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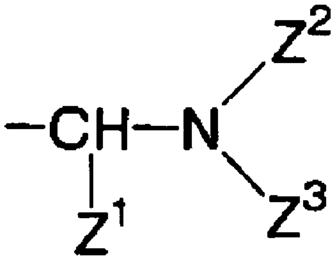
(54) Photosensitive composition and planographic printing plate precursor using the same

(57) A photosensitive composition containing: (A) a first alkaline aqueous solution-soluble resin having, on a side chain, a hydrophobic aminoalkyl group represented by the following formula (1); (B) a second alkaline aqueous solution-soluble resin, and (C) an infrared absorber:



Formula (1)

wherein Z^1, Z^2 and Z^3 each independently represent a hydrogen atom or a monovalent substituent group consisting of one or more nonmetal atoms.

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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to a photosensitive composition and a planographic printing plate precursor using the same, and in particular to a positive-type planographic printing plate precursor capable of direct plate-making by scanning with infrared laser light based on digital signals from computers etc., as well as a photosensitive composition useful as a recording layer thereof and responsive to an infrared light.

Description of the Related Art

[0002] As image formation technology has been developed in recent years, direct plate-making without using a film manuscript is possible by scanning the surface of a plate with a thin narrow beam of laser light, to form a letter manuscript, an image manuscript etc. directly on the surface of the plate. An example of plate materials used in such direct plate-making is a thermal positive-type planographic printing plate. The thermal positive-type planographic printing plate, upon irradiation with a laser light, causes light/heat conversion in a photosensitive layer thereby making the photosensitive layer alkali-soluble and forming a positive image. However, there is a problem in that the discrimination in alkali solubility between in light-exposed and light-unexposed regions is small and thus the development latitude (development stability depending on conditions used) is insufficient. This is because the principle of the image formation utilizes a slight change in interaction among binder molecules in the photosensitive layer caused by exposure to a laser light.

For such planographic printing plates, there is also a demand for resistance to a plate cleaner used when adhesion of ink is worsened during printing.

[0003] For the purpose of broadening the development latitude of alkali solubility between practically durable defmite light-exposed and light-unexposed regions, an image-recording layer forming a phase separation structure in which the image-recording layer forms a sea/island structure consisting of a highly alkali-soluble resin (sea region) and a low alkali-soluble resin (island region) is known as described for example in Japanese Patent Application Laid-Open (JP-A) No. 11-44956. However, an image-forming material forming such image-recording layer having a phase separation structure is poor in the film strength of the recording layer itself, and thus there is need for improvement of scratch resistance.

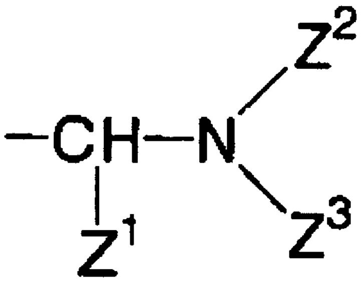
[0004] For improvement of cleaner resistance, an image forming material using an alkaline aqueous solution-soluble resin having a phenolic monomer unit in a photosensitive layer has been proposed (see, for example, EP Patent Application Laid-Open No. 1506858) wherein the improvement of cleaner resistance is reported. However, there has been a desire for the improvement of the scratch resistance of this image forming material, similarly to the image forming material described in JP-A No. 11-44956 supra.

SUMMARY OF THE INVENTION

[0005] The present invention has been made in consideration of the above circumstances, and provides a photosensitive composition and a planographic printing plate precursor using the same.

[0006] A first aspect of the invention provides a photosensitive composition comprising (A) a first alkaline aqueous solution-soluble resin having, on a side chain, a hydrophobic aminoalkyl group represented by formula (1) below (hereinafter occasionally referred to as a first alkali-soluble resin), (B) a second alkaline aqueous solution-soluble resin (hereinafter occasionally referred to as a second alkali-soluble resin), and (C) an infrared absorber.

[0007]



Formula (1)

[0008] In formula (1), Z^1, Z^2 and Z^3 each independently represent a hydrogen atom or a monovalent substituent group consisting of one or more nonmetal atoms.

[0009] A second aspect of the invention provides a positive-type planographic printing plate precursor having, on a support, a recording layer containing a photosensitive composition comprising (A) a first alkaline aqueous solution-soluble resin having, on a side chain, a hydrophobic aminoalkyl group represented by the formula (1), (B) a second alkaline aqueous solution-soluble resin, and (C) an infrared absorber.

[0010] The working mechanism of the invention is not evident but is estimated as follows:

The photosensitive composition of the invention comprises two kinds of alkali-soluble resins, one of which is the first alkali-soluble resin (A) having a hydrophobic aminoalkyl group of a specific structure. The hydrophobic aminoalkyl group of the first alkali-soluble resin (A) can interact with a functional group of the second alkali-soluble resin (B). As a result, the photosensitive composition of the invention is able to form a physically rigid film.

When the compatibility between the two alkali-soluble resins contained in the photosensitive composition of the invention is low, one of the alkali-soluble resins can form a dispersion phase thereby forming a phase separation structure (sea/island structure). It is estimated that as described above, the first alkali-soluble resin (A) has a hydrophobic aminoalkyl group thereby interacting with the functional group of the second alkali-soluble resin (B) to enhance the adhesiveness between the sea region and island region in the sea/island structure.

It is estimated that when the photosensitive composition of the invention is applied to a recording layer of a positive-type planographic printing plate precursor for infrared laser, the film strength of the recording layer as a whole is increased, and thus resistance to a plate cleaner (cleaner resistance) and scratch resistance are particularly improved; simultaneously, the resistance to an alkaline aqueous developer is improved in a light-unexposed portion, while such interaction is rapidly canceled in a light-exposed region, thus increasing discrimination and broadening development latitude.

DESCRIPTION OF THE PRESENT INVENTION

<Photosensitive composition>

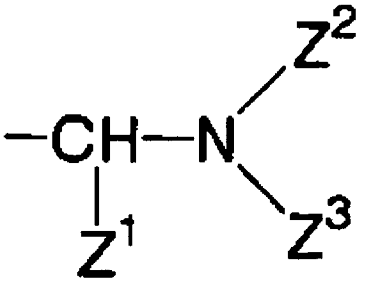
[0011] The photosensitive composition of the present invention comprises (A) a first alkaline aqueous solution-soluble resin having, on a side chain, a hydrophobic aminoalkyl group represented by the formula (1) (first alkali-soluble resin), (B) a second alkaline aqueous solution-soluble resin (second alkali-soluble resin), and (C) an infrared absorber.

Hereinafter, the respective components are described in detail.

(A) First alkaline aqueous solution-soluble resin having, on a side chain, a hydrophobic aminoalkyl group represented by the formula (1) (first alkali-soluble resin)

[0012] The hydrophobic aminoalkyl group represented by the following formula (1) is described.

[0013]



Formula (1)

[0014] In the formula (1), Z^1, Z^2 and Z^3 each independently represent a hydrogen atom or a monovalent substituent group consisting of one or more nonmetal atoms.

The monovalent substituent group consisting of one or more nonmetallic atoms represented by Z^1, Z^2 or Z^3 is preferably a substituent group having a linking portion and a terminal portion. The linking portion can be used as necessary, so the monovalent substituent group consisting of one or more nonmetallic atoms may have only the terminal portion shown below.

The monovalent substituent group consisting of one or more nonmetallic atoms may be substituted by an alkyl group, an aryl group, or the like.

[0015] Examples of the linking portion include an alkylene group, an alkenylene group, an arylene group such as phenylene or naphthalene, a heteroatom-containing heterocyclic group such as pyridyl, pyrazyl, pyrimidyl and thiazolyl, $-(C_2H_4O)_n$-group (n = 1 to 12), $-(C_2H_4S)_n$- group (n = 1 to 12), $-Ph-NHSO_2$- group, or a combination of one or more of such groups.

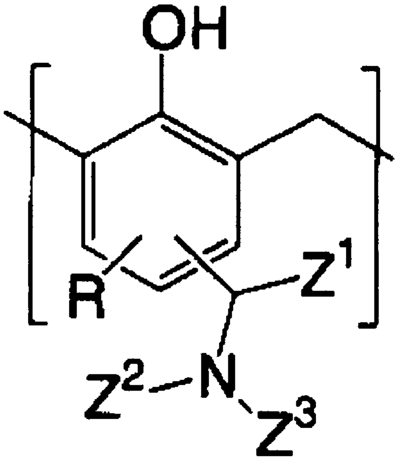
[0016] Examples of the terminal portion include a hydrogen atom, an alkyl group, an alkenyl group, a cycloalkyl group, an unsaturated cyclic hydrocarbon group, an aryl group, a heterocyclic group, an aralkyl group, $-OR^1$, $-SR^1$, $-COOR^1$, $-O-COR^1$, $-CO-R^2$, $-SO_3-R^1$, $-SO_2-R^1$, -CN, $-NO_2$, a halogen atom, a phosphate group, a phosphonate group, a t-amine group, an amide group, an imide group, and a sulfonamide group. R^1 and R^2 are independently selected from a hydrogen atom, a halogen atom, an alkyl group, an alkenyl group, a cycloalkyl group, an unsaturated cyclic hydrocarbon group, an aryl group, a heterocyclic group, an aralkyl group, and an amine group.

[0017] A hydrophobic aminoalkyl group, such as those described above, may be bound to a side chain of an alkali-soluble resin, and as the alkali-soluble resin, a conventionally known alkali-soluble resin can be used. The hydrophobic aminoalkyl group is preferably bound to a side chain of an alkali-soluble resin having a phenol structure in its repeating unit, and is more preferably bound covalently to a phenyl ring of phenol resin.

[0018] Preferable structures of the first alkali-soluble resin according to the invention are shown below, but the invention is not limited thereto.

The formula (2) below shows a preferable structure of the first alkali-soluble rein, and examples of the respective groups R, Z^1, Z^2 and Z^3 in the formula (2) are shown in Tables 1 to 3 below. The substituent groups R, Z^1, Z^2 and Z^3 shown in Tables 1 to 3 can be arbitrarily combined.

[0019]



Formula (2)

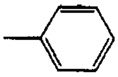
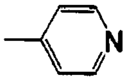
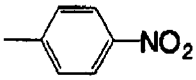
[0020]

Table 1

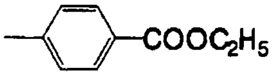
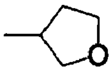
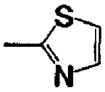
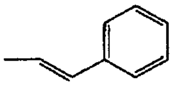
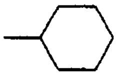
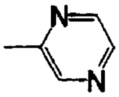
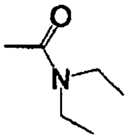
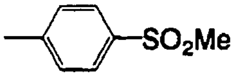
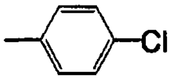
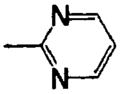
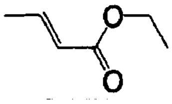
	R
R-1	-H
R-2	$-CH_3$
R-3	$-C_2H_5$
R-4	$-C_3H_8$
R-5	$-n-C_4H_9$
R-6	$-t-C_4H_9$

[0021]

Table 2

	Z^1
z^1-1	—H
Z^1-2	$—CH_3$
Z^1-3	
Z^1-4	$—C_2H_5$
Z^1-5	
Z^1-6	$—C_3H_8$
Z^1-7	$—COOC_2H_5$
Z^1-8	

(continued)

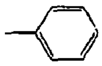
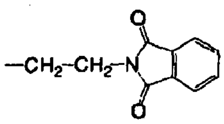
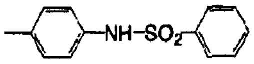
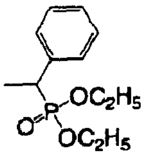
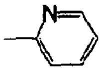
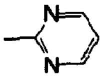
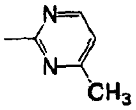
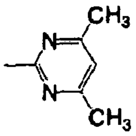
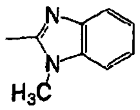
	Z^1
Z^1-9	
Z^1-10	
Z^1-11	
Z^1-12	
Z^1-13	
Z^1-14	
Z^1-15	
Z^1-16	
Z^1-17	
Z^1-18	
Z^1-19	
Z^1-20	

[0022]

Table 3

	Z^2	Z^3
Z^{23}-1	—H	—C_2H_4OH
Z^{23}-2	—H	
Z^{23}-3	—CH_3	—C_2H_4OH
Z^{23}-4	—CH_2-CH=CH_2	—CH_2-CH=CH_2

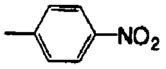
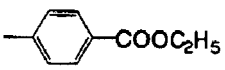
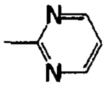
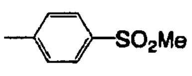
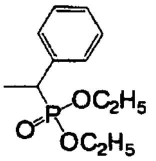
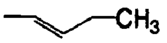
(continued)

	Z^2	Z^3
Z^{23}-5	$-COOH$	$-COOH$
Z^{23}-6	$-CH_3$	
Z^{23}-7	$-CH_3$	
Z^{23}-8	$-CH_3$	$-C_2H_4SO_2-CH_3$
Z^{23}-9	$-C_2H_4\text{-}O\text{-}C_2H_4\text{-}O\text{-}CH_3$	$-C_2H_4-O-C_2H_4-O-CH_3$
Z^{23}-10	$-CH_3$	
Z^{23}-11	$-CH_2-CH-CH_2$	
Z^{23}-12	$-C_2H_4OH$	$-C_2H_4OH$
Z^{23}-13	$-H$	$-C_2H_4\text{-}S\text{-}C_2H_4OH$
Z^{23}-14	$-H$	$-(C_2H_4\text{-}O)_3\text{-}C_2H_4OH$
Z^{23}-15	$-C_2H_4OH$	$-C_2H_4OH$
Z^{23}-16	$-H$	
Z^{23}-17	$-H$	
Z^{23}-18	$-H$	
Z^{23}-19	$-H$	
Z^{23}-20	$-H$	

[0023] Specific examples (Compound Nos. 1 to 4) of the first alkali-soluble resin represented by the formula (2) are shown in Table 4 below, but the invention is not limited thereto.

[0024]

Table 4

Compound No.	R	Z^1	Z^2	Z^3
1	—H		$—C_2H_4—O—C_2H_4—O—CH_3$	$-C_2H_4-O-C_2H_4-O-CH_3$
2	—H		—H	
3	$—CH_3$		$—CH_2—CH=CH_2$	
4	$—C_2H_5$		—H	$—C_2H_4—S—C_2H_4OH$

[0025] The method of synthesizing the first alkali-soluble resin in the invention is not particularly limited, and the first alkali-soluble resin can be produced, for example by reaction (nucleophilic addition reaction) of a phenol resin having phenoxide substituent groups with an isocyanate group-containing compound in a solvent in the presence of a Sn metal as a catalyst in order that some substituent groups of the phenol resin are substituted by specific substituent groups. The nucleophilic addition reaction of a phenoxide of a novolak-type phenol resin with an isocyanate group-containing compound can be carried out in the following manner. When some hydroxyl groups of the novolak-type phenol resin are to be substituted by specific functional groups, the novolak-type phenol resin is dissolved at a concentration of 20 to 80 wt% (preferably 30 to 70 wt%) in a solvent, and the isocyanate group-containing compound is added thereto such that the molar ratio of the isocyanate group-containing compound to the hydroxyl groups of the novolak-type phenol resin corresponds to the desired proportion of the hydroxyl groups to be substituted by the specific functional groups, and Sn metal is further added as catalyst in a molar ratio of 0.5 to 5.0% (preferably 1.0 to 2.5%) relative to the isocyanate group-containing compound under a temperature condition in the range of 10 to 200˚C, and the mixture is stirred for several hours while the temperature is kept in the above range. The reaction temperature is preferably in the range of 20 to 150˚C, more preferably in the range of 20 to 100˚C. Examples of the solvent to be used in the reaction includes chloroform, dichloromethane, dimethoxy sulfoxide (DMSO), N,N-dimethylformamide (DMF), dimethyl ether (DME), and tetrahydrofuran (THF). Among them, tetrahydrofuran (THF) is preferably used. The above-mentioned Sn metal to be used is preferably dibutyltin dilaurate.

[0026] The molecular weight of the first alkali-soluble resin in the invention is preferably 2000 or more, more preferably from 3000 to 500,000, in terms of weight-average molecular weight. The number-average molecular weight is preferably 1000 or more, more preferably from 2000 to 400,000.

[0027] The content of hydrophobic aminoalkyl group in the first alkali-soluble resin in the invention is preferably from 1 to 99 mol%, more preferably from 5 to 95 mol%, still more preferably from 20 to 95 mol%, from the viewpoint of cleaner resistance and developability.

(B) Second alkaline aqueous solution-soluble resin (second alkali-soluble resin)

[0028] The second alkali-soluble resin (B) in the invention is not particularly limited, but is preferably an alkali-soluble resin not compatible with the first alkali-soluble resin (A), and is more preferably an alkali-soluble resin which cause phase separation when mixed with the first alkali-soluble resin (A).
Preferable examples of the second alkali-soluble resin include alkali-soluble resins such as resins having an acidic group in a main chain and/or in a side chain of the polymer (for example, a phenolic resin).

[0029] Examples of the alkali-soluble resin having the acidic group in a main chain and/or side chain of the polymer include resins having the acidic group selected from the following (1) to (6) in a main chain and/or side chain of the polymer.

[0030]

(1) phenol group (-Ar-OH)
(2) sulfonamide group ($-SO_2NH-R$)
(3) substituted sulfonamide acid group (referred to hereinafter 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 ($-OPO_3H_2$)

[0031] In the foregoing (1) to (6), Ar represents a divalent aryl linking group, and R represents a hydrogen atom or a hydrocarbon group.

[0032] The alkali-soluble resin having an acidic group selected from the above-mentioned (1) to (6) is preferably an alkali-soluble resin having (1) a phenol group, (2) a sulfonamide group, or (3) an active imide group, more preferably an alkali-soluble resin having (1) a phenol group or (2) a sulfonamide group, from the viewpoint of suffciently securing solubility in an alkaline developer, development latitude, and film strength. The alkali-soluble resin having an acidic group selected from the above-mentioned (1) to (6) is most preferably an alkali-soluble resin having (1) a phenol group in a main chain and/or a side chain of the polymer.

[0033] Examples of the alkali-soluble resin having (1) a phenol group include the following resins.

Examples include novolak resin such as a condensation polymer of phenol and formaldehyde, a condensation polymer of m-cresol and formaldehyde, a condensation polymer of p-cresol and formaldehyde, a condensation polymer of a mixture of m-cresol and p-cresol with formaldehyde, a condensation polymer of phenol, m- and/or p-cresol, and formaldehyde, and a condensation polymer of pyrogallol and acetone. A copolymer obtained by copolymerizing a compound having a phenol group on a side chain thereof can also be mentioned.

[0034] In particular, the alkali-soluble resin is preferably a novolak resin in respect of relatively high discrimination of the resin itself.

Examples of the novolak resin include phenol-formaldehyde resin, m-cresol-formaldehyde resin, p-cresol-formaldehyde resin, (m- and p- mixed cresol)-formaldehyde resin, and phenol/cresol (which may be m-, p-, o-, m- p- mixed, m- o- mixed, or o- p- mixed cresol) mixed -formaldehyde resin.

[0035] The novolak resin preferably has a weight-average molecular weight of 1,500 or more and a number-average molecular weight of 300 or more. The novolak resin more preferably has a weight-average molecular weight of 3,000 to 30,000, a number-average molecular weight of 500 to 250,000, and a dispersion degree (weight-average molecular weight/number-average molecular weight) in the range of 1.1 to 10.

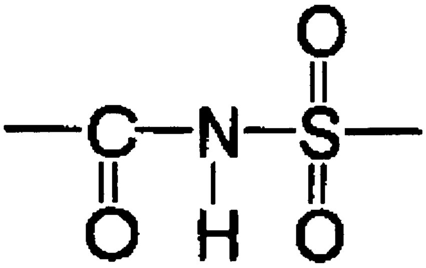
[0036] Other examples of compounds having a phenol group include a phenol group-containing acrylamide, methacrylamide, acrylate ester, methacrylate ester, or hydroxystyrene.

[0037] The alkali-soluble resin having (2) a sulfonamide group can be, for example, a polymer containing, as a main constituent component, minimum constituent units derived from a compound having a sulfonamide group. Such a compound may be, for example, a compound having, in its molecule, at least one sulfonamide group whose nitrogen atom has at least one hydrogen atom bound thereto and at least one polymerizable unsaturated group.

Particularly, m-aminosulfonyl phenyl methacrylate, N-(p-aminosulfonyl phenyl) methacrylamide, N-(p-aminosulfonyl phenyl) acrylamide, and the like can be preferably used in the invention.

[0038] The alkali-soluble resin having (3) active imide group can be, for example, a polymer containing, as a main constituent component, minimum constituent units derived from a compound having an active imide group. Such a compound may be, for example, a compound having, in its molecule, at least one active imide group represented by the structural formula below and at least one polymerizable unsaturated group.

[0039]



[0040] Specifically, N-(p-toluenesulfonyl) methacrylamide, N-(p-toluenesulfonyl) acrylamide, and the like can be suitably used.

[0041] It is not necessary that the minimum constituent units having an acidic group selected from the above-mentioned

(1) to (6), constituting the second alkali-soluble resin in the invention, be of a single kind, and a copolymer obtained by copolymerizing two or more kinds of minimum constituent units having the same acidic group or by copolymerizing two or more kinds of minimum constituent units having different acidic groups can also be used.

The copolymer preferably contains a compound having an acidic group selected from (1) to (6) as a copolymerization unit in an amount of 10 mol% or more, more preferably 20 mol% or more. When the content is less than 10 mol%, the effect on improvement of development latitude achieved by the addition of the copolymer may not be sufficiently.

The second alkali-soluble resin is preferably a copolymer of N-(4-aminosulfonyl phenyl) methacrylamide/acrylonitrile/methyl methacrylate.

[0042] The second alkali-soluble resin in the invention preferably has a weight-average molecular weight of 2,000 or more and a number-average molecular weight of 500 or more. The second alkali-soluble resin more preferably has a weight-average molecular weight of 5,000 to 300,000, a number-average molecular weight of 800 to 250,000, and a dispersion degree (weight-average molecular weight/number-average molecular weight) of 1.1 to 10.

[0043] The above-described alkali-soluble resin is particularly preferably a phenolic resin (novolak resin), which is specifically preferable in that the hydrophobic aminoalkyl groups of the first alkali-soluble resin (A) interacts with the -OH groups of the phenolic resin to form hydrogen bonds or the like, to improve the film strength of the photosensitive composition, resulting in increase in the strength of the whole photosensitive layer using this photosensitive composition and in scratch resistance.

[0044] In the photosensitive composition of the invention, the total content of the first alkali-soluble resin (A) and the alkali-soluble resin (B) is preferably in the range of 30 to 99 wt%, more preferably 40 to 95 wt%, still more preferably 50 to 90 wt%, from the viewpoint of retaining cleaner resistance and stable film properties.

[0045] The compounding ratio of the first alkali-soluble resin (A) to the second alkali-soluble resin (B) is preferably in the range of 99 : 1 to 1 : 99, more preferably in the range of 95: 5 to 55 : 45 or 5 : 95 to 45 : 55, still more preferably in the range of 90 : 10 to 60 : 40 or 10 : 90 to 40 : 60.

(C) Infrared absorber

[0046] Preferable examples of the infrared absorber (C) include a wide variety of known pigments and dyes.

[0047] The pigments may be selected from commercially-available pigments and those described in Color Index (C. I.) Handbook, "Saishin Ganryo Binran" (Newest Dye Handbook) (published in 1977 and compiled by Japanese Society of Pigment Technology), "Saishin Ganryho Oyo Gijyutsu" (Newest Pigment Applied Technology) (published in 1986 by CMC), and "Insatsu Inki Gijyutsu" (Printing Ink Technology) (published in 1984 by CMC).

[0048] Examples of usable pigments include black pigments, yellow pigments, orange pigments, brown pigments, red pigments, violet pigments, blue pigments, green pigments, fluorescent pigments, metallic powder pigments, and other pigments such as polymer-binding dyes. More specifically, examples include insoluble azo pigments, azo lake pigments, condensed azo pigments, chelate azo pigments, phthalocyanine pigments, anthraquinone pigments, perylene and perinone pigments, thioindigo pigments, quinacridone pigments, dioxazine pigments, isoindolinone pigments, quinophthalone pigments, dyed lake pigments, azine pigments, nitroso pigments, nitro pigments, natural pigments, fluorescent pigments, inorganic pigments, and carbon black.

[0049] The pigments may or may not be subjected to surface treatment before use. The method of surface treatment may be a method of coating the surface with resin or wax, a method of allowing a surfactant to adhere to the surface, and a method of bonding a reactive material (e.g., a silane coupling agent, an epoxy compound, a polyisocyanate etc.) onto the surface of the pigment. These methods of surface - treatment are described in "Kinzoku Sekken No Seishitsu To Oyo" (Properties and Application of Metallic Soap) (Sachi Shobo), "Insatsu Inki Gijyutsu" (Printing Ink Technology) (published in 1984 by CMC Shuppan) and "Saishin Ganryo Oyo Gijyutsu" (Newest Pigment Applied Technology) (published in 1986 by CMC Shuppan).

[0050] The particle diameter of the pigment is in the range of preferably 0.01 to 10 μm, more preferably 0.05 to 1 μm, still more preferably 0.1 to 1 μm. When the particle diameter is less than 0.01 μm, there may be disadvantages in the stability of the dispersion in the photosensitive layer coating solution. When the particle diameter is more than 10 μm, there may be disadvantage in the uniformity of the photosensitive layer.

[0051] As the method of dispersing the pigments, a known dispersion technique used in production of ink or toner can be used. The dispersion may involve the use of dispersing machines such as a supersonic dispersing device, a sand mill, an attritor, a pearl mill, a super mill, a ball mill, an impeller, a disperser, a KD mill, a colloid mill, a dynatron, a triple roll mill, and a press kneader. These are described in detail in "Saishin Ganryo Oyo Gijyutsu" (Newest Pigment Applied Technology) (published in 1986 by CMC Shuppan).

[0052] The dye may be selected from commercially-available dyes and known dyes described in literatures (for example, "Senryo Binran" (Dye Handbook) published in 1970 and compiled by Society of Synthetic Organic Chemistry, Japan), and examples thereof include azo dyes, metal complex salt azo dyes, pyrazolone azo dyes, anthraquinone dyes, phthalocyanine dyes, carbonium dyes, quinone imine dyes, methine dyes, and cyanine dyes. Among the pigments or dyes described above, those pigments or dyes absorbing infrared rays or near infrared rays are particularly preferable in respect of compatibility with lasers emitting infrared rays or near infrared rays.

[0053] As the pigment absorbing infrared light or near infrared light, carbon black is preferably used. Examples of dyes absorbing infrared light or near infrared light include cyanine dyes described in JP-ANo. 58-125246, JP-ANo. 59-84356, JP-A No. 59-202829, JP-A No. 60-78787 etc., methine dyes described in JP-A No. 58-173696, JP-A No. 58-181690, JP-ANo. 58-194595 etc., naphthoquinone dyes described in JP-A No. 58-112793, JP-A No. 58-224793, JP-A No. 59-48187, JP-A No. 59-73996, JP-A No. 60-52940, JP-A No. 60-63744 etc., squarylium dyes described in JP-A No. 58-112792 etc., and cyanine dyes described in U.K. Patent No. 434,875.

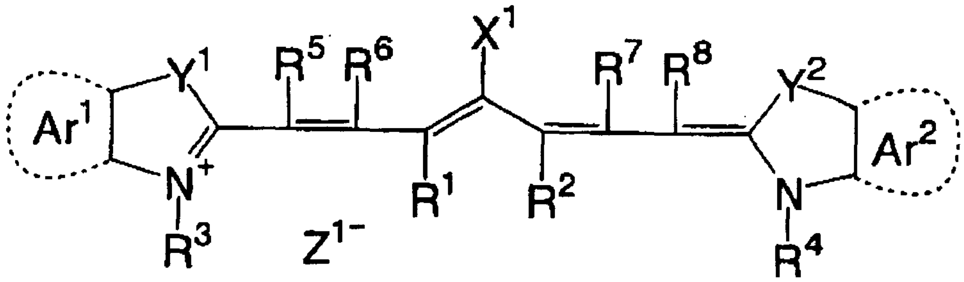
[0054] Near infrared ray-absorbing sensitizers described in U.S. Patent No. 5,156,938 are also preferable. Preferable examples also include substituted aryl benzo(thio) pyrylium salts described in U.S. Patent No. 3,881,924, trimethine thiapyrylium salts described in JP-A No. 57-142645 (U.S. Patent No. 4,327,169), pyrylium-containing compounds described in JP-A No. 58-181051, JP-A No. 58-220143, JP-A No. 59-41363, JP-A No. 59-84248, JP-A No. 59-84249, JP-A No. 59-146063, and JP-A No. 59-146061, cyanine dyes described in JP-ANo. 59-216146, pentamethine thiopyrylium salts described in U.S. Patent No. 4,283,475, pyrylium compounds described in Japanese Patent Publication (JP-B) No. 5-13514 and JP-B No. 5-19702, and commercially-available products such as EPOLIGHT III-178, EPOLIGHT III-130, EPOLIGHT III-125, and EPOLIGHT V-176A manufactured by Epoline.

[0055] Other particularly preferable examples of the dyes include the near infrared ray-absorbing dyes of formulae (I) and (II) described in U.S. Patent No. 4,756,993.

[0056] Particularly preferable among these dyes are cyanine dyes, squarylium dyes, pyrylium salts, nickel thiolate complexes and indolenine cyanine dyes.Cyanine dyes and indolenine cyanine dyes are more preferable. An example of a particularly preferable cyanine dye is represented by the following formula (i):

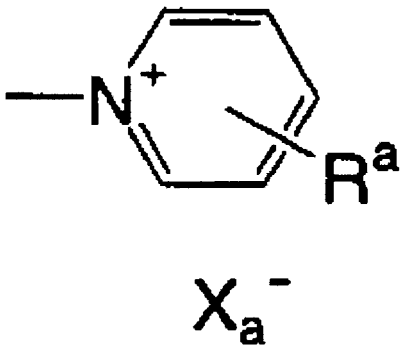
[0057]

Formula (i)



[0058] In the formula (i) above, X^1 represents a hydrogen atom, a halogen atom, $-NPh_2$, X^2-L^1, or the group shown below. X^2 represents an oxygen atom, a nitrogen atom, or a sulfur atom, and L^1 represents a C_{1-12} hydrocarbon group, an aromatic ring having a heteroatom, or a C_{1-12} hydrocarbon group containing a heteroatom. The heteroatom refers to N, S, O, a halogen atom, or Se. Xa has the same definition as that of Z^{1-} defined later, and R^a represents a substituent group selected from a hydrogen atom, an alkyl group, an aryl group, a substituted or unsubstituted amino group, or a halogen atom.

[0059]



[0060] R^1 and R^2 each independently represent a C_{1-12} hydrocarbon group. For the shelf stability of the coating liquid, each of R^1 and R^2 is preferably a hydrocarbon group containing 2 or more carbon atoms. In a particularly preferable embodiment, R^1 and R^2 are bound to each other to form a 5- or 6-memberred ring.

[0061] Ar^1 and Ar^2 may be the same or different, and each independently represent an aromatic hydrocarbon group which may have a substituent group. The aromatic hydrocarbon group is preferably a benzene ring or naphthalene ring. Preferable examples of the substituent group include a hydrocarbon group containing 12 or less carbon atoms, a halogen atom, or an alkoxy group containing 12 or less carbon atoms. Y^1 and Y^2 may be the same or different, and each independently represent a sulfur atom or a dialkyl methylene group containing 12 or less carbon atoms. R^3 and R^4 may be the same or different, and each independently represent a hydrocarbon group containing 20 or less carbon atoms, which may have a substituent group. The substituent group is preferably an alkoxy group containing 12 or less carbon atoms, a carboxyl group, or a sulfo group. R^5, R^6, R^7 and R^8 may be the same or different, and each independently represent a hydrogen atom or a hydrocarbon group containing 12 or less carbon atoms. Each of R^5, R^6, R^7 and R^8 is preferably a hydrogen atom because the starting material is easily available. Z^{1-} represents a counter anion. However, when the cyanine dye represented by the formula (a) has an anionic substituent group in its structure and neutralization of the charge is unnecessary, Z^{1-} can be omitted. Because of the shelf stability of the coating liquid, Z^{1-} is preferably a halogen ion, a perchlorate ion, a tetrafluoroborate ion, a hexafluorophosphate ion, or a sulfonate ion, particularly preferably a perchlorate ion, a hexafluorophosphate ion, or an aryl sulfonate ion.

[0062] The amount of the pigment or dye used as the infrared absorber (C) is preferably 0.01 to 50 wt%, more preferably 0.1 to 10 wt%, relative to the total solid content of the photosensitive composition. When the infrared absorber is a dye, the amount of the dye is particularly preferably 0.5 to 10 wt%. When the infrared absorber is a pigment, the amount of the pigment is particularly preferably 3.1 to 10 wt%. When the amount of the dye or pigment to be added is in the above range, it is possible to realize preferable recording sensitivity of the infrared absorber (C) when used in a positive recording layer, as well as excellent uniformity and durability of the recording layer.

<Positive-type planographic printing plate precursor>

[0063] The positive-type planographic printing plate precursor of the invention has, on a support, a recording layer containing a photosensitive composition comprising (A) a first alkaline aqueous solution-soluble resin having, on a side chain, a hydrophobic aminoalkyl group represented by the above formula (1), (B) a second alkaline aqueous solution-soluble resin, and (C) an infrared absorber.
That is, the planographic printing plate precursor of the invention contains the aforementioned photosensitive composition according to the invention in the recording layer.
Hereinafter, the planographic printing plate precursor of the invention is described in detail.

Layer constitution of the recording layer

[0064] The recording layer of the planographic printing plate precursor according to the invention can be used preferably as a photosensitive layer of phase separation structure, such as the structure described in JP-A No. 11-44956, but is not limited thereto.

Other ingredients

[0065] In addition to the above essential ingredients (A) to (C), a wide variety of additives can further be added, as necessary, to the photosensitive composition constituting the recording layer of the planographic printing plate precursor of the invention.

For regulating the solubility of the recording layer, it is preferable to add a dissolution inhibitor, which improves the function of inhibiting the dissolution of the alkali-soluble resins (A) and (B) in a developer. Examples of the dissolution inhibitor include onium salts, aromatic sulfone compounds, aromatic sulfonate esters, and multifunctional amine compounds. In particular, it is preferable to use a substance that is thermally-decomposable and substantially reduces the solubility of the alkali-soluble resin in the undecomposed state, in order to improve the ability of the composition to prevent an image region from being dissolved in a developer. Examples of such a substance include onium salts, o-quinone diazide compounds, and alkyl sulfonate esters.

[0066] Preferable examples of the onium salt used in the invention include diazonium salts described in S. I. Schlesinger, Photogr. Sci. Eng., 18, 387 (1974), T. S. Bal et al., Polymer, 21, 423 (1980), and JP-ANo. 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, p. 478, Tokyo, Oct (1988), 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, p. 31 (1988), EP Patent No. 104,143, U.S. Patent Nos. 5,041,358 and 4,491,628, JP-ANo. 2-150848 and JP-A No. 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), EU Patent Nos. 370,693, 233,567, 297,443 and 297,442, U.S. Patent No. 4,933,377, 3,902,114, 5,041,358, 4,491,628, 4,760,013, 4,734,444 and 2,833,827, and German 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) and J. V Crivello et al., J. Polymer Sci., Polymer Chem. Ed., 17, 1047 (1979), and arsonium salts described in C. S. Wen et al., Teh, Proc. Conf. Rad. Curing ASIA, p. 478, Tokyo, Oct (1988).

[0067] Among these onium salts, diazonium salts and quaternary ammonium salts are particularly preferable from the viewpoint of dissolution prevention and pyrrolysis. Preferable examples of diazonium salts include diazonium salts represented by formula (I) shown in JP-ANo. 5-158230 and diazonium salts represented by formula (1) shown in JP-A No. 11-143064, most preferably diazonium salts absorbing lights of short wavelengths in the visible light range represented by formula (1) in JP-A No. 11-143064. Examples of quaternary ammonium salts include quaternary ammonium salts shown in (1) to (10) in Chemical Formulae [5] and [6] in JP-A No. 2002-229186.

[0068] Examples of counter ions for the onium salts include tetrafluoroboric acid, hexafluorophosphoric acid, triisopropyl naphthalene sulfonic acid, 5-nitro-o-toluene sulfonic acid, 5-sulfosalicylic acid, 2,5-dimethyl benzene sulfonic acid, 2,4,6-trimethyl benzene sulfonic acid, 2-nitrobenzene sulfonic acid, 3-chlorobenzene sulfonic acid, 3-bromobenzene sulfonic acid, 2-fluorocapryl naphthalene sulfonic acid, dodecyl benzene sulfonic acid, 1-naphthol-5-sulfonic acid, 2-methoxy-4-hydroxy-5-benzoyl-benzene sulfonic acid, and p-toluene sulfonic acid. Among these, hexafluorophosphoric acid and alkyl aromatic sulfonic acids such as triisopropyl naphthalene sulfonic acid and 2,5-dimethyl benzene sulfonic acid are particularly preferable.

[0069] An example of preferable quinonediazides is an o-quinonediazide compound. The o-quinondiazide compound used in the invention can be a compound having at least one o-quinonediazide group which increases alkali solubility upon pyrrolysis, and compounds having various structures can be used. That is, o-quinone diazide facilitates dissolution of the recording layer by the following effects: the loss of dissolution inhibition ability of the binder upon pyrrolysis, and the conversion of the o-quinone diazide itself into an alkali-soluble substance.

As the o-quinone diazide compounds usable in the invention, compounds described, for example, on pages 339 to 352 in Light-Sensitive Systems authored by J. Coser (John Wiley & Sons. Inc.) can be used. In particular, o-quinone diazide sulfonates or sulfonic amides obtained by reaction with various aromatic polyhydroxy compounds or aromatic amino compounds are preferable. Further, the ester between benzoquinone(1,2)-diazide sulfonic acid chloride or naphthoquinone-(1,2)-diazide-5-sulfonic acid chloride and pyrogallol-acetone resin described in JP-B No. 43-28403 and the ester between benzoquinone-(1,2)-diazide sulfonic acid chloride or naphthoquinone-(1,2)-diazide-5-sulfonic acid chloride and phenol-formamide resin described in U.S. Patent Nos. 3,046,120 and 3,188,210 are also preferable.

[0070] The esters between naphthoquinone-(1,2)-diazo-4-sulfonic acid chloride and phenol formaldehyde resin or cresol-formaldehyde resin, and the ester between naphthoquinone-(1,2)-diazide-4-sulfonic acid chloride and pyrogallol-acetone resin are also preferable. Other useful o-quinone diazide compounds are known and reported in many patent publications. Examples thereof include those described in JP-A No. 47-5303, JP-A No. 48-63802, JP-A No. 48-63803, JP-A No. 48-96575, JP-A No. 49-38701, JP-ANo. 48-13354, JP-B No. 41-11222, JP-B No. 45-9610, JP-B No. 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, U.K. Patent Nos. 1,227,602, 1,251,345, 1,267,005, 1,329,888 and 1,330,932 and German Patent No. 854,890.

[0071] The amount of the onium salt that is a decomposable dissolution inhibitor and/or the o-quinone diazide compound to be added is in the range of preferably 1 to 10 wt%, more preferably 1 to 5 wt%, still more preferably 1 to 2 wt%, based on the total solid content of the photosensitive composition or the recording layer.

These compounds can be used alone or in the form of a mixture thereof.

[0072] The amount of a decomposable dissolution inhibitor other than onium salts and o-quinone diazide compounds is preferably from 0.1 to 5 wt%, more preferably from 0.1 to 2 wt%, still more preferably from 0.1 to 1.5 wt%.

The dissolution inhibitor in the invention is contained preferably in the same layer as the layer containing the alkali-soluble resins.

[0073] A non-decomposable dissolution inhibitor may be simultaneously used, and preferable examples thereof include a sulfonate ester, a phosphate ester, an aromatic carboxylate ester, an aromatic disulfone, a carboxylic acid anhydride, an aromatic ketone, an aromatic aldehyde, an aromatic amine, and an aromatic ether etc. described in detail in JP-A No. 10-268512, acid coloring pigments having a lactone skeleton, a N,N-diarylamide skeleton, or a diarylmethylimino skeleton and also serving as a coloring agent described in detail in JP-ANo. 11-190903, and nonionic surfactants described in detail in JP-A No. 2000-105454.

[0074] For the purpose of improving sensitivity, cyclic acid anhydrides, phenols, and organic acids can also be simultaneously used in the photosensitive composition constituting the recording layer according to the planographic printing plate precursor of the invention.

Examples of the cyclic acid anhydrides include those described in US Patent No. 4,115,128, such as phthalic anhydride, tetrahydrophthalic anhydride, 3,6-endoxy-4-tetrahydrophthalic anhydride, tetrachlorophthalic anhydride, maleic anhydride, chloromaleic anhydride, α-phenylmaleic anhydride, succinic anhydride, and pyromellitic anhydride.

Examples of the phenols include bisphenol A, p-nitrophenol, p-ethoxyphenol, 2,4,4'-trihydroxybenzophenone, 2,3,4-trihydroxybenzophenone, 4-hydroxybenzophenone, 4,4',4"-trihydroxytriphenyl methane, and 4,4',3",4"-tetrahydroxy-3,5,3',5'-tetramethyl triphenyl methane.

Examples of the organic acids include those described in JP-A No. 60-88942 and JP-A No. 2-96755, such as sulfonic acids, sulfinic acids, alkyl sulfuric acids, phosphonic acids, phosphate esters, and carboxylic acids.

The proportion of the cyclic acid anhydride, phenols, and organic acids in the recording layer is preferably from 0.05 to 20 wt%, more preferably from 0.1 to 15 wt%, still more preferably from 0.1 to 10 wt%.

[0075] In addition, epoxy compounds, vinyl ethers, and the phenol compounds having a hydroxymethyl group described in JP-A No. 8-276558, phenol compounds having an alkoxymethyl group, and the crosslinking compounds having alkali-dissolution inhibiting function described in JP-A No. 11-160860 proposed by the present inventors, can be added as necessary depending on the object.

[0076] A printing agent for giving a visible image immediately after heating by exposure to light, and a dye or pigment as an image coloring agent can be added to the photosensitive composition constituting the recording layer of the planographic printing plate precursor according to the invention.

The printing agent is typically a combination of a compound releasing an acid by heating with exposure to light (photoacid releasing agent) and an organic dye capable of forming a salt. Specific examples include a combination of o-naphthoquinonediazide-4-sulfonic acid halogenide and a salt-forming organic dye as described in JP-A No. 50-36209 and JP-A No. 53-8128 and a combination of a trihalomethyl compound and a salt-forming organic dye as described in JP-A No. 53-36223, JP-A No. 54-74728, JP-A No. 60-3626, JP-A No. 61-143748, JP-A No. 61-151644 and JP-ANo. 63-58440. The trihalomethyl compound may be an oxazole compound or a triazine compound, both of which are excellent in stability over time and give a clear print image.

[0077] As the image coloring agent, a dye different from the above-mentioned salt-formable organic dyes may be used. Preferable examples of such a dye, and of 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 (each of which is 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 recording layer at a ratio of 0.01 to 10% by mass, and preferably 0.1 to 3% by mass, relative to the total solid contents therein.

[0078] Whenever necessary, a plasticizer may be added to the photosensitive composition constituting the recording layer of the planographic printing plate according to the invention to give flexibility to a coating film. 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 olete, acrylic acid, and methacrylic acid.

[0079] Further, it is preferable to add a surfactant to the photosensitive composition constituting the recording layer of the planographic printing plate precursor according to the invention, so as to enhance the stability of the treatment under a wider range of development conditions. The surfactant is preferably a fluorine-containing surfactant.

(Coating solvent and coating method)

[0080] The planographic printing plate precursor according to the invention can be prepared by dissolving the photo-

sensitive composition according to the invention described above in a solvent, and applying the obtained solution onto an appropriate support to form a recording layer. A protective layer, a resin intermediate layer, and a backcoat layer described below can be formed as necessary in a similar manner.
Examples of usable solvents include, but are not limited to, ethylene dichloride, cyclohexanone, methylethylketone, methanol, ethanol, propanol, ethylene glycol monomethylether, 1-methoxy-2-propanol, 2-methoxyethyl acetate, 1-methoxy-2-propyl acetate, dimethoxyethane, methyl lactate, ethyl lactate, N,N-dimethylacetamide, N,N-dimethylformamide, tetramethylurea, N-methylpyrrolidone, dimethylsulfoxide, sulfolane, γ-butylolactone, and toluene. Only a single solvent may be used, or a mixture of two or more solvents may be used.
The concentration of the components (total solid content including additives) in the solvent is preferably from 1 to 50 wt %.

[0081] The amount of the recording layer (as solid matter) on the support after coating and drying may vary depending on the application, but is generally preferably from 0.5 to 5.0 g/m^2, and more preferably from 0.6 to 2.0 g/m^2 as the coating amount after drying, in view of the sensitivity and film properties.

[0082] Various methods may be used for applying the recording layer coating liquid. Examples thereof include bar coater coating, spin coating, spray coating, curtain coating, dip coating, air knife coating, blade coating, and roll coating.

(Support)

[0083] The support used in the planographic printing plate precursor according to the 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 a metal (which may be selected from the above metals) is laminated or vapor-deposited.

[0084] The support is preferably a polyester film or an aluminum plate, and more preferably an aluminum plate, since an 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 trace 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. A particularly preferable aluminum plate in the invention is a pure aluminum plate; however, since from the viewpoint of refining a completely pure aluminum cannot be easily produced, a trace amount of other elements may also be contained in the plate.
The aluminum plate used as the support is not specified in terms of the composition thereof. Thus, aluminum plates which are conventionally known can be appropriately used. The thickness of the aluminum plate used in the invention is from about 0.1 to 0.6 mm, preferably from 0.15 to 0.4 mm, and more preferably from 0.2 to 0.3 mm.

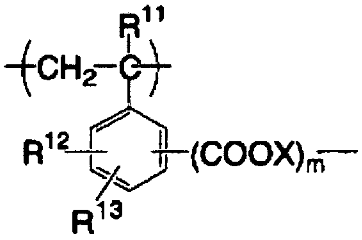
[0085] If necessary, prior to the surface-roughening treatment, the aluminum plate may optionally be subjected to degreasing treatment with a surfactant, an organic solvent, an aqueous alkaline solution or the like, in order to remove rolling oil or the like on the surface.
The surface-roughening treatment of the surface of the aluminum plate 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 the two kinds of methods may be used.
An aluminum plate whose surface is roughened as described above is if necessary subjected to alkali-etching treatment and neutralizing treatment. Thereafter, an anodizing treatment is optionally applied in order to improve the water holding capacity and wear resistance of the surface.
The electrolyte used in the anodizing treatment of the aluminum plate may be any one selected from various electrolytes which can form a porous oxide film. In general, the electrolyte is 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.

[0086] Treatment conditions for anodization cannot be specified as a general rule since conditions vary depending on the electrolyte used; however, the following range of conditions are generally suitable: an electrolyte concentration of 1 to 80% by mass, a solution temperature of 5 to 70°C, a current density of 5 to 60 A/dm^2, a voltage of 1 to 100 V, and an electrolyzing time of 10 seconds to 5 minutes. If the amount of anodic oxide film is less than 1.0 g/m^2, printing

resistance is inadequate or non-image portions of the planographic printing plate tend to become easily damaged and the so-called "blemish stains", resulting from ink adhering to damaged portions at the time of printing, are easily generated. After the anodizing treatment, the surface of the aluminum is if necessary subjected to treatment for obtaining hydrophilicity. This hydrophilicity treatment may be 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, the support is subjected to an immersing treatment or an electrolyzing treatment with an aqueous sodium silicate solution.
In addition, the following methods may also be used: a method of treating the support with potassium fluorozirconate, as disclosed in JP-B No. 36-22063, or with polyvinyl phosphonic acid, as disclosed in U.S. Patent Nos. 3,276,868, 4,153,461, and 4,689,272.

(Undercoat layer)

[0087] The planographic printing plate precursor according to the present invention is a plate having a recording layer containing the photosensitive composition as described above provided on a support, and an undercoat layer may be formed as needed between the support and the recording layer (between the support and the lowest recording layer if the recording layer has a multi-layer structure).
When formed, the undercoat layer between the support and the recording layer functions as a heat-insulating layer, inhibiting diffusion of the heat generated by exposure to an infrared laser to the support and allowing more efficient use of an infrared laser, and thus, is advantageous in improving sensitivity. When forming the undercoat layer, the recording layer according to the invention is positioned on the exposure face or in the vicinity thereof, and thus significantly retains its sensitivity to an infrared laser.
Also in the unexposed areas, the recording layer, which is resistant to penetration of the alkaline developer, functions as a protective layer for the undercoat layer, improving development stability, forming an image having superior discrimination, and ensuring image stability over time.
The undercoat layer is a layer containing an alkali-soluble polymer as its principal component and is extremely soluble in the developer. If the undercoat layer is formed close to the support, the exposed area, where the components in the photosensitive layer becomes more soluble by exposure, is dissolved or dispersed in the developer more readily without generation of undissolved film, for example, when a less active developer is used, which seems to be effective for improving developing efficiency. For that reason, the undercoat layer is thought to be useful.
[0088] Various organic compounds may be used as the components for the undercoat layer, and examples thereof include amino group-containing phosphonic acids such as carboxymethylcellulose, dextrin, gum arabic, and 2-aminoethylphosphonic acid; organic phosphonic acid that may be substituted such as phenylphosphonic acid, naphthylphosphonic acid, alkylphosphonic acids, glycerophosphonic acid, methylenediphosphonic acid and ethylenediphosphonic acid; organic phosphoric acids that may be substituted such as phenylphosphoric acid, naphthylphosphoric acid, alkylphosphoric acid and glycerophosphoric acid; organic phosphinic acids that may be substituted such as phenylphosphinic acid, naphthylphosphinic acid, alkylphosphinic acid and glycerophosphinic acid; amino acids such as glycine and β-alanine; and hydroxy group-containing amine hydrochloride salts such as triethanolamine hydrochloride salt. In an embodiment, a combination of one or more of these compounds is used.
[0089] In particular, an undercoat layer containing at least one compound selected from organic polymer compounds having the structural unit represented by the following formula is also preferable.
[0090]



[0091] In the formula above, R^{11} represents a hydrogen or halogen atom or an alkyl group; R^{12} and R^{13} each independently represent a hydrogen atom, a hydroxyl group, a halogen atom, an alkyl group, a substituted alkyl group, an aryl group, a substituted aryl group, $-OR^{14}$, $-COOR^{15}$, $-CONHR^{16}$, $-COR^{17}$ or -CN, or R^{12} and R^{13} may bind to each other forming a ring; R^{14} to R^{17} each independently represent an alkyl or aryl group; X represents a hydrogen or metal atom, or $NR^{18}R^{19}R^{20}R^{21}$; R^{18} to R^{21} each independently represent a hydrogen atom, an alkyl group, a substituted alkyl group, an aryl group or a substituted aryl group, or R^{18} and R^{19} may bind to each other forming a ring; and m represents an integer of 1 to 3.

[0092] An example of a suitable undercoat layer component for the planographic printing plate precursor according to the invention is a polymer compound having an acid group-containing structural component and an onium group-containing component described in JP-A No. 2000-241962. Specifically, it is a copolymer of an acid group-containing monomer and an onium group-containing monomer. The acid group is preferably an acid group having an acid dissociation constant (pKa) of 7 or more, more preferably -COOH, $-SO_3H$, $-OSO_3H$, $-PO_3H_2$, $-OPO_3H_2$, $-CONHSO_2-$, or $-SO_2NHSO_2-$, and particularly preferably -COOH. Specific examples of the acid group-containing monomers include acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, itaconic acid, maleic acid, maleic anhydride, and styrene derivatives having the acid group above. The onium salt is preferably an onium group having an atom in groups V and VI of the Periodic Table, more preferably an onium salt of a nitrogen, phosphorus or sulfur atom, and particularly preferably an onium salt of a nitrogen atom. Specific examples of the onium salt-containing monomers include methacrylates and methacrylamides having an ammonium group on the side chain, and styrenes having an onium group-containing substituent such as those having a quaternary ammonium group.

In addition, the compounds described in JP-A Nos. 2000-108538, 2004-94075, and 2004-73073, and others may be used as needed.

[0093] Such an undercoat layer can be formed, for example, according to the following methods: a method of dissolving the organic compound in water or in an organic solvent, such as methanol, ethanol, or methylethylketone, or in a mixed solvent of one or more of such solvents, and applying and drying the solution on an aluminum plate (support); and a method of dissolving the organic compound in water or in an organic solvent, such as methanol, ethanol, or methylethylketone, or in a mixed solvent of one or more of such solvents, immersing an aluminum plate (support) in the solution to adsorb the compound, and washing the plate with water or the like and drying it.

In the former method, it is possible to apply the solution of the organic compound at a concentration of 0.005 to 10 wt % by various methods. In the latter method, the concentration of the solution may be from 0.01 to 20 wt %, preferably from 0.05 to 5 wt %; the immersion temperature may be from 20 to 90˚C, preferably from 25 to 50˚C; and the immersion period may be from 0.1 second to 20 minutes, preferably from 2 seconds to 1 minutes. The solution used may be adjusted to a pH in the range of 1 to 12 by addition of a basic substance such as ammonia, triethylamine, or potassium hydroxide, or an acidic substance such as hydrochloric acid or phosphoric acid. A yellow dye may also be added, for improvement of tone reproducibility in the image-recording material.

The amount of the undercoat layer coated is suitably 2 to 200 mg/m^2, and preferably 5 to 100 mg/m^2, from the viewpoint of printing durability.

(Image formation)

[0094] An image can be formed thermally on the planographic printing plate precursor according to the present invention because the planographic printing plate precursor contains the photosensitive composition described above. Specifically, direct image recording with a thermal recording head or the like, scanning exposure with an infrared laser, high-illumination flash exposure with xenon discharge lamp or the like, infrared lamp exposure, or the like is used for this image formation, but exposure to a high-output infrared solid laser emitting a light at a wavelength of 700 to 1,200 nm, such as from an infrared light-emitting semiconductor laser or YAG laser is suitable.

The laser output is preferably 100 mW or more, and it is preferable to use a multi-beam laser device to shorten the exposure period. The exposure period per pixel is preferably 20 μsec or less, and the irradiation energy applied onto the recording material is preferably from 10 to 500 mJ/cm^2.

[0095] The developer usable for the developing treatment of the planographic printing plate precursor according to the invention may be a developer having a pH range of 9.0 to 14.0, preferably 12.0 to 13.5. As the developer (hereinafter the scope of this term encompasses a replenisher), a conventionally known aqueous alkali solution may be used.

Examples of the alkali agent include inorganic alkali salts such as sodium silicate, potassium silicate, trisodium phosphate, tripotassium phosphate, triammonium phosphate, disodium hydrogen phosphate, dipotassium hydrogen phosphate, diammonium hydrogen phosphate, sodium carbonate, potassium carbonate, ammonium carbonate, sodium hydrogen carbonate, potassium hydrogen carbonate, ammonium hydrogen carbonate, sodium borate, potassium borate, ammonium borate, sodium hydroxide, ammonium hydroxide, potassium hydroxide, and lithium hydroxide; and organic alkali agents such as monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, triisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethyleneimine, ethylenediamine, and pyridine. Only one alkali agent may be used, or a combination of two or more alkali agents may be used.

Among the above aqueous alkali solutions, an example of a developer which exerts the effect of the invention is a so-called "silicate developer", which is an aqueous solution of a pH 12 or higher that contains an alkali silicate as a base or contains an alkali silicate obtained by mixing a base with a silicon compound. Another example, which is more preferable, is a so-called "non-silicate developer", which does not contain alkali silicate and contains a non-reducing sugar (organic compound having buffering action) and a base.

[0096] In the former, the developing power of an aqueous solution of the alkali metal silicate can be regulated by the ratio of the silicon oxide SiO_2 as a silicate component to the alkali metal oxide M_2O (generally expressed as the molar ratio of $[SiO_2]/[M_2O]$) and by the concentration thereof Preferably used aqueous solutions include an aqueous solution of sodium silicate containing SiO_2 in an amount of 1 to 4% by weight wherein the molar ratio of SiO_2/Na_2O is 1.0 to 1.5 (that is, $[SiO_2]/[Na_2O]$ is 1.0 to 1.5) as disclosed in JP-A No. 54-62004 and an aqueous solution of an alkali metal silicate containing SiO_2 at a concentration of 1 to 4% by weight and potassium in an amount of at least 20% based on the gram atom of all alkali metals present in the developer wherein the molar ratio of $[SiO_2]/[M]$ is 0.5 to 0.75 (that is, $[SiO_2]/ [M_2O]$ is 1.0 to 1.5) as disclosed in JP-B No. 57-7427.

[0097] The alkali silicate-free "non-silicate developer" containing a non-reducing sugar and a base is also preferable for the development of the planographic printing plate material according to the invention. By development treatment of the planographic printing plate precursor with this developer, the inking property of the recording layer can be maintained in an excellent state without deteriorating the surface of the recording layer. The development latitude of the planographic printing plate material is generally narrow, and thus the width of an image line or the like significantly varies depending on the pH of the developer. However, the non-silicate developer contains a buffering non-reducing sugar that prevents pH variation, and is more advantageous than a silicate-containing developer. The non-reducing sugar, as compared with silicate, hardly contaminates a conductivity sensor or pH sensor for regulating the activity of liquid. Therefore, the non-silicate developer is advantageous also in this respect. Further, the discrimination improving effect is significant supposedly because contact (impregnation) with the developer, which is important in the invention, is mild, and thus the difference between a light-exposed region and a light-unexposed region is enhanced.

[0098] The non-reducing sugar is a sugar that does not have a free aldehyde group or a ketone group and does not show reducing properties. Non-reducing sugars can be classified into trehalose-type oligosaccharide having reducing groups bound to one another, glycoside having a sugar reducing group bound to a non-sugar, and sugar alcohol obtained by reduction through hydrogenation of a sugar moiety, each of which can be preferably used in the invention. In the invention, non-reducing sugars described in JP-A No. 8-305039 can be used preferably.

[0099] The trehalose-type oligosaccharide may be, for example, saccharose or trehalose. The glycoside may be, for example, an alkyl glycoside, a phenol glycoside, or a mustard oil glycoside. The sugar alcohol may be, for example, D, L-arabitol, ribitol, xylitol, D,L-sorbitol, D,L-mannitol, D,L-iditol, D,L-talitol, dulcitol and allodulcitol. Maltitol obtained by hydrogenation of maltose, which is a disaccharide, and a reduced body (reduced starch syrup) obtained by hydrogenation of an oligosaccharide are preferable. Among these non-reducing sugars, trehalose-type oligosaccharides and sugar alcohols are preferable, and, in particular, D-sorbitol, saccharose, and reducing starch syrup are preferable because they are inexpensive and have a buffering action in a suitable pH range.

[0100] Only a single non-reducing sugar may be used, or two or more non-reducing sugars may be used in combination. The content of the non-reducing sugar in the non-silicate developer is preferably from 0.1 to 30% by weight, more preferably from 1 to 20% by weight. When the content is less than 0.1 % by weight, the buffering property tends to be insufficient, whereas when the content is higher than 30% by weight, the developer is hard to concentrate to a high degree and tends to be high-cost.

[0101] Examples of the base that can be used in combination with the non-reducing sugar include known alkali agents such as inorganic alkali agents and organic alkali agents. Examples of inorganic alkali agents include sodium hydroxide, potassium hydroxide, lithium hydroxide, trisodium phosphate, tripotassium phosphate, triammonium phosphate, disodium phosphate, dipotassium phosphate, diammonium phosphate, sodium carbonate, potassium carbonate, ammonium carbonate, sodium hydrogen carbonate, potassium hydrogen carbonate, ammonium hydrogen carbonate, sodium borate, potassium borate, and ammonium borate.

[0102] Examples of organic alkali agents include monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, triisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethylene imine, ethylene diamine, and pyridine.

[0103] Only a single base may be used, or two or more bases may be used in combination. Among these bases, sodium hydroxide and potassium hydroxide are preferable. In the non-silicate developer in the invention, an alkali metal salt of non-reducing sugar can be used as the main component, in place of simultaneous use of non-reducing sugar and base.

[0104] Together with the non-silicate developer, an alkaline buffer solution comprising a strong base and a weak acid other than the non-reducing sugar can be used additionally. The weak acid preferably has a dissociation constant (pKa) of 10.0 to 13.2, and can be selected from those described in Ionization Constants of Organic Acids in Aqueous Solution published by Pergamon Press.

[0105] Preferable examples of the weak acid include alcohols such as 2,2,3,3-tetrafluoropropanol-1- trifluoroethanol and trichloroethanol, aldehydes such as pyridine-2-aldehyde and pyridine-4-aldehyde, compounds having a phenolic hydroxyl group such as salicylic acid, 3-hydroxy-2-naphthoic acid, catechol, gallic acid, sulfosalicylic acid, 3,4-dihydrosulfonic acid, 3,4-dihydroxybenzoic acid, hydroquinone (pKa 11.56), pyrogallol, o-, m- or p-cresol, and resorcinol, oximes such as acetoxime, 2-hydroxybenzaldehyde oxime, dimethyl glyoxime, ethane diamide dioxime, and acetophenone oxime, and nucleic acid-related substances such as adenosine, inosine, guanine, cytosine, hypoxanthine, and xanthine, as well as diethylaminomethylphosphonic acid, benzimidazole, and barbituric acid.

[0106] Various surfactants and organic solvents may be added as necessary to the developer and replenisher, for improvement or control of developing efficiency, dispersion of development scum, or improvement of the ink compatibility of the image region of a printing plate. The surfactant is preferably an anionic, cationic, nonionic or amphoteric surfactant. In addition, a reducing agent such as hydroquinone, resorcin, sodium or potassium salt of an inorganic acid such as sulfurous acid or bisulfurous acid can be may be added to the developer and replenisher as necessary. An organic carboxylic acid, an antifoaming agent, a water softener, or the like may also be added to the developer and replenisher as needed.

[0107] When the PS plate is developed in an automatic processor, it is known that it is possible to process a great number of PS plates without exchanging the developer for an extended period of time by adding to the developer an aqueous solution (replenisher) having a higher alkali strength than the developer. This replenishing method can also be favorable applied to the present invention. Various surfactants and organic solvents may be added, if needed, to the developers and replenishers for the purpose of increasing or decreasing the developing efficiency, dispersing development scum, and improving the ink compatibility on the image portions of the printing plate.

The surfactant is preferably an anionic, cationic, nonionic or amphoteric surfactant. In addition, agents selected from the following may be added to the developing and replenishers if needed: hydroquinone, resorcin, a reducing agent such as sodium or potassium salt of an inorganic acid such as sodium or potassium sulfite or bisulfite, an organic carboxylic acid, an antifoam agent, and a water softener.

The printing plate, after processing with the developers and replenishers, may be then post-treated with one or more of the following: washing water, a rinsing solution containing a surfactant or the like, and a desensitizing solution containing gum arabic or a starch derivative. The post-treatment of the printing plate precursor according to the invention may be a combination of one or more of these treatments.

[0108] In recent years, automatic processors for printing plates have been widely used for the purpose of rationalizing and standardizing the plate-making processes in the plate-making and printing industries. An automatic processor usually has a developing part and a post-treatment part. The automatic processor has a device which transfers a printing plate precursor, processing solution baths, and a spraying device. While an exposed printing plate precursor is transferred horizontally, pumped-up respective processing solutions is sprayed through spray nozzles to develop the printing plate precursors. These days, a method is known in which a planographic printing plate precursor is processed by being transferred by use of submerged guide rolls while immersed in a processing solution bath filled with a processing solution. Such automatic processing can be carried out while supplementing each processing solution with a replenishing solution, based on processed amount, operation time etc. In addition, a method of essentially using only unused treating solutions, i.e., a single-round method, may also be used.

[0109] In the present invention, if the planographic printing plate obtained after imagewise exposure, development, water washing and/or rinsing, and/or gumming has unnecessary image portions (e.g., spots made by the film edge of the original image film and the like), elimination of the unnecessary image portions is performed. Although the elimination method is preferably the method described for example in Japanese Patent Publication (JP-B) No. 2-13293, in which an image-elimination solution is applied onto the undesirable image portions and the resulting plate is then washed with water after being left for a certain period; the method described in JP-A No. 59-174842, in which the undesirable image portions are eliminated by irradiation of an activated light through an optical fiber and then the resulting plate is developed, may be also used.

[0110] The developed planographic printing plate thus obtained may, if desired, be coated with a desensitizing gum before it is sent to the printing process; or the plate is additionally subjected to a baking treatment when a planographic printing plate higher in printing durability is desired.

If the planographic printing plate is to be subjected to a baking treatment, the plate is preferably treated, before the baking treatments, with a surface conditioning solution described in JP-B No. 61-2518 JP-B No. 55-28062, JP-ANo. 62-31859, or JP-A No. 61-159655.

The treatment may involve application of the surface conditioning solution onto planographic printing plates with sponges or cotton moistened therewith, application by immersing the printing plate into a bath filled with the surface conditioning solution, or application by an automatic coater. Additionally, uniformization of the coating amount with a squeezee or a squeezee roller after application of the surface conditioning solution provides more favorable results.

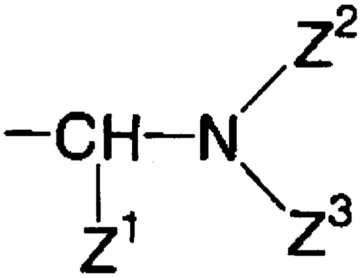
[0111] The suitable coating amount of the surface conditioning solution is generally from 0.03 to 0.8 g/m^2 (as dry weight). The planographic printing plate coated with the surface conditioning solution is then dried as needed and heated to a high temperature in a burning processor (e.g., Burning Processor BP-1300 available from Fuji Photo Film Co. Ltd.).

The temperature and the period of heating vary according to the kind of the components constituting the images, but are preferably in the range of 180 to 300°C for 1 to 20 minutes.

[0112] The planographic printing plate that has been subjected to a baking treatment may then be subjected, if needed, to treatments commonly practiced in the art such as water washing and gumming. When a surface treatment solution containing a water-soluble polymer compound or the like is used, the so-called desensitizing treatment such as gumming or the like may be eliminated. The planographic printing plate obtained after these treatments is then mounted on an offset printing machine or the like, and it is used for printing numerous sheets of paper.

[0113] Exemplary embodiments of the present invention are described in the following:

<1>. A photosensitive composition comprising (A) a first alkaline-aqueous solution-soluble resin having, on a side chain, a hydrophobic aminoalkyl group represented by the following formula (1), (B) a second alkaline aqueous solution-soluble resin, and (C) an infrared absorber:



Formula (1)

wherein Z^1, Z^2 and Z^3 each independently represent a hydrogen atom or a monovalent substituent group consisting of one or more nonmetal atoms.

<2>. The photosensitive composition of <1>, wherein the hydrophobic aminoalkyl group is bound to a side chain of an alkaline aqueous solution-soluble resin having a phenol structure in a repeating unit.

[0114]

<3>. The photosensitive composition of <1>, wherein the hydrophobic aminoalkyl group is bound covalently to a phenyl ring of a phenol resin.

<4>. The photosensitive composition of <1>, wherein the content of the hydrophobic aminoalkyl group in the first alkaline aqueous solution-soluble resin is from 5 to 95 mol%.

<5>. The photosensitive composition of <1>, wherein the content of the hydrophobic aminoalkyl group in the first alkaline aqueous solution-soluble resin is from 20 to 95 mol%.

[0115]

<6>. The photosensitive composition of <1>, wherein the second alkaline aqueous solution-soluble resin and the first alkaline aqueous solution-soluble resin cause phase separation when mixed.

<7>. The photosensitive composition of <1>, wherein the second alkaline aqueous solution-soluble resin has an acidic group in a main chain and/or side chain of a polymer.

<8>. The photosensitive composition of <7>, wherein the acidic group is selected from -Ar-OH, $-SO_2NH-R$, $-SO_2NHCOR$, $-SO_2NHSO_2R$, $-CONHSO_2R$, $-CO_2H$, $-SO_3H$, and $-OPO_3H_2$.

<9>. The photosensitive composition of <1>, wherein the second alkaline aqueous solution-soluble resin has a weight-average molecular weight of 5,000 to 300,000, a number-average molecular weight of 800 to 250,000, and a degree of dispersion of 1.1 to 10.

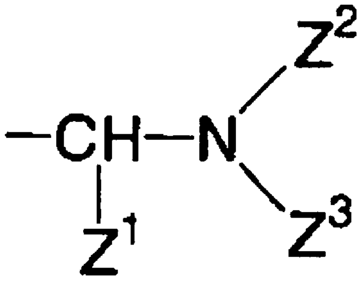
[0116]

<10>. The photosensitive composition of <1>, wherein the ratio by weight of the first alkaline aqueous solution-

soluble resin to the second alkaline aqueous solution-soluble resin is in the range of 99:5 to 55:45.

<11>. A positive-type planographic printing plate precursor comprising a support and a recording layer containing a photosensitive composition provided on the support, the photosensitive composition comprising:

(A) a first alkaline aqueous solution-soluble resin having, on a side chain, a hydrophobic aminoalkyl group represented by the following formula (1);
(B) a second alkaline aqueous solution-soluble resin; and
(C) an infrared absorber:



Formula (1)

wherein Z^1, Z^2 and Z^3 each independently represent a hydrogen atom or a monovalent substituent group consisting of one or more nonmetal atoms.

[0117]

<12>. The positive-type planographic printing plate precursor of <11>, wherein the hydrophobic aminoalkyl group is bound to a side chain of an alkaline aqueous solution-soluble resin having a phenol structure in a repeating unit.

<13>. The positive-type planographic printing plate precursor of <11>, wherein the hydrophobic aminoalkyl group is bound covalently to a phenyl ring of a phenol resin.

<14>. The positive-type planographic printing plate precursor of <11>, wherein the content of the hydrophobic aminoalkyl group in the first alkaline aqueous solution-soluble resin is from 5 to 95 mol%.

[0118]

<15>. The positive-type planographic printing plate precursor of <11>, wherein the content of the hydrophobic aminoalkyl group in the first alkaline aqueous solution-soluble resin is from 20 to 95 mol%.

<16>. The positive-type planographic printing plate precursor of <11>, wherein the second alkaline aqueous solution-soluble resin and the first alkaline aqueous solution-soluble resin cause phase separation when mixed.

<17>. The positive-type planographic printing plate precursor of <11>, wherein the second alkaline aqueous solution-soluble resin has an acidic group in a main chain and/or side chain of a polymer.

<18>. The positive-type planographic printing plate precursor of <17>, wherein the acidic group is selected from -Ar-OH, $-SO_2NH-R$, $-SO_2NHCOR$, $-SO_2NHSO_2R$, $-CONHSO_2R$, $-CO_2H$, $-SO_3H$, and $-OPO_3H_2$.

[0119]

<19>. The positive-type planographic printing plate precursor of <11>, wherein the second alkaline aqueous solution-soluble resin has a weight-average molecular weight of 5,000 to 300,000, a number-average molecular weight of 800 to 250,000, and a degree of dispersion of 1.1 to 10.

<20>. The positive-type planographic printing plate precursor of <11>, wherein the ratio by weight of the first alkaline aqueous solution-soluble resin to the second alkaline aqueous solution-soluble resin is in the range of 99:5 to 55:45.

EXAMPLES

[0120] Hereinafter, the present invention will be described with reference to Examples, but it should be understood that the scope of the invention is not restricted to these Examples.

Examples 1 to 3 and Comparative Example 1

(Preparation of support)

[0121] A support was prepared by the following process using a JIS-A-1050 aluminum plate having a thickness of 0.3 mm.

(a) Mechanical surface roughening treatment

[0122] While a suspension containing a polishing agent (silica sand) with a specific gravity of 1.12 and water was supplied as a polishing slurry onto the a surface of each aluminum plate, mechanical surface roughening was carried out by rotating roller-type nylon brushes. The average particle size of the polishing agent was 8 μm and the maximum particle size was 50 μm. The material of the nylon brushes was 6·10 nylon and hair length and hair diameters were 50 mm and 0.3 mm, respectively. The nylon brushes were produced by implanting the hairs densely in holes formed in stainless cylinders with a diameter of ϕ300 mm. Three such rotating brushes were used. Two supporting rollers (ϕ200 mm diameter) were placed in lower parts of the brushes with a separation distance of 300 mm between the supporting rollers. The brush rollers were pushed such that the load of the driving motor for rotating the brushes was increased by 7 kW or more from the load before the brush rollers were pushed against the aluminum plate. The rotation direction of the brushes was the same as the moving direction of the aluminum plate. The rotation speed of the brushes was 200 rpm.

(b) Alkaline etching treatment

[0123] Etching treatment was carried out by spraying an aqueous NaOH solution having a temperature of 70°C (NaOH concentration being 26% by weight and also containing 6.5% by weight of aluminum ion) onto the aluminum plate, to dissolve the aluminum plate by an amount of 6 g/m^2. After that, the aluminum plate was washed with sprayed well water.

(c) Desmutting treatment

[0124] The aluminum plate was subjected to a desmutting treatment by spraying an aqueous solution containing 1 wt % of nitric acid (additionally containing 0.5 wt % of aluminum ion) and having a temperature of 30°C, and then washed with sprayed water. The aqueous nitric acid solution used for desmutting was the waste water obtained in the electrochemical surface-roughening in an aqueous nitric acid solution with an alternating electrical current.

(d) Electrochemical surface-roughening treatment

[0125] The aluminum plate was further subjected to a continuous electrical surface roughening with a 60-Hz alternating current. The electrolyte used was an aqueous solution containing 10.5 g/L of nitric acid (containing additionally 5 g/L of aluminum ion) having a temperature of 50°C. The electrochemical surface roughening was performed using a trapezoidal alternating current having a trapezoidal waveform with a transition period (TP) from zero to peak currency of 0.8 msec and a duty ratio of 1:1 using a carbon electrode as the counter electrode. Ferrite was used as the auxiliary anode. The electrolytic bath used was of a radial cell type.
The electric current density was 30 A/dm^2 at peak value, and the total amount of electric current applied was 220 C/dm^2 at the time the aluminum plate served as the anode. 5% of the current from the power source was divided and sent to the auxiliary electrode.
Subsequently, the aluminum plate was washed with sprayed well water.

(e) Alkaline etching treatment

[0126] The aluminum plate was etched by being sprayed with a solution containing 26 wt % of caustic soda and 6.5 wt % of aluminum ion at 32°C to melt 0.20 g/m^2 of the aluminum plate, thereby removing the smut mainly containing aluminum hydroxide generated during the previous electrochemical surface-roughening treatment with an alternating electrical current, and smoothing the edge portion through dissolution of the edge portions of the pits generated. Subsequently, the aluminum plate was washed with sprayed well water.

(f) Desmutting treatment

[0127] The aluminum plate was desmutted by spraying an aqueous solution containing 15 wt % of nitric acid (containing additionally 4.5 wt % of aluminum ion) having a temperature of 30°C, and then washed with sprayed well water. The wastewater obtained in the electrochemical surface-roughening of the aluminum plate in an aqueous nitric acid solution with an alternating electrical current, was used as the aqueous nitric acid solution for desmutting.

(g) Electrochemical surface roughening treatment

[0128] Electrochemical surface roughening treatment was carried out continuously by using 60 Hz AC voltage. The electrolytic solution used was an aqueous solution of hydrochloric acid (the concentration thereof being 7.5 g/L and also containing 5 g/L of aluminum ion) having a temperature of 35˚C. The AC power waveform had a trapezoidal rectangular waveform and a carbon electrode was used as the counter electrode, to effect the electrochemical surface roughening treatment. Ferrite was used as an auxiliary anode. A radial cell type electrolytic bath was used for the electrochemical surface roughening.
The current density was 25 A/dm^2 at the peak value of the current and the total electricity quantity was 50 C/dm^2 at the time the aluminum plate served as the anode.
Thereafter, the aluminum plate was washed with sprayed well water.

(h) Alkali etching treatment

[0129] Etching treatment was carried out at 32˚C on the aluminum plate by spraying a solution containing 26 wt. % of sodium hydroxide and 6.5 wt. % of aluminum ion onto the aluminum plate, to dissolve 0.10 g/m^2 of the aluminum plate, thereby removing the smut mainly composed of aluminum hydroxide produced during the previous electrochemical roughening treatment with an alternating current, and smoothing the edges through the dissolution of the edge portions of the generated pits. Thereafter, the aluminum plate was washed with sprayed well water.

(i) Desmutting treatment

[0130] A desmutting treatment was is carried out by spraying an aqueous solution containing 25% by weight of sulfuric acid and 0.5% by weight of aluminum ion having a temperature of 60˚C. Then, the aluminum plate was washed with sprayed well water.

(j) Anodization treatment

[0131] As the electrolytic solution, sulfuric acid was used. The electrolytic solution contained 170 g/L of sulfuric acid and 0.5% by weight of aluminum ion. The temperature of the electrolytic solution was 43˚C. After the anodization, the aluminum plate was washed with sprayed well water.
[0132] The electric current density was about 30 A/dm^2. The final oxide film thickness was 2.7 g/m^2.

<Support A>

[0133] Each of the foregoing (a) through (j) steps was sequentially carried out, in which the amount of etching in the step (e) was 3.4 g/m^2, to give support A.

<Support B>

[0134] Support B was prepared by sequentially carrying out the aforementioned steps but omitting the steps (g), (h), and (i).

<Support C>

[0135] The respective steps were successively performed except that steps (a), (g), (h), and (i) were omitted, to give support C.

<Support D>

[0136] The respective steps were successively performed except that steps (a), (d), (e), and (f) were omitted, in which the sum of the quantity of electricity in step (g) was adjusted to be 450C/dm^2, to give support D.
Supports A, B, C, and D as obtained above were subsequently subjected to the following hydrophilization treatment (k) and undercoating treatment.

(k) Alkali metal silicate treatment

[0137] The aluminum supports obtained by the anodizing treatment were subjected to an alkali metal silicate treatment (silicate treatment) by being dipped in a treatment bath containing 1 wt% aqueous solution of sodium silicate No. 3 having a temperature of 30°C for 10 seconds. Thereafter, the aluminum supports were washed with sprayed well water. The amount of silicate adhered was 3.6 mg/m^2.

Undercoating treatment

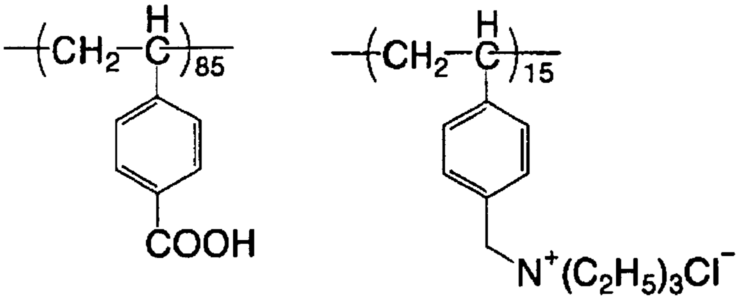
[0138] After the alkali metal silicate treatment, the resulting aluminum supports were coated with an undercoat solution having the following composition, and then dried at 80°C for 15 seconds. The amount of the coating after drying was 15 mg/m^2.

(Undercoat solution)

[0139]

The following polymer compound (I or II)	0.3 g
Methanol	100 g
Water	1 g

[0140]



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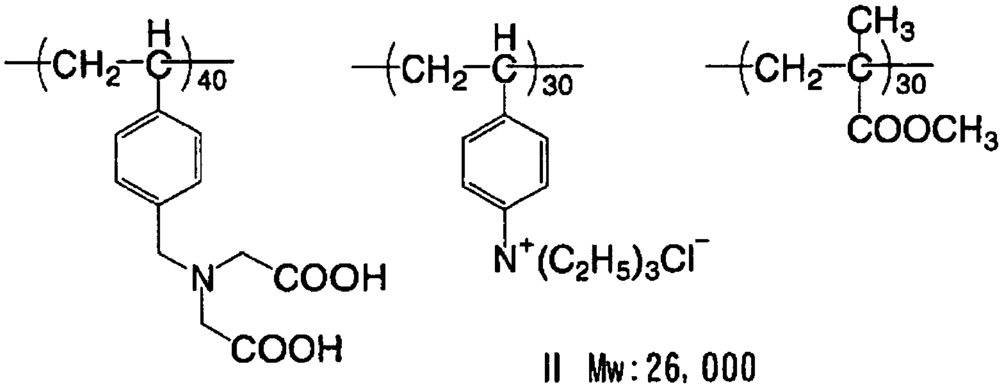

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(Formation of recording layer)

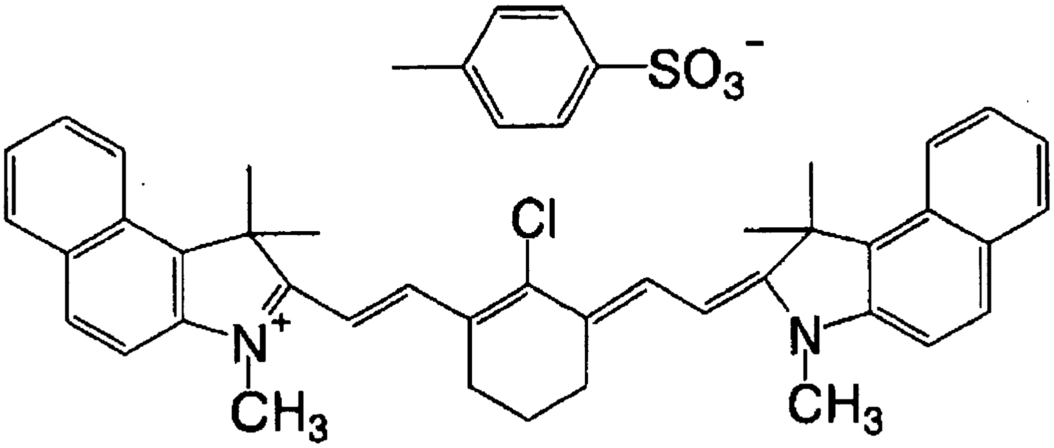
[0141] Then, each of the supports having the undercoat layer obtained above was coated with the coating liquids A, B, or C having the following composition using a wire bar, and was dried for 50 seconds in a drying oven at 140°C, such that the total coating amount was 1.00 g/m^2.
The types of the coating liquids used in Examples and Comparative Examples are shown in Table 5 below.

<Coating liquid A>

[0142]

·(A) First alkali-soluble resin (compound described in Table 5) 0.75 g
.(B) Second alkali-soluble resin (compound described in Table 5) 0.25 g
·(C) Cyanine dye P (the structure below) 0.017 g
·p-Toluenesulfonic acid 0.003 g
·Tetrahydrophthalic anhydride 0.03 g
·Victoria Pure Blue in which the counter-ion of BOH was replaced by 1-naphthalene sulfonate anion 0.015 g
·γ-Butyrolactone 10 g
·Methyl ethyl ketone 10 g
·1-Methoxy-2-propanol 1 g

[0143]



Cyanine Dye P

<Coating liquid B>

[0144]

·(A) First alkali-soluble resin (compound described in Table 5)	0.60 g
·(B) Second alkali-soluble resin (compound described in Table 5)	0.40 g
·(C) Cyanine dye P (the above structure)	0.017 g
·p-Toluenesulfonic acid	0.003 g
·Tetrahydrophthalic anhydride	0.03 g
·Victoria Pure Blue in which the counter-ion of BOH was replaced by 1-naphthalene sulfonate anion	0.015 g
·γ-Butyrolactone	10 g

·Methyl ethyl ketone	10 g
·1-Methoxy-2-propanol	1 g

<Coating liquid C>

[0145]

·(A) First alkali-soluble resin (compound described in Table 5)	0.25 g
·(B) Second alkali-soluble resin (compound described in Table 5)	0.75 g
·(C) Cyanine dye P (the above structure)	0.017 g
·p-Toluenesulfonic acid	0.003 g
·Tetrahydrophthalic anhydride	0.03 g
·Victoria Pure Blue in which the counter-ion of BOH was replaced by 1-naphthalene sulfonate anion	0.015 g
·γ-Butyrolactone	10 g
·Methyl ethyl ketone	10 g
·1-Methoxy-2-propanol	1 g

Evaluation of planographic printing plate precursor

[0146] Then, the performance of the positive-type planographic printing plate precursor obtained in each of Examples 1 to 7 and Comparative Examples 1 to 3 was evaluated.
The evaluation test was carried out on the planographic printing precursor stored for 14 days at 25˚C after coating with the recording layer.

(Evaluation of development latitude)

[0147] The positive-type planographic printing plate precursor obtained in each of Examples 1 to 7 and Comparative Examples 1 to 3 was exposed to light with a beam intensity of 10.0 W at a drum revolution number of 250 rpm with TRENDSETTER 800 manufactured by Creo to draw an imagewise test pattern thereon (Exposure step).
Then, the planographic printing plate precursor was developed at a development temperature of 30˚C for a development time of 12 seconds with PS Processor LP-940HII charged with an aqueous dilution of developer DT-2R (diluted at 1 : 9, manufactured by Fuji Photo Film Co., Ltd.) containing carbon dioxide gas blown to adjust the electrical conductivity to 37 mS/cm and with an aqueous dilution of Finisher FG-1 (diluted at 1 : 1, manufactured by Fuji Photo Film Co., Ltd.).
Separately, each planographic printing plate precursor having an imagewise test pattern drawn thereon was developed with a developer prepared by adding a suitable amount of the aqueous dilution of DT-2R (diluted at 1 : 9) to the above developer to adjust the electrical conductivity to 39 mS/cm.
This development operation was repeated while increasing the electrical conductivity of the developer serially by 2 mS/cm, until the wear of the coating by development of the image became considerably noticeable.
[0148] The surface of the planographic printing plate precursor in each of the Examples and Comparative Examples developed at each electrical conductivity was observed through a magnifying lens (x50) to confirm whether tinting or coloring due to a residual film in the non-image region caused by insufficient development had occurred or not, thereby determining the electrical conductivity of the developer with which excellent development could be conducted. Then, the electrical conductivity at which the wear of the developed film in the light-unexposed region had not occurred was determined; specifically, the electrical conductivity of the developer with which a solid region having an image density lower by at least 0.10 than the image density of a solid region before development, as determined with GRETAG reflection densitometer D 196 (manufactured by Gretag Macbeth), had been formed was determined.
The latitude (difference) between the lowest electrical conductivity of the developer at which excellent development could be conducted and the highest electrical conductivity at which the film in the non-exposed region was retained after development was regarded as development latitude. A larger numerical value is indicative of excellent development latitude. The results are shown in Table 5.

(Evaluation of cleaner resistance)

[0149] A cleaner solution ("Plate Cleaner CL2" manufactured by Fuji Photo Film) was dropped onto the positive-type planographic printing plate precursor in each of Examples 1 to 7 and Comparative Examples 1 to 3, and 1 minute thereafter, a change in the density of the region onto which the cleaner had dropped was observed with the naked eye and evaluated under the following criteria. The results are shown in Table 5.

A: No change in density.
B: Only a slight change in density.
C: Significant change in density

(Evaluation of scratch resistance)

[0150] The surface of the recording layer of the positive-type planographic printing plate precursor in each of Examples 1 to 7 and Comparative Examples 1 to 3 was scratched with a rubber needle loaded with a weight, and the planographic printing plate precursor was developed at a development temperature of 30˚C for a development time of 12 seconds with PS Processor LP940HII (manufactured by Fuji Photo Film Co., Ltd.) charged with an aqueous dilution of developer DT-2R (diluted at 1 : 9) containing a carbon dioxide gas blown to adjust the electrical conductivity to 47 mS/cm. Then, the scratched region was checked visually, and when no scratch was observed, the surface was scratched with a rubber needle with a heavier loading, then developed in the same manner as above, and visually checked. This operation was repeatedly carried out, and the maximum loading with which no scratch had been observed was determined. A greater value is indicative of excellent scratch resistance. The results are shown in Table 5.

[0151]

Table 5

	Support	Compound contained in undercoat layer	Coating liquid	First alkali-soluble resin	Second alkali-soluble resin	Development latitude (mS/cm)	Cleaner resistance	Scratchresistance (g)
Example 1	A	I	A	Compound No. 1	(Resin (1))	12	A	20
Example 2	B	II	A	Compound No. 2	(Resin (2))	12	A	20
Example 3	C	I	A	Compound No. 3	(Resin (3))	10	A	25
Example 4	D	II	A	Compound No. 4	(Resin (1))	10	A	20
Example 5	A	I	A	Compound No. 1	(Resin (2))	10	A	20
Example 6	A	I	B	Compound No. 1	(Resin (1))	10	A	20
Example 7	A	I	C	Compound No. 1	(Resin (1))	9	A	20
Comparative Example 1	A	I	A	none	(Resin (1))	5	C	15
Comparative Example 2	A	I	A	Compound No. 1	none	6	A	10
Comparative Example 3	A	I	A	(Resin (3))	(Resin (1))	7	A	5

[0152] The first alkali-soluble resins in Table 5 refers to specific examples shown in Compound Nos. 1 to 4 in Table 4. The other alkali-soluble resins described in Table 5 represent the followings.

Resin (1): m-/p-cresol novolak resin
(m-cresol/p-cresol ratio = 6/4; Mw: 5000)
Resin (2): phenol/m-cresol/p-cresol novolak resin
(phenol/m-cresol/p-cresol ratio = 5/3/2; Mw: 5000)
Resin (3): N-(4-aminosulfonyl phenyl) methacrylamide/acrylonitrile/methyl methacrylate
(molar ratio 36 : 34 : 30, weight-average molecular weight 50,000)

[0153] In the coating liquid A used in Comparative Example 1, the first alkali-soluble resin was not used, and 1.00 g of the resin (1) corresponding to the second alkali-soluble resin was used.

[0154] In the coating liquid A used in Comparative Example 2, the second alkali-soluble resin was not used, and 1.00 g of Compound No. 1, which serves as the first alkali soluble resin, was used.

[0155] As is evident from Table 5, the planographic printing plate precursors of Examples 1 to 7according to the invention gave planographic printing plates having broad development latitude and excellent in cleaner resistance and scratch resistance. As can be seen from this result, the photosensitive composition according to the invention can form a physically rigid film durable to an alkaline developer, but cancels its development resistance rapidly upon exposure to infrared light, thus making being preferable for use in the recording layer of the positive-type planographic printing plate precursor.

On the other hand, the planographic printing plate precursor according to Comparative Example 1 containing only novolak resin showed inferior development latitude, inferior cleaner resistance, and inferior scratch resistance.

The planographic printing plate precursor according to Comparative Example 2, containing the first alkali-soluble resin (A) in the invention but not containing the second alkali-soluble resin, showed excellent cleaner resistance, but was inferior in development latitude and in scratch resistance.

The planographic printing plate precursor according to Comparative Example 3, containing two kinds of alkali-soluble resins outside of the scope of the invention, showed excellent cleaner resistance, but was inferior in development latitude and was significantly inferior in scratch resistance.

[0156] According to the invention, there can be provided a photosensitive composition useful as a recording layer for a positive-type planographic printing plate precursor for infrared laser, which has broad development latitude and is excellent in cleaner resistance and scratch resistance, as well as a positive-type planographic printing plate precursor using the same.

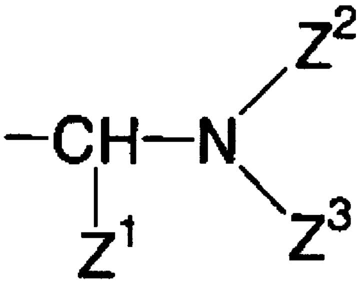
According to the invention, there can be provided a photosensitive composition useful as a recording layer of a positive-type planographic printing plate precursor for infrared laser, which can form a physically rigid film durable to an alkaline developer but cancels its development resistance rapidly upon exposure to infrared light, to give a significant difference in solubility in an alkaline developer between a light-exposed region and a light-unexposed region.

The planographic printing plate precursor according to the invention having a recording layer containing the photosensitive composition described above has broad development latitude and is excellent in cleaner resistance and scratch resistance.

Claims

1. A photosensitive composition comprising:

(A) a first alkaline aqueous solution-soluble resin having, on a side chain, a hydrophobic aminoalkyl group represented by the following formula (1);
(B) a second alkaline aqueous solution-soluble resin; and
(C) an infrared absorber:



Formula (1)

wherein Z^1, Z^2 and Z^3 each independently represent a hydrogen atom or a monovalent substituent group consisting of one or more nonmetal atoms.

2. The photosensitive composition of claim 1, wherein the hydrophobic aminoalkyl group is bound to a side chain of an alkaline aqueous solution-soluble resin having a phenol structure in a repeating unit.

3. The photosensitive composition of claim 1, wherein the hydrophobic aminoalkyl group is bound covalently to a phenyl ring of a phenol resin.

4. The photosensitive composition of claim 1, wherein the content of the hydrophobic aminoalkyl group in the first alkaline aqueous solution-soluble resin is from 5 to 95 mol%.

5. The photosensitive composition of claim 1, wherein the content of the hydrophobic aminoalkyl group in the first alkaline aqueous solution-soluble resin is from 20 to 95 mol%.

6. The photosensitive composition of claim 1, wherein the second alkaline aqueous solution-soluble resin and the first alkaline aqueous solution-soluble resin cause phase separation when mixed.

7. The photosensitive composition of claim 1, wherein the second alkaline aqueous solution-soluble resin has an acidic group in a main chain and/or side chain of a polymer.

8. The photosensitive composition of claim 7, wherein the acidic group is selected from -Ar-OH, $-SO_2NH-R$, $-SO_2NHCOR$, $-SO_2NHSO_2R$, $-CONHSO_2R$, $-CO_2H$, $-SO_3H$, or $-OPO_3H_2$.

9. The photosensitive composition of claim 1, wherein the second alkaline aqueous solution-soluble resin has a weight-average molecular weight of 5,000 to 300,000, a number-average molecular weight of 800 to 250,000, and a degree of dispersion of 1.1 to 10.

10. The photosensitive composition of claim 1, wherein the ratio by weight of the first alkaline aqueous solution-soluble resin to the second alkaline aqueous solution-soluble resin is in the range of 99:5 to 55:45.

11. A positive-type planographic printing plate precursor comprising a support and a recording layer containing the photosensitive composition of claim 1 provided on the support.

12. The positive-type planographic printing plate precursor of claim 11, wherein the hydrophobic aminoalkyl group is bound to a side chain of an alkaline aqueous solution-soluble resin having a phenol structure in a repeating unit.

13. The positive-type planographic printing plate precursor of claim 11, wherein the hydrophobic aminoalkyl group is bound covalently to a phenyl ring of a phenol resin.

14. The positive-type planographic printing plate precursor of claim 11, wherein the content of the hydrophobic aminoalkyl group in the first alkaline aqueous solution-soluble resin is from 5 to 95 mol%.

15. The positive-type planographic printing plate precursor of claim 11, wherein the content of the hydrophobic aminoalkyl group in the first alkaline aqueous solution-soluble resin is from 20 to 95 mol%.

16. The positive-type planographic printing plate precursor of claim 11, wherein the second alkaline aqueous solution-soluble resin and the first alkaline aqueous solution-soluble resin cause phase separation when mixed.

17. The positive-type planographic printing plate precursor of claim 11, wherein the second alkaline aqueous solution-soluble resin has an acidic group in a main chain and/or side chain of a polymer.

18. The positive-type planographic printing plate precursor of claim 17, wherein the acidic group is selected from -Ar-OH, $-SO_2NH-R$, $-SO_2NHCOR$, $-SO_2NHSO_2R$, $-CONHSO_2R$, $-CO_2H$, $-SO_3H$, and $-OPO_3H_2$.

19. The positive-type planographic printing plate precursor of claim 11, wherein the second alkaline aqueous solution-soluble resin has a weight-average molecular weight of 5,000 to 300,000, a number-average molecular weight of 800 to 250,000, and a degree of dispersion of 1.1 to 10.

20. The positive-type planographic printing plate precursor of claim 11, wherein the ratio by weight of the first alkaline aqueous solution-soluble resin to the second alkaline aqueous solution-soluble resin is in the range of 99:5 to 55:45.

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EUROPEAN SEARCH REPORT

Application Number
EP 06 01 3360

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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	11 September 2006	Bacon, Alan

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