was 50 μm . The nylon brush was made of 6·10 nylon, the length of the brush hair was 50 mm, and the diameter of the brush hair was 0.3 mm. The nylon brush had hairs arranged densely in holes in a stainless steel cylinder of $\phi 300$ mm. Three rotating brushes were used. The distance between two supporting rollers ($\phi 200$ mm) under the brushes was 300 mm. The brush roller was pressed against the aluminum plate until the load of a driving motor for rotating the brush was increased by 7 kW relative to the load before the brush roller was pressed against the aluminum plate. The direction 30 of rotation of the brush was the same as the direction of movement of the aluminum plate. The number of revolutions of the brush was 200 rpm.

(b) Alkali etching treatment

35 **[0201]** The aluminum plate obtained above was subjected to etching treatment by spraying with an aqueous solution of sodium hydroxide at a concentration of 2.6 wt% and aluminum ions at a concentration of 6.5 wt% at a temperature of 70°C, whereby the aluminum plate was dissolved in an amount of 10 g/m². Thereafter, the aluminum plate was washed by spraying with water.

40 (c) Desmut treatment

[0202] The aluminum plate was subjected to desmut treatment with an aqueous solution (containing 0.5 wt% aluminum ion) of 1 wt% nitric acid at a temperature of 30°C and then washed by spraying with water. The aqueous solution of nitric acid used in the desmut treatment was waste liquid resulted from the process of electrochemical surface roughening 45 treatment with an alternating current in an aqueous solution of nitric acid.

(d) Electrochemical surface roughening treatment

[0203] The plate was subjected to continuous electrochemical surface roughening treatment with an alternating voltage 50 of 60 Hz. The electrolyte used was 10.5 g/L aqueous nitric acid solution (containing 5 g/L aluminum ion and 0.007 wt% ammonium ion) at a temperature of 80°C. The electrochemical surface roughening treatment was carried out with a carbon electrode as a counter electrode wherein the alternating current power source waveform had a waveform as shown in Fig. 1, the time required for the electric current to reach from 0 to the peak was 0.8 msec., the duty ratio was 1:1, and a trapezoidal rectangular wave alternating current was used. Ferrite was used as an auxiliary anode. The 55 electrolyte chamber used was as shown in Fig. 2. The current density was 30 A/dm² in terms of the electric current peak, and the electrical quantity was 220 C/dm² in terms of the total electrical quantity when the aluminum plate was an anode. 5% of the electric current from the power source was fed through the auxiliary anode. Thereafter, the plate was washed by spraying with water.

(e) Alkali etching treatment

[0204] The aluminum plate was subjected to etching treatment by spraying with an aqueous solution of sodium hydroxide at a concentration of 26 wt% and aluminum ions at a concentration of 6.5 wt% at a temperature of 32°C, whereby the aluminum plate was dissolved in an amount of 0.20 g/m². Smut components, composed in the main of aluminum hydroxide formed by the electrochemical surface roughening treatment using the alternating current in the previous stage, were removed, and the edges of the pits formed were dissolved to smooth the edge. Thereafter, washing by spraying with water was carried out.

(f) Desmut treatment

[0205] The aluminum plate was subjected to desmut treatment with an aqueous solution of 25 wt% nitric acid (containing 0.5 wt% aluminum ions) at a temperature of 30°C and then washed by spraying with water.

(g) Anodizing treatment

[0206] Anodizing treatment was carried out with an anodizing apparatus for two-step current feeding which has a structure with first and second electrolyte zones of 6 m in length each, first and second current feeding zones of 3 m in length, and first and second current feeding zones of 2.4 m in length. The electrolytes supplied to the first and second electrolytic zones were sulfuric acid. Both the electrolytes were 170 g/L sulfuric acid (containing 0.5 wt% aluminum ions) at a temperature of 43°C. Thereafter, washing by spraying with water was carried out. The final anodized coating was 2.7 g/m².

(h) Alkali metal silicate treatment

[0207] The aluminum support obtained by the anodizing treatment was subjected to alkali metal silicate treatment (silicate treatment) by dipping it in a treatment bath of 1 wt% aqueous sodium silicate No. 3 at a temperature of 30 °C for 10 seconds. Thereafter, the aluminum support was washed by spraying with water

(i) Formation of Undercoat layer

[0208] After the alkali metal silicate treatment, the resulting aluminum support was coated with an undercoat liquid having the following formulation and then dried at 80 °C for 15 seconds, to form a coating thereon. The amount of the coating (undercoat layer) after drying was 15 mg/m².

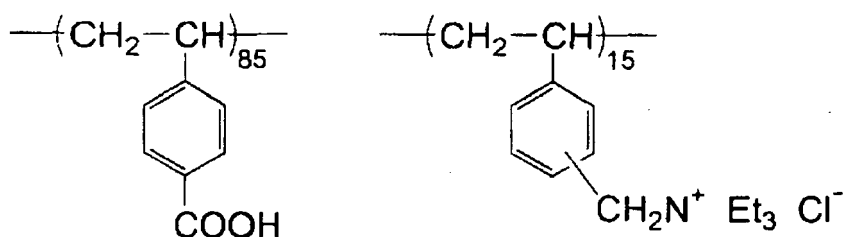
Formulation of Undercoat liquid

[0209]

- Polymer compound 1 (weight average molecular weight: 28,000) 0.3 g
- Methanol 100 g
- Water 1 g

[0210]

Polymer compound 1



(ii) Formation of Positive recording layer

[0211] The coating liquid for the lower recording layer having the following formulation was applied to the thus obtained support such that the application amount thereof was 0.85 g/m², and then dried at 140°C for 50 seconds with PERFECT OVEN PH200 (trade name, manufactured by TABAI) by setting the level of wind control thereof to seven. Thereafter, the following coating liquid for the upper recording layer having the following formulation was applied to the resulting coating film such that the application amount thereof was 0.15 g/m², and then dried at 120°C for 1 minute, so as to provide planographic printing plate precursors of Examples 1 to 5 and Comparative Examples 1 to 4.

Formulation of Coating liquid for Lower recording layer

[0212]

- Two polymers shown in Table 1 (mixing ratio of the two: shown in Table 1) 2.15 g
- Cyanine dye A (the following structure) 0.13 g
- 4,4'-Bishydroxyphenyl sulfone 0.11 g
- Tetrahydrophthalic anhydride 0.15 g
- p-Toluenesulfonic acid 0.01 g
- 3-Methoxy-4-diazodiphenylamine hexafluorophosphate 0.03 g
- Ethyl Violet in which counter ion was replaced by 0.10 g 4-hydroxy-1-sulfonic acid
- Fluorine surfactant (surfactant for improving surface conditions) (trade name: MEGAFAC F-781F, manufactured by DIC Corporation) 0.035 g
- Methyl ethyl ketone 24 g
- 2-Hydroxy-1-propanol 13 g
- γ -Butyrolactone 14 g

[0213]

Cyanine dye A

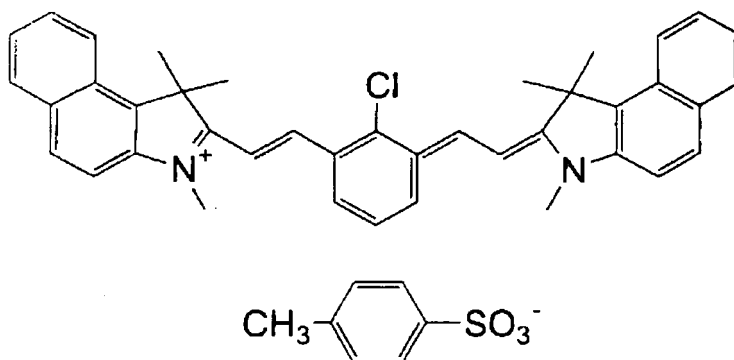
**[0214]**

Table 1

	Polymer 1	Polymer 2	Polymer 3	Polymer 4	Novolak A	Novolak B	Novolak C	Novolak D
Example 1	95	-	-	-	5	-	-	-
Example 2	70	-	-	-	-	30	-	-
Example 3	60	-	-	-	-	-	40	-
Example 4	-	80	-	-	20	-	-	-
Example 5	-	-	75	-	-	25	-	-

(continued)

	Polymer 1	Polymer 2	Polymer 3	Polymer 4	Novolak A	Novolak B	Novolak C	Novolak D
Comparative Example 1	100	-	-	-	-	-	-	-
Comparative Example 2	50	-	-	-	50	-	-	-
Comparative Example 3	70	-	-	-	-	-	-	30
Comparative Example 4	-	-	-	70	30	-	-	-

The values shown in Table 1 denote a mass ratio of the respective polymer in the mixture of the polymer(s) used in each of the Examples/Comparative examples.

[0215] Details of each of the polymers shown in Table 1 are as follows.

- Polymers 1 to 3: Specific polymers synthesized as described above
- Polymer 4: N-(4-aminosulfonylphenyl)methacrylamide/acrylonitrile/methyl methacrylate (mole ratio: 36/34/30, weight average molecular weight: 100,000, acid value: 2.65)
- Novolak A: 2,5-xyleneol/m/p-cresol novolak (mole ratio: 5/55/40, weight average molecular weight: 6,500)
- Novolak B: m/p-cresol novolak (mole ratio: 60/40, weight average molecular weight: 3,500)
- Novolak C: phenol/m/p-cresol novolak (mole ratio: 20/50/30, weight average molecular weight: 5,000)
- Novolak D: phenol novolak (weight average molecular weight: 4,500)

Formulation of Coating liquid for Upper recording layer

[0216]

- m, p-cresol novolak 0.2846 g (m/p ratio=6/4, weight average molecular weight: 4,500, containing 0.8% by mass of unreacted cresol)
- Cyanine dye A (having the structure described above) 0.075 g
- Behenic acid amide 0.060 g
- Fluorine type surfactant (surface-improving surfactant) 0.022 g (MEGAFAC F781F: described above)
- Image formation-improving fluorine type surfactant 0.120 g (MEGAFAC F780 (30%): described above)
- Methyl ethyl ketone 15.1 g
- 1-Methoxy-2-propanol 7.7 g

Confirmation of Dispersion phase

[0217] The planographic printing plate precursors of Examples 1 to 5 and Comparative examples 1 to 4 were respectively cut with a microtome. The resulting section of the recording layer of each was made electroconductive, and then photographs thereof were taken with a scanning electron microscope (SEM) and observed. As a result, the presence of a dispersion phase in the lower recording layer in Examples 1 to 5 was confirmed. The size of the dispersion phase was in the range of 0.05 to 0.55 μm . In contrast, the lower recording layers of Comparative examples 1 to 4 has uniform phases which lack a dispersion phase.

Evaluation of the Planographic printing plate precursor

[0218] Each of the resulting planographic printing plate precursors of Examples 1 to 5 and Comparative examples 1 to 4 was subjected to evaluations with respect to the small dot reproducibility, printing durability and chemical resistance in accordance with the following manners.

1. Evaluation of Small dot reproducibility

[0219] A test pattern was drawn to each of the resulting planographic printing plate precursors of Examples 1 to 5 and

Comparative examples 1 to 4 by imagewise exposure using TRENDSETTER (trade name, manufactured by KGC) with a beam intensity of 9 W at a drum revolution of 250 rpm and a screen (trade name: STACCATO 10, manufactured by Creo Inc.) with an output of 1% to 99% gradation. The thus exposed precursors were then developed by using a developing solution DT-2 (trade name, manufactured by FUJIFILM Corporation: diluted with water to provide an electrical conductivity of 43 ms/cm) charged in a PS processor (trade name: 940HII, manufactured by FUJIFILM Corporation) with a developing time of 12 seconds at a temperature of 30°C. The smallest gradation value (dot coverage area percentage) reproduced upon the development was evaluated as the index of the small dot reproducibility. The smaller the dot coverage area percentage is, the better in the small dot reproducibility. The results are shown below in Table 2.

2. Evaluation of Printing durability

[0220] The respective planographic printing plate precursors obtained in Examples 1 to 5 and Comparative Examples 1 to 4 were drawn on (exposed) and developed in the same manner as in 1. above to provide planographic printing plates. Printing was performed on high quality paper with a KOR-D machine (trade name, manufactured by Heidelberger Druckmaschinen AG) using the obtained planographic printing plates. Evaluation of printing durability was conducted by counting the number of sheets until image-lackness occurred; namely, until the recording layer of the planographic printing plates is reduced in thickness and ink does not attach in places. The results are shown below in Table 2.

3. Evaluation of Chemical resistance

[0221] Chemical resistance was evaluated by the following evaluation method and evaluation criteria using the following testing liquids 1-3. The results are shown below in Table 2.

Testing liquids

[0222] Testing liquid 1: 50 wt% aqueous solution of isopropanol

Testing liquid 2: EMERALD® PREMIUM MXEH (trade name, commercially available from ANCHOR)

Testing liquid 3: ANCHOR AQUA AYDE (trade name, commercially available from ANCHOR)

Method of evaluation of Chemical resistance

[0223] 40 µL of droplets of each of testing liquids 1-3 was dripped onto different portions of the surface of the recording layer of the obtained planographic printing plate precursors. After three minutes had elapsed, the droplets were wiped from the recording layer surface using a cotton pad. Damage to the recording layer caused by the testing liquids was visually observed and evaluated according to the following criteria.

Evaluation criteria for Chemical resistance

[0224]

0: no damage

1: variation in the sheen of the recording layer surface

2: minor damage to the recording layer (reduction in thickness)

3: significant damage to the recording layer

4: complete dissolution of the recording layer

[0225]

Table 2

	Small dot reproducibility	Printing Durability (10,000 sheets)	Chemical Resistance		
			Testing liquid 1	Testing liquid 2	Testing liquid 3
Example 1	1%	10	1	1	1
Example 2	1%	10	1	1	1
Example 3	1%	10	1	1	1
Example 4	1%	10	1	1	1

(continued)

	Small dot reproducibility	Printing Durability (10,000 sheets)	Chemical Resistance		
			Testing liquid 1	Testing liquid 2	Testing liquid 3
Example 5	1%	10	1	1	1
Comparative Example 1	4%	10	1	1	1
Comparative Example 2	2%	6	3	4	3
Comparative Example 3	4%	10	1	1	1
Comparative Example 4	1%	8	2	2	2

[0226] As is evident from Table 2, it is found that any of the planographic printing plate precursors in Examples 1 to 5 are superior in both of small dot reproducibility, printing durability and chemical resistance as comparing to Comparative Examples 1 and 4.

Claims

1. A planographic printing plate precursor comprising:

a support; and

two or more positive recording layers respectively comprising a resin and an infrared absorber, each of the layers having a solubility with respect to an aqueous alkali solution that is increased by exposure to infrared laser light, wherein:

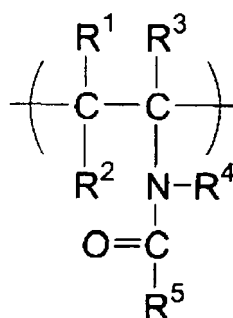
of the two or more positive recording layers, a positive recording layer that is nearest to the support comprises two resins;

the two resins each comprise a polymer comprising a structural unit represented by the following Formula (I);

one of the two resins constitutes a dispersion phase that is dispersed in a matrix phase; and

the matrix phase serves as a dispersing medium and comprises the other of the two resins:

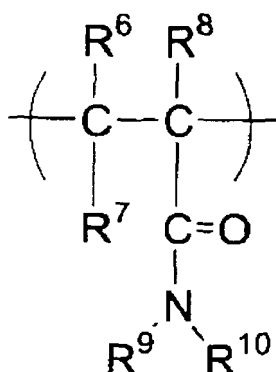
Formula (I)



wherein each of R¹, R² and R³ independently represents a hydrogen atom, a substituted or unsubstituted alkyl group; each of R⁴ and R⁵ independently represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted arylalkyl group; and R⁴ and R⁵ may be bonded together to form a ring structure.

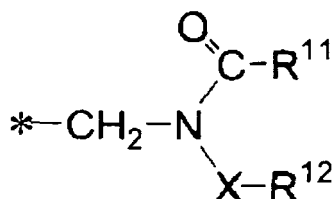
2. The planographic printing plate precursor of claim 1, wherein the polymer comprising a structural unit represented by Formula (I) comprises a structural unit represented by the following Formula (II):

Formula (II)



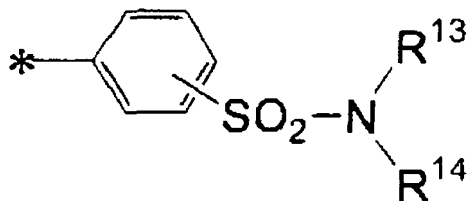
wherein each of R⁶, R⁷ and R⁸ independently represents a hydrogen atom or a substituted or unsubstituted alkyl group; R⁹ represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted arylalkyl group; and R¹⁰ represents a group represented by the following Formula (III) or (IV):

Formula (III)



wherein "*" represents the position at which R¹⁰ is bonded with the nitrogen atom in Formula (II); X represents -C(=O) or -SO₂-; each of R¹¹ and R¹² independently represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted arylalkyl group, or a substituted or unsubstituted heteroaryl group; and R¹¹ and R¹² may be bonded together to form a ring structure:

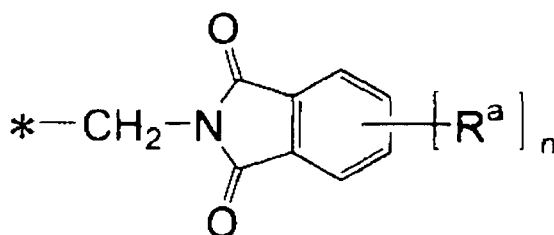
Formula (IV)



wherein "*" represents the position at which R¹⁰ is bonded with the nitrogen atom in Formula (II); each of R¹³ and R¹⁴ independently represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted arylalkyl group, or a substituted or unsubstituted heteroaryl group; and R¹³ and R¹⁴ may be bonded together to form a ring structure.

3. The planographic printing plate precursor of claim 2, wherein R¹⁰ in Formula (II) is a group represented by the following Formula (V):

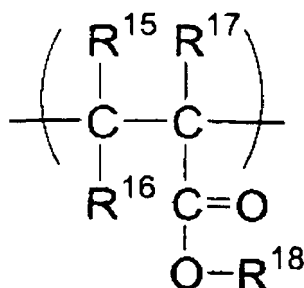
Formula (V)



wherein "*" represents the position at which R¹⁰ is bonded with the nitrogen atom in Formula (II); n represents 0, 1, 2, 3 or 4; R^a represents a hydrogen atom, a halogen atom, -CN, -NO₂, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted heterocyclic group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heteroaryl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted heteroaralkyl group, -O-R^b, -S-R^c, -SO₃-R^d, -CO-O-R^e, -O-CO-R^f, -NR^gR^h, -NRⁱ-CO-R^j, -NR^k-SO₂-R^l, -CO-R^m, -CO-NRⁿR^o, -SO₂-NR^pR^q, or -P(=O)(-O-R^r)(-O-R^s); each of R^b to R^s independently represents a hydrogen atom, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl group; and when there is more than one R^a, respective groups represented by R^a may be the same as or different from each other.

4. The planographic printing plate precursor of claim 1, wherein the polymer comprising a structural unit represented by Formula (I) comprises a structural unit represented by the following Formula (VI):

Formula (VI)



wherein each of R¹⁵, R¹⁶ and R¹⁷ independently represents a hydrogen atom or a substituted or unsubstituted alkyl group; and R¹⁷ represents a hydrogen atom, a metal ion having a positive electric charge, an ammonium ion, a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted arylalkyl group.

5. The planographic printing plate precursor of claim 1, wherein at least one of the two resins is insoluble in water and soluble in an aqueous alkali solution.
6. The planographic printing plate precursor of claim 5, wherein the matrix phase comprises the one of the two resins that is insoluble in water and soluble in an aqueous alkali solution.
7. The planographic printing plate precursor of claim 6, wherein the dispersion phase includes a compound that generates an acid or a radical when irradiated with an infrared laser.
8. The planographic printing plate precursor of claim 6, wherein the dispersion phase includes a compound having an alkali solubility that is changed by irradiation with an infrared laser.
9. The planographic printing plate precursor of claim 1, wherein the rate of dissolution with respect to an alkaline aqueous solution of the resin constituting the dispersion phase is slower than that of the resin included in the matrix

phase.

10. The planographic printing plate precursor of claim 1, wherein the resin constituting the dispersion phase comprises a novolak resin.

11. The planographic printing plate precursor of claim 1, wherein the ratio between the content of the resin constituting the matrix phase and that of the resin constituting the dispersion phase is from 95:5 to 50:50 in terms of mass ratio.

12. The planographic printing plate precursor of claim 1, wherein the maximum major axis of the dispersion phase is from 0.1 μm to 0.8 μm , and the average major axis thereof is from 0.05 μm to 0.6 μm .

13. A method of forming the planographic printing plate precursor of any one of claims 1 to 12, the method comprising forming the dispersion phase by either (1) using a combination of the resin constituting the dispersion phase and the resin constituting the matrix phase, wherein the two resins are incompatible with each other, or (2) dispersing, in the resin constituting the matrix phase, the resin constituting the dispersion phase in microcapsule or latex form.

FIG. 1

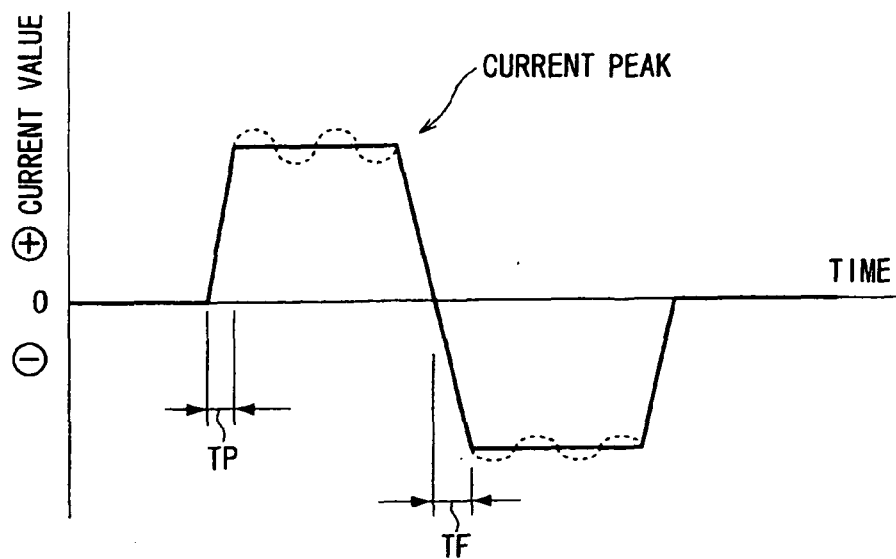
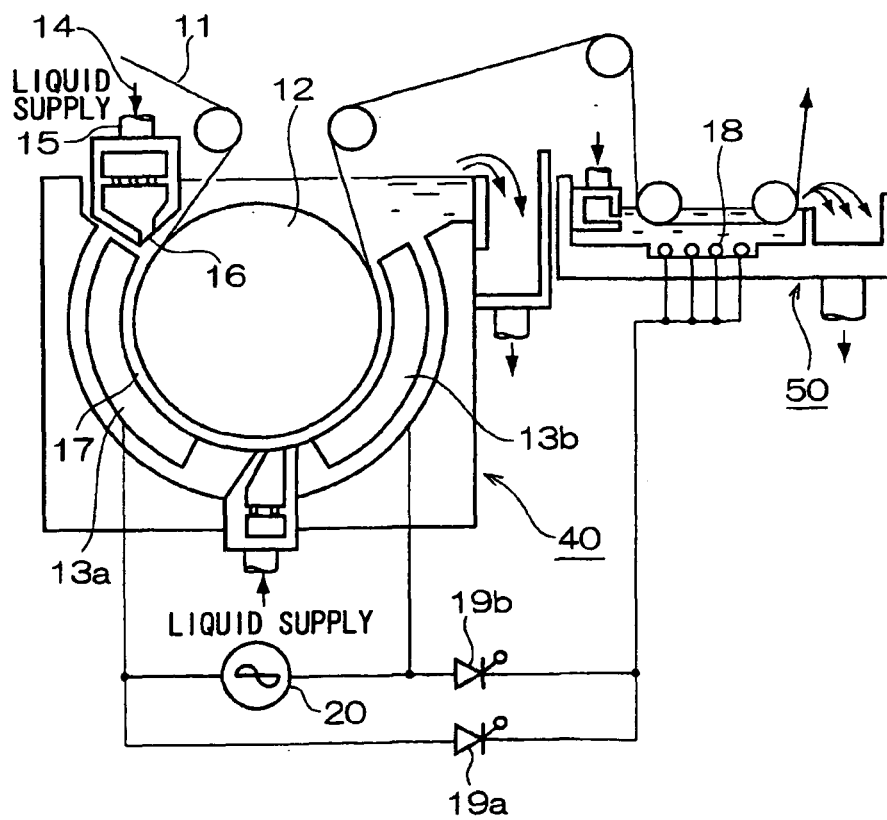


FIG. 2



REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 11218914 A [0008]
- US 20040003870 A1 [0008]
- US 4123279 A [0069] [0076] [0104]
- JP 9090610 A [0080]
- JP 63124047 A [0103]
- JP 63287946 A [0103]
- JP 2000866 A [0103]
- JP 2156241 A [0103]
- JP 1145190 A [0107]
- JP 10265710 A [0107]
- JP 10270233 A [0107]
- JP 5002281 A [0107]
- JP 11095415 A [0109]
- JP 7020629 A [0109]
- US 4708925 A [0113]
- JP 58125246 A [0118]
- JP 59084356 A [0118]
- JP 59202829 A [0118]
- JP 60078787 A [0118]
- JP 58112793 A [0118]
- JP 58224793 A [0118]
- JP 59048187 A [0118]
- JP 59073996 A [0118]
- JP 60052940 A [0118]
- JP 60063744 A [0118]
- JP 58112792 A [0118]
- GB 434875 A [0118]
- US 5156938 A [0119]
- US 3881924 A [0119]
- JP 57142645 A [0119]
- US 4327169 A [0119]
- JP 58181051 A [0119]
- JP 58220143 A [0119]
- JP 59041363 A [0119]
- JP 59084248 A [0119]
- JP 59084249 A [0119]
- JP 59146063 A [0119]
- JP 59146061 A [0119]
- JP 59216146 A [0119]
- US 4283475 A [0119]
- JP 5013514 B [0119]
- JP 5019702 B [0119]
- US 4756993 A [0120]
- JP 11338131 A [0128] [0128]
- JP 11291652 A [0129]
- JP 11288093 A [0137] [0138] [0153]
- JP 2000187318 A [0137]
- JP 5158230 A [0143] [0145]
- US 4069055 A [0143] [0143]
- US 4069056 A [0143] [0143]
- JP 3140140 A [0143]
- EP 104143 A [0143]
- US 5041358 A [0143] [0144]
- US 4491628 A [0143] [0144]
- JP 2150848 A [0143]
- JP 2296514 A [0143]
- EP 370693 A [0144]
- EP 233567 A [0144]
- EP 297443 A [0144]
- EP 297442 A [0144]
- US 4933377 A [0144]
- US 3902114 A [0144]
- US 4760013 A [0144]
- US 4734444 A [0144]
- US 2833827 A [0144]
- DE 2904626 [0144]
- DE 3604580 [0144]
- DE 3604581 [0144]
- JP 4328403 B [0146]
- JP 47005303 A [0147]
- JP 48063802 A [0147]
- JP 48063803 A [0147]
- JP 48096575 A [0147]
- JP 49038701 A [0147]
- JP 48013354 A [0147]
- JP 4111222 B [0147]
- JP 459610 B [0147]
- JP 49017481 B [0147]
- US 2797213 A [0147]
- US 3454400 A [0147]
- US 3544323 A [0147]
- US 3573917 A [0147]
- US 3674495 A [0147]
- US 3785825 A [0147]
- GB 1227602 A [0147]
- GB 1251345 A [0147]
- GB 1267005 A [0147]
- GB 1329888 A [0147]
- GB 1330932 A [0147]
- DE 854890 [0147]
- JP 2000087318 A [0149]
- US 4115128 A [0150]
- JP 60088942 A [0150]
- JP 2096755 A [0150]
- JP 62293247 A [0151]
- JP 62251740 A [0153]
- JP 3208514 A [0153]
- JP 59121044 A [0153]

- JP 4013149 A [0153]
- EP 950517 A [0153]
- JP 50036209 A [0156]
- JP 53008128 A [0156]
- JP 53036223 A [0156]
- JP 54074728 A [0156]
- JP 60003626 A [0156]
- JP 61143748 A [0156]
- JP 61151644 A [0156]
- JP 63058440 A [0156]
- JP 55062444 A [0156]
- JP 55077742 A [0156]
- JP 62170950 A [0168]
- JP 54063902 A [0171]
- US 2714066 A [0173]
- US 3181461 A [0173]
- US 3280734 A [0173]
- US 3902734 A [0173]
- JP 3622063 B [0173]
- US 3276868 A [0173]
- US 4153461 A [0173]
- US 4689272 A [0173]
- JP 2013293 B [0186]
- JP 59174842 A [0186]
- JP 61002518 B [0187]
- JP 55028062 A [0187]
- JP 62031859 A [0187]
- JP 61159655 A [0187]

Non-patent literature cited in the description

- Dye Handbook. Society of Synthesis Organic Chemistry, 1970 [0117]
- Latest Pigment Handbook. Japan Pigment Technique Association, 1977 [0122]
- Latest Pigment Applied Technique. CMC Publishing Co., Ltd, 1986 [0122] [0124] [0126]
- Printing Ink Technique. CMC Publishing Co., Ltd, 1984 [0122]
- Nature and Application of Metal Soap. Printing Ink Technique. CMC Publishing Co., Ltd, 1984 [0124]
- S. I. SCHLESINGER. *Photogr. Sci. Eng.*, 1974, vol. 18, 387 [0143]
- T. S. BAL et al. *Polymer*, 1980, vol. 21, 423 [0143]
- D. C. NECKER et al. *Macromolecules*, 1984, vol. 17, 2468 [0143]
- C. S. WEN et al. *Teh, Proc. Conf. Rad. Curing ASIA*, 1988, 478 [0143]
- J. V. CRIVELLO et al. *Macromolecules*, 1977, vol. 10 (6), 1307 [0143] [0144]
- *Chem. & Eng. News*, November 1988, vol. 28, 31 [0143]
- J. V. CRIVELLO et al. *Polymer J.*, 1985, vol. 17, 73 [0144]
- J. V. CRIVELLO et al. *J. Org. Chem.*, 1978, vol. 43, 3055 [0144]
- W. R. WATT et al. *J. Polymer Sci., Polymer Chem. Ed.*, 1984, vol. 22, 1789 [0144]
- J. V. CRIVELLO et al. *Polymer Bull.*, 1985, vol. 14, 279 [0144]
- J. V. CRIVELLO et al. *Macromolecules*, 1981, vol. 14 (5), 1141 [0144]
- J. V. CRIVELLO et al. *J. Polymer Sci., Polymer Chem.*, 1979, vol. 17, 2877 [0144]
- J. V. CRIVELLO et al. *J. Polymer Sci., Polymer Chem.*, 1979, vol. 17, 1047 [0144]
- C. S. WEN et al. *The Proc. Conf. Rad. Curing ASIA*, October 1988, 478 [0144]
- J. COSER. *Light-Sensitive Systems*. John Wiley & Sons. Inc, 339-352 [0146]