(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 2 042 305 A2**

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
01.04.2009 Bulletin 2009/14

(51) Int Cl.:
B41C 1/10 *(2006.01)*

(21) Application number: **08016207.6**

(22) Date of filing: **15.09.2008**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MT NL NO PL PT RO SE SI SK TR
Designated Extension States:
AL BA MK RS

(30) Priority: **28.09.2007 JP 2007255972**

(71) Applicant: **FUJIFILM Corporation**
Minato-ku
Tokyo (JP)

(72) Inventor: **Nagashima, Akira**
Haibara-gun
Shizuoka-ken (JP)

(74) Representative: **HOFFMANN EITLE**
Patent- und Rechtsanwälte
Arabellastraße 4
81925 München (DE)

(54) Planographic printing plate precursor

(57) A planographic printing plate precursor comprises a substrate and a positive recording layer prepared on the substrate, the positive recording layer comprising two kinds of polymer including specific copolymer components and a compound that absorbs light and generates heat, and the solubility thereof in an alkaline developer being improved by light-exposure or heating. A planographic printing plate precursor has a positive recording layer which is a strong film (image area) having excellent chemical resistance and resistance to alkaline developers and from which resistance to alkaline developers can be quickly eliminated by exposure, and that suppresses the occurrence of abrasion during exposure.

Printed by Jouve, 75001 PARIS (FR)

Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to a positive planographic printing plate precursor, the solubility of which can be improved with respect to an aqueous alkaline solution by imparting energy thereto, such as by exposure to light, and, specifically, to a positive planographic printing plate precursor that can directly make a plate, namely, that is capable of so-called "direct plate-making", by scanning with a laser light based on digital signals from a computer or the like.

Description of the Related Art

[0002] In recent years, progress in laser technology has been remarkable, particularly in higher-output and smaller-size solid state and semiconductor lasers having an emission wavelength in the range from the near-infrared to infrared regions. Accordingly, when plate making is performed directly from digital data from a computer or the like, these lasers are extremely useful as an exposure-light source.

[0003] A positive planographic printing plate for use with an infrared laser that uses an infrared laser having an emission in the infrared region as an exposure source is an image-forming material containing, as essential components, a binder resin soluble in an aqueous alkaline solution, and an infrared-absorbent dye or the like that absorbs light and generates heat. When the positive planographic printing plate material for use with an infrared laser is exposed by the infrared laser, the infrared-absorbent dye or the like in the material functions as a solubilization inhibitor which substantially reduces the solubility of the binder resin in a unexposed area (image area) due to the interaction of the infrared-absorbent dye with the binder resin. On the other hand, in the exposed area (non-image area), the infrared-absorbent dye or the like in the material absorbs light and generate heat, lowering the interaction of the infrared-absorbent dye or the like with the binder resin. Accordingly, during development, the exposed area (non-image area) is solubilized in an alkaline developer and removed to form a planographic printing plate.

However, these materials for positive planographic printing plates for use with infrared lasers have been inferior to those for a positive planographic printing plate material for use with ultraviolet light exposure, because the binder resin thereof must have higher solubility in a solvent such as an alkaline developer. Since this kind of resin possesses a low resistance to chemicals such as a plate cleaner used when ink receptivity become worse during printing, the photosensitive composition in the positive planographic printing plate material tends to be eluted when the plate surface is wiped with the cleaner.

[0004] In order to improve the resistance to the plate cleaner, a photosensitive composition using a polymer containing a structural unit having a specific functional group has been proposed (see, for example, U.S. Patent No. 6,475,692 and EP Patent publication No. 1738900), for which improvement in resistance to plate cleaner has been reported. However, in a planographic printing plate precursor having this kind of image forming layer, abrasion tends to occur when irradiation by infrared laser is performed and the setter (the exposure device) can be contaminated by scattered infrared-absorbent dye or the like, thus impairing the functions of optical systems such as lenses or the like.

SUMMARY OF THE INVENTION

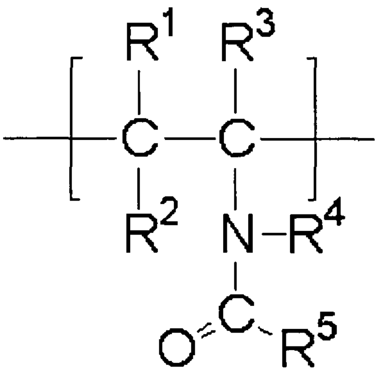
[0005] The present invention provides a planographic printing plate precursor that has a positive recording layer which is a strong film (image area) having excellent chemical resistance and resistance to alkaline developers and from which resistance to alkaline developers can be quickly eliminated by exposure, and that suppresses the occurrence of abrasion during exposure.

In other words, the present invention provides a planographic printing plate precursor having excellent printing durability and chemical resistance and that suppresses the occurrence of abrasion during exposure.

[0006] As a result of intensive research by the present inventors, it was found that the above issue(s) could be resolved by using two kinds of polymer including specific copolymer components.

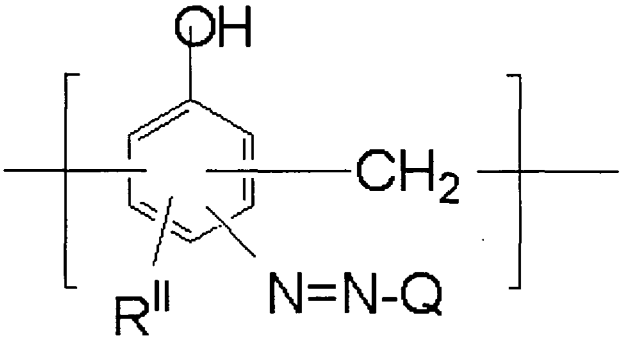
[0007] The present invention provides a planographic printing plate precursor comprising a substrate and a positive recording layer prepared on the substrate, the positive recording layer comprises a polymer (A) including a structural unit represented by the following Formula (I), a polymer (B) including a structural unit represented by the following Formula (II), and a compound (C) that absorbs light and generates heat, and the solubility of the positive recording layer being increased with respect to an alkaline developer by exposure to light or heating.

Formula (I)



In Formula (I), each of R^1, R^2 and R^3 independently represents a hydrogen atom, or 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.

Formula (II)



In Formula (II), R^{II} represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms and Q represents a monovalent substituent group including an aromatic ring structure.

[0008] While the mechanism of the present invention has yet to be fully elucidated, it is presumed to be as follows. In the planographic printing plate precursor of the present invention, specific polymer (A), which is included in the positive recording layer thereof, includes a structural unit represented by Formula (I) and, consequently, a film having excellent solvent resistance and resistance to alkali development can be formed; however, it does not have properties that enable formation of a film that can suppress scattering (abrasion) of a low molecular-weight compound (C) such as a compound that absorbs light and generates heat, when the positive recording layer reaches a high temperature due to exposure (to, for example, infrared irradiation). Further, specific polymer (B), while also effective for obtaining solvent resistance and alkali resistance and having excellent developability due to having a novolac resin skeleton and having a substituent group with excellent alkali solubility in a side chain, exhibits insufficient suppression of abrasion, similarly to specific polymer (A).

As a result of intensive research by the present inventors, the surprising discovery was made that use of both specific polymer (A) and specific polymer (B) together dramatically improved the abrasion suppression effect. While the reason for this is uncertain, it is thought that some kind of interaction is created between the respective polymers, whereby a film is formed that is remarkably more dense than when either of the polymers are used singly and even when localized generation of heat occurs due to infrared laser exposure and the recording layer reaches a high temperature, scattering of a low molecular-weight compound (C) such as a compound that absorbs light and generates heat, in other words, the occurrence of abrasion, is effectively suppressed by the superior film properties.

Consequently, in a planographic printing plate precursor having this kind of positive recording layer, a strong film with excellent resistance to alkali developer and chemical resistance can be maintained in a unexposed area and, in addition, in an infrared laser exposed area, for example, the occurrence of abrasion can be suppressed. Further, as an additional effect, when the interaction is eliminated, the alkali solubility of the specific polymer (B) is manifested and a photosensitive layer in the exposed area is quickly removed and the planographic printing plate precursor is thought to exhibit excellent image forming properties as a result.

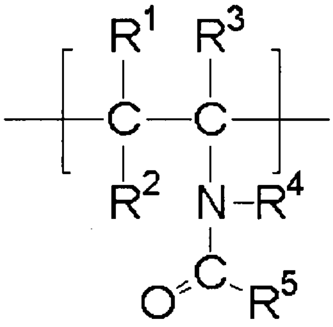
DETAILED DESCRIPTION OF THE INVENTION

[0009] The planographic printing plate precursor of the present invention includes a polymer having a structural unit represented by the following Formula (I) (specific polymer (A)), a polymer having a structural unit represented by the following Formula (II) (specific polymer (B)), and a compound (C) that absorbs light and generates heat, and has a positive recording layer, the solubility of which with respect to an alkaline developer is improved by exposure or heating. In the following, the respective components included in the positive recording layer (hereinafter also referred to simply as the "recording layer") of the planographic printing plate precursor of the present invention are explained in turn.

Specific polymer (A)

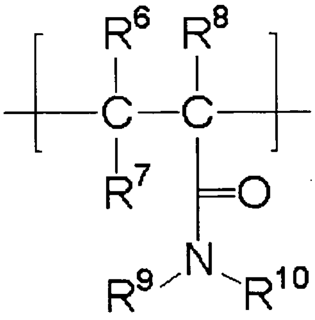
[0010] Specific polymer (A) used in the present invention has a structural unit represented by the following Formula (I).
[0011]

Formula (I)



[0012] In Formula (1), each of R^1, R^2 and R^3 independently represents a hydrogen atom or 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.
Further, the ring structure formed by R^4 and R^5 is preferably a ring structure that has at least 5 carbon atoms.
[0013] The structural unit represented by Formula (I) is more preferably a structural unit derived from vinyl caprolactam. The content of the structural unit represented by Formula (I) in specific polymer (A) is preferably from 3 mol% to 75 mol%, more preferably from 4 mol% to 60 mol% and yet more preferably from 5 mol% to 50 mol%.
[0014] Specific polymer (A) preferably further contains a structural unit represented by the following Formula (III).
[0015]

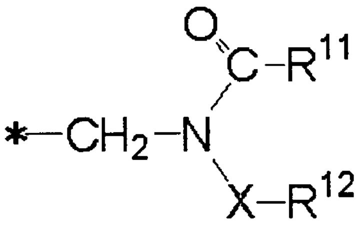
Formula (III)



[0016] In Formula (III), 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 (IV) or Formula (V).

[0017]

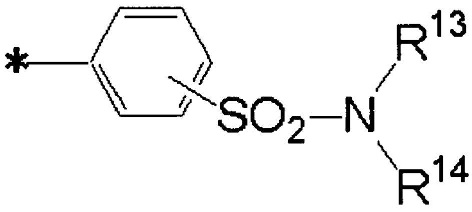
Formula (IV)



[0018] In Formula (IV), the symbol "*" represents a position bonded with the nitrogen atom in Formula (III). X represents -C(=O)- or $-SO_2-$. 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.

[0019]

Formula (V)

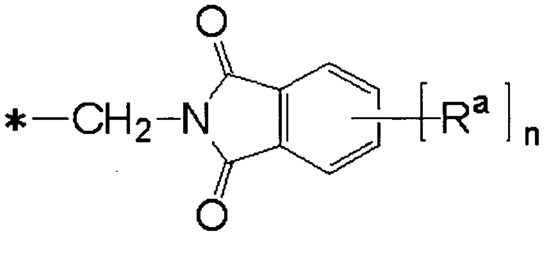


[0020] In Formula (V), the symbol "*" represents a position bonded with the nitrogen atom in Formula (III). Each of R^{13} and R^{14} independently represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted arylalkyl group, or a substituted or unsubstituted heteroaryl group, and R^{13} and R^{14} may be bonded together to form a ring structure.

[0021] In Formula (II), R^{10} is preferably a group represented by the following Formula (VI).

[0022]

Formula (VI)



[0023] In Formula (VI), the symbol "*" represents a position bonded with the nitrogen atom in Formula (III). n represents 0, 1, 2, 3 or 4. R^a represents a hydrogen atom, a halogen atom, -CN, $-NO_2$, 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, $-O-R^b$, $-S-R^c$, $-SO_3-R^d$, $-CO-O-R^e$, $-O-CO-R^f$, $-NR^gR^h$, $-NR^i-CO-R^j$, $-NR^k-SO_2-R^1$, $-CO-R^m$, $-CO-NR^nR^o$, $-SO_2-NR^pR^q$, 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.

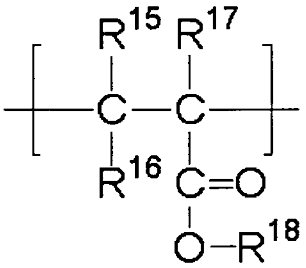
[0024] The structural unit represented by Formula (III) is more preferably a structural unit derived from N-acroyl aminomethyl phthalimide or N-methacroyl aminomethyl phthalimide.

[0025] The content of the structural unit represented by Formula (III) in specific polymer (A) is preferably from 5 mol% to 95 mol%, more preferably from 10 mol% to 85 mol% and yet more preferably from 20 mol% to 75 mol%.

[0026] Specific polymer (A) preferably further contains a structural unit represented by the following Formula (VII).

[0027]

Formula (VII)



[0028] In Formula (VII), each of R^{15}, R^{16} and R^{17} independently represents a hydrogen atom or a substituted or unsubstituted alkyl group. R^{18} represents a hydrogen atom, a positively-charged metal ion, 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.

[0029] The structural unit represented by Formula (VII) is more preferably a structural unit derived from (meth)acrylic acid, or a salt or alkyl ester thereof.

[0030] The content of the structural unit represented by Formula (VII) in specific polymer (A) is preferably from 2 mol% to 70 mol%, more preferably from 4 mol% to 60 mol% and yet more preferably from 6 mol% to 50 mol%.

[0031] A favorable embodiment of specific polymer (A) is a polymer containing a combination of a structural unit represented by Formula (I), a structural unit represented by Formula (III) and a structural unit represented by Formula (VII). With regard to the three types of structural unit, a polymer containing the structural unit represented by Formula (I) in an amount in a range of from 5 mol% to 50 mol%, the structural unit represented by Formula (III) in a range of from 20 mol% to 75 mol% and the structural unit represented by Formula (VII) in a range of from 3 mol% to 40 mol% is preferable as this kind of specific polymer (A).

[0032] A more favorable embodiment of specific polymer (A) is a polymer containing a combination of structural units respectively derived from N-vinyl caprolactam, N-(meth)acroyl aminomethyl phthalimide and (meth)acrylic acid. A polymer containing the structural unit derived from N-vinyl caprolactam in a range of from 5 mol% to 50 mol% (more preferably from 10 mol% to 40 mol%), the structural unit derived from N-(meth)acroyl aminomethyl phthalimide in a range of form 20 mol% to 75 mol% (more preferably from 30 mol% to 70 mol%), and the structural unit derived from (meth)acrylic acid in a range of from 3 mol% to 35 mol% (more preferably from 5 mol% to 30 mol%) is preferable as this kind of specific polymer (A).

[0033] In the present invention, the specific polymer (A) preferably has a weight-average molecular weight of from 3000 to 300000 and more preferably of from 30000 to 100000.

The weight-average molecular weight can be measured by a gel permeation chromatography method using polystyrene as a reference sample.

[0034] In the present invention, one kind of the specific polymer (A) may be used singly or two or more kinds thereof may be used in a suitable mixture.

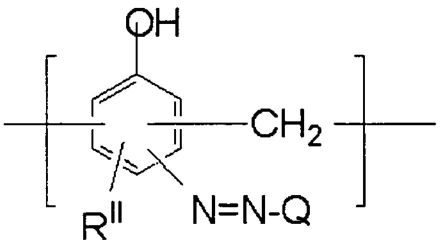
In the present invention, the content of the specific polymer (A) is preferably in the range of from 5 mass% to 80 mass% with respect to the total solid content of the composition forming the positive recording layer, and more preferably from 20 mass% to 70 mass%, in view of developability and suppressing the occurrence of abrasion.

Specific polymer (B)

[0035] Specific polymer (B) used in the present invention has a structural unit represented by the following Formula (II).

[0036]

Formula (II)



[0037] In Formula (II), R^{II} represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms and Q represents a monovalent substituent group including an aromatic ring structure.

Here, R^{II} is preferably a hydrogen atom or an alkyl group having a carbon number of 1to 3, more preferably a hydrogen atom, a methyl group or an ethyl group, and yet more preferably a hydrogen atom.

The substitution position when R^{II} represents an alkyl group is not particularly limited but is preferably the third or fourth position.

[0038] In the present invention, specific polymer (B) is characterized in that, in a resin including a phenol structure such as a novolac resin, a substituent group -N=N-Q is covalently bonded to a carbon atom of a phenyl group.

As a result of the specific polymer (B) having the above structure, the introduction of a bulky organic substituent group achieves improved resistance to alkali development and resistance to cleaner in an unexposed area and, in an exposed area, when the interaction that manifests resistance to alkali development is eliminated, the functions of alkali soluble groups such as phenolic hydroxyl groups in the novolac resin are rapidly manifested and excellent solubility with respect to alkali developer is manifested, enabling image formation at high sensitivity.

[0039] In the structural unit of specific polymer (B) represented by Formula (II), Q represents a monovalent substituent group including an aromatic ring structure. While there needs to be at least one aromatic ring in the structure of the substituent group, the number of aromatic rings is preferably from 1 to 3 and is more preferably 1.

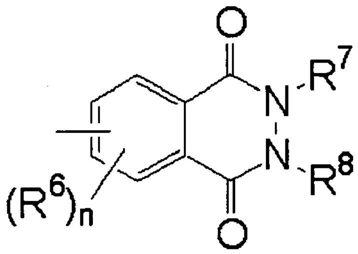
The aromatic ring may have a single ring structure, a multiple ring structure or a condensed ring structure and, in addition, may be a complex aromatic ring including a heteroatom such as a nitrogen atom, oxygen atom or sulfur atom inside the ring structure. Among these, a complex aromatic ring and a single ring structure are preferable.

Specific examples of the aromatic ring that may be introduced as Q include benzene rings and pyridine rings, and benzene rings and the like are preferable.

Among these, Q is preferably a substituent group having a structure represented by the following Formula (II-1).

[0040]

Formula (II-1)



[0041] In Formula (II-1), n represents an integer of 0, 1, 2 or 3, preferably 0. R^6 represents a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, a cycloalkyl group, a heterocyclic group, an aryl group, a heteroaryl group, an aralkyl group, a heteroaralkyl group, $-SO_2-NH-R^9$, $-NH-SO_2-R^{11}-$, $-CO-NR^9-R^{10}$, $-NR^9-CO-R^{11}$, $-O-CO-R^{11}$, $-CO-O-R^9$, $-CO-R^9$, $-SO_3-R^9$, $-SO_2-R^9$, -SO-R", $-P(=O)(-O-R^9)(-O-R^{10})$, $-NR^9-R^{10}$, $-O-R^9$, $-S-R^9$, -CN, $-NO_2$, a halogen atom, -N-phthalimidyl, -M-N-phthalimidyl or $-M-R^9$. Here, M represents a divalent linking group having a carbon number of 1 to 8, each of R^9 and R^{10} independently represents a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, a cycloalkyl group, a heterocyclic group, an aryl group, a heteroaryl group, an aralkyl group, or a heteroaralkyl group. R^{11} represents an alkyl group, an alkenyl group, an alkynyl group, a cycloalkyl group, a heterocyclic group, an aryl group, a heteroaryl group, an aralkyl group, or a heteroaralkyl group. When there are a plurality of groups represented by R^6, respective groups represented by R^6 may be the same as or different from each other, and may be bonded together to form a ring structure.

[0042] R^6 is preferably a hydrogen atom or a methyl group and is more preferably a hydrogen atom.
Further, when any of the above R^6 to R^{11} represents a substituent group other than a hydrogen atom, these substituent groups may have a further substituent group.
For example, in the case of an alkyl group, the alkyl group may be nonsubstituted or have a substitutent group. Examples of substituent groups that may be introduced in this respect include alkoxy groups such as a methoxy group and halogen atoms such as a chlorine atom.

[0043] Each of R^7 and R^8 independently represents a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, a cycloalkyl group, a heterocyclic group, an aryl group, a heteroaryl group, an aralkyl group, or a heteroaralkyl group, and preferably a hydrogen atom or an alkyl group. A combination of two or more groups selected from the groups represented by R^6, R^9, R^{10} or R^{11} may be bonded together to form a ring structure. The group represented by R^7 and the group represented by R^8 may be bonded together to form a ring structure.

[0044] A more favorable embodiment of specific polymer (B) is a polymer containing a structural unit in which R^{II} and Q in Formula (II) respectively represent a hydrogen atom and a substituent group having a structure represented by Formula (II-1), and each of R^6, R^7 and R^8 in Formula (II-1) represents a hydrogen atom.

[0045] In the present invention, the specific polymer (B) preferably has a number-average molecular weight (Mn) of from 300 to 50000, more preferably of from 500 to 5000 and yet more preferably from 500 to 2500, and preferably has a weight-average molecular weight (Mw) of from 400 to 100000, more preferably of from 800 to 20000 and yet more preferably from 800 to 12000.
The number-average molecular weight and the weight-average molecular weight can be measured by a gel permeation chromatography method using polystyrene as a reference sample.

[0046] In the present invention, one kind of the specific polymer (B) may be used singly or two or more kinds thereof may be used in a suitable mixture.
In the present invention, the content of the specific polymer (B) is preferably in the range of from 5 mass% to 80 mass% with respect to the total solid content of the composition forming the positive recording layer, and more preferably from 20 mass% to 60 mass%, in view of developability and suppressing the occurrence of abrasion.

[0047] The content ratio of specific polymer (A) to specific polymer (B) is preferably within the range of from 30 to 70 by mass ratio to 70 to 30 by mass ratio.

Compound (C) that absorbs light and generates heat

[0048] The recording layer of the present invention needs to contain a compound (C) that absorbs light and generates heat (hereinafter, it may be referred to as "photo-thermal conversion agent") in addition to specific polymer (A) and specific polymer (B).
The photo-thermal conversion agent that can be used in the present invention includes compound that generates heat by exposure to light used for image formation from a light source. it is preferable to use an infrared light absorbent which has a light absorption region in an infrared region of 700 nm or more, preferably from 750 nm to 1200 nm, and exhibits a photo-thermal conversion property by the light within the above range of the wavelengths since images are formed by exposure to infrared laser light in the planographic printing plate precursor of the present invention. Specifically, various dyes or pigments that absorb the light in the above wavelength range to generate heat can be used.

[0049] 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, oxonol dyes, diimonium dyes, aminium dyes, and croconium dyes.

[0050] 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-A Nos. 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; squalirium dyes described in JP-A No. 58-112792; and cyanine dyes described in GB Patent No. 434,875.

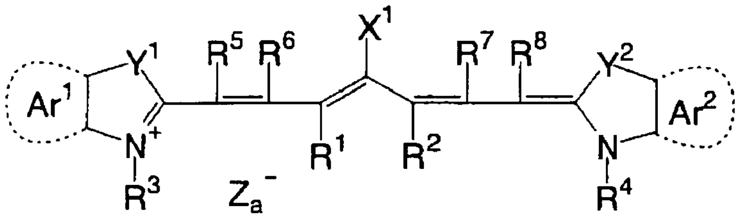
[0051] Other preferable examples of the dye include near infrared absorbing sensitizers described in U.S. Patent No. 5,156,938; substituted arylbenzo(thio)pyrylium salts described in U.S. Patent No. 3,881,924; trimethinethiapyrylium salts described in JP-A No. 57-142645 (U.S. Patent No. 4,327,169); pyrylium type compounds described in JP-A Nos. 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.

[0052] Additional preferable examples of the dye include near infrared absorbing dyes represented by formulae (I) and (II) as described in U.S. Patent No. 4,756,993.

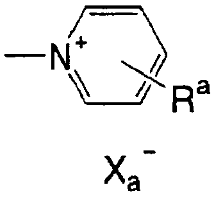
[0053] Among these dyes, cyanine dyes, phthalocyanine dyes, oxonol dyes, squarylium dyes, pyrylium salts, thiopyrylium dyes, and nickel thiolate complexes are particularly preferable. Dyes represented by the following Formulae (a) to (e) are also preferable since such dyes are excellent in photo-thermal conversion efficiency. The cyanine dyes represented by the following Formula (a) are most preferable because: when the dyes are used for the positive recording layer of planographic printing plate precursor of the present invention, they manifest a high degree of interaction with an alkali-soluble resin; and the dyes are excellent in terms of stability and economy.

[0054]

Formula (a)



[0055] In Formula (a), X^1 represents a hydrogen atom, a halogen atom, -NPh_2, X^2-L^1 (wherein X^2 represents an oxygen atom or a sulfur atom, L^1 represents a hydrocarbon group having 1 to 12 carbon atoms, an aromatic cyclic group having a heteroatom, or a hydrocarbon group containing a heteroatom and having 1 to 12 carbon atoms, and the heteroatom referred to herein is N, S, O, a halogen atom, or Se), or a group represented by the following:



wherein Xa^- is equivalent to Za^- described below, and R^a represents a substituent selected from a hydrogen atom, an alkyl group, an aryl group, a substituted or unsubstituted amino group, or a halogen atom.

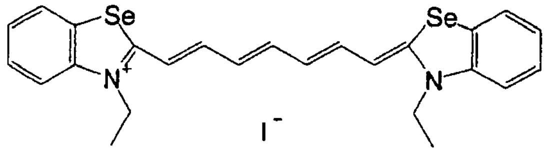
[0056] In Formula (a), each of R^1 and R^2 independently represents a hydrocarbon group having 1 to 12 carbon atoms, and from a viewpoint of the storage stability of the coating solution for a recording layer, each of R^1 and R^2 independently represents a hydrocarbon group preferably having 2 or more carbon atoms, and more preferably R^1 and R^2 are bonded together to form a 5-membered or 6-membered ring.

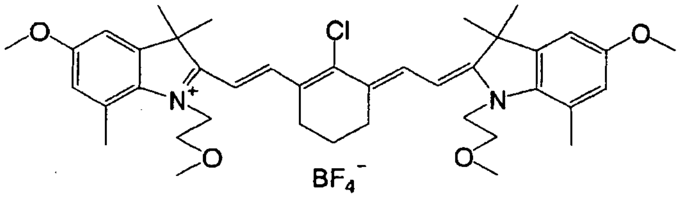
[0057] Ar^1 and Ar^2 may be the same as or different from each other, and respectively represent an aromatic hydrocarbon group which may have a substituent. Preferable examples of the aromatic hydrocarbon group include benzene and naphthalene rings. Preferable examples of the substituent include hydrocarbon groups having 12 or fewer carbon atoms, halogen atoms, and alkoxy groups having 12 or fewer carbon atoms. Y^1 and Y^2 may be the same as or different from each other, and respectively represent a sulfur atom, or a dialkylmethylene group having 12 or fewer carbon atoms. R^3 and R^4 may be the same as or different from each other, and respectively represent a hydrocarbon group having 20 or fewer carbon atoms which may have a substituent. Preferable examples of the substituent include alkoxy groups having 12 or fewer carbon atoms, a carboxyl group, and a sulfo group. R^5, R^6, R^7 and R^8 may be the same as or different from each other, and respectively represent a hydrogen atom or a hydrocarbon group having 12 or fewer carbon atoms. From a viewpoint of availability of raw materials, each of R^5, R^6, R^7 and R^8 preferably represents a hydrogen atom. Za^-

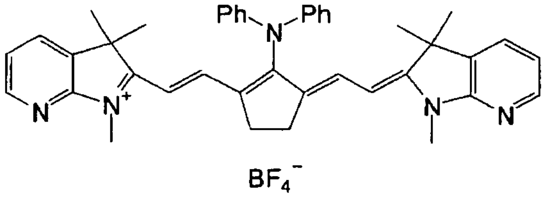
represents a counter anion. When the cyanine dye represented by Formula (a) has an anionic substituent in the structure thereof and does not require charge neutralization, Za$^-$ is unnecessary. From a viewpoint of the storage stability of the coating solution for the recording layer, Za$^-$ is preferably a halogen ion, a perchlorate ion, tetrafluroborate ion, hexafluorophosphate ion, or sulfonate ion, and is more preferably a perchlorate ion, hexafluorophosphate ion, or aryl sulfonate ion.

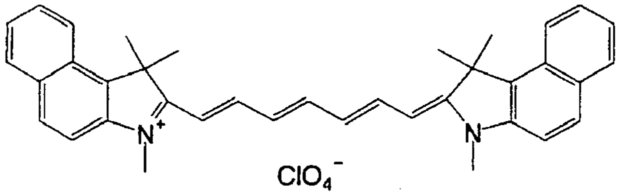
[0058] Preferable examples of the cyanine dye represented by Formula (a) that can be used in the present invention include dyes in JP-A No. 2001-133969 (paragraphs [0017] to [0019]), JP-A No. 2002-40638 (paragraphs [0012] to [0038]), and JP-A No. 2002-23360 (paragraphs [0012] to [0023]), as well as dyes shown below.

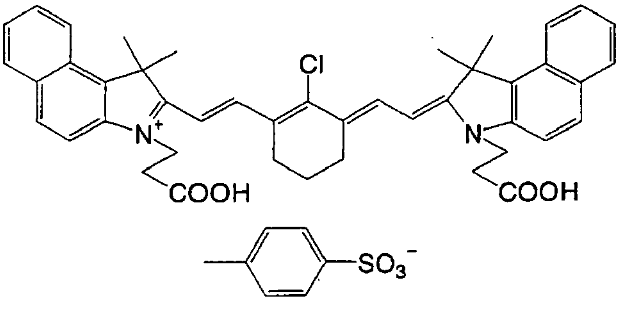
[0059]



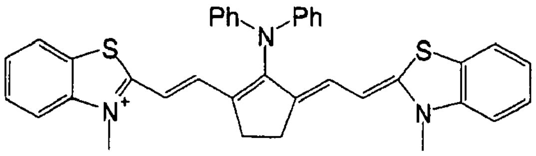




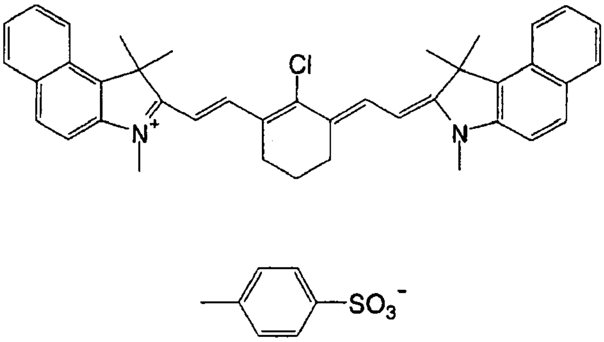


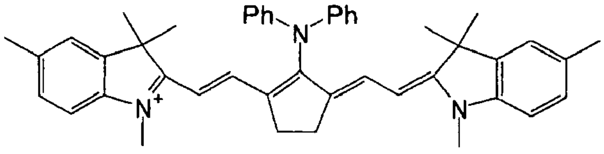


[0060]

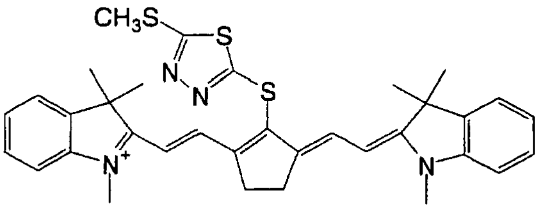


ClO_4^-

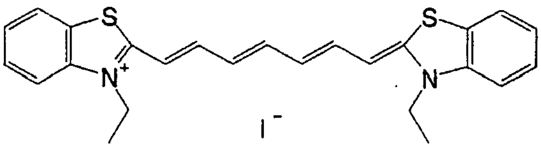




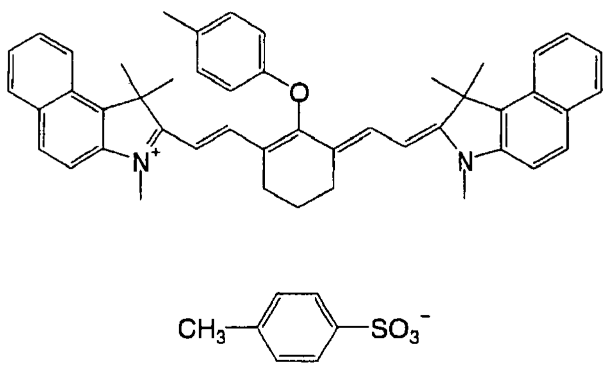
BF_4^-

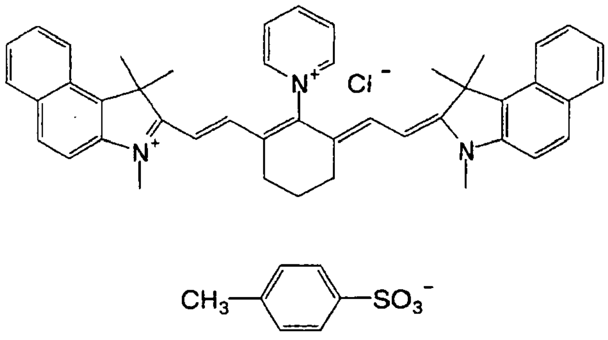


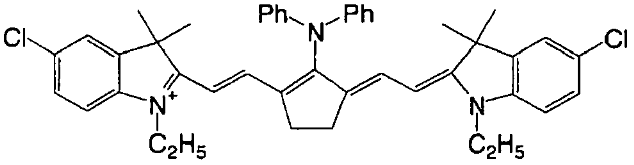
ClO_4^-



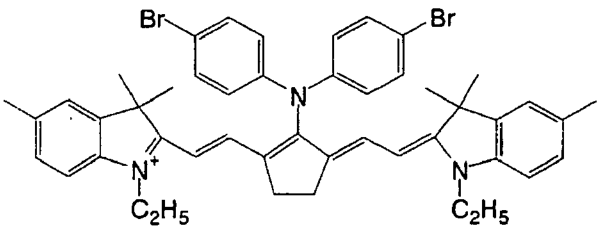
[0061]







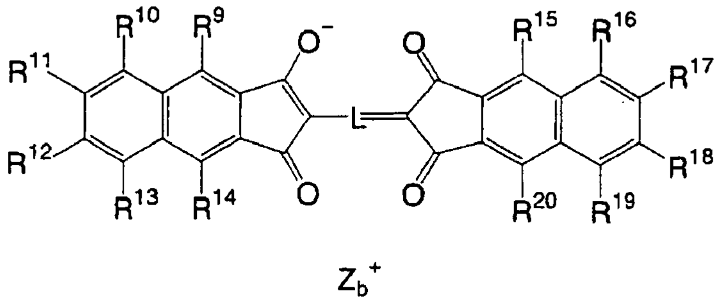
$CF_3SO_3^-$



ClO_4^-

[0062]

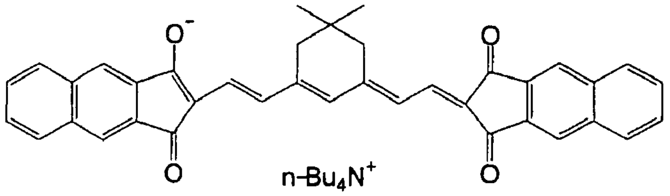
Formula (b)

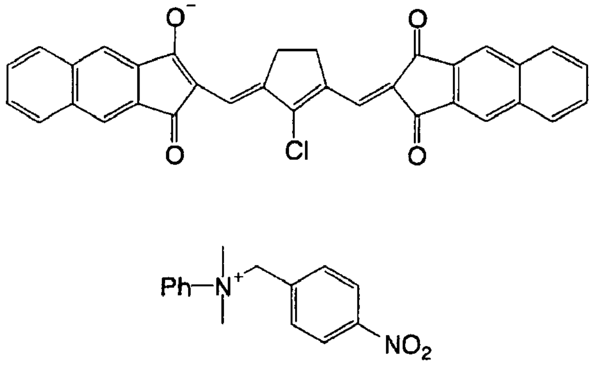


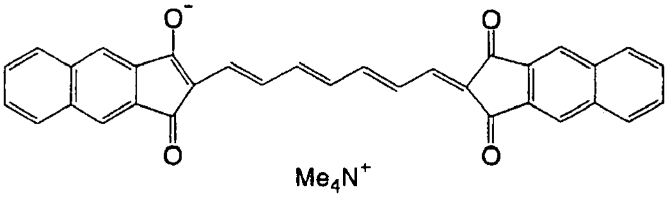
[0063] In Formula (b), L represents a methine chain having 7 or more conjugated carbon atoms, and the methine chain may have one or more substituent. The substituents may be bonded together to form a ring structure. Zb^+ represents a counter cation. Preferable examples of the counter cation include ammonium ions, iodonium ions, sulfonium ions, phosphonium ions and pyridinium ions, and alkali metal cations (such as Ni^+, K^+ and Li^+). R^9 to R^{14} and R^{15} to R^{20} each independently represent a hydrogen atom or a halogen atom; a substituent selected from a cyano group, an alkyl group, an aryl group, an alkenyl group, an alkynyl group, a carbonyl group, a thio group, a sulfonyl group, a sulfinyl group, an oxy group, or an amino group; or a combination of two or three thereof. Two or three of R^9 to R^{14} and, further, two or three of R^{15} to R^{20} may be bonded together to form a ring structure. From a viewpoint of availability and effects, among dyes represented by the above Formula (b), a dye wherein L represents a methine chain having 7 conjugated carbon atoms, and each of R^9 to R^{14} and R^{15} to R^{20} represents a hydrogen atom, is preferable.

[0064] Preferable examples of the dye represented by Formula (b) that can be used in the present invention are shown below.

[0065]

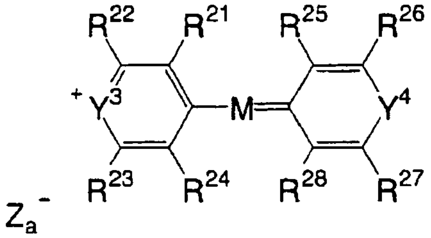






[0066]

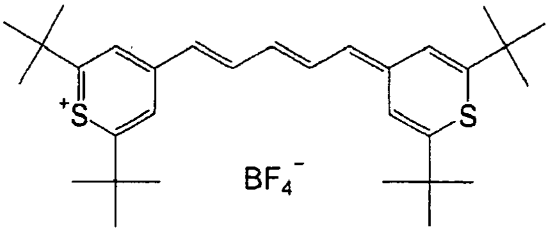
Formula (c)

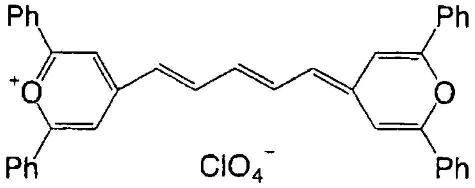


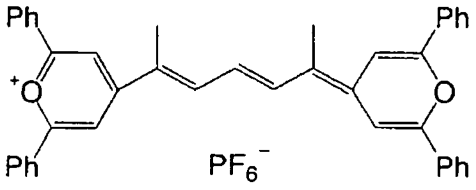
[0067] In Formula (c), each of Y^3 and Y^4 independently represents an oxygen atom, a sulfur atom, a selenium atom or a tellurium atom. M represents a methine chain having 5 or more conjugated carbon atoms. R^{21} to R^{24} and R^{25} to R^{28} may be the same as or different from each other, and each represents a hydrogen atom, a halogen atom, a cyano group, an alkyl group, an aryl group, an alkenyl group, an alkynyl group, a carbonyl group, a thio group, a sulfonyl group, a sulfinyl group, an oxy group, or an amino group. Za^- represents a counter anion, and is equivalent to Za^- in Formula (a).

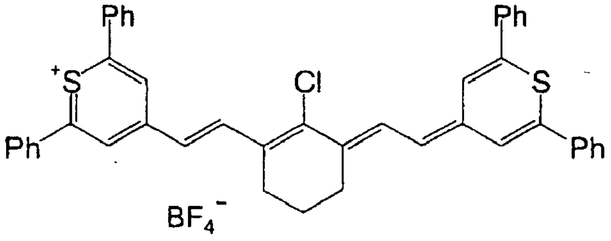
[0068] Preferable examples of the dye represented by Formula (c) that can be used in the present invention are shown below.

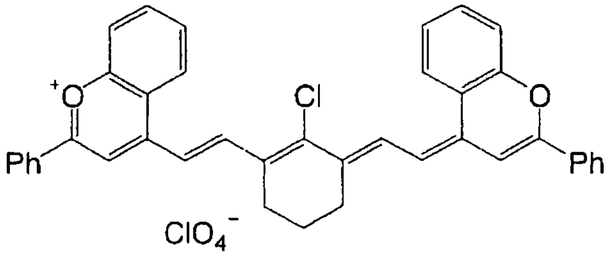
[0069]





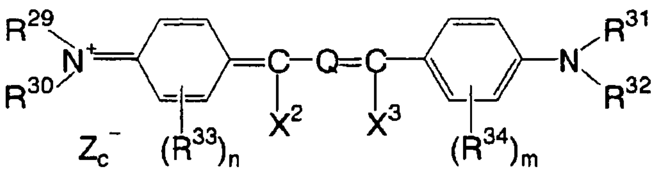






[0070]

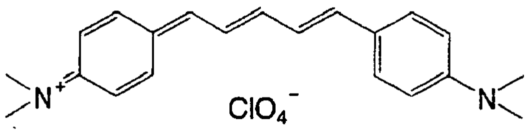
Formula (d)

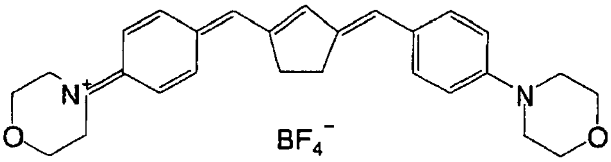


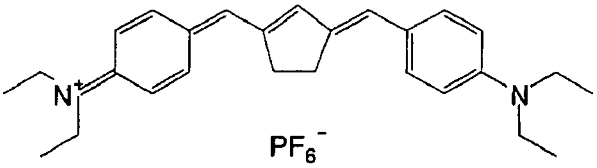
[0071] In Formula (d), R^{29} to R^{32} each independently represent a hydrogen atom, an alkyl group or an aryl group. Each of R^{33} and R^{34} independently represents an alkyl group, a substituted oxy group, or a halogen atom. Each of n and m independently represents an integer of from 0 to 4. R^{29} and R^{30}, or R^{31} and R^{32}, may be bonded together to form a ring structure, or R^{29} and/or R^{30} may be bonded to R^{33} to form a ring structure and R^{31} and/or R^{32} may be bonded to R^{34} to form a ring structure. When there are a plurality of groups represented by R^{33} or R^{34}, respective groups represented by R^{33} may be bonded together to form a ring structure, and respective groups represented by R^{34} may be bonded together to form a ring structure. X^2 and X^3 each independently represent a hydrogen atom, an alkyl group or an aryl group, and at least one of X^2 and X^3 represents a hydrogen atom or an alkyl group. Q represents a trimethine group or a pentamethine group which may have a substituent, and may be combined with a bivalent organic group to form a cyclic structure. Zc^- represents a counter anion and is equivalent to Za^- in Formula (a).

[0072] Preferable examples of the dye represented by Formula (d) that can be used in the present invention are shown below.

[0073]

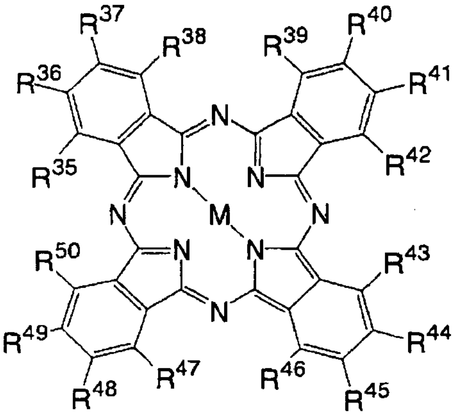






[0074]

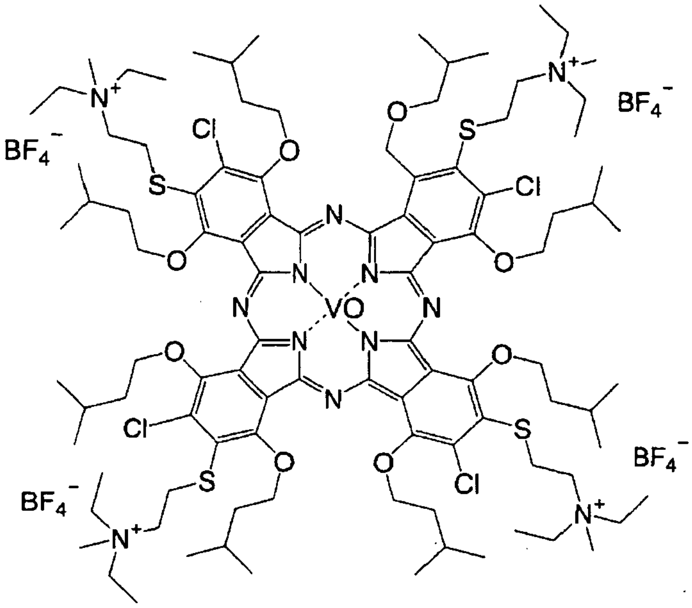
Formula (e)

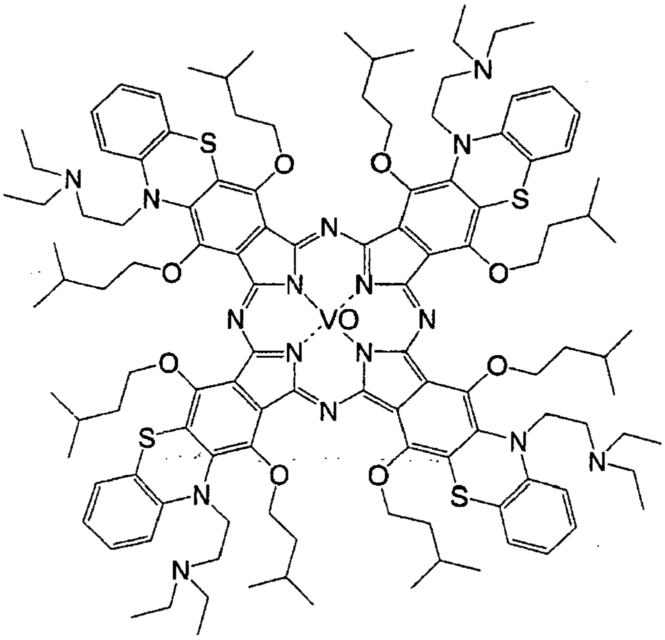


[0075] In Formula (e), R^{35} to R^{50} each independently represent a hydrogen atom, a halogen atom, a cyano group, an alkyl group, an aryl group, an alkenyl group, an alkynyl group, a hydroxyl group, a carbonyl group, a thio group, a sulfonyl group, a sulfinyl group, an oxy group, an amino group, or an onium salt structure, and each of which may have a substituent. M represents two hydrogen atoms, a metal atom, a halo metal group, or an oxy metal group. Examples of the metal include atoms in IA, IIA, IIIB and IVB groups in the periodic table, transition metals in the first, second and third periods therein, and lanthanoid elements. Among these examples, copper, magnesium, iron, zinc, cobalt, aluminum, titanium, and vanadium are preferable.

[0076] Preferable examples of the dye represented by Formula (e) that can be used in the present invention are shown below.

[0077]





[0078] As the above pigment, 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) can be used.

[0079] 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.

[0080] These pigments may be used with or without surface treatment. Examples of 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" (by Saiwai Shobo), "Printing Ink Technique" (by CMC Publishing Co., Ltd. in 1984), and "Latest Pigment Applied Technique" (by CMC Publishing Co., Ltd. in 1986).

[0081] From a viewpoint of stability of a dispersed particle in a coating solution and uniformity of a recording layer, a particle diameter of pigments is preferably in a range of from 0.01 μm to 10 μm, more preferably in a range of from 0.05 μm to 1 μm, and particularly preferably in a range of from 0.1 μm to 1 μm.

[0082] As the method for dispersing the pigment, a known technique used for producing ink or toner can be used. Examples of a dispersing machine that can be used, 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).

[0083] In view of the balance between the sensitivity, uniformity and durability of the film to be formed, the pigment or dye (photo-thermal conversion agent) is included in the recording layer in an amount of from 0.01 mass % to 50 mass% with respect to the total solid content of the composition forming the recording layer, and preferably of from 0.1 mass % to 10 mass%. The dye is particularly preferably included in an amount of from 0.5 mass% to 10 mass%, and the pigment is particularly preferably included in an amount of from 0.1 mass% to 10 mass%, relative to the total solid content of the recording layer.

Other components

[0084] In the recording layer of the planographic printing plate precursor according to the present invention, various compounds can be used as necessary in combination with the essential components (specific polymer (A), specific polymer (B) and compound (C) that absorbs light and generates heat), as long as the effects of the present invention are not adversely affected in any way.

[0085] For example, resins other than the specific polymer (A) and specific polymer (B), which are soluble in an aqueous alkaline solution, can be incorporated into the recording layer as required. In this case, there is no restriction as to the other alkali-soluble resins, but general-purpose novolac resins are preferred.

[0086] Example of the novolac resins include, for example, phenol/formaldehyde resin, m-cresol/formaldehyde resin, p-cresol/formaldehyde resin, m-/p-mixed cresol/formaldehyde resin, phenol/cresol (may be any of m-, p-, o-, m-/p-mixture, m-/o-mixture, or o-/p-mixture) mixed formaldehyde resin. They may be used singly or two or more kinds thereof may be used in combination.

[0087] Among the novolac resins, those having a weight-average molecular weight of 1500 or more and a number-average molecular weight of 300 or more are preferred. More preferred are those having a weight-average molecular weight of from 3,000 to 300,000 and a number-average molecular weight of from 500 to 250,000 with a degree of dispersion (weight-average molecular weight / number-average molecular weight) of from 1.1 to 10.

[0088] Examples of preferred alkali-soluble resins that can be used in combination with the resins of the present invention include polymers which have, at the main chain and/or a side chain thereof, an acidic group selected from the following (1) to (6).

(1) Phenol group (-Ar-OH)
(2) Sulfonamide group ($-SO_2NH-R$)
(3) Substituted sulfonamide acid groups (hereinafter, referred to as active imide group; $-SO_2NHCOR$, $-SO_2NHSO_2R$, $-CONHSO_2R$)
(4) Carboxylic acid group ($-CO_2H$)
(5) Sulfonic acid group ($-SO_3H$)
(6) Phosphoric acid group ($-OPO_3H_2$)

In the above (1) to (6), Ar represents a bivalent aryl linking group which may have a substituent. R represents a hydrogen atom or a hydrocarbon group which may have a substituent.

[0089] Among these alkali-soluble resins having an acidic group selected from the above (1) to (6), alkali-soluble resins having (1) a phenol group, (2) a sulfonamide group and (3) an active imide group are preferable. In particular, alkali-soluble resins having (1) a phenol group and (2) a sulfonamide group are most preferable from a viewpoint of sufficient solubility in an alkaline developer, developing latitude, and film strength.

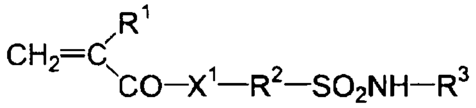
[0090] Examples of the alkali-soluble resins having an acidic group selected from the above items (1) to (6) are shown in the following.

Examples of the alkali-soluble resins having a phenol group in the item (1) include the novolac resins 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. Further, copolymers obtained by copolymerization of compounds having a phenol group at the main chain may be included. Alternatively, copolymers obtained by copolymerization of compounds having a phenol group at the side chain may be used.

[0091] Examples of the compounds having a phenol group include acrylamide, methacrylamide, acrylic acid ester, methacrylic acid ester, hydroxystyrene and the like.

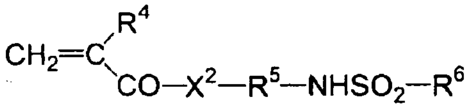
[0092] Examples of the alkali-soluble resins having a sulfonamide group in the item (2) include a polymer having, as the main component, a minimum structural unit derived from a compound having a sulfonamide group. Examples of such compounds include those having in the molecule thereof one or more sulfonamide group in which at least one hydrogen atom is bonded to the nitrogen atom thereof, and one or more unsaturated groups which can be polymerized with the sulfonamide group(s). Among them, a low molecular-weight compound having in molecules thereof an acryloyl group, an allyl group, or a vinyloxy group or a substituted or monosubstituted aminosulfonyl group, or a substituted sulfonylimino group is preferable. Examples thereof include the compounds represented by any one of the following Formulae (i) to (v).

[0093]



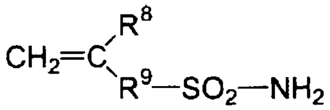
$$CH_2=C(R^1)-CO-X^1-R^2-SO_2NH-R^3$$

Formula (i)



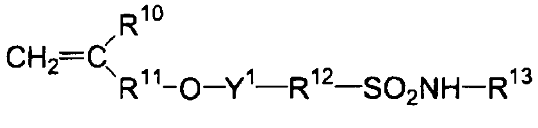
$$CH_2=C(R^4)-CO-X^2-R^5-NHSO_2-R^6$$

Formula (ii)



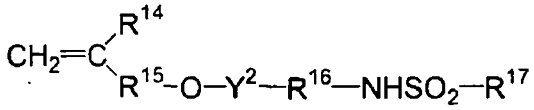
$$CH_2=C(R^8)-R^9-SO_2-NH_2$$

Formula (iii)



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

Formula (iv)



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

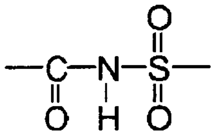
Formula (v)

[0094] In Formulae (i) to (v), each of X^1 and X^2 independently represents -O-or $-NR^7-$. Each of R^1 and R^4 independently represents a hydrogen atom or $-CH_3$. Each of R^2, R^5, R^9, R^{12} and R^{16} independently represents an alkylene group which has 1 to 12 carbon atoms and may have a substituent. Each of R^3, R^7 and R^{13} independently represents a hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group or an aralkyl group which has 1 to 12 carbon atoms and may have a substituent. Each of R^6 and R^{17} independently represents an alkyl group, a cycloalkyl group, an aryl group or aralkyl group which has 1 to 12 carbon atoms and may have a substituent. Each of R^8, R^{10} and R^{14} independently represents a hydrogen atom or $-CH_3$. Each of R^{11} and R^{15} independently represents a single bond, or an alkylene group, a cycloalkylene group, an arylene group or an aralkylene group which has 1 to 12 carbon atoms and may have a substituent. Each of Y^1 and Y^2 independently represents a single bond or -CO-.

[0095] Among the compounds represented by Formulae (i) to (v), m-aminosulfonylphenyl methacrylate, N-(p-aminosulfonylphenyl)methacrylamide and N-(p-aminosulfonylphenyl)acrylamide are preferably used for the planographic printing plate precursor of the present invention.

[0096] Examples of the alkali-soluble resins having an active imide group in the item (3) include a polymer having, as the main component, a minimum structural unit derived from a compound having an active imide group. Examples of such compounds include those having in the molecule thereof one or more active imide groups represented by the following structural formula and one or more unsaturated groups which can be polymerized with the active imide group(s).

[0097]



$$-C(=O)-N(H)-S(=O)_2-$$

[0098] Specifically, N-(p-toluenesulfonyl)methacrylamide, N-(p-toluenesulfonyl)acrylamide and the like can be preferably used.

[0099] Examples of the alkali-soluble resins having a carboxylic acid group in the item (4) include a polymer having, as the main component, a minimum structural unit derived from a compound having in the molecule thereof one or more carboxylic acid groups and one or more unsaturated groups which can be polymerized with the carboxylic acid group(s).
Examples of the alkali-soluble resins having a sulfonic acid group in the item (5) include a polymer having, as the main component, a minimum structural unit derived from a compound having in the molecule thereof one or more sulfonic acid groups and one or more unsaturated groups which can be polymerized with the sulfonic acid group(s).
Examples of the alkali-soluble resins having a phosphoric acid group in the item (6) include a polymer having, as the main component, a minimum structural unit derived from a compound having in the molecule thereof one or more phosphoric acid group and one or more unsaturated groups which can be polymerized with the phosphoric acid group(s).

[0100] The minimum structural unit having at least one acidic group selected from (1) to (6) is not necessarily limited to one particular unit, but a copolymer obtained by copolymerizing two or more types of minimum structural units having the same acidic group, or by copolymerizing two or more types of minimum structural units having different acidic groups can be used.

[0101] The above copolymer preferably contains the compound having the acidic group selected from (1) to (6) to be copolymerized in an amount of 10 mol% or more, and more preferably in an amount of 20 mol% or more. When the amount is 10 mol% or less, the development latitude cannot be improved sufficiently.

[0102] Examples of monomer components which are copolymerized with the above compounds having a phenolic hydroxyl group, a sulfonamide group, or an active imide group include one or more monomers selected from (meth) acrylic acid esters; alkyl acrylates; alkyl methacrylates; acrylamide or methacrylamide; vinyl ethers; vinyl esters; styrenes; vinyl ketones; olefins; n-vinylpyrrolidone, acrylonitrile and methacrylonitrile; unsaturated imides; unsaturated carboxylic acid; and the like.

[0103] As the alkali-soluble resins of the present invention, the homopolymers or copolymers of the above-mentioned polymerizable monomers having a phenolic hydroxyl group or an activated imide group are preferable, and the homopolymers or copolymers of the polymerizable monomers having a sulfonamide group such as m-aminosulfonylphenyl methacrylate, N-(p-aminosulfonylphenyl) methacrylamide, N-(p-aminosulfonylphenyl) acrylamide, or the like are especially preferable. Further, those with a weight-average molecular weight of 2,000 or more and a number-average molecular weight of 500 or more are preferable, and those with a weight-average molecular weight of from 5,000 to 300,000 and a number-average molecular weight of from 800 to 250,000 and a degree of dispersion (weight-average molecular weight/number-average molecular weight) of from 1.1 to 10 are more preferable. Further, when the alkali-soluble resin in the present invention is a resin such as a phenolformaldehyde resin or a cresol aldehyde resin, the weight-average molecular weight thereof is preferably from 500 to 20,000 and the number-average molecular weight thereof is preferably from 200 to 10,000.

[0104] One kind of these alkali-soluble resins may be used singly or two or more kinds thereof may be used in combination and, with respect to the total solid content of the composition forming the recording layer, are included in the recording layer in an amount of from 5 mass% to 70 mass%, preferably from 5 mass% to 60 mass% and particularly preferably from 10 mass% to 40 mass%. The amount of alkali-soluble resin added is preferably within this range since an appropriate addition amount of the specific polymer (A), which is an essential component of the present invention, can be maintained and the effects of the present invention can be sufficiently exhibited thereby and, in addition, when used as the recording layer of the planographic printing plate precursor, the effect of improved durability of the recording layer can also be achieved.

[0105] Further, for adjusting the solubility of the recording layer, it is preferable to add a so-called solubilization inhibitor that improves the function of inhibiting solubility of the aqueous alkaline polymer (alkali-soluble resin) in the developer. Examples of the solubilization inhibitor include onium salts, aromatic sulfone compounds, aromatic sulfonate ester compounds, and polyfunctional amine compounds. Among these, in order to improve the solubility inhibiting property of the image forming area with respect to the developer, the combined use of a substance that is thermally-decomposable and can substantially lower the solubility of the alkali-soluble resin in an un-decomposed state, such as onium salts, o-quinonediazide compounds, alkyl sulfonate ester, and the like is preferable.

[0106] Preferable examples of the onium salts used in the present 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., Teh, 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), EP No. 104,143, U.S. Patent Nos. 5,041,358 and 4,491,628, and JP-A Nos. 2-150848 and 2-296514; sulfonium salts described in J. V. Crivello et al., Polymer J. 17, 73 (1985), J. V. Crivello et al., J. Org. Chem., 43, 3055 (1978), W. R. Watt et al., J. Polymer Sci., Polymer Chem. Ed., 22, 1789 (1984), J. V. Crivello et al., Polymer Bull., 14, 279 (1985), J. V. Crivello et al., Macromolecules, 14 (5), 1141 (1981), J. V. Crivello et al., J. Polymer Sci., Polymer Chem. Ed., 17, 2877 (1979), EP 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); arsonium salts described in C. S. Wen et al., and The Proc. Conf. Rad. Curing ASIA, p478, Tokyo, Oct (1988).

Among these onium salts, in view of the solubility inhibiting property and thermally-decomposablility, diazonium salts and quaternary ammonium salts are particularly preferable. As diazonium salts, the diazonium salts represented by formula (I) as described in JP-A No. 5-158230 and the diazonium salts represented by formula (1) as described in JP-A No. 11-143064 are preferable, and diazonium salts which have a small absorption wavelength in the visible radiation region as represented by formula (1) as described in JP-A No. 11-143064 are most preferable. As quaternary ammonium salts, quaternary ammonium salts represented by items (1) to (10) in [Formula 5] and [Formula 6] as described in JP-A No. 2002-229186 are preferable.

[0107] Examples of the counter ion of the onium salt include tetrafluoroboric acid, hexafluorophosphoric acid, triisopropylnaphthalenesulfonic acid, 5-nitro-o-toluenesulfonic acid, 5-sulfosalicylic acid, 2,5-dimethylbenzenesulfonic acid, 2,4,6-trimethylbenzenesulfonic acid, 2-nitrobenzenesulfonic acid, 3-chlorobenzenesulfonic acid, 3-bromobenzenesulfonic acid, 2-fluorocaprylnaphthalenesulfonic acid, dodecylbenzenesulfonic acid, 1-naphthol-5-sulfonic acid, 2-methoxy-4-hydroxy-5-benzoyl-benzenesulfonic acid, and p-toluenesulfonic acid. Among these examples, hexafluorophosphoric acid, and alkylaromatic sulfonic acids such as triisopropylnaphthalenesulfonic acid and 2,5-dimethylbezenesulfonic acid are particularly preferable.

[0108] Preferable examples of the quinonediazide compounds include an o-quinonediazide compounds. The o-quinonediazide compounds used in the present invention have at least one o-quinonediazide group, an alkali-solubility thereof is increased by the thermal decomposition, and can be used in various structures. The o-quinonediazide compounds can improve the solubility of the photosensitive material by the both effects that the o-quinonediazide compounds are thermally decomposed, and thereby causing the lost of the solubility inhibiting property of the binder, and that o-quinonediazide compounds themselves are changed into an alkali-soluble material. Preferable examples of the o-quinonediazide compounds used in the present invention include compounds described in J. Coser, "Light-Sensitive Systems" (John Wiley & Sons. Inc.), pp. 339 to 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 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 as in described in US 3,046,120 and US 3,188,210.

[0109] Furthermore, preferable examples include an ester made from naphthoquinone-(1,2)-diazide-4-sulfonic acid chloride and phenol-formaldehyde resin or cresolformaldehyde 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 thereof 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.

[0110] The amount of onium salt and/or o-quinonediazide compounds added as the decomposable solubilization inhibitor(s) is preferably from 1 mass% to 10 mass% in the total solid content of the recording layer, more preferably from 1 mass% to 5 mass%, and even more preferably from mass% to 2 mass%. The onium salts and the o-quinonediazide compounds may be used either independently or in the form of mixtures of two or more thereof.

[0111] The amount of additives other than o-quinone diazide compounds added is preferably from0.1 mass% to 5 mass%, more preferably from 0.1 mass% to 2 mass%, and even more preferably from 0.1 mass% 1.5 mass%. The additives and the binder used in the present invention are preferably incorporated into the same layer.

[0112] A solubilization inhibitor having no decomposability may be used in combination. Preferable examples thereof include sulfonic acid esters, phosphoric acid esters, aromatic carboxylic acid esters, aromatic disulfones, carboxylic acid anhydrides, aromatic ketones, aromatic aldehydes, aromatic amines, and aromatic ethers, details of which are described in JP-A No. 10-268512; acidic color-developable dyes which have a lactone skeleton, an N,N-diarylamide skeleton or a diarylmethylimino skeleton and also function as a coloring agent, details of which are described in JP-A No. 11-190903; and nonionic surfactants described, details of which are described in JP-A No. 2000-105454.

[0113] From a viewpoint of improving sensitivity, preferable examples of additives for use in the uppermost layer of the recording layer include a cyclic acid anhydride, a phenolic compound , an organic acid, or the like. Further, a surfactant, an image colorant, and a plasticizer, each to be described later, can also be used as additives to the positive recording layer.

Examples of cyclic acid anhydride include phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, 3,6-endooxy-Δ4-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, and 4,4’, 3",4"-tetrahydroxy-3,5,3’,5’-tetramethyltriphenylmethane. Examples of the organic acid include sulfonic acids, sulfinic acids, alkylsulfuric acids, phosphonic acids, phosphates, and carboxylic acids, which are described in JP-A No. 60-88942 or 2-96755.

The amount of cyclic acid anhydride, phenolic compound, or organic acid included in the composition forming the recording layer is preferably from 0.05 mass% to 20 mass%, more preferably from 0.1 mass% to 15 mass%, and even more preferably from 0.1 mass% to 10 mass%.

[0114] Other than the above agents, epoxy compounds, vinyl ethers, and phenolic compounds having a hydroxymethyl group as described in Japanese Patent Application Laid-Open No. 8-276558, phenolic compounds having an alkoxymethyl group, and crosslinking compounds proposed by inventors which have the function of inhibiting the solubility in alkaline solution as described in Japanese Patent Application Laid-Open No. 11-160860 may be added.

[0115] A printing-out agent for obtaining a visible image immediately after the heating of the photosensitive composition by exposure to light, or a dye or a pigment as an image coloring agent can be added to the imaging layer of the present invention.

A typical example of a printing-out agent is a combination of a compound which is heated by exposure to light, thereby emitting an acid (an optically acid-generating agent), and an organic dye which can form salts (salt formable organic dye). Specific examples thereof 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 a vivid printed-out image that is excellent in stability over the passage of time.

[0116] As the image coloring agent, a dye other than the above salt-formable organic dye may be used. Preferable examples of the dye and the salt-formable organic dye include oil-soluble dyes and basic dyes. Specific examples thereof 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 (all manufactured by Orient Chemical Industries Ltd.); Victoria Pure Blue, Crystal Violet (CI42555), Methyl Violet (CI42535), Ethyl Violet, Rhodamine B (CI145170B), Malachite Green (CI42000), and Methylene Blue (CI52015). Dyes described in JP-A No. 62-293247 are particularly preferable. These dyes may be added to the recoding layer at a ratio of from 0.01 mass% to 10 mass%, and preferably from 0.1 mass% to 3 mass%, with respect to the total solid content of the composition forming the recording layer.

[0117] As necessary, to give flexibility to a coating film, a plasticizer may be added to the uppermost layer of the recording layer of the planographic printing plate precursor of the present invention. 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 methacrylic acid.

Production of Planographic printing plate precursor

Coating solvents and coating methods

[0118] A planographic printing plate precursor according to the present invention can be formed by dissolving the constituent components of the recording layer described above into a solvent and coating them onto an appropriate support. Further, a protective layer, a resin intermediate layer, a back coating layer, and the like, which are described later, are provided in the planographic printing plate precursor depending on the purpose and can be formed in the same manner.

The solvents to be used in such cases may be ethylene dichloride, cyclohexanone, methyl ethyl ketone, methanol, ethanol, propanol, ethylene glycol monomethyl ether, 1-methoxy-2-propanol, 2-methoxyethyl acetate, 1-methoxy-2-propyl acetate, dimethoxyethane, methyl lactate, ethyl lactate, N,N-dimethylacetamide, N,N-dimethylformamide, tetramethylurea, N-methylpyrrolidone, dimethyl sulfoxide, sulfolane, γ-butyrolactone, and toluene, however the solvents should not be limited to these examples. These solvents may be used alone or in form of mixtures.

The concentration of the above-mentioned components (the solid components including the additives) in the solvent is preferably from 1 mass% to 50 mass%.

Layer constitution of Positive recording layer

[0119] The positive recording layer of the planographic printing plate precursor of the present invention can use any one of either in a single-layer structure, a phase-separated structure, and a multi-layer structure.

The single-layer type recording layer can use a photosensitive layer described, for example, in Japanese Patent Application Laid-Open No. 7-285275 and pamphlet of International Publication 97/39894; the phase-separated type recording layer can used a photosensitive layer described, for example, in Japanese Patent Application Laid-Open No. 11-44956; and the multi-layer type recording layer can use a photosensitive layer described, for example, in Japanese Patent Application Laid-Open No. 11-218914, United States Patents Nos. 6352812B1, 6352811B1, 6358669B1, and 6535238B1, and European Patent No. 864420B1, but are not limited to these examples.

In the case of a multi-layer structure, the essential components (A) and (B) of the present invention are not restricted to the lower layers and the uppermost layer, but can be included in any layer; but in view of the effects, it is preferable to include components (A) and (B) in the top layer.

Further, although the amount of recording layer coating (solid content) on the support obtained after coating and drying differs depends on the use, it is generally preferable that such amount of film coating (total amount of all layers in the case of multi-layers) after drying is from 0.5 g/m^2 to 5.0 g/m^2, and more preferably from 0.6 g/m^2 to 2.0 g/m^2.

[0120] Various methods can be used to apply the recording layer coating liquid, including, for example, bar-coater coating, rotary coating, spray coating, curtain coating, dip coating, air knife coating, blade coating, roll coating, and the like. Although the apparent sensitivity becomes larger as the amount of coating applied decreases, the special characteristics of the film are rather reduced.

Support

[0121] The support used in the planographic printing plate precursor of the present invention is a plate having dimensional stability. A plate satisfying required physical properties such as strength and flexibility can be used without any restriction. Examples thereof include paper, plastic (such as polyethylene, polypropylene or polystyrene)-laminated papers, metal plates (such as aluminum, zinc and copper plates), plastic films (such as cellulose biacetate, cellulose triacetate, cellulose propionate, cellulose lactate, cellulose acetate lactate, cellulose nitrate, polyethylene terephthalate, polyethylene, polystyrene, polypropylene, polycarbonate, and polyvinyl acetate films), and papers or plastic films on which, as described above, a metal is laminated or vapor-deposited.

The support is preferably a polyester film or an aluminum plate. The aluminum plate is more preferable, since the aluminum plate is superior 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 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. While a pure aluminum is particularly preferable for use in aluminum plate of the invention, a very small amount of other elements may also be contained in the plate since production of a completely pure aluminum is difficult due to limitation of the refining technology.

The composition of aluminum plate used for the support is not specifically limited, but the known aluminum plates can be used arbitrarily. 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.

[0122] As necessary, prior to the surface-roughening treatment, the aluminum plate may optionally be subjected to degreasing 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, and 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 both methods may be used. As necessary, the aluminum plate obtained by the above surface-roughening treatment may be subjected to alkali-etching treatment and neutralizing treatment. Thereafter, if required, an anodizing treatment may be subjected to the aluminum plate in order to improve the water holding capacity and wear resistance of the surface thereof. 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.

[0123] 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 from 1 mass% to 80 mass%, a solution temperature of from 5°C to 70°C, a current density of from 5 A/dm^2 to 60 A/dm^2, a voltage of from 1 V to 100 V, and an electrolyzing time of from 10 seconds to 5 minutes. When the amount of anodic oxide film is 1.0 g/m^2 or less, printing resistance is inadequate or non-image areas 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. After the anodizing treatment, the surface of the aluminum may be subjected as necessary to a hydrophilic treatment. Examples of hydrophilic treatments used in the present invention include an alkali metal silicate (for example, an aqueous sodium silicate solution) method, as disclosed in U.S. Patent Nos. 2,714,066, 3,181,461, 3,280,734, and 3,902,734. In this method, a support is subjected to an immersing treatment or an electrolyzing treatment with an aqueous sodium silicate solution. In addition, potassium fluorozirconate described in JP-B No. 36-22063, or polyvinyl phosphonic acid described in U.S. Patent Nos. 3,276,868, 4,153,461, and 4,689,272 can be used for treating a support.

Undercoat layer

[0124] In the planographic printing plate precursor of the present invention, although a recording layer is provided on the support, an undercoat layer can be disposed, when required, between the support and the recording layer (lower layer). The provision of the undercoat layer offers the benefit that: the undercoat layer functions as a heat-insulating layer between the support and the lower layer so that the heat generated by the exposure of the infrared laser does not diffuse into the support, thus providing higher sensitivity due to the efficient use of the heat. Further, when this undercoat layer is provided in the recording layer according to the present invention, the recording layer is situated still at the exposure surface or near thereat and thus the sensitivity to the infrared laser can be favorably maintained.

In an unexposed area, it is assumed that, since the recording layer itself is impervious to the alkaline developer and functions as a protective layer for the undercoat layer, the stability of image development is improved while images of excellent discrimination are formed and the stability over time can be ensured. In an exposed area, the solubility inhibiting property is diminished, and the components of the recording layer are rapidly solubilized and dispersed in the developer. Further, the undercoat layer itself, which exists adjacent to the support, is an alkali-soluble polymer having favorable solubility in the developer, and thus is rapidly solubilized without generating a residual film even if a developer with lowered activity is used, contributing the improvement of the developability. Therefore, the undercoat layer is useful.

[0125] As components of the undercoat layer, various organic compounds can be used. 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 singly or two or more kinds thereof may be used in combination.
The appropriate coated amount of undercoat layer is from 2 mg/m^2 to 200 mg/m^2, and preferably from 5 mg/m^2 to 100 mg/m^2. When the coating amount is 2 mg/m^2 or less, sufficient printing endurance cannot be obtained. The same applies when the coating amount is 200 mg/m^2 or more.

[0126] The planographic printing plate precursor of the present invention has images formed by heat. Specifically, direct imagewise recording by a thermal recording head or the like, scan-exposure by infrared laser, high-luminosity flash exposure by a xenone discharge lamp or the like, infrared lamp exposure, or the like are employed. Exposure by a solid high-output infrared laser such as a semiconductor laser which emits infrared beams, a YAG laser, and the like having a wavelength of from 700 nm to 1200 nm is preferable.

[0127] A laser output of 100 mW or more is preferable, and for shortening the exposure time, use of a multi-beam laser device is preferable. Further, the exposure time per 1 pixel is preferably within 20 μsec, and the energy irradiated onto the positive recording material is preferably from10 mJ/cm^2 to 500 mJ/cm^2.

[0128] The developer which can be used for developing the planographic printing plate precursor of the present invention is a developer having a pH of from 9.0 to 14.0, preferably of form 12.0 to 13.5. The developer, the category of which includes not only developer but also replenisher hereinafter, may be an aqueous alkaline solution that has been known so far. Examples thereof include aqueous solutions of inorganic alkali salts such as sodium silicate, potassium silicate, sodium triphosphate, potassium triphosphate, ammonium triphosphate, sodium biphosphate, potassium biphosphate, ammonium biphosphate, sodium carbonate, potassium carbonate, ammonium carbonate, sodium hydrogencarbonate, potassium hydrogencarbonate, ammonium hydrogencarbonate, sodium borate, potassium borate, ammonium borate, sodium hydroxide, ammonium hydroxide, potassium hydroxide and lithium hydroxide; and organic alkali agents such as monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, ethyleneimine, ethylenediamine, or pyridine. These aqueous alkaline solutions may be used singly or two or more kinds thereof may be used in combination.

[0129] Of these aqueous alkaline solutions, one preferable developer which can exert the effects of the present invention is a so-called "silicate developer", which contains an alkali silicate as a base or an alkali silicate obtained by mixing a base with a silicon compound, and has a pH of 12 or more. Another preferable developer is a so-called "non-silicate developer", which does not contain an alkali silicate but contains a nonreducing sugar (as an organic compound having a buffer effect) and a base.

[0130] In the silicate developer, the developer property of the alkali metal silicate solution can be controlled by adjusting the ratio of silicon oxide (SiO_2), which are components of the silicate, to alkali metal oxide (M_2O) (generally, the ratio is represented by the molar ratio of $[SiO_2]/[M_2O]$) and the concentration of the alkali metal silicate. For example, the following is preferably used: an aqueous solution of sodium silicate wherein the molar ratio of SiO_2/Na_2O ($[SiO_2]/[Na_2O]$) is from 1.0 to 1.5 and the content of SiO_2 is from 1 mass% to 4 mass%, as disclosed in JP-A No. 54-62004; or alkali metal silicate solution wherein the molar ratio of $[SiO_2]/[M\ ]$is from 0.5 to 0.75 (that is, the molar ratio of $[SiO_2]/[M_2O]$ is from 1.0 to 1.5), the content of SiO_2 is from 1 mass% to 4 mass%, and the content of potassium is at least 20% with respect to the total gram-atomic weight of all alkali metals in the solution, as disclosed in JP-B No. 57-7427.

[0131] The so-called "non-silicate developer", which does not contain an alkali silicate but contains a nonreducing sugar and a base, is preferably used for developing the planographic printing plate precursor of the present invention. When the non-silicate developer is used for developing the planographic printing plate precursor, ink-adsorbing property of the positive recording layer can be kept better without deteriorating the surface of the recording layer. Further, while a planographic printing precursor generally has a narrow development latitude and the scanning width and the like are altered depending on the pH value of the developer, the non-silicate developer have an advantage over a developing liquid containing a silicate, since the non-silicate developer contains a nonreducing sugar having a buffering property to suppress the pH fluctuation. In addition, the non-silicate developer has an advantage in that the nonreducing sugar is hardly contaminate a conductivity sensor, a pH sensor, or the like which control the liquid activity, as compared with a silicate. Further, the non-silicate developer can produce the excellent discrimination-improving effect. It is assumed that such effect can be obtained by the mild contact (permeation) between the developer and the positive recording layer, which is an important aspect in the present invention and enables the difference between an exposed area and an unexposed area to be clear.

[0132] The nonreducing sugar belongs to sugars which do not have free aldehyde groups or ketone groups and show a non-reducing property; these sugars are classified into trehalose-type oligo-saccharides in which reducing groups are bonded together, glucosides in which reducing group of sugars and non-sugar material are bonded, and sugar alcohols formed by reducing sugars with hydrogenation, each of which can be used suitably in the present invention. In the present invention, nonreducing sugars described in Japanese Patent Application Laid-Open No. 8-305039 can be used suitably.

[0133] Examples of the trehalose type oligosaccharides include saccharose and trehalose. Examples of the glucosides include alkylglucosides, phenolglucosides, and mustard seed oil glucoside. Examples of the sugar alcohols include D, L-arabitol, ribitol, xylitol, D, L-sorbitol, D, L-mannitol, D, L-iditol, D, L-talitol, dulcitol, and allodulcitol. Furthermore, maltitol, obtained by hydrogenating maltose that is 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.

[0134] These nonreducing sugars may be used singly or two or more kinds thereof may be used in combination. The content of the nonreducing sugar in the non-silicate developer is preferably from 0.1 mass% to 30 mass% and, more preferably, from 1 mass% to 20 mass%. When the content is 0.1 mass% or less, a sufficient buffering effect may not be obtained. When the content is 30 mass% or more, making high concentrations may become difficult, resulting in higher cost of the materials.

[0135] The base combined with the nonreducing sugar(s) may be an alkali agent that has been known so far. 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 and ammonium borate.

[0136] Examples of organic alkali agents include monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, triisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethyleneimine, ethylenediamine, and pyridine.

[0137] The bases may be used singly or two or more kinds thereof may be used in combination. Among the bases, sodium hydroxide or potassium hydroxide is preferred. In the present invention, instead of the combined use of the nonreducing sugar and the base, it is possible to use a non-silicate developer whose main component is an alkaline metal salt of a nonreducing sugar.

[0138] Further, for the non-silicate developer, an alkaline buffer solution composed of a weak acid and a strong base other than the nonreducing sugar can be used in combination. As the weak acid, those having a dissociation constant (pKa) of from 0.0 to 13.2 are preferred, and can be selected from the acids described in "Ionization Constants of Organic Acids in Aqueous Solution" published by Pergamon Press, or the like.

[0139] For the purpose of promoting or suppressing image development, dispersing development scum, or improving the ink-affinity of the printing plate image forming area, various surfactants or organic solvents can be added to the developer and a replenisher as required. As the surfactant, anionic, cationic, nonionic, and amphoteric surfactants are preferable. Further, as the organic solvent, reducing agents such as hydroquinone, resorcin, or sodium salts or potassium salts of inorganic acids such as sulfurous acid or hydrogen sulfurous acid; organic carboxylic acids; defoamers; or softening agents for hard water, can be added to the developer and the replenisher.

[0140] The planographic printing plate developed by using the above developer or the replenisher is subjected to the post-treatment with washing water, a rinsing solution containing a surfactant or the like, or a desensitizing solution containing gum arabic or starch derivative. Various combinations of these can be used for the post-treatment.

[0141] In the case of carrying out development by using an automatic developing apparatus, it is known that a large quantity of PS plates can be treated without replacing the developer in a developer tank for a long duration by adding, to the developer, aqueous solution (a replenisher) having a higher alkalinity than that of the developer. In the present invention, this replenishing method is preferably employed. To promote or suppress the developability of the developer or the replenisher and improve the dispersion of development scum and affinity of the image forming area of the printing plate to ink, a variety of surfactants and organic solvents may be added as required.

Examples of preferable surfactants include anionic, cationic, nonionic and amphoteric surfactants. In addition, to the developer or the replenisher, reducing agents such as hydroquinone, resorcin, or sodium salts or potassium salts of inorganic acids such as sulfurous acid, hydrogen sulfurous acid; organic carboxylic acid; defoaming agents; and water hardening or softening agents may be added as required.

The printing plate treated by using the developer or the replenisher is washed with water and post-treated with rinsing solutions containing the surfactants or the like, and desensitizing solutions containing gum arabic and starch derivatives. The post-treatment of the image recording material of the invention can be carried out by using these treatments in combinations.

[0142] Recently, for rationalization or standardization of the printing plate production work in printing plate-producing or printing industries, automatic developing apparatuses for printing plates have been used widely. An automatic developing apparatuses generally includes a development section and a post-treatment section. More specifically, an automatic developing apparatus includes a unit for transferring the printing plates, tanks for respective treatment solutions, and a spraying apparatus. The automatic developing apparatus transfers the exposed printing plates horizontally and at the same time carries out development treatment by spraying the respective treatment solutions pumped up by pumps, to the printing plate, through spray nozzles. Recently, there is also known a method for carrying out treatment by transporting the printing plates by under-solution guide rolls while the printing plates are immersed in the treatment solution tanks filled with the treatment solutions. In such automatic treatment, the replenishers may be replenished to the respective treatment solutions depending on the treatment quantity, operation times, and the like. Alternatively, so-called disposable treatment method in which treatment is carried out using substantially unused treatment solutions can be employed.

[0143] In the planographic printing plate precursor of the present invention, the planographic printing plate precursor is imagewise exposed, developed, washed with water and/or rinsed and/or gum-coated to obtain a planographic printing plate. When unnecessary image forming area (e.g. film edge trace of a master film) is present in the planographic printing plate, the unnecessary image forming area is erased. Such erasing is preferably carried out by a method of applying an erasing solution as described in JP-B No. 2-13293 to the unnecessary image areas and washing with water after a prescribed duration. A method of radiating active light beam led through optical fibers to the unnecessary image forming area and then carrying out development as described in JP-A No. 59-174842 may also be employed.

[0144] The planographic printing plate produced in such a manner is coated with a desensitizing gum as necessary and supplied to printing steps. In order to further improve the printing durability of planographic printing plate, baking treatment may be carried out as required.

When the baking treatment of the planographic printing plate is carried out, it is preferable to treat, prior to the baking treatment, the planographic printing plate with surface conditioning solutions described in JP-B Nos. 61-2518 and 55-28062 and JP-A Nos. 62-31859 and 61-159655.

Examples of the methods that can be used include a method for applying the surface conditioning solutions to the planographic printing plate by sponge or degreased cotton doped with the solutions, a method for immersing the printing plate in a vat filled with the surface conditioning solutions, and a method for applying the surface conditioning solutions using automatic coaters. To obtain a better result, after the above application, the amount of solution applied is made uniform with a squeegee or a squeegee roller.

[0145] In general, proper amount of surface-adjusting solution applied is from 0.03 g/m^2 to 0.8 g/m^2 (by dry mass). As 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 baking processor (for example, BP-1300 (trade name, manufactured by FUJIFILM Corporation)) or the like. In this case, the heating temperature and the heating time, which depend on the kind of image forming components, are preferably from 180°C to 300°C and from 1 minute to 20 minutes, respectively.

[0146] As necessary, a planographic printing plate subjected to a baking treatment can be subjected to treatments which have been conventionally conducted, such as a water-washing treatment and gum coating. However, when 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 precursor of the present invention is processed into a planographic printing plate. This planographic printing plate is then placed on an offset printing machine or the like, and used for printing large quantities of sheets. The planographic printing plate precursor of the present invention has the advantages of excellent chemical resistance, excellent printing endurance in the image forming area, wide image development latitude, and excellent image reproducibility.

EXAMPLES

[0147] The present invention will be explained in conjunction with examples, but the invention is not restricted to such examples.

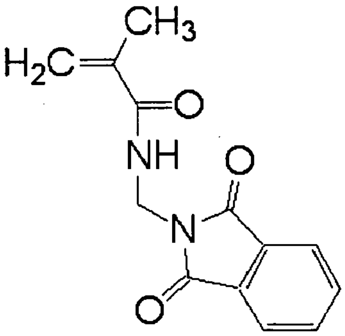
Synthesis Example 1

Synthesis of specific polymer (A-1)

[0148] Specific polymer (A-1) was prepared according to the method shown in the following. Specific polymer (A-1) is a copolymer ofN-vinyl caprolactam, monomer 1 having the following structure, and methacrylic acid. Further, the copolymer molar ratio of the respective structural units included in specific polymer (A-1) (N-vinyl caprolactam/ monomer 1/ methacrylic acid) is 33/57/10.

[0149]

Monomer 1



[0150] 9.48 g (0.0681 mol) of N-vinyl caprolactam, 28.74 g (0.118 mol) of monomer 1 and 1.78 g (0.0206 mol) of methacrylic acid were added to a sealed reaction container equipped with a water-cooled condenser tube, a temperature gauge, a nitrogen-inlet tube and a mechanical stirrer and into which 129.6 g of y-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: V601, an azo initiator available from Wako Pure Chemical Industries Co., Ltd.) were dissolved in 28.9 g of y-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%.

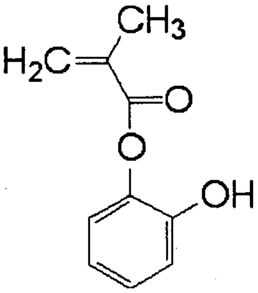
Synthesis Example 2

Synthesis of specific polymer (A-2)

[0151] Specific polymer (A-2) was prepared according to the method shown in the following. Specific polymer (A-2) is a copolymer of monomer 1 having the above structure and monomer 2 having the following structure. Further, the copolymer molar ratio of the respective structural units included in specific polymer (A-2) (monomer 1/ monomer 2) is 57/43.

[0152]

Monomer 2



[0153] 23.33 g (0.096 mol) of monomer 1 and 12.84 g (0.072 mol) of monomer 2 were added to a sealed reaction container equipped with a water-cooled condenser tube, a temperature gauge, a nitrogen-inlet tube and a mechanical stirrer and into which 116.35 g of γ-butyrolactone had already been added. The resultant mixture was heated at 90°C

and stirred until it became a transparent solution.
1.37 g of dimethyl-2,2'-azobisisobutyrate (trade name: V601, an azo initiator available from Wako Pure Chemical Industries Co., Ltd.) were dissolved in 26.1 g of y-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 Example 3

Synthesis of specific polymer (A-3)

[0154] Specific polymer (A-3) was prepared according to the method shown in the following. Specific polymer (A-3) is a copolymer of N-vinyl caprolactam, monomer 1 having the above structure, monomer 2 having the above structure, and methacrylic acid. Further, the copolymer molar ratio of the respective structural units included in specific polymer (A-3) (N-vinyl caprolactam/ monomer 1/ monomer 2/ methacrylic acid) is 9/57/19/15.
[0155] 3.16 g (0.0227 mol) of N-vinyl caprolactam, 35.07 g (0.1436 mol) of monomer 1, 8.53 g (0.0479 mol) of monomer 2, and 3.25 g (0.0378 mol) of methacrylic acid were added to a sealed reaction container equipped with a water-cooled condenser tube, a temperature gauge, a nitrogen-inlet tube and a mechanical stirrer and into which 162 g of γ-butyrolactone had already been added. The resultant mixture was heated at 90°C and stirred until it became a transparent solution.
1.9 g of dimethyl-2,2'-azobisisobutyrate (trade name: V601, an azo initiator available from Wako Pure Chemical Industries Co., Ltd.) were dissolved in 36.1 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%.

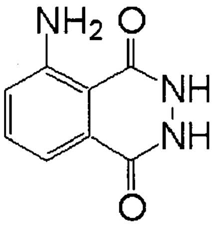
Synthesis Example 4

Synthesis of specific polymer (B-1)

Specific polymer (B-1) was prepared as follows.

(Preparation of diazonium solution)

[0156] A mixture of 2.6 g of compound AM-10 having the following structure, 25 ml of acetic acid and 37.5 ml of water was stirred, mixed and cooled to 15°C. Subsequently, 2.5 ml of concentrated HCl were added and the mixture was further cooled to 0°C.
Then, a solution obtained by dissolving 1.1 g of $NaNO_2$ in 3 ml of water was dripped into the mixture and stirring was further continued for 30 minutes, whereby a diazonium solution was obtained.
[0157]



(AM-10)

Preparation of phenolic polymer solution

[0158] A mixture of 45.9 g of a solution of 40 weight% novolac resin (trade name: ALNOVOL SPN452, manufactured by Clariant GmbH) in DOWANOL PM (trade name, manufactured by Dow Chemical Co., Ltd.)(solvent), 16.3 g of NaOAc-$3H_2O$, and 200 ml of 1-methoxy-2-propanol was stirred and cooled to 10°C.
Over a period of 30 minutes, all of the diazonium solution obtained as above was dripped into the phenolic polymer mixed liquid cooled to 10°C as above and, then, stirring was continued for 120 minutes while maintaining the temperature at 15°C. The resultant mixture was added to 2 liters of ice-cold water over a period of 30 minutes while performing

continuous stirring. The polymer was precipitated from the aqueous vehicle and isolated by filtration. Specific polymer (B-1) was obtained by washing with water and then drying at 45°C (95% yield). Further, the weight-average molecular weight of specific polymer (B-1) was 8000 and the number-average molecular weight thereof was 3000.

Examples 1 to 3

Preparation of substrate

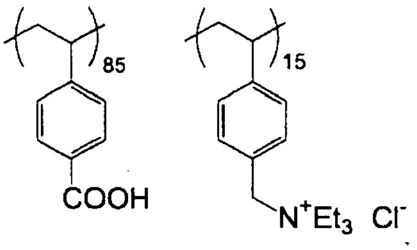
[0159] An aluminum plate (material composition: Al: 99.50% or more; Si: 0.25%; Fe: 0.40%; Cu: 0.05%; Mn: 0.05%; Mg: 0.05%; Zn: 0.05%; Ti: 0.03%) having a thickness of 0.3 mm was subjected to etching treatment for 10 seconds using a solution having a caustic soda concentration of 30 g/l, an aluminum ion concentration of 10 g/l and a solution temperature of 60°C, washed with running water, neutralized by washing with a 10 g/l solution of nitric acid, and then washed with water. Using a sinusoidal alternating waveform current at an applied voltage Va of 20V, this was subjected to electrochemical roughening treatment at an quantity of electricity of 400 C/dm^2 in an aqueous solution with a hydrogen chloride concentration of 15 g/l, an aluminum ion concentration of 10 g/l and a solution temperature of 30°C, and washed. Next, the plate was subjected to etching treatment for 10 seconds using a solution having a caustic soda concentration of 30 g/l, an aluminum ion concentration of 10 g/l and a solution temperature of 40°C, and washed with running water. Then, the plate was subjected to desmat treatment using a sulfuric acid aqueous solution having a sulfuric acid concentration of 15 mass% and a solution temperature of 30°C, and washed. In addition, the plate was subjected to anodization treatment in a 10 mass% sulfuric acid aqueous solution having a solution temperature of 20°C with direct current at a current density of 6 A/dm^2 such that the amount of the anodized film corresponded to 2.5 g/m^2, washed and dried. Then the plate was treated with a 1.0 mass% sodium silicate aqueous solution at 30°C for 10 seconds, whereby a substrate (a) that has been subjected to hydrophilic treatment was obtained.
The centerline average roughness of the substrate (a) was measured using a 2 μm diameter needle and was found to be 0.48 μm.

Formation of Undercoat Layer

[0160] The substrate (a) obtained in this manner was coated with the following undercoating solution and dried at 80°C for 30 seconds to provide an undercoat layer. The dried coating amount of the undercoat layer was 17 mg/m^2.
[0161] Formulation of the undercoating solution

- The following compound 0.3 g
- Methanol 100 g
- Water 1 g

[0162]



Weight-average molecular weight: 28,000

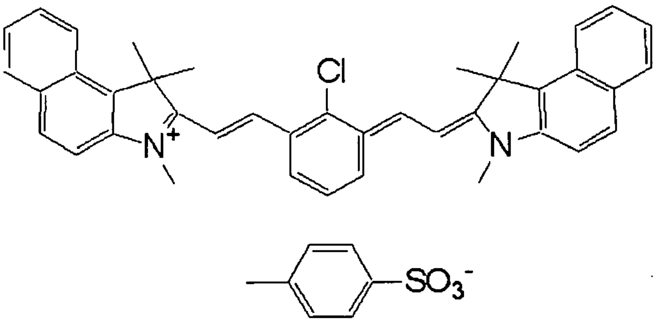
Formation of Recording Layer

[0163] The substrate having the undercoat layer obtained in the this manner was coated with the following coating solution for a positive recording layer and dried at 150°C for 1 minute in an oven, whereby a photosensitive planographic printing plate precursor having a positive recording layer was obtained. The dried coating amount of the positive recording layer was 1.5 g /m^2.
[0164] Formulation of the positive recording layer coating solution 1

- Specific polymer (A) 0.5 g (a compound described in the following Table 1)
- Specific polymer (B) 0.35g (specific polymer (B-1) obtained in Synthesis Example 4)
- Novolac resin A 0.1 g (m-/p-mixed cresol (6/4), weight-average molecular weight; 7,000, unreacted cresol; 0.3 mass %)
- Cyanine dye A 0.07 g ((C) photo-thermal conversion agent having the following structure)
- Phthalic anhydride 0.04 g
- Ethyl violet 0.02 g
- A fluorinated polymer 0.015 g (trade name: Defenser F-780 F (solid content: 30%), manufactured by DIC Corporation)
- Methyl ethyl ketone 5 g
- γ-butyrolactone 8 g

[0165]

Cyanine dye A



[0166] Further, the specific polymer (A) and specific polymer (B) of the present invention shown in the following table are specific polymers (A-1) to (A-3) and specific polymer (B-1) obtained by the above synthesis examples.

Comparative Examples 1 to 5

[0167] The planographic printing plate precursor of Comparative Example 1 was obtained in a similar manner to in Example 1 except that 0.35 g of specific polymer (A-1) was used instead of 0.35 g of specific polymer (B-1) in the positive recording layer coating solution 1 used in Example 1.
The planographic printing plate precursor of Comparative Example 2 was obtained in a similar manner to in Example 2 except that 0.35 g of specific polymer (A-2) was used instead of 0.35 g of specific polymer (B-1) in the positive recording layer coating solution 1 used in Example 2.
The planographic printing plate precursor of Comparative Example 3 was obtained in a similar manner to in Example 3 except that 0.35 g of specific polymer (A-3) was used instead of 0.35 g of specific polymer (B-1) in the positive recording layer coating solution 1 used in Example 3.
The planographic printing plate precursor of Comparative Example 4 was obtained in a similar manner to in Example 1 except that 0.5 g of specific polymer (B-1) was used instead of 0.5 g of specific polymer (A-1) in the positive recording layer coating solution 1 used in Example 1.
The planographic printing plate precursor of Comparative Example 5 was obtained in a similar manner to in Example 1 except that 0.85 g of Novolac resin A (m-/p-mixed cresol (6/4), weight-average molecular weight; 7,000, unreacted cresol; 0.3 mass %) was used instead of 0.5 g of specific polymer (A-1) and 0.35 g of specific polymer (B-1) in the positive recording layer coating solution 1 used in Example 1.
In Table 1, a comparative polymer is denoted by an asterisk.

Evaluation of printing durability and chemical resistance

[0168] A test pattern was drawn as an image on the obtained photosensitive planographic printing plate precursor using a Trendsetter (trade name, manufactured by Creo Co., Ltd.) at a beam strength of 9 W and a drum rotation speed of 150 rpm.
After that, the planographic printing plate precursor was developed using a PS processor 900H (trade name, manufactured by FUJIFILM Corporation), into which an alkaline developer having the following composition had been fed, while the temperature of the developer was kept at 30°C with a developing time of 20 seconds. The image in the obtained

planographic printing plate was printed using a Lithron printing machine manufactured by Komori Corporation using a black ink (trade name: DIC-GEOS (N), manufactured by DIC Corporation), and the printing durability was evaluated by the number of printed sheets until the point in time when it was visually recognized that the density of the solid image began to become low. Results of the evaluation are shown in Table 1.
With the addition of a step of wiping the plate surface with a cleaner (multi-cleaner manufactured by FUJIFILM Corporation) after every 5000 sheets printed, the printing endurance was evaluated in the same manner as above. The former printing durability is referred to as "usual printing durability" and the latter printing durability is referred to as "cleaner printing durability". Results of the evaluation are shown in Table 1. It is evaluated that the higher the cleaner printing durability is, the better the chemical resistance is.

Formulation of alkaline developer

[0169]

- SiO_2- K_2O (K_2O/SiO_2 = 1/1 (mol ratio))	4.0 mass%
- Citric acid	0.5 mass%
- Polyethylene glycol lauryl ether (weight-average molecular weight: 1,000)	0.5 mass%
- Water	95.0 mass %

Evaluation of Abrasion

[0170] Full surface exposure was performed on 50 planographic printing plate precursors (each having a width of 600 mm and a length of 800 mm) in an exposure device (trade name: Trendsetter, manufactured by Creo Co., Ltd.) at a beam strength of 13 W and drum rotation speed of 150 rpm. The level of contamination of the filter was observed before and after exposure and compared. When there was hardly any difference in the level of contamination before and after exposure a grade of A was given, and when there was clearly more contamination after exposure a grade of X was given. Results of the evaluation are shown in Table 1.
[0171]

Table 1

	Specific Polymer (A) or Comparative Polymer *	Specific Polymer (B) or Comparative Polymer *	Usual Printing Durablility (10,000 sheets)	Cleaner Printing Durablility (10,000 sheets)	Abrasion
Example 1	Specific Polymer (A-1)	Specific Polymer (B-1)	10	9	A
Example 2	Specific Polymer (A-2)	Specific Polymer (B-1)	10	9	A
Example 3	Specific Polymer (A-3)	Specific Polymer (B-1)	11	10	A
Comparative Example 1	Specific Polymer (A-1)	Specific Polymer (A-1)*	10	7	X
Comparative Example 2	Specific Polymer (A-2)	Specific Polymer (A-2)*	10	7	X
Comparative Example 3	Specific Polymer (A-3)	Specific Polymer (A-3)*	11	7	X
Comparative Example 4	Specific Polymer (B-1)*	Specific Polymer (B-1)	7	4	X
Comparative Example 5	Novolac resin A*	Novolac resin A*	5	2	X

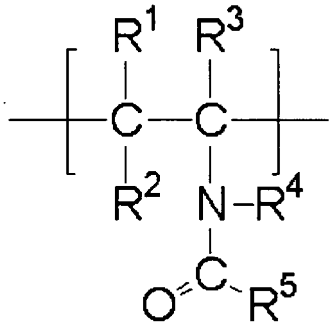
[0172] From Table 1, it is evident that the planographic printing plate precursors of Examples 1 to 3 according to the

present invention respectively exhibit excellent cleaner printing durability in addition to usual printing durability, in other words, exhibiting excellent chemical resistance, and, further, that abrasion was not caused by laser exposure.
Further, in Comparative Examples 1 to 3, which did not include specific polymer (B), while printing durability was favorable, cleaner printing durability was somewhat inferior. In Comparative Example 4, which did not include specific polymer (A), both printing durability and cleaner printing durability were somewhat inferior. In addition, abrasion was caused by laser exposure in each of Comparative Examples 1 to 4. Further, in Comparative Example 5, in which equivalent amounts of Novolac Resin A were used in place of specific polymer (A) and specific polymer (B), abrasion occurred and chemical resistance was significantly inferior.

Claims

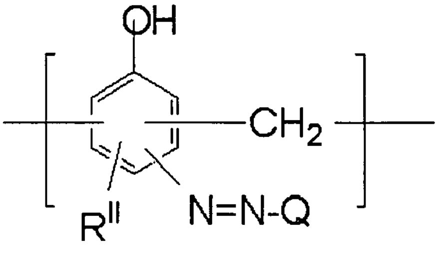
1. A planographic printing plate precursor comprising:

   a substrate; and
   a positive recording layer provided on the substrate,
   the positive recording layer comprising: a polymer (A) comprising a structural unit represented by the following Formula (I); a polymer (B) comprising a structural unit represented by the following Formula (II); and a compound (C) that absorbs light and generates heat, and the solubility of the positive recording layer being increased with respect to an alkaline developer by exposure to light or heating:

   Formula (I)

   wherein in Formula (I), each of R^1, R^2 and R^3 independently represents a hydrogen atom or 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;

   Formula (II)

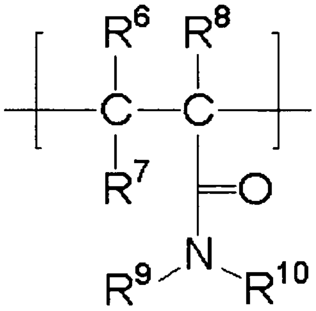
   wherein in Formula (II), R^{II} represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms and Q represents a monovalent substituent group comprising an aromatic ring structure.

2. The planographic printing plate precursor according to claim 1, wherein the structural unit represented by Formula (I) is a structural unit derived from N-vinyl caprolactam, N-(meth)acroyl aminomethyl phthalimide or (meth)acrylic acid.

3. The planographic printing plate precursor according to claim 1, wherein the content of the structural unit represented

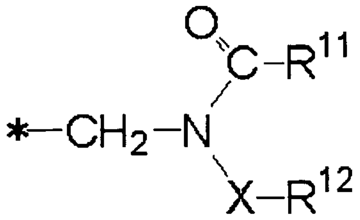
by Formula (I) in the polymer (A) is from 3 mol% to 75 mol%.

4. The planographic printing plate precursor according to claim 1, wherein the polymer (A) further comprises a structural unit represented by the following Formula (III):



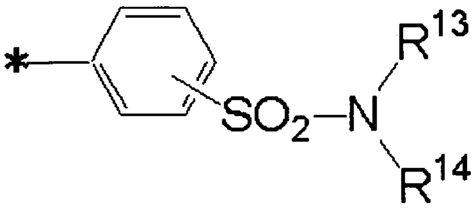
Formula (III)

wherein in Formula (III), 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; and R^{10} represents a group represented by the following Formula (IV) or Formula (V):



Formula (IV)

wherein in Formula (IV), the symbol "*" represents a position bonded with the nitrogen atom in Formula (III); X represents -C(=O)- or -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;



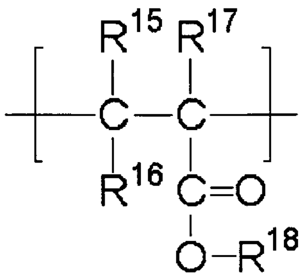
Formula (V)

wherein in Formula (V), the symbol "*" represents a position bonded with the nitrogen atom in Formula (III); each of R^{13} and R^{14} 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 R^{13} and R^{14} may be bonded together to form a ring structure.

5. The planographic printing plate precursor according to claim 1, wherein the content of the structural unit represented by Formula (III) in the polymer (A) is from 5 mol% to 95 mol%.

6. The planographic printing plate precursor according to claim 1, wherein the polymer (A) further contains a structural

unit represented by the following Formula (VII):



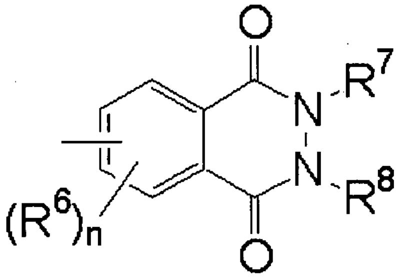
$$\left[-\overset{R^{15}}{\underset{R^{16}}{C}}-\overset{R^{17}}{\underset{C(=O)-O-R^{18}}{C}}- \right]$$

Formula (VII)

wherein in Formula (VII), each of R^{15}, R^{16} and R^{17} independently represents a hydrogen atom or a substituted or unsubstituted alkyl group; R^{18} represents a hydrogen atom, a positively-charged metal ion, 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.

7. The planographic printing plate precursor according to claim 1, wherein the content of the polymer (A) is in the range of from 5 mass% to 80 mass% with respect to the total solid content of a composition forming the positive recording layer.

8. The planographic printing plate precursor according to claim 1, wherein Q in Formula (II) is a monovalent substituent group represented by the following Formula (II-1):



Formula (II-1)

wherein in Formula (II-1), n represents an integer of 0, 1, 2 or 3; R^6 represents a hydrogen atom, a halogen atom, an alkyl group, an alkenyl group, an alkynyl group, a cycloalkyl group, a heterocyclic group, an aryl group, a heteroaryl group, an aralkyl group, a heteroaralkyl group, -SO$_2$-NH-R^9, -NH-SO$_2$-R^{11}-, -CO-NR^9-R^{10}, -NR^9-CO-R^{11}, - O-CO-R'', -CO-O-R^9, -CO-R^9, -SO$_3$-R^9, -SO$_2$-R^9, -SO-R^{11}, -P(=O)(-O-R^9)(-O-R^{10}), - NR^9-R^{10}, -O-R^9, -S-R^9, -CN, -NO$_2$, -N-phthalimidyl, -M-N-phthalimidyl or -M-R^9, wherein M represents a divalent linking group having 1 to 8 carbon atoms, and when there are a plurality of groups represented by R^6, respective groups represented by R^6 may be the same as or different from each other, and may be bonded together to form a ring structure; each of R^9 and R^{10} independently represents a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, a cycloalkyl group, a heterocyclic group, an aryl group, a heteroaryl group, an aralkyl group, or a heteroaralkyl group; R^{11} represents an alkyl group, an alkenyl group, an alkynyl group, a cycloalkyl group, a heterocyclic group, an aryl group, a heteroaryl group, an aralkyl group, or a heteroaralkyl group; each of R^7 and R^8 independently represents a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, a cycloalkyl group, a heterocyclic group, an aryl group, a heteroaryl group, an aralkyl group, or a heteroaralkyl group; a combination of two or three groups selected from the groups represented by R^6, R^9, R^{10} or R^{11} may be bonded together to form a ring structure; and the group represented by R^7 and the group represented by R^8 may be bonded together to form a ring structure.

9. The planographic printing plate precursor according to claim 1, wherein the content of the polymer (B) is in the range of from 5 mass% to 80 mass% with respect to the total solid content of a composition forming the positive recording layer.

10. The planographic printing plate precursor according to claim 1, wherein the content ratio of the polymer (A) to the polymer (B) is within the range of from 30 to 70 by mass ratio to from 70 to 30 by mass ratio.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 6475692 B **[0004]**
- EP 1738900 A **[0004]**
- JP 58125246 A **[0050]**
- JP 59084356 A **[0050]**
- JP 59202829 A **[0050]**
- JP 60078787 A **[0050]**
- JP 58173696 A **[0050]**
- JP 58181690 A **[0050]**
- JP 58194595 A **[0050]**
- JP 58112793 A **[0050]**
- JP 58224793 A **[0050]**
- JP 59048187 A **[0050]**
- JP 59073996 A **[0050]**
- JP 60052940 A **[0050]**
- JP 60063744 A **[0050]**
- JP 58112792 A **[0050]**
- GB 434875 A **[0050]**
- US 5156938 A **[0051]**
- US 3881924 A **[0051]**
- JP 57142645 A **[0051]**
- US 4327169 A **[0051]**
- JP 58181051 A **[0051]**
- JP 58220143 A **[0051]**
- JP 59041363 A **[0051]**
- JP 59084248 A **[0051]**
- JP 59084249 A **[0051]**
- JP 59146063 A **[0051]**
- JP 59146061 A **[0051]**
- JP 59216146 A **[0051]**
- US 4283475 A **[0051]**
- JP 5013514 B **[0051]**
- JP 5019702 B **[0051]**
- US 4756993 A **[0052]**
- JP 2001133969 A **[0058]**
- JP 2002040638 A **[0058]**
- JP 2002023360 A **[0058]**
- JP 5158230 A **[0106] [0106]**
- US 4069055 A **[0106] [0106]**
- US 4069056 A **[0106] [0106]**
- JP 3140140 A **[0106]**
- EP 104143 A **[0106]**
- US 5041358 A **[0106] [0106]**
- US 4491628 A **[0106] [0106]**
- JP 2150848 A **[0106]**
- JP 2296514 A **[0106]**
- EP 370693 A **[0106]**
- EP 233567 A **[0106]**
- EP 297443 A **[0106]**
- EP 297442 A **[0106]**
- US 4933377 A **[0106]**
- US 3902114 A **[0106]**
- US 4760013 A **[0106]**
- US 4734444 A **[0106]**
- US 2833827 A **[0106]**
- DE 2904626 **[0106]**
- DE 3604580 **[0106]**
- DE 3604581 **[0106]**
- JP 11143064 A **[0106] [0106]**
- JP 2002229186 A **[0106]**
- JP 4328403 B **[0108]**
- US 3046120 A **[0108]**
- US 3188210 A **[0108]**
- JP 47005303 A **[0109]**
- JP 48063802 A **[0109]**
- JP 48063803 A **[0109]**
- JP 48096575 A **[0109]**
- JP 49038701 A **[0109]**
- JP 48013354 A **[0109]**
- JP 4111222 B **[0109]**
- JP 459610 B **[0109]**
- JP 49017481 B **[0109]**
- US 2797213 A **[0109]**
- US 3454400 A **[0109]**
- US 3544323 A **[0109]**
- US 3573917 A **[0109]**
- US 3674495 A **[0109]**
- US 3785825 A **[0109]**
- GB 1227602 A **[0109]**
- GB 1251345 A **[0109]**
- GB 1267005 A **[0109]**
- GB 1329888 A **[0109]**
- GB 1330932 A **[0109]**
- DE 854890 **[0109]**
- JP 10268512 A **[0112]**
- JP 11190903 A **[0112]**
- JP 2000105454 A **[0112]**
- US 4115128 A **[0113]**
- JP 60088942 A **[0113]**
- JP 2096755 A **[0113]**
- JP 8276558 A **[0114]**
- JP 11160860 A **[0114]**
- JP 50036209 A **[0115]**
- JP 53008128 A **[0115]**
- JP 53036223 A **[0115]**
- JP 54074728 A **[0115]**
- JP 60003626 A **[0115]**
- JP 61143748 A **[0115]**
- JP 61151644 A **[0115]**

- JP 63058440 A **[0115]**
- JP 62293247 A **[0116]**
- JP 7285275 A **[0119]**
- JP 9039894 A **[0119]**
- JP 11044956 A **[0119]**
- JP 11218914 A **[0119]**
- US 6352812 B1 **[0119]**
- US 6352811 B1 **[0119]**
- US 6358669 B1 **[0119]**
- US 6535238 B1 **[0119]**
- EP 864420 B1 **[0119]**
- JP 54063902 A **[0122]**
- US 2714066 A **[0123]**
- US 3181461 A **[0123]**
- US 3280734 A **[0123]**
- US 3902734 A **[0123]**
- JP 3622063 B **[0123]**
- US 3276868 A **[0123]**
- US 4153461 A **[0123]**
- US 4689272 A **[0123]**
- JP 54062004 A **[0130]**
- JP 57007427 B **[0130]**
- JP 8305039 A **[0132]**
- JP 2013293 B **[0143]**
- JP 59174842 A **[0143]**
- JP 61002518 B **[0144]**
- JP 55028062 B **[0144]**
- JP 62031859 A **[0144]**
- JP 61159655 A **[0144]**

Non-patent literature cited in the description

- Dye Handbook. 1970 **[0049]**
- Latest Pigment Handbook. 1977 **[0078]**
- Latest Pigment Applied Technique. CMC Publishing Co., Ltd, 1986 **[0078] [0080] [0082]**
- Printing Ink Technique. CMC Publishing Co., Ltd, 1984 **[0078]**
- Nature and Application of Metal Soap. **SAIWAI SHOBO.** Printing Ink Technique. CMC Publishing Co., Ltd, 1984 **[0080]**
- **S. I. SCHLESINGER.** *Photogr. Sci. Eng.,* 1974, vol. 18, 387 **[0106]**
- **T. S. BAL et al.** *Polymer,* 1980, vol. 21, 423 **[0106]**
- **D. C. NECKER et al.** *Macromolecules,* 1984, vol. 17, 2468 **[0106]**
- **C. S. WEN et al.** *Teh, Proc. Conf. Rad. Curing ASIA,* October 1988, 478 **[0106]**
- **J. V. CRIVELLO et al.** *Macromolecules,* 1977, vol. 10 (6), 1307 **[0106] [0106]**
- *Chem. & Eng. News,* November 1988, vol. 28, 31 **[0106]**
- **J. V. CRIVELLO et al.** *Polymer J.,* 1985, vol. 17, 73 **[0106]**
- **J. V. CRIVELLO et al.** *J. Org. Chem.,* 1978, vol. 43, 3055 **[0106]**
- **W. R. WATT et al.** *J. Polymer Sci., Polymer Chem. Ed.,* 1984, vol. 22, 1789 **[0106]**
- **J. V. CRIVELLO et al.** *Polymer Bull.,* 1985, vol. 14, 279 **[0106]**
- **J. V. CRIVELLO et al.** *Macromolecules,* 1981, vol. 14 (5), 1141 **[0106]**
- **J. V. CRIVELLO et al.** *J. Polymer Sci., Polymer Chem. Ed.,* 1979, vol. 17, 2877 **[0106]**
- **J. V. CRIVELLO et al.** *J. Polymer Sci., Polymer Chem. Ed., 17,* 1979, 1047 **[0106]**
- **C. S. WEN et al.** *The Proc. Conf. Rad. Curing ASIA,* October 1988, 478 **[0106]**
- **J. COSER.** Light-Sensitive Systems. John Wiley & Sons. Inc, 339-352 **[0108]**
- Ionization Constants of Organic Acids in Aqueous Solution. Pergamon Press **[0138]**