Planographic printing plate precursor

The planographic printing plate precursor of the invention contains a substrate and a positive recording layer prepared on the substrate, and the recording layer contains (A) a polymer having a urea bond in a side chain, (B) a photothermal conversion agent, and (C) an amino compound having a methylol group or an alkoxymethyl group, and its solubility in an alkaline developing solution is improved by light-exposure or heating.
DESCRIPTION

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to a positive planographic printing plate precursor whose solubility in an aqueous alkaline solution is improved by infrared ray exposure, and particularly to a positive planographic printing plate precursor that can directly make a plate, that is, capable of so-called "direct plate-making", by scanning with an infrared laser light based on digital signals from a computer or the like.

Description of the Related Art

[0002] The development of lasers in recent years has been remarkable. Especially, there is progress in higher output and miniaturized solid lasers and semiconductor lasers whose light-emitting regions are in the near-infrared to infrared regions. Consequently, these lasers are extremely useful as an exposure light source when making a plate directly from the digital data from a computer or the like.

[0003] A positive planographic printing plate material for use with an infrared laser, which uses the aforementioned infrared laser whose light-emitting region is in the infrared region as an exposure light source, is a planographic printing plate material that has a binder resin soluble in an aqueous alkaline solution, an IR dye which absorbs light and generates heat, and the like as essential components.

[0004] When the positive planographic printing plate material for use with an infrared laser is exposed by the infrared laser, in a unexposed portion (image portion), the IR dye and the like in the positive planographic printing plate material for use with an infrared laser works as a dissolution inhibitor that substantially reduces the solubility of the binder resin by an interaction with the binder resin. On the other hand, in the exposed portion (non-image portion), because the IR dye and the like absorb light and generate heat, the interaction between the IR dye and the like and the binder resin is weakened. Consequently, during developing, the exposed portion (non-image portion) dissolves in an alkaline developer, thus forming a planographic printing plate.

[0005] However, in such a positive planographic printing plate material for use with an infrared laser, compared with a positive planographic printing plate material made by UV light exposure, a resin with high solubility in solvents, such as an alkaline developer, must be used as the binder resin. Therefore, there was a problem that such a resin possesses a low resistance to a plate cleaner which is used when ink receptivity is bad during printing, and, as a result, the photosensitive composition is eluted when the plate surface is wiped with the cleaner.

[0006] For the purpose of improving this cleaner resistance, a photosensitive composition, which uses a polymer containing a structural unit having a specific functional group that can form a hydrogen bond in the recording layer, has been proposed (see, for example, U.S. Patent No. 6,475,692), and it is reported that cleaner resistance was improved.

[0007] However, in such a positive planographic printing plate precursor for use with an infrared laser, there was a problem that the strength of the recording layer was low and printing durability deteriorated. Moreover, the polymer described here has the function of increasing the difference in alkali solubilization between the exposed portion and the non-exposed portion (discrimination), but this is insufficiently effective, so a technique had been desired to further improve the stability of development in accordance with the fluctuations of the conditions of use (development latitude).

[0008] Similarly, for the purpose of improving the printing durability, a technique that uses a polymer having a urea bond in a side chain has been proposed (see, for example, Japanese Patent Application Laid-Open (JP-A) No. 2000-330265). Though an effect of improving the printing durability of the unexposed portion was obtained by use of this polymer, for practical purposes, a further substantial improvement was desired, and, in addition, there was further room for improvement of discrimination from the viewpoint of the developing property of the exposed portion.

[0009] Moreover, for the purpose of improving the discrimination, a technique of adding a specific surfactant to a positive recording layer has been proposed (see, for example, JP-A No. 2002-122982), but there are concerns that containing a hydrophilic surfactant in the recording layer may make the surface of the recording layer hydrophilic and thereby lower the alkaline developer resistance in the image portion.

SUMMARY OF THE INVENTION

[0010] The object to be attained by the present invention is to overcome the above-mentioned weaknesses of the related art to provide a positive planographic printing plate precursor capable of forming an image using an infrared laser that not only can form a strong film being excellent in chemical resistance and alkaline developer resistance, but has a recording layer whose alkaline developer resistance is rapidly removed by infrared-light exposure, and has superior printing durability and chemical resistance, and excellent discrimination.
As a result of intensive research, the inventors attained the object of overcoming the above-mentioned problems by the combined use of a polymer having a specific structural unit and a specific crosslinking agent, and have completed the present invention.

That is, the planographic printing plate precursor of the present invention has a substrate and a positive recording layer prepared on the substrate, the recording layer comprises (A) a polymer having a urea bond in a side chain, (B) a photothermal conversion agent, and (C) an amino compound having a methoxymethyl group or an alkoxymethyl group, and the solubility thereof in an alkaline developer is improved by light-exposure or heating.

The mechanism of the present invention is not fully clear, but is presumed to be as follows.

In the planographic printing plate precursor of the invention, (A) a polymer having a urea bond in a side chain, which is contained in the positive recording layer, is improved in terms of chemical resistance and strength (hardness) in a non-exposed portion by the properties of the urea bond group introduced in the side chain. Moreover, because the urea bond itself does not act as a group soluble in an aqueous alkaline solution, the alkaline developer resistance of the polymer is not impaired. In addition, a strong interaction is formed by the hydrogen bond between the nitrogen atom or oxygen atom present in the urea bond group in the side chain and (C) the amino compound having a methoxymethyl group or an alkoxymethyl group, the urea bond group and the amino compound being used in combination, and as a result, a film more excellent in alkaline developer resistance and chemical resistance is formed due to the high dissolution suppressing function.

On the other hand, such an interaction is easily released by exposure to light or heat, and when the interaction is released, (A) the polymer having an urea bond group and (C) the amino compound reveal the hydrophilic properties which they have originally possessed, and rapidly dissolve in the developer.

Consequently, the non-exposed portion of the planographic printing plate precursor having such a positive recording layer maintains a strong film having excellent alkaline developer resistance and chemical resistance. And, the solubility of the exposed portion in the developer is remarkably improved owing to the release of the interaction and the hydrophilicity that the compounds have by nature. It is thought that, therefore, the difference of the solubility of the non-exposed portion and that of the exposed portion in an alkaline developer is large, and thereby the planographic printing plate precursor has excellent image reproducibility and printing durability.

In short, in the non-exposed portion in the planographic printing plate precursor of the present invention, a strong film having excellent chemical resistance and alkaline developer resistance is formed. And, when this non-exposed portion is exposed to infrared light, the solubility of the exposed area to a developer is remarkably improved. Thus, according to the present invention, a positive planographic printing plate precursor for use with an infrared laser that has wide development latitude and has excellent chemical resistance and printing durability can be provided.

The planographic printing plate precursor of the invention has a substrate and a positive recording layer prepared on the substrate, and the recording layer comprises (A) a polymer having a urea bond in a side chain (hereinafter, it may be referred to as "a specific polymer"), (B) a photothermal conversion agent, and (C) an amino compound having a methoxymethyl group or an alkoxymethyl group (hereinafter, it may be referred to as "a specific amino compound"), and the solubility thereof in an alkaline developer is improved by light-exposure or heating.

Hereinafter, each component contained in the recording layer in the planographic printing plate precursor of the present invention will be described in order.

[(A) A polymer having a urea bond in a side chain (a specific polymer)]

Though the specific polymer (A) used in the invention is not especially limited as long as it is a polymer having a urea bond in a side chain, among such polymers, it is preferable to use a polymer that is insoluble in water and soluble to aqueous alkaline solution.

As such polymers, known polymers can be used. Especially, in view of chemical resistance at the time of printing while a printing chemical is used, vinyl polymerized or condensation polymerized high-molecular compounds having a constitutional unit shown by any of the following formulas of (1-a) to (1-c), or novolac resins having a urea bond in the side chain can be preferably cited.

Moreover, in addition to a urea bond, the existence of a functional group that will contribute to the solubility to aqueous alkaline solution in a side chain is preferable in view of the improvement of sensitivity.
In the formulas of (1-a) to (1-c), R\textsubscript{1} and R\textsubscript{2} indicate independently a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a carboxyl group, or their salts, respectively. R\textsubscript{3} indicates a hydrogen atom, a halogen atom, an alkyl group, or an aryl group. X indicates a bivalent linkage group, of which suitable examples are an alkylene group, a phenylene group or the like that may have a substituent. Y indicates a bivalent aromatic group that may have a substituent, of which suitable examples are a phenylene group, a naphthylene group or the like that may have a substituent.

As the content of the constitutional unit shown by any of the formulas of (1-a) to (1-c) in the specific polymer (A), the constitutional unit in the copolymer is preferably 10 to 80 mol % in the feed ratio, more preferably 15 to 70 mol %, and in particular preferably 20 to 60 mol %.

When the content is less than 10 mol %, the specific polymer is poor in chemical resistance, and when more than 80 mol %, the solubility to aqueous alkaline solution is low and the sensitivity may be low.

The method for manufacturing the high-molecular compounds having a constitutional unit shown by any of the formulas of (1-a) to (1-c) is not especially limited, they can be manufactured by various sorts of known methods, for example, a method of polymerizing a polymerizable monomer using a polymerization initiator in a solvent, and the like can be cited.

In the method of polymerizing the polymerizable monomer using a polymerization initiator in a solvent, the polymerizable monomer is a monomer having one or more urea bonds and one or more polymerizable unsaturated bonds in one molecule, for example, compounds shown by the following formula (1-d) and the like can be suitably cited.

In the formula (1-d), R\textsuperscript{4} indicates a hydrogen atom or an alkyl group. X indicates a bivalent linkage group, for example, an alkylene group or a phenylene group that may have a substituent can be cited. Y indicates a bivalent aromatic group that may have a substituent, for example, a phenylene group, a naphthylene group or the like that may have a substituent can be cited.

Compounds shown by the formula (1-d) include, for example, acrylate derivatives such as 1-(N'-(4-hydroxyphenyl) ureido) methyl acrylate, 1-(N'-(3-hydroxyphenyl) ureido) methyl acrylate, 1-(N'-(3-hydroxy-4-methylphenyl) ureido) methyl acrylate, 1-(N'-(2-hydroxy-5-methylphenyl) ureido) methyl acrylate, 1-(N'-(5-hydroxynaphthyl) ureido) methyl acrylate, 1-(N'-(2-hydroxy-5-phenylphenyl) ureido) methyl acrylate, 2-(N'-(4-hydroxyphenyl) ureido) ethyl acrylate, 2-(N'-(3-hydroxyphenyl) ureido) ethyl acrylate, 2-(N'-(2-hydroxy-5-methylphenyl) ureido) ethyl acrylate, 2-(N'-(5-hydroxynaphthyl) ureido) ethyl acrylate, 2-(N'-(2-hydroxy-5-phenylphenyl) ureido) ethyl acrylate, 4-(N'-(4-hydroxyphenyl) ureido) butyl acrylate, 4-(N'-(3-hydroxyphenyl) ureido) butyl acrylate, 4-(N'-(2-hydroxy-5-methylphenyl) ureido) butyl acrylate, 4-(N'-(5-hydroxynaphthyl) ureido) butyl acrylate, and 4-(N'-(2-hydroxy-5-phenylphenyl) ureido) butyl acrylate.
urea bond in the area of 1600 to 1700 cm\(^{-1}\).

4-(N'-(2-ethyl acrylate); methacrylates having no acid group such as 2-(N'-(2-ethyl acrylate), 2-(N'-(2-propyl ureido) ethyl acrylate, 2-(N'-(phenyl ureido) ethyl acrylate, 2-(N'-(4-methylphenyl) ureido) ethyl acrylate, 2-(N'-(hydroxyphenyl) ureido) ethyl acrylate).

4-(N'-(hydroxy-5-phenyl) ureido) ethyl methacrylate, 2-(N'-(hydroxy-5-phenyl) ureido) ethyl methacrylate, 2-(N'-(5-methylphenyl) ureido) ethyl methacrylate, 2-(N'-(2-hydroxy-5-phenyl) ureido) ethyl methacrylate, 2-(N'-(2-hydroxy-5-phenyl) ureido) ethyl methacrylate, 2-(N'-(4-hydroxy-5-phenyl) ureido) ethyl methacrylate, 2-(N'-(2-hydroxy-5-phenyl) ureido) ethyl methacrylate, 2-(N'-(2-hydroxy-5-phenyl) ureido) ethyl methacrylate, 2-(N'-(2-hydroxy-5-phenyl) ureido) ethyl methacrylate, 2-(N'-(2-hydroxy-5-phenyl) ureido) ethyl methacrylate, 2-(N'-(2-hydroxy-5-phenyl) ureido) ethyl methacrylate, 2-(N'-(2-hydroxy-5-phenyl) ureido) ethyl methacrylate, 2-(N'-(2-hydroxy-5-phenyl) ureido) ethyl methacrylate, 2-(N'-(2-hydroxy-5-phenyl) ureido) ethyl methacrylate, 2-(N'-(2-hydroxy-5-phenyl) ureido) ethyl methacrylate, 2-(N'-(2-hydroxy-5-phenyl) ureido) ethyl methacrylate, 2-(N'-(2-hydroxy-5-phenyl) ureido) ethyl methacrylate, 2-(N'-(2-hydroxy-5-phenyl) ureido) ethyl methacrylate, 2-(N'-(2-hydroxy-5-phenyl) ureido) ethyl methacrylate.

[note]

Because the above-mentioned polymerizable monomers have a characteristic absorption band based on the urea bond in the area of 1600 to 1700 cm\(^{-1}\) in their infrared absorption spectrum, they can be identified by the measurement of their infrared absorption spectra. Moreover, they can be identified by the measurement of their melting points, proton NMR and the like.

For example, among the concrete examples described above, 2-(N'-(4-hydroxyphenyl) ureido) ethyl methacrylate has a melting point of 131 to 133°C, and can be identified by the measurement of their IR absorption spectrum based on the hydroxyl group and the urea bond.

Furthermore, besides the compounds shown by the formula (1-\(d\)), polymerizable monomers preferably include, for example, acrylates having an acid group such as 2-(N'-(4-carboxyphenyl) ureido) ethyl acrylate, 2-(N'-(4-sulfamoylphenyl) ureido) ethyl acrylate, 2-(N'-(sulfophenyl) ureido) ethyl acrylate, and 2-(N'-(4-phosphonophenyl) ureido) ethyl acrylate; methacrylates having an acid group such as 2-(N'-(4-carboxyphenyl) ureido) ethyl methacrylate, 2-(N'-(4-sulfamoylphenyl) ureido) ethyl methacrylate, 2-(N'-(sulfophenyl) ureido) ethyl methacrylate, 2-(N'-(4-phosphonophenyl) ureido) ethyl methacrylate; acrylates having no acid group such as 2-(N'-(methyl ureido) ethyl acrylate, 2-(N'-(propyl ureido) ethyl acrylate, 2-(N'-(phenyl ureido) ethyl acrylate, 2-(N'-(4-methylphenyl) ureido) ethyl acrylate, 2-(N'-(2-methylphenyl) ureido) ethyl acrylate, 2-(N'-(naphthyl ureido) ethyl acrylate, and 2-(N'-(2-phenylphenyl) ureido) ethyl acrylate; methacrylates having no acid group such as 2-(N'-(methyl ureido) ethyl methacrylate, 2-(N'-(propyl ureido) ethyl methacrylate, 2-(N'-(phenyl ureido) ethyl methacrylate, 2-(N'-(4-methylphenyl) ureido) ethyl methacrylate, 2-(N'-(2-methylphenyl) ureido) ethyl methacrylate, 2-(N'-(2-phenylphenyl) ureido) ethyl methacrylate, 2-(N'-(naphthyl ureido) ethyl methacrylate, and 2-(N'-(2-phenylphenyl) ureido) ethyl methacrylate.

Among the concrete examples described above, 2-(N'-(4-carboxyphenyl) ureido) ethyl methacrylate has a decomposition temperature of 220°C, and can be identified by the absorption of IR spectrum based on the carboxyl group and the urea bond.

The method for manufacturing the above-mentioned polymerizable monomers is not especially limited. For example, the known manufacturing method of reacting an isocyanate compound shown by the following formula (1-\(e\)) with an amine compound shown by the following formula (1-\(f\)), and the like can be suitably cited.

\[\text{R}^5\]
\[\text{CH}_2\]
\[\text{O} - \text{C} - \text{O} - \text{X} - \text{NCO}\]

\[\text{R}^6\]
\[\text{H} - \text{N} - \text{Y} - \text{Z}\]

In formula (1-\(e\), R\(^5\)) indicates a hydrogen atom or an alkyl group. X is the same as that in formula (1-\(d\)). In formula (1-\(f\), R\(^6\)) indicates a hydrogen atom, or an alkyl group that may have a substituent. Y is the same as that in formula (1-\(d\)). Z indicates a hydroxyl group, a carboxyl group, or a sulfonamide group.

In the above-mentioned manufacturing method, a polymerizable monomer shown by formula (1-\(d\)) can be suitably obtained by the use of a compound of formula (1-\(e\)) and a compound of formula (1-\(f\)) in which Z is a hydroxyl group and R\(^6\) is a hydrogen atom.
In the above-mentioned manufacturing method, because an amino group in formula (1-f) is more active to an isocyanate group compared to an a hydroxy group, a carboxyl group, -NH-CO- group, or the like, such polymerizable monomers as shown by formula (1-d) can be easily obtained.

Moreover, if desired, the reaction can be more effectively advanced by excessively using an amine compound shown by formula (1-f) and by slowly adding an isocyanate compound shown by formula (1-e) to the amine compound.

The above-mentioned solvent is not especially limited as long as it is a known organic solvent. Such solvents suitably include those having no active hydrogen atom, for example, ethylene dichloride, cyclohexanone, methyl ethyl ketone, acetone, methanol, ethanol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, 2-methoxyethyl acetate, 1-methoxy-2-propanol, 1-ethoxy-2-propanol, 1-methoxy-2-propanol acetate, 1-methoxy-2-propyl acetate, 1-ethoxy-2-propyl acetate, dimethyl sulfoxide, toluene, ethyl acetate, methyl lactate, ethyl lactate, and dioxane. One of these solvents may be used separately, or 2 or more of them may be used at the same time.

The reaction only has to be performed until the isocyanate compound shown by formula (1-e) runs out, or the amount of the urea bond becomes constant, and the time is usually 15 minutes to 24 hours.

Moreover, the temperature of the reaction is preferably 0 to 40°C.

For the purpose of removing unreacted raw material components and by-products when the reaction was performed in an excessive condition of the amine compound shown by formula (1-f), if desired, the reaction mixture is neutralized with an acidic compound, including dilute hydrochloric acid, to make the salt of the amine compound shown by formula (1-f), and then water washing, filtering, and vacuum drying of the reaction mixture will make the above-mentioned polymerizable monomer have high purity.

Although the specific polymer (A) concerned in the invention may be a homopolymer or a copolymer of 2 or more monomers from among the polymerizable monomers, each of which contains the urea bond (for example, monomers shown by formulae (1-a) to (1-c), and the like), the polymer is preferably a copolymer with a compound that has one or more polymerizable unsaturated bond(s) and does not contain a urea bond in view of printing durability. The copolymer may be any of a block copolymer, a random copolymer, a graft copolymer and the like.

The above-mentioned copolymer is preferably copolymerized by use of 10 to 80 mol % of the polymerizable monomer in a total 100 mol % of the polymerizable monomer and a compound that has one or more polymerizable unsaturated bond(s) and does not contain a urea bond.

The polymerizable compounds that have an unsaturated bond and do not contain a urea bond include, for example, acrylate compounds such as methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, amyl acrylate, ethylhexyl acrylate, octyl acrylate, t-octyl acrylate, chloroethyl acrylate, 2,2-dimethylhydroxypropyl acrylate, 5-hydroxypentyl acrylate, trimethylolpropane monoacrylate, pentaerythritol monoacrylate, glycidyl acrylate, benzyl acrylate, methoxybenzyl acrylate, and tetrahydro acrylate; aryl acrylate compounds such as phenyl acrylate, and furfuryl acrylate; methacrylate compounds such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, chlorobenzyl methacrylate, octyl methacrylate, 4-hydroxybutyl methacrylate, 5-hydroxypentyl methacrylate, 2,2-dimethyl-3-hydroxypropyl methacrylate, trimethylolpropane monomethacrylate, pentaerythritol monomethacrylate, glycidyl methacrylate, furfuryl methacrylate, and tetrahydrofurfuryl methacrylate; aryl methacrylate compounds such as phenyl methacrylate, cresyl methacrylate, and naphthyl methacrylate; acrylamide or its derivatives including N-alkyl acrylamide compounds such as N-methyl acrylamide, N-ethyl acrylamide, N-propyl acrylamide, N-butyl acrylamide, N-t-butyl acrylamide, N-octyl acrylamide, N-cyclohexyl acrylamide, and N-benzyl acrylamide; N-aryl acrylamide compounds such as N-phenyl acrylamide, N-tolyl acrylamide, N-nitrophenyl acrylamide, N-naphthyl acrylamide, and N-hydroxyphenyl acrylamide; N-dialkyl acrylamide compounds such as N,N-dimethyl acrylamide, N,N-diethyl acrylamide, N,N-dibutyl acrylamide, N,N-diisobutyl acrylamide, N,N-dimethylhexyl acrylamide, and N,N-dicyclohexyl acrylamide; N,N-aryl acrylamide compounds such as N,N-dimethyl-N-phenyl acrylamide, N,N-dimethyl-N-nitrophenyl acrylamide, and N-2-acetamidoethyl-N-acetyl acrylamide; methacrylamide or its derivatives include, N-alkyl methacrylamide compounds such as N,N-ethylenediamine-N-methylacrylamide, N,N-methylenediamine-N-methylacrylamide, N,N-dimethylenediamine-N-methylacrylamide, and N,N-diethylenediamine-N,N-dimethylacrylamide; N,N-dimethylethylenediamine-N-methylacrylamide, N,N-diethylethylenediamine-N-methylacrylamide, N,N-dicyclohexylmethacrylamide, N-aryl methacrylamide, N,N-propyl methacrylamide, N,N-butyl methacrylamide, N,N-t-butyl methacrylamide, N,N-ethylenehexyl methacrylamide, N,N-dihydroxymethacrylamide, and N,N-cyclohexyl methacrylamide; N-aryl methacrylamide compounds such as N-phenyl methacrylamide, and N,N-dialkyl methacrylamide compounds such as N,N-dimethyl methacrylamide, N,N-dipropyl methacrylamide, and N,N-dibutyl methacrylamide; N,N-diaryl methacrylamide compounds such as N,N-diphenyl methacrylamide; methacrylamide derivatives such as N-hydroxymethyl-N-methyl methacrylamide, N-methyl-N-phenyl methacrylamide, and N-ethyl-N-phenyl methacrylamide; allyl compounds such as allyl acetate, allyl caproate, allyl caprylate, allyl laurate, allyl palmitate, allyl stearate, allyl benzoate, allyl acetoacetate, allyl lactate, and allyl o xoethanol; vinyl ether compounds such as hexyl vinyl ether, octyl vinyl ether, dodecyl vinyl ether, ethylhexyl vinyl ether, methoxyethyl vinyl ether, ethoxyethyl vinyl ether, chloroethyl vinyl ether, 1-methyl-2,2-dimethylpropyl vinyl ether, 2-ethylbutyl vinyl ether, hydroxyethyl vinyl ether, diethylene glycol vinyl ether, dimethylaminoothyl vinyl ether, diethyldiaminoothyl vinyl ether, butylaminoothyl vinyl ether, benzyl vinyl ether, tetrahydrofururyl vinyl ether, vinyl phenyl ether, vinyl tolyl ether, vinyl chlorophenyl ether, vinyl-2,4-dichlorophenyl ether, vinyl naphthyl ether, and vinyl antranil ether; vinyl ester compounds such as vinyl butyrate, vinyl iso-
butylate, vinyl trimethyl acetate, vinyl diethyl acetate, vinyl caproate, vinyl chloroacetate, vinyl methoxy-acetate, vinyl butoxyacetate, vinyl phenylacetate, vinyl acetoacetate, vinyl lactate, vinyl-β-phenyl butylate, vinyl cyclohexyl carboxylate, vinyl benzoate, vinyl salicylate, vinyl chlorobenzoate, vinyl tetrachlorobenzoate, and vinyl naphthoate; Styrene compounds such as methylstyrene, dimethylstyrene, trimethylstyrene, ethylstyrene, diethylstyrene, isopropylstyrene, butylstyrene, hexylstyrene, cyclohexylstyrene, dodecylstyrene, benzylstyrene, chloromethylstyrene, trifluoromethylstyrene, ethoxymethylstyrene, acetoxyethylstyrene, methoxy styrene, 4-methoxy-3-methyl styrene, dimethoxy styrene, chlorostyrene, dichlorostyrene, trichlorostyrene, tetrachlorostyrene, pentachlorostyrene, bromostyrene, dibromostyrene, iodostyrene, fluoro styrene, 2-bromo-4-trifluoromethyl styrene, and 4-fluoro-3-trifluoromethyl styrene; crotonate compounds such as butyl crotonate, hexyl crotonate, crotonic acid, and glycerin monocrotonate; dialkyl itaconate compounds such as dimethyl itaconate, diethyl itaconate, and dibutyl itaconate; dialkyl compounds of maleic acid or fumaric acid such as dimethyl maleate, and dibutyl fumarate; maleimide compounds such as maleimide, N-phenyl maleimide, N-2-methylphenyl maleimide, N-2,6-diethylphenyl maleimide, N-2-chlorophenyl maleimide, N-cyclohexyl maleimide, N-lauryl maleimide, and N-hydroxyphenyl maleimide; and other compounds including N-vinylpyrrolidone, N-vinylpyridine, acrylonitrile, and methacrylonitrile. One sort of these compounds may be used separately, and 2 or more sorts of them may be used at the same time.

[0047] Among these compounds, (meth)acrylate compounds, (meth)acrylamide compounds, maleimide compounds, and (meth)acrylonitrile compounds are especially preferable.

[0048] Further, in the present specification, when both or any one of acrylate and methacrylate are indicated, they may be described as (meth)acrylate. Similarly, both or any one of acrylic acid and methacrylic acid may be called as (meth)acrylic acid, both or any one of acrylonitrile and methacrylonitrile as (meth)acrylonitrile, and both or any one of acrylamide and methacrylamide as (meth)acrylamide, respectively.

[0049] Hereinafter, preferable examples of the specific polymer (A) concerned with the present invention will be cited together with their weight-average molecular weight (Mw) and number-average molecular weight (Mn) by their constitutional units and the mole ratios in polymerization, though the present invention is not limited to these examples.
\[ \text{Mw} = 400,000 \]
\[ \text{Mn} = 100,000 \]

\[ \text{Mw} = 150,000 \]
\[ \text{Mn} = 30,000 \]

\[ \text{Mw} = 110,000 \]
\[ \text{Mn} = 50,000 \]

\[ \text{Mw} = 380,000 \]
\[ \text{Mn} = 130,000 \]
The molecular weight of the specific polymer (A) of the present invention is preferably 2,000 or more in weight-average molecular weight, and more preferably 3,000 to 500,000, while in number-average molecular weight, it is preferably 1,000 or more, and more preferably 2,000 to 400,000.

The content of the specific polymer (A) of the present invention in the recording layer is 3 to 97 mass % in the total solid content of the compositions constituting the recording layer, and preferably 10 to 90 mass %, and more preferably 30 to 80 mass %.

(B) A photothermal conversion agent

The recording layer of the present invention needs to contain a photothermal conversion agent (B) in addition to the specific polymer (A).

As a photothermal conversion agent usable in the invention, it is possible to use any compound that generates heat by being exposed to a light source used for image forming. However, because the planographic printing plate precursor of the present invention can form an image by being exposed to an infrared laser, it is preferable to use an infrared-light absorbing agent that has a light absorption range in the infrared region of 700 nm or more, preferably 750 to 1,200 nm, and that reveals a photothermal conversion function through light in the wavelengths of this range. In concrete terms, it is possible to use various sorts of dyes or pigments that absorb light in the above-mentioned wavelength band and generate heat.

As a dye, commercially available dyes and the known dyes described in the publication such as "Dye Handbook" (edited by The Society of Synthetic Organic Chemistry, Japan, published in 1970) can be utilized. Examples include dyes such as azo dyes, metal complex salt azo dyes, pyrazolone azo dyes, naphthoquinone dyes, anthraquinone dyes, phthalocyanine dyes, carbonium dyes, quinoneimine dyes, methine dyes, squarylium pigments, pyrrole salts, metal thiolate complexes, oxomol dyes, diimonium dyes, aminium dyes, and croconium dyes.


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

Among these dyes, particularly preferable are cyanine dyes, phthalocyanine dyes, oxonol dyes, squarylium dyes, pyrylium salts, thiopyrylium dyes, and nickel thiolate complexes. Dyes represented by the following general formulae (a) to (e) are also preferable since such dyes are excellent in terms of photothermal conversion efficiency. The cyanine dyes represented by the following general formula (a) are most preferable because: when the dyes are used with the image forming material of the invention, they manifest a high degree of interaction with an alkali-soluble resin; and the dyes are excellent in terms of stability and economy.

**General formula (a)**

![Diagram of General Formula (a)]

In general formula (a), $X^1$ represents a hydrogen atom, a halogen atom, $-\text{NPh}_2$, $X^2-L^1$ (wherein $X^2$ represents an oxygen atom or a sulfur atom, $L^1$ represents a hydrocarbon group having 1 to 12 carbon atoms, an aromatic cyclic group having a heteroatom, or a hydrocarbon group containing a heteroatom and having 1 to 12 carbon atoms, and the heteroatom referred to herein is N, S, O, a halogen atom, or Se), or a group represented by the following:

![Diagram of General Formula (a) with $X_{a-}$ and $R^a$]

wherein $X_{a-}$ has the same definition as $Z_{a-}$, which will be described at a later time, and $R^a$ represents a substituent selected from a hydrogen atom, an alkyl group, an aryl group, a substituted or unsubstituted amino group, or a halogen atom;

R$^1$ and R$^2$, each independently represents a hydrocarbon group having 1 to 12 carbon atoms, and from the viewpoint of the storage stability of the photosensitive composition of the invention when it is used in a coating solution for forming a recording layer of a planographic printing plate precursor, it is preferable that R$^1$ and R$^2$ each independently represents a hydrocarbon group having 2 or more carbon atoms, and more preferably R$^1$ and R$^2$ are bonded to each other to form a 5-membered or 6-membered ring.

Ar$^1$ and Ar$^2$, which may be the same or different, each represents an aromatic hydrocarbon group which may have a substituent. Preferable examples of the aromatic hydrocarbon group include benzene and naphthalene rings. Preferable examples of the substituent include hydrocarbon groups having 12 or less carbon atoms, halogen atoms, and alkoxy groups having 12 or less carbon atoms.

Y$^1$ and Y$^2$, which may be the same or different, each represents a sulfur atom, or a dialkylmethylene group having 12 or less carbon atoms.

R$^3$ and R$^4$, which may be the same or different, each represents a hydrocarbon group which has 20 or less carbon atoms and may have a substituent. Preferable examples of the substituent include alkoxy groups having 12 or less carbon atoms, a carboxyl group, and a sulfo group. R$^5$, R$^6$, R$^7$ and R$^8$, which may be the same or different, each represents a hydrocarbon group having 12 or less carbon atoms, and since the raw materials thereof can easily be obtained, each preferably represents a hydrogen atom.

Z$^a$ represents a counter anion. However, in a case where the cyanine dye represented by general formula (a) has an anionic substituent in the structure thereof and there is accordingly no need to neutralize electric charges in the dye, Z$^a$ is not required. From the viewpoint of the storage stability of the recording layer coating solution, Z$^a$ is preferably an ion of a halogen, perchlorate, tetrafluoroborate, hexafluorophosphate, carboxylate or sulfonate. From the viewpoints of compatibility of the dye with the alkali-soluble resin and solubility in the coating solution, Z$^a$ is preferably a halogen.
ion, or an organic acid ion such as a carboxylic acid ion or sulfonic acid ion, more preferably a sulfonic acid ion, and even more preferably an arylsulfonic acid ion.

Specific examples of the cyanine dye represented by general formula (a), and which can be preferably used in the invention, include dyes in JP-A No. 2001-133969 (paragraphs [0017] to [0019]), JP-A No. 2002-40638 (paragraphs [0012] to [0038]), and JP-A No. 2002-23360 (paragraphs [0012] to [0023]), as well as dyes illustrated below.
In general formula (b), L represents a methine chain having 7 or more conjugated carbon atoms, and the methine chain may have one or more substituent. The substituents may be bonded to each other to form a cyclic structure. Zb+ represents a counter cation. Preferable examples of the counter cation include ammonium, iodonium, sulfonium, phosphonium and pyridinium ions, and alkali metal cations (such as Na+, K+ and Li+).

R9 to R14 and R15 to R20 each independently represents a substituent selected from hydrogen atom, halogen atom, cyano, alkyl, aryl, alkenyl, alkynyl, carbonyl, thio, sulfonyl, sulfanyl, oxy and amino groups; or a substituent obtained by combining two or three among these substituents. Two or three of R9 to R14 and R15 to R20 may be bonded to each other to form a cyclic structure.

A dye wherein L in general formula (b) represents a methine chain having 7 conjugated carbon atoms, and each of R9 to R14 and R15 to R20 represents a hydrogen atom, is preferable since such a dye can be easily obtained and exhibits advantageous effects.

Specific examples of the dye represented by general formula (b), and which can be preferably used in the invention, are illustrated below.
In general formula (c), \(Y_3\) and \(Y_4\) each independently represent an oxygen, sulfur, selenium or tellurium atom; \(M\) represents a methine chain having 5 or more conjugated carbon atoms; \(R_{21}\) to \(R_{24}\) and \(R_{25}\) to \(R_{28}\), which may be the same or different, each represents a hydrogen or halogen atom, or a cyano, alkyl, aryl, alkenyl, alkynyl, carbonyl, thio, sulfonyl, sulfanyl, oxy or amino group; and \(Z_a^-\) represents a counter anion, and has the same meaning as \(Z_a^-\) in general formula (a).

Specific examples of the dye which is represented by general formula (c) and which can be preferably used in the present invention, are illustrated below.
In general formula (d), R\textsubscript{29} to R\textsubscript{31} each independently represents a hydrogen atom, an alkyl group or an aryl group; R\textsubscript{33} and R\textsubscript{34} each independently represents an alkyl group, a substituted oxy group, or a halogen atom; n and m each independently represents an integer of 0 to 4; and R\textsubscript{29} and R\textsubscript{30}, or R\textsubscript{31} and R\textsubscript{32} may be bonded to each other to form a ring, or R\textsubscript{29} and/or R\textsubscript{30} may be bonded to R\textsubscript{33} to form a ring and R\textsubscript{31} and/or R\textsubscript{32} may be bonded to R\textsubscript{34} to form a ring. When plural R\textsubscript{33}'s and R\textsubscript{34}'s are present, R\textsubscript{33}'s may be bonded to each other to form a ring, or R\textsubscript{34}'s may be bonded to each other to form a ring.

X\textsubscript{2} and X\textsubscript{3} each independently represents a hydrogen atom, an alkyl group or an aryl group, and at least one of X\textsubscript{2} and X\textsubscript{3} represents a hydrogen atom or an alkyl group.

Q represents a trimethine group or a pentamethine group which may have a substituent, and may be combined with a bivalent organic group to form a cyclic structure. Z\textsubscript{c} represents a counter anion and has the same meanings as Z\textsubscript{a} in general formula (a).

Specific examples of the dye represented by general formula (d) and which can be preferably used in the present invention, are illustrated below.
In general formula (e), $R^{35}$ to $R^{50}$ each independently represents a hydrogen or halogen atom, or a cyano, alkyl, aryl, alkenyl, alkynyl, hydroxyl, carbonyl, thio, sulfonyl, sulfanyl, oxy or amino group, or an onium salt structure, each of which may have a substituent; M represents two hydrogen atoms, a metal atom, a halo metal group, or an oxy metal group. Examples of the metal contained therein include atoms in IA, IIA, IIIB and IVB groups in the periodic table, transition metals in the first, second and third periods therein, and lanthanoid elements.

Among these examples, preferable are copper, magnesium, iron, zinc, cobalt, aluminum, titanium, and vanadium.

Specific examples of the dye represented by general formula (e) and which can be preferably used in the present invention, are illustrated below.
The pigment used as the infrared absorbent in the invention may be a commercially available pigment or a pigment described in publications such as Color Index (C.I.) Handbook, "Latest Pigment Handbook" (edited by Japan Pigment Technique Association, and published in 1977), "Latest Pigment Applied Technique" (by CMC Publishing Co., Ltd. in 1986), and "Printing Ink Technique" (by CMC Publishing Co., Ltd. in 1984).

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

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

From a viewpoint of stability of a dispersion in a recording layer coating solution, and uniformity of a recording layer, a particle diameter of pigments is preferably in a range of 0.01 μm to 10 μm, further preferably in a range of 0.05 μm to 1 μm, particularly preferably in a range of 0.1 μm to 1 μm.

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

From the viewpoints of sensitivity, uniformity of the film to be formed and durability, the pigment or dye can be added to the recording layer in a ratio of 0.01 to 50%, preferably 0.1 to 10%, and more preferably 0.5 to 10% in the case of dye and 0.1 to 10% in the case of pigment by mass, relative to the total solid contents of the recording layer.

[(C) An amino compound having a methylol group or an alkoxymethyl group (the specific amino compound)]

In the present invention, the recording layer needs to contain (C) an amino compound having a methylol group or an alkoxymethyl group (the specific amino compound) together with the (A) the specific polymer and (B) a photothermal conversion agent.

Here, the specific amino compound is preferably an amino compound having at least 2 groups selected from the group comprising of methylol groups and alkoxymethyl groups.

More preferably, the specific amino compound in the present invention is an amino compound containing the structure shown by the following formula (I).
(In the formula (I), \(T_1\) and \(T_2\) independently indicate a hydrogen atom, an alkyl group, an alkenyl group, an acyl group, and an acetyl group, respectively.)

[0087] Here, when \(T_1\) and \(T_2\) in formula (I) are alkyl groups, the number of carbon atoms in the alkyl group is preferably 1 to 8, and more preferably 1 to 4. In concrete terms, a methyl group, an ethyl group, an isopropyl group, a tertiary butyl group, and the like are preferable.

[0088] And, when \(T_1\) and \(T_2\) are alkenyl groups, the number of carbon atoms in the alkenyl group is preferably 2 to 18, and more preferably 2 to 4.

[0089] Further, when \(T_1\) and \(T_2\) are acyl groups, the number of carbon atoms in the acyl group is preferably 2 to 18, and more preferably 2 to 4.

[0090] Concrete examples of the structure shown by the formula (I) include a methoxymethylolamine group, a dimethoxymethylamino group, a dimethylolamino group (a dihydroxyamino group), and a diethoxymethylamino group.

[0091] As compounds having two or more of the structures shown by formula (I) in the molecules, compounds having a melamine skeleton, compounds having a benzoguanamine skeleton, compounds having a glycoluryl skeleton, and compounds having a urea skeleton can be cited. Further, condensation products, which are made by condensing the structure shown by formula (I) and any of compounds cited here through a bivalent linkage group, may be accepted.

[0092] Moreover, in the present invention, among these compounds, amino compounds shown by the following formula (II) are preferable.

(In formula (II), \(R_1\) to \(R_6\) independently indicate a hydrogen atom, an alkyl group, an alkenyl group, an acyl group, and an acetyl group, respectively.)

[0093] Here, a hydrogen atom, an alkyl group, an alkenyl group, an acyl group, and an acetyl group in \(R_1\) to \(R_6\) of the formula (II) have the same meaning as a hydrogen atom, an alkyl group, an alkenyl group, an acyl group, and an acetyl group in \(T_1\) and \(T_2\) of formula (I).

[0094] In the following, concrete examples of the specific amino compounds suitably used in the present invention will be cited, though the invention is not limited to these examples.
The specific amino compound in the present invention is preferably added by 0.5 to 30 mass % in the total
solid content constituting the recording layer in view of printing durability and chemical resistance, and more preferably added by the ratio of 1 to 10 mass %.

[Other components]

[0096] In the recording layer in the planographic printing plate precursor of the present invention, in addition to the essential components of (A) to (C), various sorts of compounds may be further used at the same time if needed.

[0097] For example, besides the specific polymer (A), any of the other resins soluble in an aqueous alkaline solution can be contained in the recording layer if needed. In this case, other resins soluble in an aqueous alkaline solution are not particularly limited, but general-purpose novolac resins are preferable.

[0098] As novolac resins, for example, phenol-formaldehyde resin, m-cresol-formaldehyde resin, p-cresol-formaldehyde resin, m-/p-mixed cresol-formaldehyde resin, phenol/cresol (any of m-, p-, o-, m-/p-mixed, m-/o-mixed, and o-/p-mixed may be accepted) mixed formaldehyde resin can be cited. One of these compounds may be used separately, and 2 or more may be used at the same time.

[0099] Among these novolac resins, those with weight-average molecular weight of 1,500 or more and number-average molecular weight of 300 or more are preferable, and those with weight-average molecular weight of 3,000 to 300,000, number-average molecular weight of 500 to 250,000 and the degree of dispersion (weight-average molecular weight/number-average molecular weight) of 1.1 to 10 are more preferable.

[0100] Moreover, as preferable resins which are soluble in an aqueous alkaline solution and can be used with the essential components (A) to (C), resins having any of the acidic groups shown in the following (1) to (6) in the principal chain and/or a side chain of the polymer can be cited.

(1) a phenolic hydroxyl group (-Ar-OH),
(2) a sulfonamide group (-SO₂NH-R),
(3) a substituted sulfonamide acidic group (referred to as an “active imide group” hereinafter; -SO₂NHCOR, -SO₂NH₂SO₂R, -CONHSO₂R),
(4) a carboxylic acid group (-CO₂H),
(5) a sulfonic acid group (-SO₃H), and
(6) a phosphoric acid group (-OPO₃H₂).

[0101] In (1) to (6), Ar represents a divalent aryl linking group that may be substituted, and R represents a hydrogen atom or a hydrocarbon group that may be substituted.

[0102] Among alkali-soluble resins having acidic groups selected from the (1) to (6), alkali-soluble resins having (1) a phenol group, (2) a sulfonamide group and (3) an active imide group are preferable. In particular, alkali-soluble resins having (1) a phenol group or (2) a sulfone amide group are most preferable from a viewpoint of sufficient solubility in an alkaline developer, developing latitude, and film strength.

[0103] As the alkali-soluble resin comprising the acidic group selected from the above-mentioned (1) to (6), the following can be exemplified.

(1) Examples of the alkali-soluble resin comprising phenol group may include the aforementioned novolak resin or the like such as condensation polymers of phenol and formaldehyde; condensation polymers of m-cresol and formaldehyde; condensation polymers of p-cresol and formaldehyde; condensation polymers of m-/p-mixed cresol and formaldehyde; and condensation polymers of phenol, cresol (m-, p-, or m-/p-mixture) and formaldehyde; and condensation copolymers of pyrogallol and acetone. Further, copolymers obtained by copolymerizing compound comprising phenol groups in the side chains can be exemplified. Or, copolymers obtained by copolymerizing compounds comprising phenol groups in the side chains can also be used. As the compounds comprising phenol group, acrylamide, methacrylamide, acrylic acid ester, methacrylic acid ester, or hydroxystyrene can be exemplified.

(2) Examples of the alkali-soluble resin comprising sulfonamide group may include polymers obtained by using the minimum component units derived from compounds comprising sulfonamide group as main constituent components. Examples of such compounds include those having at least one sulfonamide group comprising at least one hydrogen atom bonded to the nitrogen atom and at least one polymerizable unsaturated group, in the molecules. Among them, low molecular weight compounds comprising acryloyl, allyl, or vinylxoy group as well as substituted or mono-substituted aminosulfonyl group or a substituted sulfonylimino group in molecules are preferable and the following compounds defined by the following (i) to (v) can be exemplified.
In the formulae (i) to (v), $X_1$ and $X_2$ each represents, independently, -O- or -NR$_7$. $R_1$ and $R_4$ each represents, independently, a hydrogen atom or -CH$_3$. $R_2$, $R_5$, $R_9$, $R_{12}$ and $R_{15}$ each represents, independently, an alkylene group of a carbon number of 1 to 12 optionally having a substituent, a cycloalkylene group, an arylene group or an aralkylene group. $R_3$, $R_7$ and $R_{13}$ each represents, independently, a hydrogen atom, an alkyl group of a carbon number of 1 to 12 optionally having a substituent, a cycloalkyl group, an aryl group or an aralkyl group. $R_6$ and $R_{17}$ each represents, independently, an alkyl group of a carbon number of 1 to 12 optionally having a substituent, a cycloalkyl group, an aryl group or an aralkyl group. $R_8$, $R_{10}$ and $R_{14}$ each represents, independently, a hydrogen atom or -CH$_3$. $R_9$ and $R_{16}$ each represents, independently, a single bond, or an alkylene group of a carbon number of 1 to 12 optionally having a substituent, a cycloalkylene group, an arylene group or an aralkylene group. $Y_1$ and $Y_2$ each represents, independently, a single bond or -CO-.

Among compounds represented by the formula (i) to the formula (v), in the planographic printing plate precursor of the invention, particularly, m-aminosulfonylphenyl methacrylate, N-(p-aminosulfonylphenyl) methacrylamide, and N-(p-aminosulfonylphenyl)acrylamide can be suitably used.

Examples of the alkali-soluble resin having an active imide group in the item (3) include a polymer having as the main component a minimum structural unit derived from a compound having an active imide group. Examples of such a compound include a compound having in the molecule thereof one or more active imide groups represented by the following structural formula and one or more unsaturated groups which can be polymerized with the active imide group(s):
Specifically, N-(p-toluenesulfonyl)methacrylamide, N-(p-toluenesulfonyl)acrylamide and others can be preferably used.

Examples of the monomer having a carboxylic acid group in the item (4) include compounds each having in the molecule thereof one or more carboxylic acid groups and one or more unsaturated groups which can be polymerized with the carboxylic acid group(s).

Examples of the monomer having a sulfonic acid group in the item (5) include compounds each having in the molecule thereof one or more sulfonic acid groups and one or more unsaturated groups which can be polymerized with the sulfonic acid group(s).

Examples of the monomer having a phosphoric acid group in the item (6) include compounds each having in the molecule thereof a phosphoric acid group and one or more unsaturated groups which can be polymerized with the phosphoric acid group(s).

The minimum constituent unit comprising acidic group selected from (1) to (6) is not necessarily limited to one particular unit, but can be those obtained by copolymerizing two or more types of minimum constituent units comprising the same acidic group or two or more types of minimum constituent units comprising different acidic groups.

The above-mentioned copolymer contains the compound having the acidic group selected from (1) to (6) to be copolymerized in an amount preferably 10% by mole or more, more preferably 20% by mole or more. If it is less than 10% by mole, the development latitude tends to be improved insufficiently.

As monomer components which are copolymerized with the polymerizable monomers having a phenolic hydroxyl group, a sulfonamide group, or an activated imide group, for example, monomers shown in the following (m1) to (m12) can be used, though the monomer components should not be limited to them.

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

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

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

\[(m4)\] Acrylamide or methacrylamide such as acrylamide, methacrylamide, N-methyl acrylamide, N-ethyl acrylamide, N-hexyl methacrylamide, N-cyclohexylacrylamide, N-hydroxyethyl acrylamide, N-phenyl acrylamide, N-nitrophenylacrylamide, and N-ethyl-N-phenylacrylamide.

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

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

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

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

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

\[(m10)\] N-vinylpyrrolidone, acrylonitrile, and methacrylonitrile.

\[(m11)\] Unsaturated imides such as maleimide, N-acryloylacrylamide, N-acryloylmethacrylamide, N-propionylmethacrylamide, and N-(p-chlorobenzoyl)methacrylamide.

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

As the resins soluble in an aqueous alkaline solution in the present invention, the homopolymers or copolymers of the above-mentioned polymerizable monomers having a phenolic hydroxyl group or an activated imide group are preferable, and the homopolymers or copolymers of the polymerizable monomers having a sulfonamide group such as m-aminosulfonylphenyl methacrylate, N-(p-aminosulfonylphenyl) methacrylamide, N-(p-aminosulfonylphenyl) acrylamide, or the like are especially preferable. Further, those with a weight-average molecular weight of 2,000 or more and a number-average molecular weight of 500 or more are preferable, and those with a weight-average molecular weight of 5,000 to 300,000 and a number-average molecular weight of 800 to 250,000 and a degree of dispersion (weight-average molecular weight/number-average molecular weight) of 1.1 to 10 are more preferable.

One of these resins soluble in an aqueous alkaline solution may be used respectively, or two or more types
thereof may be used in combination. The amount of these resins to be added is 5 to 90 mass % in the total solid amount of the above-mentioned recording layer, preferably 10 to 85 mass %, and in particular preferably 15 to 80 mass %. If the amount added of a resin soluble in an aqueous alkaline solution is insufficient, when using the resin as the recording layer in a planographic printing plate precursor, the durability of the recording layer is deteriorated. If the amount is too much, the content of "a specific polymer (A)" as an essential component in the invention is relatively reduced, whereby it is difficult to obtain the effect of the present invention. Both states of which are not preferable.

[0116] For example, it is preferable to add a so-called dissolution inhibitor that enhances the effect of inhibiting dissolution of the alkaline solution-soluble polymer (alkaline soluble resin) in the developer when added, such as other onium salts, aromatic sulfone compounds, aromatic sulfonate ester compounds, polyfunctional amine compounds, or the like. Among these, the combined use of a substance that is heat-decomposing and substantially lowers the solubility of the alkaline soluble resin in an un-decomposed state, such as onium salts, o-quinonediazide compounds, alkyl sulfonate ester, and the like is preferable for the aim of improving the solubility inhibiting property of the image area with regard to the developer.


[0118] Among these onium salts, in view of the dissolution-inhibiting function and pyrolyzable property, diazonium salts and quaternary ammonium salts are especially preferable. Especially as diazonium salts, the diazonium salts shown by the formula (I) described in JP-A No. 5-158230 and the diazonium salts shown by the formula (1) described in JP-Ano. No. 11-143064 are preferable, and diazonium salts which have a small absorption wavelength in the visible radiation region and shown by the formula (1) described in JP-A No. 11-143064 are most preferable. And as quaternary ammonium salts, quaternary ammonium salts described as (1) to (10) in [Formula 5] and [Formula 6] in JP-Ano. 2002-229186 are preferable.

[0119] Examples of the counter ion of the onium salt include tetrafluoroboric acid, hexafluorosilicic acid, trisopropylphosphonic acid, 5-nitro-o-toluenesulfonic acid, 5-sulfosalicylic acid, 2,5-dimethylbenzenesulfonic acid, 2,4,6-trimethylbenzenesulfonic acid, 2-nitrobenzenesulfonic acid, 3-chlorobenzenesulfonic acid, 3-bromobenzenesulfonic acid, 2-fluorocaprylnaphthalenesulfonic acid, dodecylbenzenesulfonic acid, 1-naphthol-5-sulfonic acid, 2-methoxy-4-hydroxy-5-benzoyl-benzenesulfonic acid, and p-toluenesulfonic acid. Among these examples, hexafluorophosphoric acid, and alkylaromatic sulfonic acids such as trisopropylphosphonohesulfonic acid and 2,5-dimethylbenzenesulfonic acid are particularly preferable.

[0120] The quinonediazide is preferably an o-quinonediazide compound. The o-quinonediazide compound used in the invention is a compound having at least one o-quinonediazide group and having an alkali-solubility increased by being thermally decomposed. The compound may be any one of compounds having various structures.

[0121] In other words, the o-quinonediazide compound assists the solubility of the photosensitive material both from the viewpoint of the effects of being thermally decomposed, and thereby losing the function of suppressing the dissolution of the binder, and the effect that the o-quinonediazide itself is changed into an alkali-soluble material.

[0122] Preferable examples of the o-quinonediazide compound used in the invention include compounds described in J. Coser. "Light-Sensitive Systems" (John Wiley & Sons. Inc.), pp. 339-352. Particularly preferable are sulfonic acid esters or sulfonamides of o-quinonediazide made to react with various aromatic polyhydroxy compounds or with aromatic amino compounds.

[0123] Further preferable examples include an ester made from benzoquinone-(1,2)-diazide-5-sulfonic acid chloride or naphthoquinone-(1,2)-diazide-5-sulfonic acid chloride and pyrogallol-acetone resin, as described in JP-B No. 43-28403; and an ester made from benzoquinone-(1,2)-diazidesulfonic acid chloride or naphthoquinone-(1,2)-diazide-5-sulfonic acid chloride and phenol-formaldehyde resin as in described in US 3,046,120 and US 3,188,210.

[0124] Additional preferable examples include an ester made from naphthoquinone-(1,2)-diazide-4-sulfonic acid chloride and phenol-formaldehyde resin or cresol-formaldehyde resin; and an ester made from naphthoquinone-(1,2)-diazide-4-sulfonic acid chloride and pyrogallol-acetone resin.

[0126] The amount of onium salts and/or o-quinone diazide compounds that is added, which are decomposable dissolution inhibitors is preferable in the range of 1 to 10 mass % in the total solid content of the recording layer, is further preferably in the range of 1 to 5 mass %, and especially preferably in the range of 1 to 2 mass %. Though these compounds can be used alone, they may be used as a mixture of several of these compounds.

[0127] The amount added of additives other than o-quinone diazide compounds that is added is preferably 0.1 to 5 mass %, further preferably 0.1 to 2 mass %, and in particular preferably 0.1 to 1.5 mass %. The additives and binders in the present invention are preferably contained in the same layer.

[0128] Moreover, a dissolution inhibitor not having resolvability may be used at the same time. Preferable dissolution inhibitors include compounds described in detail in JP-A No. 10-268512 such as sulfonates, phosphates, aromatic carboxylates, aromatic disulfones, carboxylic acid anhydrides, aromatic ketones, aromatic aldehydes, aromatic amines, and aromatic ethers, compounds similarly described in detail in JP-A No. 11-190903 such as acid coloring dyestuffs having a lactone skeleton, a N,N-diallyl amide skeleton, and diaryl methylimino skeleton and combining a coloring agent, and nonionic surfactants similarly described in detail in JP-ANo. 2000-105454.

[0129] Moreover, as preferable additives used in the top layer of the recording layer, cyclic acid anhydrides, phenol compounds, organic acids and the like can be cited in view of improving sensitivity. Further, surfactants, image coloring agents and plasticizers, which will be described later, can be also used as an additive in the positive recording layer.

[0130] Examples of cyclic acid anhydride include phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, 3,6-endooxy-A4-tetrahydrophthalic anhydride, tetrachlorophthalic anhydride, maleic anhydride, chloromaleic anhydride, α-phenylmaleic anhydride, succinic anhydride, and pyromellitic anhydride which are described in U.S. Patent No. 4,115,128.

[0131] Examples of phenolic compound include bisphenol A, p-nitrophenol, p-ethoxyphenol, 2,4,4'-trihydroxybenzophenone, 2,3,4-trihydroxybenzophenone, 4-hydroxybenzophenone, 4,4',4''-trihydroxytriphenylmethane, and 4,4',3',4''-tetrahydroxy-3,5,3',5'-tetramethyltriphenylmethane.

[0132] Examples of the organic acid include sulfonic acids, sulfuric acids, alkylsulfuric acids, phosphonic acids, phosphates, and carboxylic acids, which are described in JP-A No. 60-88942 or 2-96755.

[0133] When the cyclic acid anhydride, the phenol or the organic acid is added to a recording layer of a planographic printing plate precursor, the ratio thereof in the recording layer is preferably from 0.05 to 20%, more preferably from 0.1 to 15%, and even more preferably from 0.1 to 10% by mass.

[0134] In addition to the above, the following may be appropriately added to the composition, depending on the objective: an epoxy compound; a vinyl ether; a phenol compound having a hydroxymethyl group and a phenol compound having an alkoxymethyl group, described in JP-A No. 8-276558; and a cross-linkable compound having an effect of suppressing dissolution in an alkali, described in JP-A No. 11-160860, and which was previously proposed by the present inventors.

[0135] To the photosensitive composition of the present invention may be added a printing-out agent for obtaining a visible image immediately after the photosensitive composition of the invention has been heated by exposure to light, or a dye or pigment as an image coloring agent.

[0136] A typical example of a printing-out agent is a combination of a compound which is heated by exposure to light, thereby emitting an acid (an optically acid-generating agent), and an organic dye which can form salts (salt formable organic dye).

[0137] Specific examples thereof include combinations of an o-napthoquinonediazide-4-sulfonic acid halogenide with a salt-formable organic dye, described in JP-A Nos. 50-36209 and 53-8128; and combinations of a trihalomethyl compound with a salt-formable organic dye, described in each of JP-ANos. 53-36223, 54-74728, 60-3626, 61-143748, 61-151644 and 63-58440.

[0138] The trihalomethyl compound is classified into an oxazol compound or a triazine compound. Both of the compounds provide excellent in stability over the passage of time and produce a vivid printed-out image.

[0139] As the image coloring agent, a dye different from the above-mentioned salt-formable organic dye may be used. Preferable examples of such a dye, and of the salt-formable organic dye, include oil-soluble dyes and basic dyes.

[0140] 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 (CI45170B), Malachite Green (CI42000), and Methylene Blue (CI52015).

[0141] Dyes described in JP-A No. 62-293247 are particularly preferable. These dyes may be added to the photosensitive composition 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.
Whenver necessary, a plasticizer may be added to the uppermost layer of the recording layer of the planographic printing plate precursor of 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, diocetyl phthalate, tricresyl phosphate, tributyl phosphate, trioctyl phosphate, tetrahydrofurfuryl oleate, and acrylic acid and methacrylic acid.

[The manufacture of the planographic printing plate precursor]

(Coating solvents and coating methods)

The planographic printing plate precursor of the present invention can be formed in such a way that the above-mentioned constituent in the recording layer is dissolved in a solvent and the solution is applied on a suitable substrate. Moreover, a protective layer, a intermediate resin layer, a backcoating layer and the like, which are provided in the planographic printing plate precursor according to the purpose and will be described later, can also be formed similarly.

Examples of a solvent which can be used in the present invention include, though not limited thereto, ethylene dichloride, cyclohexanone, methyl ethyl ketone, methanol, ethanol, propanol, ethylene glycol monomethyl ether, 1-methoxy-2-propanol, 2-methoxyethyl acetate, 1-methoxy-2-propyl acetate, dimethoxyethane, methyl lactate, ethyl lactate, N,N-dimethylacetamide, N,N-dimethylformamide, tetramethyurea, N-methylpyrrolidone, dimethylsulfoxide, sulfolane, γ-butylrolactone and toluene. These solvents may be used either singly or in combination. The concentration of the above components (total solid content including the additives) in the solvent is preferably 1 to 50 mass%.

[The layer constitution of the recording layer]

The recording layer in the planographic printing plate precursor of the present invention can be used in any of a single layer structure, a phase separation structure, or a multilayer structure. Although the recording layer can use a single layer type recording layer, for example, in the photosensitive layers described in JP-A No. 7-285275 and International Publication No. 97/39894 pamphlet, as a phase separation type recording layer, for example, in the photosensitive layer described in JP-A No. 11-44956, or as a multilayer type recording layer, for example, in the photosensitive layers described in JP-A No. 11-218914, U.S. Patent Nos. 6352812B1, 6352811B1, 6358669B1 and 6534238B1, and European Patent Application No. 864420B1, but is not limited to them.

Moreover, in the case of a multilayer structure, the components (A) to (C), which are essential components in the present invention, may be contained in any layer without being limited to being in a lower layer or the top layer, but are preferably in the lower layers in view of their effect.

And, the coated amount of the recording layer (solid content) on the substrate obtained after coating and drying is different according to the use, but generally, the amount of film after drying (the total amount in the case of a multilayer structure) is preferably 0.5 to 5.0 g/m², and more preferably 0.6 to 2.0 g/m².

It is possible to employ various methods for applying a recording layer coat. For example, bar coater coating, spin coating, spray coating, curtain coating, dip coating, air-knife coating, blade coating, roll coating and the like can be cited. As the coating amount becomes small, apparent sensitivity becomes high, but filming characteristics lower.

Support

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

The support is preferably a polyester film or an aluminum plate, 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 very small amount of other elements. A plastic film on which aluminum is laminated or vapor-deposited may also be used.

Examples of other elements contained in the aluminum alloys include silicon, iron, manganese, copper, magnesium, chromium, zinc, bismuth, nickel, and titanium. The content by percentage of different elements in the alloy is at most 10% by mass. A particularly preferable aluminum plate in the present invention is a pure aluminum plate; however, since from the viewpoint of refining a completely pure aluminum cannot be easily produced, a very small amount of other
elements may also be contained in the plate.

0154 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 present 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.

0155 If necessary, prior to the surface-roughening treatment, the aluminum plate may optionally be subjected to degreasing treatment, in order to remove rolling oil or the like on the surface, with a surfactant, an organic solvent, an aqueous alkaline solution or the like.

0156 The surface-roughening treatment of the aluminum surface can be performed by various methods such as a mechanical surface-roughening method, a method of dissolving and roughening the surface electrochemically, and a method of dissolving the surface selectively in a chemical manner.

0157 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.

0158 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.

0159 The electrolyte used in the anodizing treatment of the aluminum plate is any one selected from various electrolytes which can form a porous oxide film. Among which in general use are electrolytes of sulfuric acid, phosphoric acid, oxalic acid, chromic acid, or a mixed acid thereof. The concentration of the electrolyte may be appropriately decided depending on the kind of electrolyte selected.

0160 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/dm², 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/m², 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.

0161 After the anodizing treatment, the surface of the aluminum is if necessary subjected to treatment for obtaining hydrophilicity. This securance of 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.

0162 In addition, the following methods may also be used: a method of treating the support with potassium fluoro-zirconate, 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)

0163 In the planographic printing plate precursor of the present invention, in which a recording layer is provided on the support, an undercoat layer may further be disposed, when required, between the support and the recording layer (lower layer). The provision of the undercoat layer offers the benefit that: the undercoat layer functions as a heat-insulating layer between the support and the lower layer so that the heat generated by the exposure of the infrared laser does not diffuse into the support, thus providing higher sensitivity due to the efficient use of the heat. Further, when this undercoat layer is provided in the recording layer according to the present invention, the recording layer is situated still at the exposure surface or near thereto and thus the sensitivity to the infrared laser can be favorably maintained.

0164 In the unexposed areas, it is assumed that, since the recording layer itself is impervious to the alkaline developer and functions as a protective layer for the undercoat layer, the stability of image development is improved while images of excellent discrimination are formed and the stability over time can be ensured.

0165 In the exposed areas, the components of the recording layer which have been released from the solubility suppressing effect are rapidly dissolved and dispersed in the developer. Further, the undercoat layer itself, which exists adjacent to the support, is an alkaline soluble polymer having favorable solubility in the developer, and thus is rapidly dissolved without generating a residual film even if a developer with lowered activity is used, contributing the improvement of the developability. That is, the undercoat layer is useful.

0166 As components of the undercoat layer, various organic compounds can be used. Examples thereof include carboxymethylcellulose, dextrin, gum arabic, phosphonic acids having an amino group, such as 2-aminoethylphosphonic acid, organic phosphonic acids which may have a substituent, such as phenyl phosphonic acid, naphthylphosphonic acid, alkylphosphonic acid, glycerophosphonic acid, methylenediphosphonic acid and ethylenediphosphonic acid, or-
organic phosphoric acids which may have a substituent, such as phenylphosphoric acid, naphthylphosphoric acid, alkyl-
phosphoric acid and glycerophosphoric acid, organic phosphinic acids which may have a substituent, such as phenyl-
phosphinic acid, naphthylphosphinic acid, alkylphosphinic acid and glycerophosphinic acid, amino acids such as glycine
and β-alanine, and hydrochlorides of amines having a hydroxyl group, such as a hydrochloride of triethanolamine. These
organic compounds may be used alone or in the form of a mixture of two or more thereof.

[0167] The appropriate coated amount of undercoat layer is from 2 to 200 mg/m², and preferably from 5 to 100 mg/m².
When the coating amount is less than 2 mg/m², sufficient printing endurance cannot be obtained. The same applies
when the coating amount is more than 200 mg/m².

[0168] In a planographic printing plate precursor of the present invention, an image is formed with heat. Concrete
methods for forming the image include direct image-like recording by a thermal recording head and the like, scanning
exposure by an infrared laser, high illumination flash exposure by a xenon discharge lamp and the like, and infrared
lamp exposure, but it is preferable to use exposure with solid high-energy infrared lasers such as a semiconductor laser,
YAG laser, or the like which emit infrared rays of 700 to 1200 nm wavelength.

[0169] The output power of a laser is preferably 100 mW or more, and it is preferable to use a multibeam laser device
to shorten the exposure time. Furthermore, the exposure time per pixel is preferably within 20 µs and energy radiated
onto a recording material is preferably 10 to 500 mJ/cm².

[0170] The developer which can be used for the planographic printing plate precursor of the invention is a developer
having a pH of 9.0 to 14.0, preferably 12.0 to 13.5. The developer, the category of which includes not only developer
but also replenisher hereinafter, may be an aqueous alkaline solution that has been known so far. Examples thereof
include aqueous solutions of inorganic alkali salts such as sodium silicate, potassium silicate, sodium triphosphate,
sodium carbonate, sodium borate, ammonium carbonate, sodium hydrogencarbonate, potassium hydrogencarbonate,
ammonium hydrogencarbonate, sodium borate, potassium borate, ammonium borate, sodium hydroxide, ammonium
hydroxide, potassium hydroxide and lithium hydroxide; and organic alkali agents such as monomethylamine,
dimethylamine, trimethylamine, mononethylamine, diethylamine, monoisopropylamine, diisopropylamine,
ethyleneimine, ethylenediamine, and pyridine. These aqueous alkaline solutions may be used alone or in combination
of two or more thereof.

[0171] Of the above-mentioned aqueous alkaline solutions, one preferable developer, which exhibits the effects of
the invention effectively, is an aqueous solution having a pH of 12 or more and comprising alkali silicate as a base or
alkali silicate obtained by mixing a base with a silicon compound. The aqueous solution is the so-called "silicate developer".
Another preferable developer is the so-called "non-silicate developer", which does not comprise any alkali silicate but
comprises a nonreducing sugar (organic compound having a buffering effect) and a base.

[0172] About the former, the developing power of aqueous solution of alkali metal silicate can be adjusted by adjusting
the ratio between silicon oxide SiO₂ and alkali metal oxide M₂O, which are components of the silicate, (generally, the
mole ratio of [SiO₂]/[M₂O]), and the concentration of the alkali metal silicate. For example, the following is preferably
used: an aqueous solution of sodium silicate wherein the mole ratio of SiO₂/Na₂O ([SiO₂]/[Na₂O]) is from 1.0 to 1.5 and
the content by percentage of SiO₂ is from 1 to 4% by mass, as disclosed in JP-A No. 54-62004; or an aqueous solution
of alkali metal silicate wherein the mole ratio of SiO₂/M₂O is from 0.5 to 0.75 (that is, the mole ratio of SiO₂/M₂O is from
1.0 to 1.5), the content by percentage of SiO₂ is from 1 to 4% by mass, and the content by percentage of potassium in
all alkali metals is 20% by gram atom, as disclosed in JP-B No. 57-7427.

[0173] The so-called "non-silicate developer", which does not comprise any alkali silicate but comprises a nonreducing
sugar and a base, is also preferable for being used to develop the first and second planographic printing plate precursors
of the invention. When this developer is used to develop any one of the planographic printing plate precursors, ink-
adsorbing power of the recording layer can be kept better without deteriorating the surface of the recording layer.

[0174] Further, although a planographic printing plate material generally has a narrow development latitude and ex-
periences a large change in scanning width and the like depending on the pH value of the developer, since a non-silicate
developer contains a non-reducing sugar having a buffering property to suppress the pH fluctuation, use of a non-silicate
developer is advantageous, as compared with using a developing liquid containing a silicate. Further, since a non-
reducing sugar is unlikely to contaminate a conductivity sensor, a pH sensor, or the like which control the liquid activity,
as compared with a silicate, a non-silicate developer is more advantageous than a silicate developer in this regard, as
well. Further, the discrimination-improving effect of a non-silicate developer is remarkable in the planographic printing
plate material of the present invention. It is assumed that such a good discrimination-improving effect is obtained because
contact with the developer (permeation), which is an important aspect in the present invention, is made moderate and
the difference between the exposed areas and the non-exposed areas can be expressed more easily.

[0175] The aforementioned non-reducing sugar belongs to sugars which do not have free aldehyde groups or ketone
groups and show a non-reducing property; these sugars are classified into trehalose-type oligo-saccharides in which
reducing groups are bonded to each other, glucoisides in which reducing group of sugars and non-sugar material are
bonded, and sugar alcohols formed by reducing sugars with hydrogenation, each of which can be used suitably in the
present invention. In the present invention, non-reducing sugars described in Japanese Patent Application Laid-Open No. 8-305039 can be used suitably.

[0176] Examples of the trehalose type oligosaccharides include saccharose and trehalose. Examples of the glucosides include alkylglycosides, phenolglycosides, and mustard seed oil glucoside. Examples of the sugar alcohols include D, L-arabitol, ribitol, xylitol, D, L-sorbitol, D, L-mannitol, D, L-iditol, D, L-talitol, dulcitol, and alloidulcitol. Furthermore, maltitol, obtained by hydrogenating maltose that is a disaccharide, and a reductant obtained by hydrogenating an oligosaccharide (i.e., reduced starch syrup) are preferable. Of these examples, sugar alcohol and saccharose are more preferable. D-sorbitol, saccharose, and reduced starch syrup are even more preferable since they have buffer effect within an appropriate pH range and are inexpensive.

[0177] These non-reducing sugars may be used alone or two or more may be used in combination. The content of the non-reducing sugar in the non-silicate developer is preferably from 0.1 to 30 mass% and, more preferably, from 1 to 20 mass%. When the content is less than 0.1 mass%, a sufficient buffering effect may not be obtained. When the content exceeds 30 mass%, making high concentrations may become difficult, resulting in higher cost of the materials.

[0178] The base combined with the nonreducing sugar(s) may be an alkali agent that has been known so far. Examples thereof include inorganic alkali agents such as sodium hydroxide, potassium hydroxide, lithium hydroxide, trisodium phosphate, tripotassium phosphate, trimmonium 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; and organic alkali agents such as monomethylamine, dimethylamine, trimethylamine, monoethyamine, diethyamine, triethylamine, monoisoamylamine, diisoamylamine, triisoamylamine, monoisopropanolamine, disopropanolamine, ethyleneimine, ethylenediamine, and pyridine.

[0179] The bases may be used each alone or two or more may be used in combination. Among the bases, sodium hydroxide or potassium hydroxide is preferred. In the present invention, instead of the combined use of the non-reducing sugar and the base, it is possible to use a non-silicate developer whose main component is an alkaline metal salt of a non-reducing sugar.

[0180] Further, an alkaline buffer solution comprising a weak acid and a strong base other than the non-reducing sugar can be used in combination as the non-silicate developer. As the weak acid, those having a dissociation constant (pKa) of 10.0 to 13.2 are preferred, and can be selected from among those described, for example, in "Ionization Constants of Organic Acids in Aqueous Solution" published by Pergamon Press, or the like.

[0181] For the purpose of promoting or suppressing image development, dispersing development scum, or improving the ink-affinity of the printing plate image area, various surfactants or organic solvents can be added to the developer and a replenisher as required. As the surfactant, anionic, cationic, nonionic, and amphoteric surfactants are preferred. Further, as the organic solvent, reducing agents such as hydroquinone, resorcin, and sodium salts or potassium salts of inorganic acids such as sulfuric acid or hydrogen sulfurous acid, and further, organic carboxylic acids, defoamers, softening agents for hard water, can be added to the developer and the replenisher.

[0182] The planographic printing plate developed using the developer and the replenisher described above is post-treated with washing water, a rinsing solution containing a surfactant or the like, and a desensitizing solution containing gum arabic or starch derivative. Various combinations of these can be used for the post-treatment.

[0183] In the case of carrying out development by using an automatic developing apparatus, it is known that a large quantity of PS plates can be treated without replacing the developer in a developer tank for a long duration by adding, to the developer, aqueous solution (a replenisher) with a higher alkalinity than that of the developer. In the invention, this replenishing method is preferably employed. To promote or suppress the developability of the developer or the replenisher and improve the dispersion of development scum and affinity of the image forming portion of the printing plate to ink, a variety of surfactants and organic solvents may optionally be added.

[0184] As preferable surfactants, anionic, cationic, nonionic and amphoteric surfactants can be exemplified. Further, to the developer or the replenisher, reducing agents of such as hydroquinone, resorcin, sodium salt or potassium salt of inorganic acids such as sulfuric acid, hydrogen sulfurous acid, and further organic carboxylic acid, defoaming agents, and water hardening or softening agents may be added.

[0185] The printing plate treated by using the developer or the replenisher is washed with water and post-treated with rinsing solutions containing the surfactants or the like, and desensitizing solutions containing gum arabic and starch derivatives. The post-treatment of the image recording material of the invention can be carried out by using these treatments in combinations.

[0186] Recently, for rationalization or standardization of the printing plate production work in printing plate-producing or printing industries, automatic developing apparatuses for printing plates have been used widely. An automatic developing apparatus generally comprise a development section and a post-treatment section. More specifically, an automatic developing apparatus includes a unit for transferring the printing plates, tanks for respective treatment solutions, and a spraying apparatus. The automatic developing apparatus transfers the exposed printing plates horizontally and at the same time carries out development treatment by spraying the respective treatment solutions pumped up by pumps,
to the printing plate, through spray nozzles. Recently, there is also known a method for carrying out treatment by transporting the printing plates by under-solution guide rolls while the printing plates are immersed in the treatment solution tanks filled with the treatment solutions. In such automatic treatment, the replenishers may be replenished to the respective treatment solutions depending on the treatment quantity, operation times, and the like. Alternatively, so-called disposable treatment method in which treatment is carried out using substantially unused treatment solutions can be employed.

[0187] In the planographic printing plate precursor of the present invention, the planographic printing plate precursor is imagewise exposed, developed, washed with water and/or rinsed and/or gum-coated to obtain a planographic printing plate. If unnecessary image portions (e.g. film edge trace of a master film) are present in the planographic printing plate, the unnecessary image portions are erased. Such erasing is preferably carried out by a method of applying an erasing solution as described in JP-B No. 2-13293 to the unnecessary image portions and washing with water after a prescribed duration. A method of radiating active light beam led through optical fibers to the unnecessary image portions and then carrying out development as described in JP-A No. 59-174842 may also be employed.

[0188] The planographic printing plate produced in such a manner is coated with a desensitizing gum if necessary and supplied to printing steps. In a case where a planographic printing plate with further improved printing durability is to be obtained, baking treatment is optionally carried out.

[0189] In the case where the baking treatment of the planographic printing plate is carried out, it is preferable to treat, prior to the baking treatment, the planographic printing plate with surface conditioning solutions described in JP-B Nos. 61-2518 and 55-28062 and JP-A Nos. 62-31859 and 61-159655.

[0190] Examples of a method for effecting such a pre-baking treatment include a method of applying the surface conditioning solutions to the planographic printing plate by sponge or degreased cotton doped with the solutions, a method of immersing the printing plate in a vat filled with the surface conditioning solutions, a method of applying the surface conditioning solutions using automatic coaters. In a case where after application the amount of solution applied is made uniform with a squeegee or a squeegee roller, a better result can be obtained.

[0191] In general, the amount of surface-adjusting solution applied is suitably from 0.03 to 0.8 g/m² (dry mass). If necessary the planographic printing plate onto which the surface-adjusting solution is applied can be dried, and then the plate is heated to a high temperature by means of a baking processor (for example, a baking processor (BP-1300) sold by Fuji Photo Film Co., Ltd.) or the like. In this case, the heating temperature and the heating time, which depend on the kind of components forming the image, are preferably from 180 to 300°C and from 1 to 20 minutes, respectively.

[0192] If necessary, a planographic printing plate subjected to a baking treatment can be subjected to treatments which have been conventionally conducted, such as a water-washing treatment and gum coating. However, in a case where a surface-adjusting solution containing a water soluble polymer compound or the like is used, the so-called desensitizing treatment (for example, gum coating) can be omitted.

[0193] The planographic printing plate precursor of the present invention is processed into a planographic printing plate. This planographic printing plate is then placed on an offset printing machine and the like, and used for printing large quantities of sheets. The planographic printing plate precursor of the present invention has the advantages of excellent chemical resistance and printing endurance in the image area, wide image development latitude, and excellent image reproducibility.

EXAMPLES

[0194] The present invention will be explained in conjunction with examples, but the invention is not restricted to such examples.

(Synthesis example 1)

<Synthesis example 1: Synthesis of (A) polymer 1 having a urea bond in a side chain>
- Synthesis of a high molecular compound containing a polymerizable monomer -

[0195] After 15.5 g of methacryloyloxethyl isocyanate and 15.0 g of 4-aminobenzoic acid were added and dissolved in 150 g of dioxane solvent, the solution was stirred for 2 hours to give 28.0 g of 2-(N’-(4-carboxyphenyl) ureido) ethyl methacrylate having the following constituent units.
The obtained 2-(N'-(4-carboxyphenyl) ureido) ethyl methacrylate and N-phenyl maleimide (a compound having one or more polymerizable unsaturated linkages and containing no urea bond) were polymerized in the weight ratio (2-(N'-(4-carboxyphenyl) ureido) ethyl methacrylate/N-phenyl maleimide) of 75/25 to give 20 g of (A) polymer 1 having a urea bond in a side chain (weight-average molecular weight (Mw) = 15,000).

Polymer 2 was synthesized in the same way as the synthesis of the high molecular compound containing a polymerizable monomer in Synthesis example 1, except for the use of 15.5 g of methacryloyloxyethyl isocyanate, 12.0 g of 4-aminophenol, and 140 g of dioxane solvent, such that 25.0 g of 2-(N'-(4-hydroxyphenyl)ureido) ethyl methacrylate having the following constituent unit was obtained.

Next, a high molecular compound containing a polymerizable monomer was synthesized in the same way as in the synthesis of the resin 1 soluble in an aqueous alkaline solution in Synthesis example 1, except for the use of 2-(N'-(4-hydroxyphenyl)ureido) ethyl methacrylate, such that 20 g of (A) polymer 2 having a urea bond in a side chain (weight-average molecular weight (Mw) = 16,000) was obtained.

Polymer 3 was synthesized in the same way as the synthesis of the (A) polymer 1 having a urea bond in a side chain in Synthesis example 1, except for the use of N-phenyl maleimide and methacrylamide as compounds having no urea bond and performing the polymerization in the weight ratio (2-(N'-(4-carboxyphenyl)ureido) ethyl methacrylate/N-phenyl maleimide/methacrylamide) of 75/13/12, such that 20 g of (A) polymer 3 having a urea bond in a side chain (weight-average molecular weight (Mw) = 34,000) was obtained.

Polymer 4 was synthesized in the same way as the synthesis of the (A) polymer 2 having a urea bond in a side chain in Synthesis example 2, except for the use of methacrylate and methacrylamide as compounds having no urea bond and performing the polymerization in the weight ratio (2-(N'-(4-carboxyphenyl)ureido) ethyl methacrylate/methyl methacrylate/methacrylamide) of 72/14/14, such that 20 g of (A) polymer 4 having a urea bond in a side chain (weight-average molecular weight (Mw) = 68,000) was obtained.

Polymer 5 was synthesized in the same way as the synthesis of the (A) polymer 2 having a urea bond in a side chain in Synthesis example 2, except for the use of acrylonitrile and methacrylamide as compounds having no urea bond and performing the polymerization in the weight ratio (2-(N'-(4-carboxyphenyl)ureido) ethyl methacrylate/acrylonitrile/methacrylamide) of 65/20/15, such that 20 g of (A) polymer 5 having a urea bond in a side chain (weight-average molecular weight (Mw) = 45,000) was obtained.
<Synthesis example 6: Synthesis of (A) polymer 6 having a urea bond in a side chain>

[0202] After 11.9 g of phenyl isocyanate and 12.0 g of 4-aminophenol were added and dissolved in 120 g of dioxane solvent, the solution was stirred for 2 hours to give 22.0 g of 4-(N'-phenyl ureido) phenol.

[0203] After 18.3 g of the obtained 4-(N'-phenyl ureido) phenol and 2.40 g of paraformaldehyde were dissolved in 100 g of oxalic acid and the solution was stirred, the solution was heated to 100°C and 20 g of polymer 6 represented by the following structural formula and having a urea bond in a side chain (A) (weight-average molecular weight (Mw) = 2,000) was obtained.

[0204] In the above-mentioned structural formula, n is 1 to 15, and the Ph within the parenthesis is a benzene ring.

[Examples 1 to 12, Comparative examples 1 to 6]

[The manufacture of a substrate]

[0205] An aluminum plate (material quality: JIS A 1050) of 0.3 mm thickness was etched using a liquid with a caustic soda concentration of 30 g/l and an aluminum ion concentration of 10 g/l at 60°C for 10 seconds, washed with flowing water, and then neutralized with nitric acid of 10 g/l. After that, the plate was rinsed in water. Electrochemical surface roughening of the plate was carried out with an electrical charge of 400C/dm² using an alternating sinusoidal waveform under the condition of applied voltage = 20 V in an aqueous solution of hydrogen chloride concentration of 15 g/l and an aluminum ion concentration of 10 g/l and being kept at 30°C, and then the plate was rinsed in water. Next, the plate was etched using a liquid with a caustic soda concentration of 30 g/l and an aluminum ion concentration of 10 g/l at 40°C for 10 seconds, and washed with flowing water. Then, the plate was subjected to desmutting treatment in sulfuric acid solution of 15 mass % concentration at a temperature of 30°C, and was rinsed in water. Furthermore, the plate was anodized in sulfuric acid aqueous solution of 10 mass % concentration at the temperature of 20°C under the condition of a direct current density of 6A/dm² so that the amount of anodic oxide film was 2.5 g/m², and then rinsed in water and dried. After that, the plate was treated with a sodium silicate aqueous solution of 1.0 mass % concentration at 30°C for 10 seconds to manufacture a hydrophilic substrate (a).

[0206] The average center line roughness of this substrate (a), (Ra), was measured using a needle of 2 μm diameter, and the result was 0.43 μm.

[The formation of a primer layer]

[0207] The substrate (a) thus obtained was coated with the following primer coat liquid and then dried at 80°C for 30 seconds to prepare a primer layer. The dried coated amount of the primer layer was 17 mg/m².

(The composition of the prime coat liquid)

[0208]

- The following compound 0.3 g
- Methanol 100 g
- Water 1 g
[The formation of a recording layer]

The substrate having the primer layer obtained in the above-mentioned manner was coated with a coating liquid for a positive recording layer and dried at 150°C for 1 minute in an oven to give a positive photosensitive planographic printing plate having a positive recording layer of 1.5 g/m² in dried coating amount.

[A coating liquid for a positive recording layer 1]

[0210] - Novolac resin A
  (m/p-cresol (6/4), weight-average molecular weight; 7,000, unreacted cresol; 0.5 mass %) 0.15 g
  - (A) The specific polymer
    (a compound described in the following Table 1) 0.7 g
  - (B) Cyanine dye A (the following structure) 0.07 g
  - (C) The specific amino compound
    (a compound described in the following Table 1) 0.05 g
  - Tetrahydro phthalic anhydride 0.04 g
  - Ethyl violet 0.02 g
  - A fluorinated polymer
    (trade name: Defenser F-780 F (solid content; 30%), manufactured by Dainippon Ink And Chemicals, Inc.) 0.015 g
  - Methyl ethyl ketone 12 g

[Cyanine dye A]

[0211] Further, the structure of polymers 1 to 6 having a urea bond in a side chain in the present invention, which are described in the following Table 1, was described in the above-mentioned synthesis examples, and (C) a specific amino compound is indicated by the exemplary compounds prefixed with "C" described above.

[Evaluation of printing durability and chemical resistance]

[0212] A test pattern was drawn as an image on the obtained photosensitive planographic printing plate precursor using a Trendsetter manufactured by Creo Co., Ltd. at a beam intensity of 9 W and a drum rotation speed of 150 rpm. [0213] After that, the planographic printing plate precursor was developed using a PS processor 900H (trade name, manufactured by Fuji Photo Film Co., Ltd.), into which an alkaline developer having the following composition had been fed, while the temperature of the developer was kept at 30°C with a developing time of 20 seconds. The image in the
obtained planographic printing plate was printed using a Lithron printing machine manufactured by Komori Corporation using DIC-GEOS (N) (trade name) black ink manufactured by Dainippon Ink And Chemicals, Inc., and the printing durability was evaluated by the number of printed sheets until the point in time when it was visually recognized that the density of the solid image began to become low. The result was shown in the following Table 2.

Moreover, a process was added of wiping the printing plate surface with a cleaner (a multicleaner manufactured by Fuji Photo Film Co., Ltd.) every time 5,000 sheets are printed, and the printing durability was evaluated in the same way as that mentioned above. The former printing durability is referred to as "usual printing durability" and the latter printing durability is referred to as "cleaner printing durability", and their results are shown in Table 2. It is evaluated that the higher the cleaner printing durability is, the better the chemical resistance is.

<Alkaline developer composition>

- SiO$_2$ K$_2$O (K$_2$O/SiO$_2$ = 1/1 (mol ratio)) 4.0 mass %
- Citric acid 0.5 mass %
- Polyethylene glycol lauryl ether (weight-average molecular weight: 1,000) 0.5 mass %
- Water 95.0 mass %

[Evaluation of development latitude]

Exposure and development were performed on the obtained photosensitive planographic printing plate precursor in the same method as the above-mentioned evaluation method for printing durability and chemical resistance. After that, while the conductivity of the developer was raised by a constant value by suitably adding a potassium hydroxide aqueous solution of 3 mass % to the developer, development operations were carried out using the developer of each conductivity value. Moreover, while the conductivity of the developer was lowered by a constant value by blowing carbon dioxide gas into the alkaline developer and several developers having low conductivity (that is, developers with low activity) were prepared, development operations were carried out using the developer of each conductivity value.

In these development operations, among those developers with which good development could be achieved, that is, the image portions were not eluted out and there were no stains and coloring caused by the film remaining in the photosensitive layer due to bad development on the non-image portions, the difference between the highest conductivity and the lowest conductivity was made the index of development latitude. It was evaluated that the larger the difference was, the better the development latitude was. The results are shown in the following Table 1.

<table>
<thead>
<tr>
<th>Example</th>
<th>(A) The specific polymer</th>
<th>(C) The specific amino compound</th>
<th>Usual printing durability (Ten thousand sheets)</th>
<th>Cleaner printing durability (Ten thousand sheets)</th>
<th>Development latitude (ms/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polymer 1</td>
<td>C-1</td>
<td>11</td>
<td>10</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>Polymer 2</td>
<td>C-1</td>
<td>12</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
<td>Polymer 3</td>
<td>C-1</td>
<td>10</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>Polymer 4</td>
<td>C-1</td>
<td>11</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>5</td>
<td>Polymer 5</td>
<td>C-1</td>
<td>12</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>6</td>
<td>Polymer 6</td>
<td>C-1</td>
<td>11</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>Polymer 1</td>
<td>C-2</td>
<td>10</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>8</td>
<td>Polymer 3</td>
<td>C-2</td>
<td>11</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>9</td>
<td>Polymer 3</td>
<td>C-5</td>
<td>10</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>10</td>
<td>Polymer 4</td>
<td>C-11</td>
<td>12</td>
<td>11</td>
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<td>Polymer 5</td>
<td>C-12</td>
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<tr>
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<td>Polymer 6</td>
<td>C-16</td>
<td>10</td>
<td>9</td>
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</table>
As clearly shown in Table 1, it was obvious that the planographic printing plate precursors of the present invention in Examples 1 to 12 were especially excellent in cleaner printing durability, that is, chemical resistance. On the other hand, it was known that Comparative examples 1 to 6 that did not contain the specific amino compound, which is an additive in the present invention, were inferior in chemical resistance even if the specific polymer was used.

Moreover, it was found that the planographic printing plate precursors in Examples 1 to 12 were good also in usual printing durability and development latitude compared with Comparative Examples 1 to 6.

**Claims**

1. A planographic printing plate precursor comprising a substrate and a positive recording layer prepared on the substrate, the planographic printing plate precursor is characterized in that the recording layer comprises (A) a polymer having a urea bond in the side chain, (B) a photothermal conversion agent, and (C) an amino compound having a methylol group or an alkoxymethyl group, and the solubility thereof in an alkaline developer is improved by light-exposure or heating.

2. The planographic printing plate precursor according to claim 1, wherein the polymer (A) is a vinyl-polymerized or condensation-polymerized high molecular polymer having a constituent unit shown by any of the following formulas of (1-a) to (1-c):

   ![Formula (1-a)](image)

   ![Formula (1-b)](image)
wherein in the formulas of (1-a) to (1-c), R¹ and R² indicate independently a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a carboxyl group, or their salts, respectively, R³ indicates a hydrogen atom, a halogen atom, an alkyl group, or an aryl group, X indicates a bivalent linkage group, for example, an alkylene group, a phenylene group or the like that may have a substituent, and Y indicates a bivalent aromatic group that may have a substituent, for example, a phenylene group, a naphthylene group or the like that may have a substituent.

3. The planographic printing plate precursor according to claim 2, wherein the content of the constituent unit shown by any of the formulas of (1-a) to (1-c) in the polymer (A) is 10 to 80 mol % in feed ratio.

4. The planographic printing plate precursor according to claim 1, wherein the polymer (A) is a novolac resin having a urea bond in a side chain.

5. The planographic printing plate precursor according to any of claims 1 to 4, wherein the polymer (A) has a functional group that will contribute to solubility to aqueous alkaline solution, in addition to a urea bond, in a side chain.

6. The planographic printing plate precursor according to claim 1, wherein the amino compound (C) has at least 2 substituents selected from the group consisting of methylol groups and alkoxyethyl groups.

7. The planographic printing plate precursor according to claim 1, wherein the amino compound (C) comprises the structure shown by the following formula (I):

\[
\begin{align*}
\text{Formula (I)}
\end{align*}
\]

wherein in the formula (I), T¹ and T² indicate independently a hydrogen atom, an alkyl group, an alkenyl group, an acyl group, and an acetyl group.

8. The planographic printing plate precursor according to claim 7, wherein T¹ and T² in formula (I) are alkyl groups having 1 to 8 carbon atoms.

9. The planographic printing plate precursor according to claim 7, wherein T¹ and T² in formula (I) are alkenyl groups having 2 to 18 carbon atoms.

10. The planographic printing plate precursor according to claim 7, wherein T¹ and T² in formula (I) are acyl groups having 2 to 18 carbon atoms.

11. The planographic printing plate precursor according to claim 7, wherein the amino compound (C) is an amino compound represented by the following formula (II):
wherein in formula (II), R\textsuperscript{1} to R\textsuperscript{6} indicate independently a hydrogen atom, an alkyl group, an alkenyl group, an acyl group, and acetyl group.
## DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category</th>
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<th>Relevant to claim</th>
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<tr>
<td>X</td>
<td>US 2002/086233 A1 (FUJI PHOTO FILM CO LTD) 4 July 2002 (2002-07-04) * claim 3 * * claim 5 * * paragraph [0109] * * paragraph [0215] * * sentence 3, paragraph 227 - sentence 9 * * paragraph [0108]; compound 9 *</td>
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<td>US 2003/162126 A1 (KODAK POLYCHROME GRAPHICS, LLC) 28 August 2003 (2003-08-28) * claim 1 * * paragraph [0027] * * paragraph [0031] * * paragraph [0056] * * sentence 1, paragraph 44 - sentence 3 * * sentence 7, paragraph 116 *</td>
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The present search report has been drawn up for all claims.

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<td>2 June 2006</td>
<td>Dardel, B</td>
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### CATEGORY OF CITED DOCUMENTS

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**02-06-2006**

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