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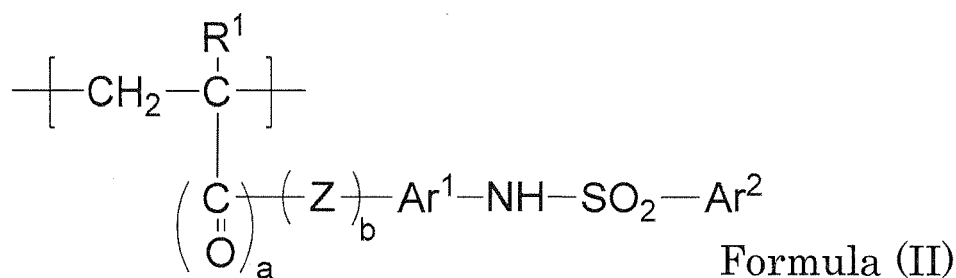
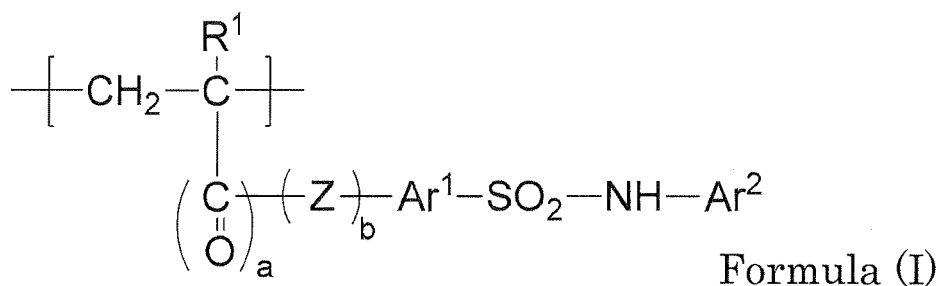
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(84) Designated Contracting States: AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR Designated Extension States: BA ME (30) Priority: 23.03.2012 JP 2012068241 (71) Applicant: Fujifilm Corporation Minato-ku Tokyo (JP)	(72) Inventors: • Yasuhara, Yuichi Shizuoka-ken (JP) • Taguchi, Yoshinori Shizuoka-ken (JP) (74) Representative: HOFFMANN EITLE Patent- und Rechtsanwälte Arabellastrasse 4 81925 München (DE)
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(54) **Method of producing planographic printing plate and planographic printing plate**

(57) A planographic printing plate precursor includes a substrate having a hydrophilic surface; and two or more recording layers provided on the substrate and each independently containing an alkali-soluble resin, in which at least one of the two or more recording layers is a positive-working recording layer including an infrared absorbing agent, and in which, of the two or more recording layers, a recording layer provided in closest proximity to the substrate includes a resin (A) having an onium salt structure and a (meth)acrylic resin (B) having at least one repeating unit selected from a structural unit represented by the following Formula (I) or a structural unit represented by the following Formula (II):



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wherein, R^1 represents a hydrogen atom or an alkyl group; Z represents -O- or -N(R^2)- wherein R^2 represents a hydrogen atom, an alkyl group, or the like; Ar^1 and Ar^2 each independently represent an aromatic group, and at least one of Ar^1 or Ar^2 is a heteroaromatic group; and a and b each independently represent 0 or 1.

Description**BACKGROUND OF THE INVENTION**

Field of the Invention

[0001] The invention relates to a planographic printing plate precursor and a method of producing a planographic printing plate using the planographic printing plate precursor. More specifically, the invention relates to an infrared laser-sensitive positive-working planographic printing plate precursor for so-called direct platemaking, in which platemaking can be carried out directly from a digital signal sent from a computer or the like, and to a method for producing a planographic printing plate using the plate precursor.

Description of the Related Art

[0002] The development of lasers in recent years has been remarkable and, in particular, with regard to solid-state lasers or semiconductor lasers capable of emitting light in the range from near-infrared to infrared, compact devices having high output are readily available. Conventionally, a variety of photosensitive compositions have been used as visible image forming materials or materials forming a recording layer of a planographic printing plate precursor. These lasers are very useful as exposure light sources when carrying out direct forming of an image on the photosensitive compositions based on a digital data signal sent from a computer or the like.

[0003] A positive-working planographic printing plate precursor for an infrared laser contains as essential components an alkali-soluble binder resin, an infrared absorbing agent (IR dye) that absorbs infrared light and generates heat, or the like. In unexposed areas (image areas) the IR dye or the like functions as a dissolution inhibitor that substantially decreases the solubility of a binder resin with respect to a developer by interacting with the binder resin. Meanwhile, in exposed areas (non-image areas), heat generated therein weakens the interaction between the IR dye or the like and the binder resin, whereby the exposed region dissolves in an alkaline developer to form a planographic printing plate.

[0004] In such an infrared laser-sensitive positive-working planographic printing plate precursor, a difference (hereinafter may be referred to as "dissolution discrimination") between the dissolution resistance of unexposed areas (image areas) in a developer and the solubility of exposed areas (non-image areas) under various conditions of use is required to be large. In order to improve the difference between the dissolution resistance and the solubility, addition of various kinds of dissolution inhibitors has been studied. Among these, it is known that onium salt-based dissolution inhibitors have a very strong dissolution inhibiting ability.

[0005] When a conventional onium salt compound is used as a dissolution inhibitor, the effect of improving the dissolution resistance of unexposed areas can be obtained since this compound has a favorable dissolution inhibiting ability. However, when an exposed plate precursor is not developed immediately after exposure but is developed after a certain period of time, deterioration in developability can be caused by the reformation of undesired interactions in the unexposed areas. Therefore, there has been a problem that an increased degree of change in developability due to the elapse of time after exposure reduces productivity due, for example, to difficulties in adjusting development conditions. Therefore, a planographic printing plate precursor in which deterioration in developability over a predetermined period of time after exposure is suppressed (in other words, a planographic printing plate precursor having "excellent post-exposure stability") has been demanded.

[0006] To overcome these problems, there is disclosed a novel photosensitive material in which a specific onium salt is used as a dissolution inhibitor. For example, a technique has been proposed that achieves both favorable dissolution inhibiting ability with respect to imaged areas and excellent post-exposure stability by the addition of a quaternary ammonium salt having a specific structure to an image-forming layer (see Japanese Patent Nos. 3, 917, 422 and 4, 043, 898).

SUMMARY OF THE INVENTION

[0007] However, in the photosensitive material using the onium salt-based dissolution inhibitor, while the post-exposure stability is improved to some extent, the improvement of the post-exposure stability cannot be said sufficient to form a sharp and favorable image regardless of change in developer activity. In addition, further improvement in dissolution discrimination has also been required.

The invention has been made in consideration of the above problems and provides a planographic printing plate precursor having a sufficient difference (dissolution discrimination) between the dissolution resistance of unexposed areas (image areas) in a developer and the solubility of exposed areas (non-image areas), in which deterioration in developability is suppressed when it is not developed immediately after exposure but is developed after a certain period of time.

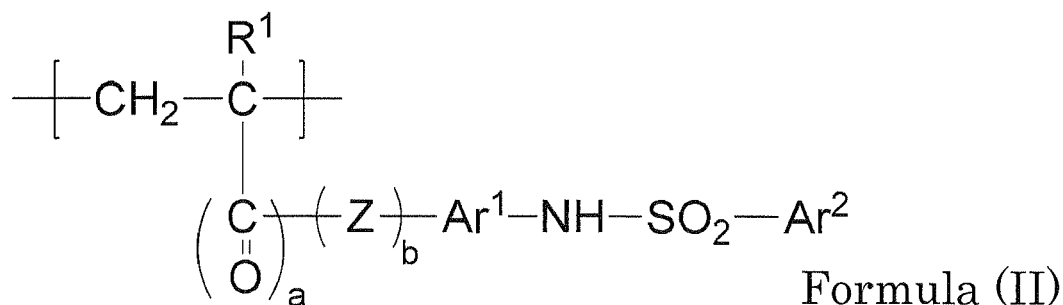
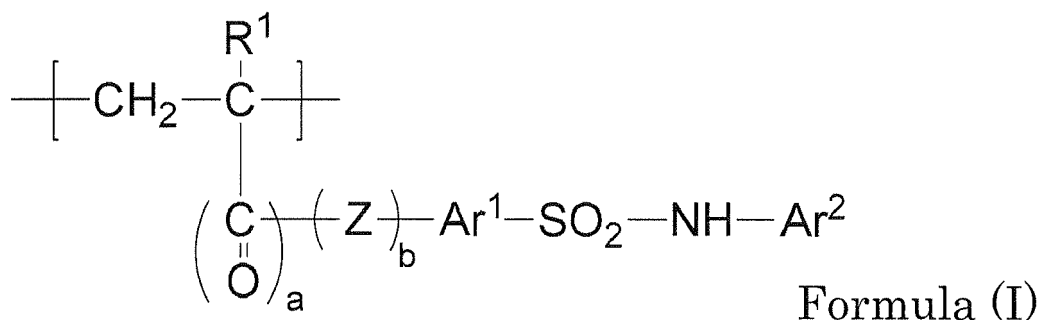
The invention also provides a method for producing a planographic printing plate precursor, by which a high quality

planographic printing plate in which deterioration in developability of exposed areas is suppressed can be produced even when the exposed planographic printing plate precursor is not developed immediately after exposure but is developed after a certain period of time (i.e., developed after so-called "post-exposure storage").

[0008] After the intensive and extensive studies, the inventors have found that the above-mentioned problems can be solved by using, in positive-working recording layers having a layered structure, two specific resins in combination in a recording layer provided in closest proximity to a substrate, and have achieved the invention.

According to a first aspect of the invention, there is provided a planographic printing plate precursor including a substrate having a hydrophilic surface; and two or more recording layers provided on the substrate and each containing an alkali-soluble resin, in which at least one of the two or more recording layers is a positive-working recording layer containing an infrared absorbing agent, and in which, of the two or more recording layers, a recording layer provided in closest proximity to the substrate includes a resin (A) having an onium salt structure and a (meth)acrylic resin (B) having at least one repeating unit selected from a structural unit represented by the following Formula (I) or a structural unit represented by the following Formula (II).

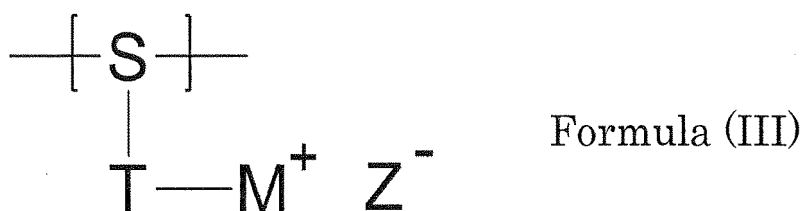
[0009]



[0010] In Formulae (I) and (II), R¹ represents a hydrogen atom or an alkyl group; Z represents -O- or -N(R²)- wherein R² represents a hydrogen atom, an alkyl group, an alkenyl group, or an alkynyl group; Ar¹ and Ar² each independently represent an aromatic group, and at least one of Ar¹ or Ar² is a heteroaromatic group; and a and b each independently represent 0 or 1.

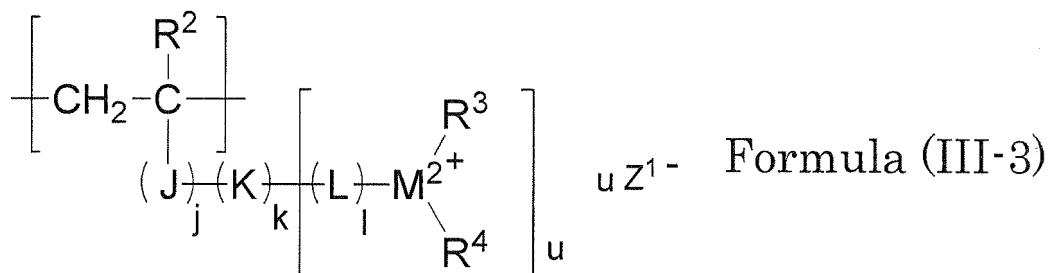
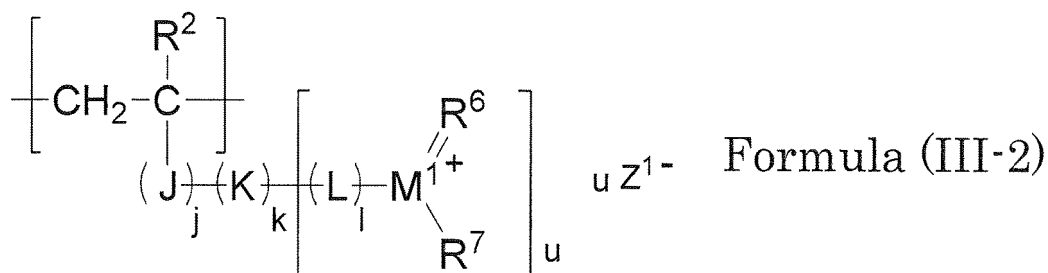
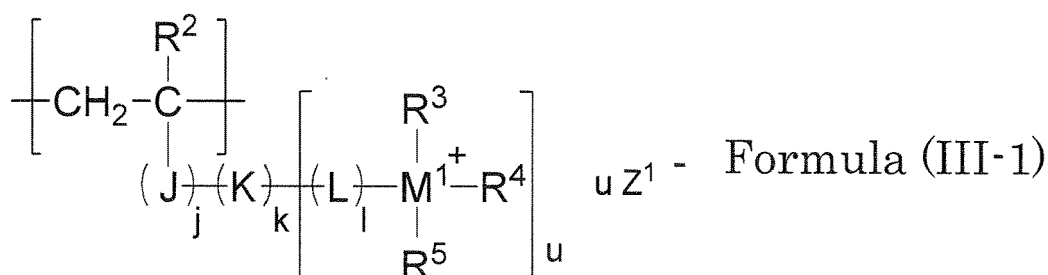
The resin (A) having an onium salt structure is preferably a resin including a repeating unit represented by the following Formula (III). More specifically, the resin (A) having an onium salt structure is preferably a resin including at least one of a repeating unit represented by the following Formula (III-1), (III-2), or (III-3).

[0011]



[0012] In Formula (III), S represents a linking group forming the polymer main chain; T represents a single bond linking S and M or a di- or higher-valent linking group; M represents a substituent including an onium structure; Z represents a substituent including an anion structure; and M⁺ and Z⁻ together form an onium salt structure.

[0013]



[0014] In Formula (III-1), R² represents a hydrogen atom, an alkyl group, or a halogen atom; J represents a divalent linking group; K represents an aromatic group; L represents a divalent linking group; M¹ represents an atom belonging to group 15 of the periodic table; Z¹⁻ represents a counter anion; R³, R⁴, and R⁵ each independently represent a hydrogen atom, an alkyl group, an aromatic group, or an aralkyl group, R³ and R⁴ may be linked to each other to form a ring, and R⁴ and R⁵ may be linked to each other to form a ring; j, k, and l each independently represent 0 or 1 provided that j and k are not 0 at the same time; and u represents an integer of 1 to 3.

In Formula (III-2), R², J, K, L, M¹, Z¹⁻, j, k, l, and u have the same definitions as R², J, K, L, M¹, Z¹⁻, j, k, l, and u in Formula (III-1), respectively; R⁶ represents an alkylidyne group; and R⁷ represents a hydrogen atom, an alkyl group, an aromatic group, or an aralkyl group. R⁶ and R⁷ may be linked to each other to form a ring.

In Formula (III-3), R², J, K, L, Z¹⁻, j, k, l, and u have the same definitions as R², J, K, L, Z¹⁻, j, k, l, and u in Formula (III-1), respectively; and R³ and R⁴ each independently represent a hydrogen atom, an alkyl group, an aromatic group, or an aralkyl group. R³ and R⁴ may be linked to each other to form a ring. M² represents a sulfur atom.

[0015] In the recording layer provided in closest proximity to the substrate, a content ratio (A:B) of the resin (A) having an onium salt structure and the (meth)acrylic resin (B) having at least one repeating unit selected from the structural unit represented by Formula (I) or the structural unit represented by Formula (II) in terms of mass is preferably from 1.0:0.1 to 1.0:8.0.

[0016] According to another aspect of the present invention, there is provided a method for producing a planographic printing plate, the method including in this order: image-wise exposing the planographic printing plate precursor according to the invention; storing the planographic printing plate precursor after the exposure; and developing the planographic printing plate precursor after the storage, using an aqueous alkaline solution.

DETAILED DESCRIPTION OF THE INVENTION

[0017] Hereinbelow, the invention is described in detail.

Although the explanation of the constituent features described hereinbelow are made based on representative embodiments of the invention, the invention is not limited unless departing from the scope of the invention.

In this specification, the notation "A to B" expressing numerical range represents a range including the numerical values A and B, as the minimum value and the maximum value, respectively.

With regard to the amount of a component of a composition, when plural substances corresponding to the same component exist in the composition, the amount of the component refers to a total amount of the plural substances in the composition unless otherwise specified.

[0018] With regard to the notation of a group (including an atomic group), the notation without "substituted" or "unsubstituted" includes both a group with a substituent and a group without a substituent. For example, an "alkyl group" includes not only an alkyl group having no substituent (unsubstituted alkyl group) but also an alkyl group having a substituent (substituted alkyl group).

As used herein, the term "process" indicates not only a separate process but also a process that is not clearly distinguished from other process as long as the desired effect of the process is obtained therefrom.

[0019] As used herein, the term "(meth)acrylic acid" indicates both or any one of acrylic acid and methacrylic acid, and the term "(meth)acrylate" indicates both or any one of acrylate and methacrylate.

As used herein, unless otherwise specified, the term "content" refers to a content in terms of mass, the term "% by mass" refers to the proportion of each component with respect to a total mass of a composition, and the term "solid content" refers to a total amount of the ingredients included in a composition other than solvent(s).

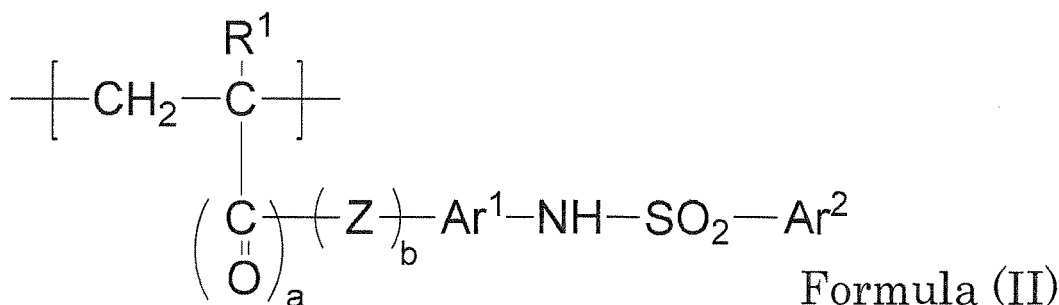
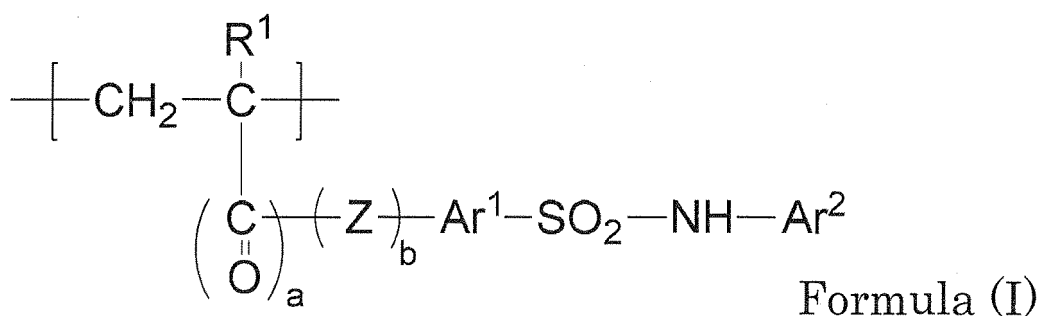
[0020] Hereinafter, in the specification, the "recording layer provided in closest proximity to the substrate" may be also referred to as a "lower layer" or a "lower recording layer".

[0021] On the hydrophilic surface of the substrate having the hydrophilic surface of the planographic printing plate precursor of the invention, another layer such as a surface protective layer or an undercoat layer may be provided if necessary in addition to the two or more recording layers, as long as the effects of the invention are not impaired. On a surface of the substrate opposed to the surface where there is the two or more recording layers, a backcoat layer or the like may be provided if necessary.

Planographic printing plate precursor

[0022] The planographic printing plate precursor according to the invention includes a substrate having a hydrophilic surface; and two or more recording layers provided on the substrate and each containing an alkali-soluble resin, in which at least one of the two or more recording layers is a positive-working recording layer containing an infrared absorbing agent, and, of the two or more recording layers, a recording layer provided in closest proximity to the substrate includes a resin (A) having an onium salt structure (hereinafter may be referred to as an "onium-containing resin") and a (meth) acrylic resin (B) (hereinafter may be referred to as a "specific acrylic resin") having at least one repeating unit selected from a structural unit represented by the following Formula (I) or a structural unit represented by the following Formula (II).

[0023]



[0024] In Formulae (I) and (II), R^1 represents a hydrogen atom or an alkyl group; Z represents -O- or -N(R^2)- wherein R^2 represents a hydrogen atom, an alkyl group, an alkenyl group, or an alkynyl group; Ar^1 and Ar^2 each independently represent an aromatic group, at least one of Ar^1 or Ar^2 is a heteroaromatic group; and a and b each independently represent 0 or 1.

In Formulae (I) and (II), each group represented by R^1 , R^2 , Ar^1 , or Ar^2 may further have a substituent.

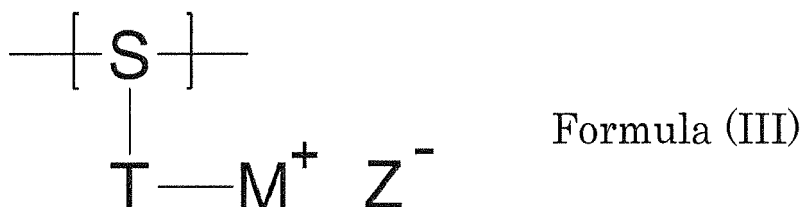
[0025] Although the specifics of the mechanism of the invention are uncertain, the mechanism is thought to be as follows. A sulfonamide portion having a specific structure in the specific acrylic resin (B) exhibits a strong static interaction with a cationic center portion of the resin (A) having an onium salt structure, whereby these resins form a pseudo-crosslinking structure therebetween. The pseudo-crosslinking structure imparts a strong dissolution inhibiting effect (inhibition) with respect to a developer, thereby improving the development resistance of unexposed areas and the strength of obtained image areas. On the other hand, in an area subjected to heat-mode exposure, due to three-dimensional bulkiness around the cationic center portion of the resin (A), it becomes difficult for an interaction (inhibition) between the resins that has been cancelled to be formed again, thus inhibiting the reformation of the undesired interaction. Therefore, both dissolution resistance of image areas (unexposed areas) and excellent solubility of non-image areas (exposed areas) in the developer are achieved, so that high dissolution discrimination is obtained, and post-exposure stability is improved.

In summary, the planographic printing plate precursor according to the invention shows excellent dissolution discrimination, has good image formability regardless of the physical properties of developer, is excellent in terms of both the strength of image areas and the developability of non-image areas, and has excellent post-exposure stability. Accordingly, the planographic printing plate precursor of the invention is suitably applicable not only to conventional platemaking methods but also to a method for producing a planographic printing plate in which the exposed planographic printing plate precursor is stored for a certain period of time before a development treatment.

Resin (A) having onium salt structure (Onium-containing resin)

[0026] The onium-containing resin that can be used in the invention is not specifically limited as long as it is a resin including at least one onium salt structure in the molecule thereof. From the viewpoint of advantageous effect, the onium-containing resin (A) is preferably a polymer including a repeating unit having an onium salt structure. Preferable examples of such polymer include a resin including a repeating unit represented by the following Formula (III).

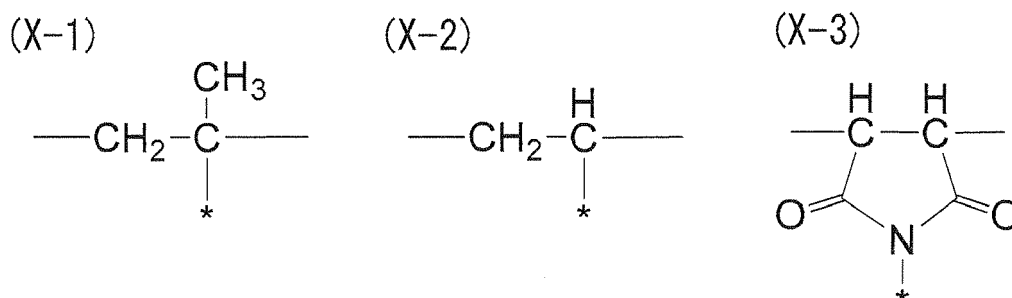
[0027]



[0028] In Formula (III), S represents a linking group forming the polymer main chain; T represents a single bond linking S and M, or a di- or higher-valent linking group; M represents a substituent including a cationic structure; Z represents a substituent including an anionic structure; and M^+ and Z^- together form an onium salt structure.

S represents a linking group forming the main chain, and examples thereof include structures represented by the following Formulae (X-1) to (X-3). In Formulae (X-1) to (X-3), the symbol "*" represents a position at which S is linked with T.

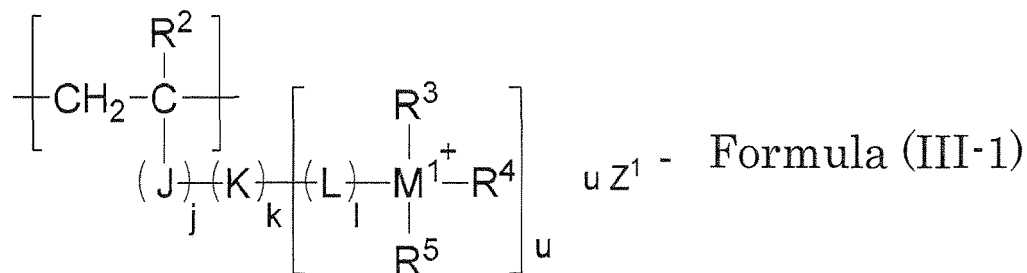
[0029]



[0030] Specific examples of the repeating unit having an onium salt structure include repeating units represented by

the following Formulae (III-1) to (III-3).

[0031]



[0032] In Formula (III-1), R² represents a hydrogen atom, an alkyl group, or a halogen atom, in which an hydrogen atom, a methyl group, or an ethyl group is preferable, and a hydrogen atom or a methyl group is more preferable.

J represents a divalent linking group. The divalent linking group is preferably -COO- or -CONH-.

K represents an aromatic group and is preferably a phenylene group. The phenylene group may have an optional substituent. Examples of the optional substituent that can be introduced in the phenylene group include a hydroxy group, a halogen atom, and an alkyl group.

L represents a divalent linking group, and examples thereof include an alkylene group having 1 to 12 carbon atoms, or a divalent linking group consisting of a combination of two or more of an alkylene group having 1 to 12 carbon atoms, -O-, -S-, and -NH-.

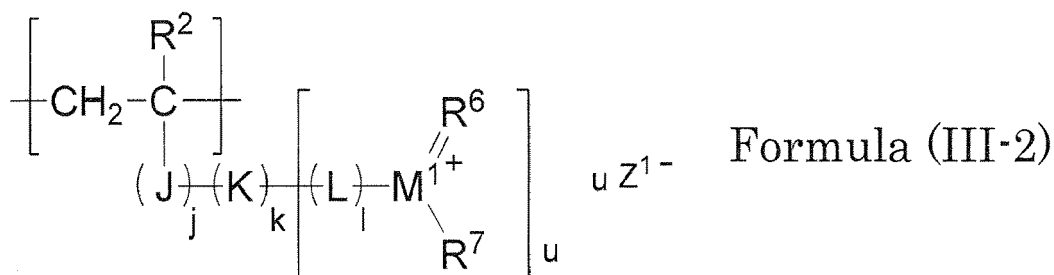
M¹ represents an atom belonging to group 15 of the periodic table and preferably represents a nitrogen atom or a phosphorous atom.

[0033] R³, R⁴, and R⁵ each independently represent a hydrogen atom, an alkyl group, an aromatic group, or an aralkyl group. The alkyl group is preferably an alkyl group having 1 to 10 carbon atoms. When R³, R⁴, and R⁵ each independently represent an alkyl group, an aromatic group, or an aralkyl group, each of these groups themselves may have an optional substituent. Examples of the optional substituent that can be introduced in these groups include an alkyl group, an aromatic group, an alkoxy group, a carboxy group, an amino group, an imino group, and a nitro group. R³ and R⁴ may be linked to each other to form a ring, and R⁴ and R⁵ may be linked to each other to form a ring.

Z¹⁻ represents a counter anion. The counter anion is preferably a halogen ion, PF₆⁻, BF₄⁻, or R⁸SO₃⁻. R⁸ represents an alkyl group having 1 to 10 carbon atoms, an aromatic group, or an aralkyl group, and each of these groups may have an optional substituent such as the optional substituent mentioned regarding R³ to R⁵.

j, k, and l each independently represents 0 or 1 provided that j and k are not 0 at the same time. u represents an integer of 1 to 3.

[0034]



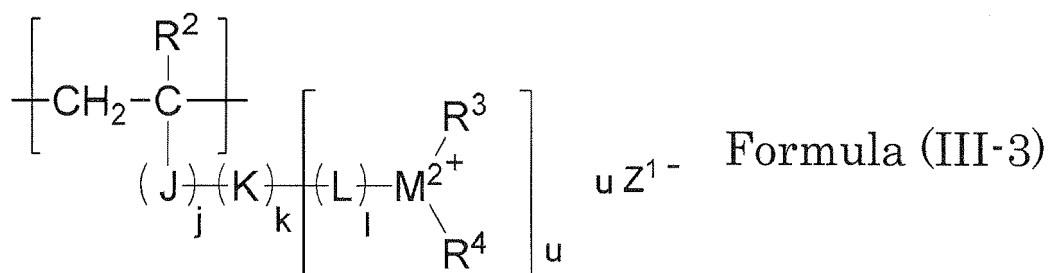
[0035] In Formula (III-2), R², J, K, L, M¹, Z¹⁻, j, k, l, and u have the same definitions as R², J, K, L, M¹, Z¹⁻, j, k, l, and u in Formula (III-1) respectively, and have the same preferable definitions as R², J, K, L, M¹, Z¹⁻, j, k, l, and u in the formula (III-1) respectively.

R⁶ represents an alkylidyne group and preferably represents an alkylidyne group having 1 to 10 carbon atoms. The alkylidyne group may have an optional substituent. Examples of the optional substituent that can be introduced in the alkylidyne group include an alkyl group, an aromatic group, an alkoxy group, a carboxy group, an amino group, an imino group, and a nitro group.

R⁷ represents a hydrogen atom, an alkyl group, an aromatic group, or an aralkyl group. The alkyl group is preferably an alkyl group having 1 to 10 carbon atoms. When R⁷ represents an alkyl group, an aromatic group, or an aralkyl group, each of these groups may have an optional substituent. Examples of a substituent that can be introduced in these groups include an alkyl group, an aromatic group, an alkoxy group, a carboxy group, an amino group, an imino group, and a

nitro group. R⁶ and R⁷ may be linked to each other to form a ring.

[0036]



[0037] In Formula (III-3), R², J, K, L, Z¹⁻, j, k, l, and u have the same definitions as R², J, K, L, Z¹⁻, j, k, l, and u in Formula (III-1) respectively. When R³ and R⁴ each independently represent a hydrogen atom, an alkyl group, an aromatic group, or an aralkyl group, each of these groups may have an optional substituent. Examples of the optional substituent that can be introduced in these groups include an alkyl group, an aromatic group, an alkoxy group, a carboxy group, an amino group, an imino group, and a nitro group. R³ and R⁴ may be linked to each other to form a ring. M²⁺ represents a sulfur atom.

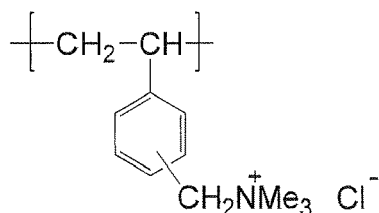
[0038] As shown above, the repeating units represented by Formula (III-1) and Formula (III-2) correspond to an example including a phosphonium salt structure and an example including an ammonium salt structure, respectively. The repeating unit represented by Formula (III-3) corresponds to an example including a sulfonium salt structure. M⁺ Z⁻ in Formula (III) may form a structure including, for example, an iodonium salt or a pyridinium salt.

[0039] As preferable examples of the onium-containing resin (A) that can be used in the invention, resins (A-1) to (A-22) are shown in terms of the repeating units included in the resins and the weight-average molecular weights (Mw) of the resins. However, it should be noted that the onium-containing resin (A) is not limited thereto.

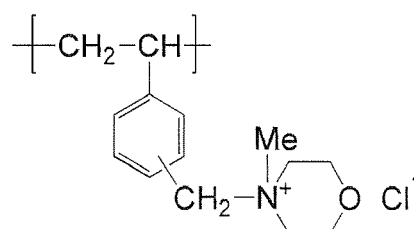
Here, the weight-average molecular weights of the resins are values measured by gel permeation chromatography (GPC) in terms of the polystyrene equivalent.

[0040]

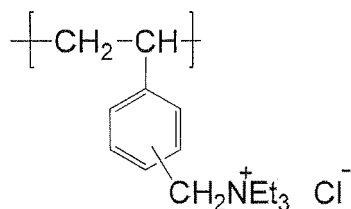
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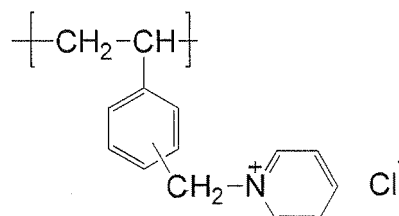
(A-2) Mw: 30,000



(A-3) Mw: 40,000

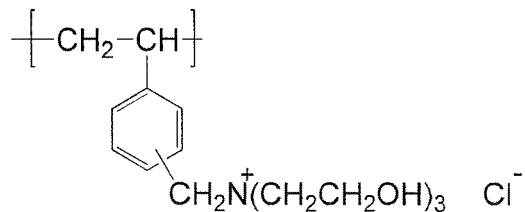
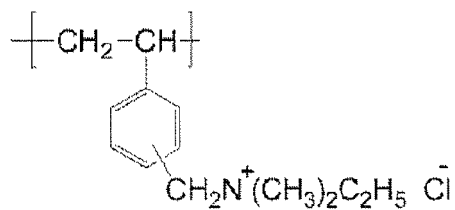


(A-4) Mw: 18,000



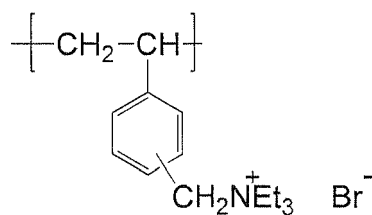
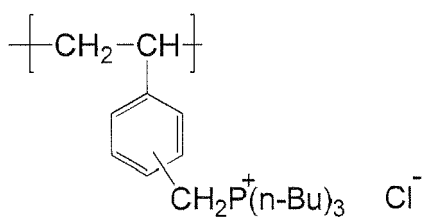
(A-5) Mw: 30,000

(A-6) Mw: 60,000



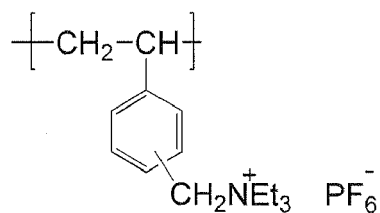
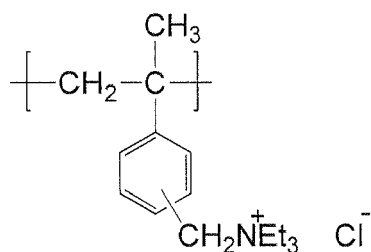
(A-7) Mw: 40,000

(A-8) Mw: 25,000



(A-9) Mw: 20,000

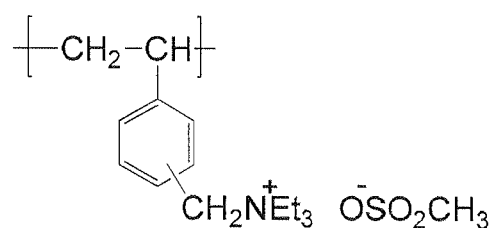
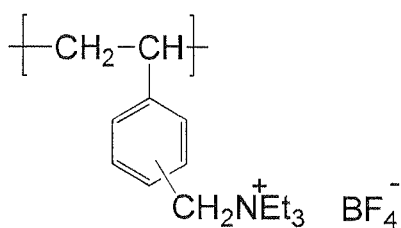
(A-10) Mw: 30,000



[0041]

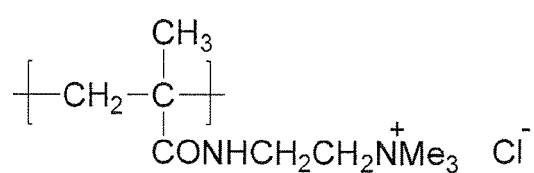
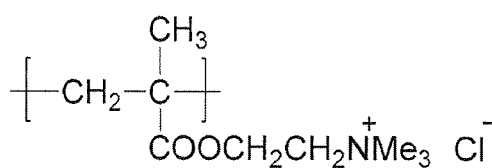
(A-11) Mw: 30,000

(A-12) Mw: 40,000



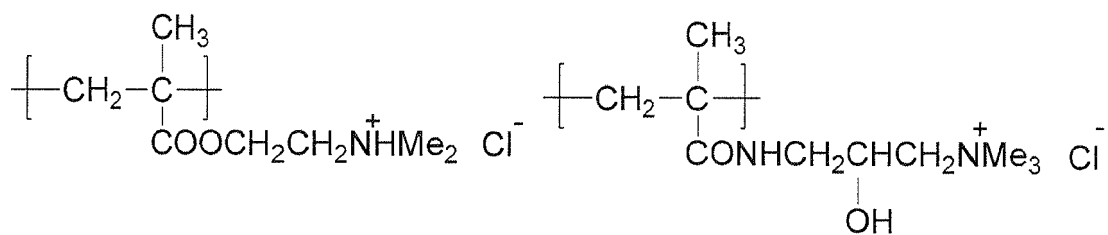
(A-13) Mw: 55,000

(A-14) Mw: 40,000



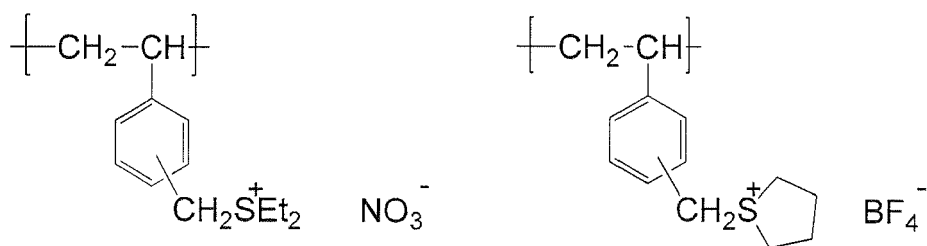
(A-15) Mw: 18,000

(A-16) Mw: 20,000

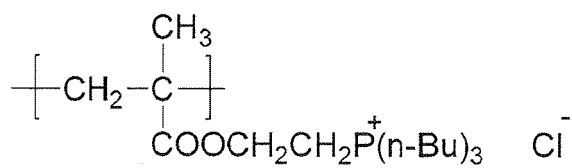


(A-17) Mw: 18,000

(A-18) Mw: 20,000



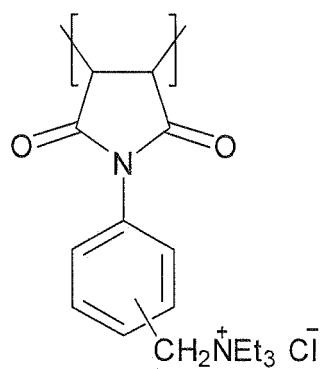
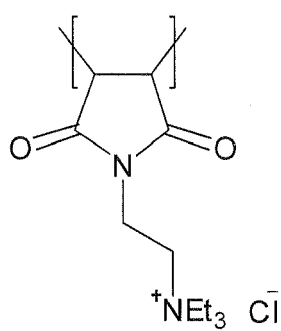
(A-19) Mw: 30,000



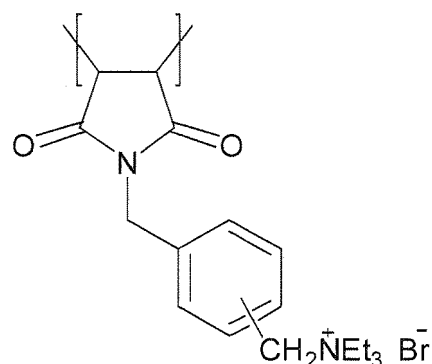
[0042]

(A-20) Mw: 40,000

(A-21) Mw: 50,000



(A-22) Mw: 40,000



[0043] The above examples of the onium-containing resin (A) are homo-polymers of a repeating unit including an onium salt structure, but the onium-containing resin (A) of the invention is not limited thereto.

The onium-containing resin (A) may contain single kind of the repeating unit having an onium salt structure, as shown in the above specific examples, or a combination of two or more kinds thereof. Alternatively, the onium-containing resin (A) may be a copolymer including a repeating unit having an onium salt structure and another repeating unit (not having an onium salt structure).

[0044] In the resin (A) having an onium salt structure, a known polymerizable monomer for forming the another repeating unit (not having an onium salt structure), that may be optionally included is not specifically restricted, as long as it is a monomer for forming a copolymer together with the aforementioned repeating unit having an onium salt structure. Examples of the monomer include (meth) acrylic acid esters, N- substituted (meth) acrylamides, acrylonitrile, styrene-based compounds, maleimides, (meth) acrylamide, glycidyl (meth) acrylate, N- substituted maleimides, a (meth) acrylic acid ester having a polyoxyethylene chain, 2- hydroxyethyl (meth) acrylate, vinylpyridine, N- vinyl caprolactam, and N- vinyl pyrrolidine.

[0045] When the resin (A) having an onium salt structure includes the another repeating unit (not having an onium salt structure), the content of the repeating unit represented by Formula (III), preferably, the total content of at least one repeating unit selected from the repeating unit represented by Formula (III-1), (III-2), or (III-3) is appropriately from 15% by mole to 90% by mole, preferably from 20% by mole to 80% by mole, and more preferably from 20% by mole to 70% by mole.

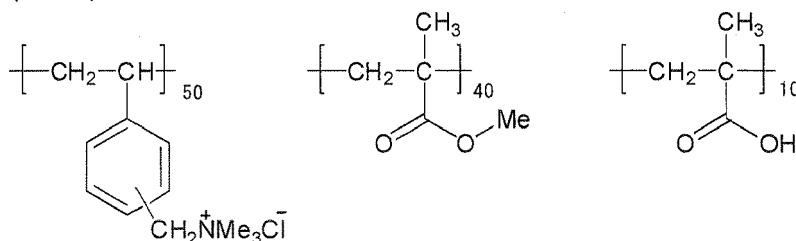
[0046] As preferable examples of the resin (A) having an onium salt structure that includes the another repeating unit (not having an onium salt structure) that can be used in the invention, resins (A-23) to (A-23) are shown in terms of the repeating units of the respective resins and the weight-average molecular weights (Mw) of the resins. However, it should be noted that the onium-containing resin (A) is not limited to thereto.

Here, the weight-average molecular weights of the resins are values measured by GPC in terms of the polystyrene equivalent.

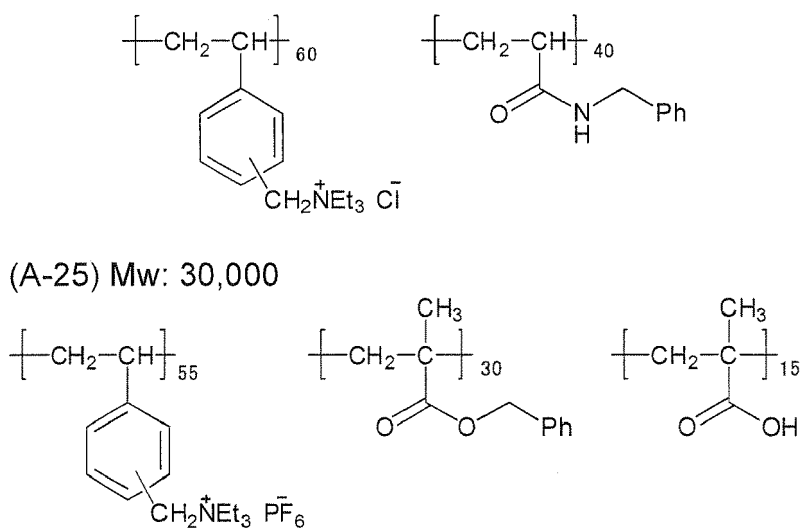
A numerical value in each of the repeating units represents a mole ratio.

[0047]

(A-23) Mw: 30,000



(A-25) Mw: 30,000


$$\begin{array}{ccc} \left[\text{CH}_2 - \underset{\text{Ph}}{\text{CH}} \right]_{50} & \left[\text{CH}_2 - \underset{\text{CONHCH}_2\text{Ph}}{\text{CH}} \right]_{40} & \left[\text{CH}_2 - \underset{\text{C}_6\text{H}_4\text{COOH}}{\text{CH}} \right]_{10} \\ \text{Ph} & \text{O} & \text{O} \\ \text{CH}_2 - \text{N}^+ \text{Me} & & \\ | & & \\ \text{CH}_2 & & \end{array}$$
$$\begin{array}{ccc} \left[\text{CH}_2 - \underset{\text{C}_6\text{H}_4 - \text{CH}_2 - \text{N}^+ \text{C}_6\text{H}_5}{\text{CH}} \right]_{40} & \left[\text{CH}_2 - \underset{\text{C}(=\text{O})\text{NH} - \text{C}(\text{CH}_3)_3}{\text{CH}} \right]_{40} & \left[\text{CH}_2 - \underset{\text{C}(=\text{O})\text{OH}}{\overset{\text{CH}_3}{\text{C}}} \right]_{20} \\ & \text{Cl}^- & \end{array}$$
$$\begin{array}{cc} \left[\text{CH}_2 - \underset{\text{C}_6\text{H}_4\text{CH}_2\text{P}^+(\text{n-Bu})_3\text{Cl}^-}{\text{CH}} \right]_{70} & \left[\text{CH}_2 - \underset{\text{NHCH}_2\text{Ph}}{\text{CH}} \right]_{30} \end{array}$$

13

(A-29) Mw: 40,000

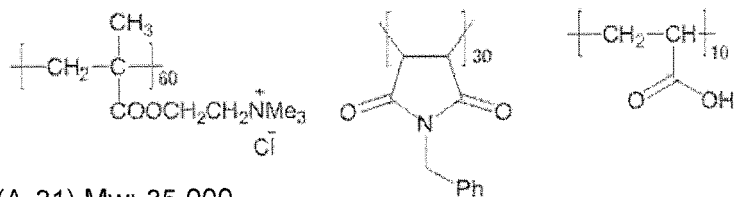
5

10



(A-30) Mw: 50,000

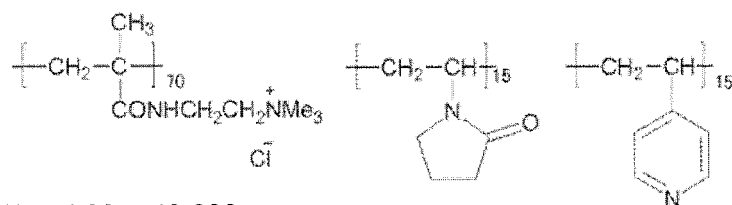
15



(A-31) Mw: 35,000

20

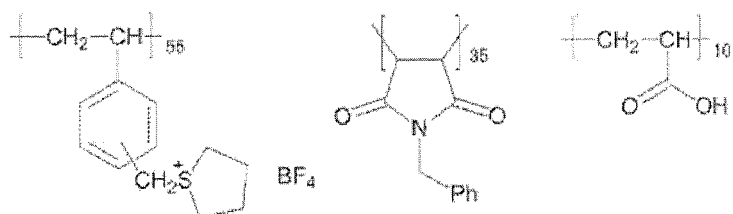
25



(A-32) Mw: 40,000

30

35



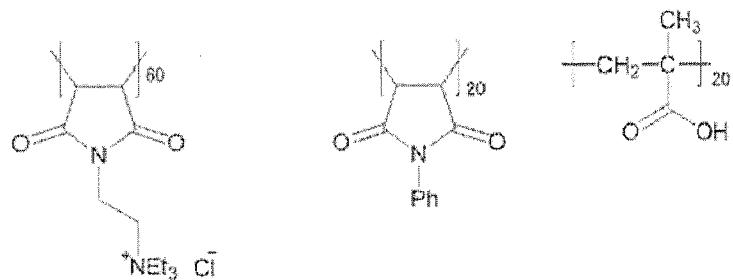
(A-33) Mw: 40,000

40

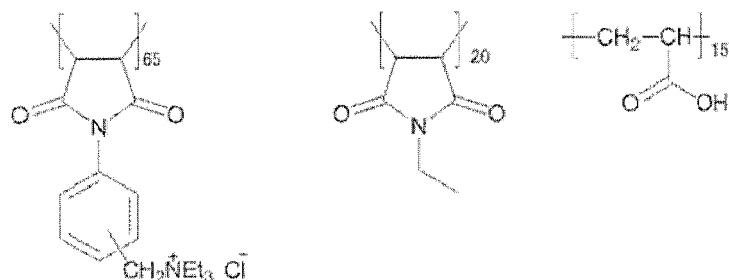
45

50

55



(A-34) Mw: 35,000



[0049] Among these, the onium salt structure is preferably the (A-1), (A-2), (A-4), (A-7), (A-23), (A-24), (A-26), (A-27), or (A-33), from the viewpoint of further improving post-exposure stability.

The weight-average molecular weight (Mw) of the resin (A) having an onium salt structure used in the invention is from 5,000 to 1,000,000, preferably from 7,000 to 500,000, and more preferably from 10,000 to 300,000.

In the specification, the molecular weight may be determined by gel permeation chromatography (GPC) using N-methylpyrrolidone as an eluent. In this case, monodispersed polystyrene may be used as a standard for molecular weight.

[0050] The onium- containing resin (A) used in the invention may be synthesized based on, for example, a synthesis method described in "Ikeda, T., Makromol, Chem, Rapid Commun., P4, 459 (1983)". As the known onium- containing resins that can be used in the invention, onium salt- containing resins such as those described in JP- A- 2000- 108538 and JP- A- 2004- 094075 are preferably used.

[0051] In the invention, the content of the resin (A) having an onium salt structure is preferably from 5% by mass to 95% by mass, and more preferably from 10% by mass to 90% by mass, with respect to a total solid content of the recording layer provided in closest proximity to the substrate.

When content of the onium-containing resin (A) is 5% by mass or more, the obtained recording layer exhibits favorable strength of images in unexposed areas and excellent developability in exposed areas. When the amount thereof is 95% by mass or less, the recording layer has excellent sensitivity.

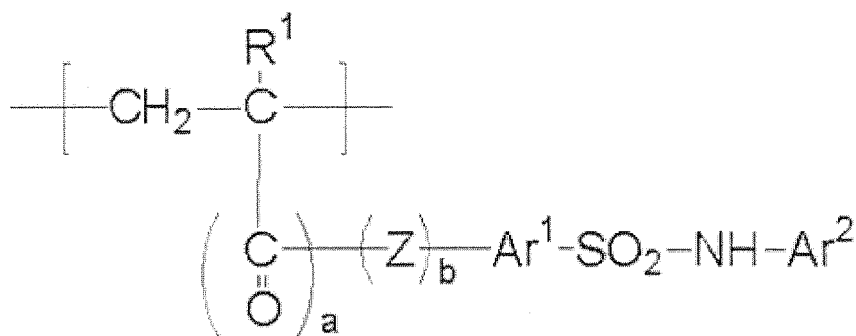
(Meth)acrylic resin (Specific acrylic resin) (B) having at least one repeating unit selected from a structural unit represented by Formula (I) or a structural unit represented by Formula (II)

[0052] Hereinbelow, the specific acrylic resin is described in detail.

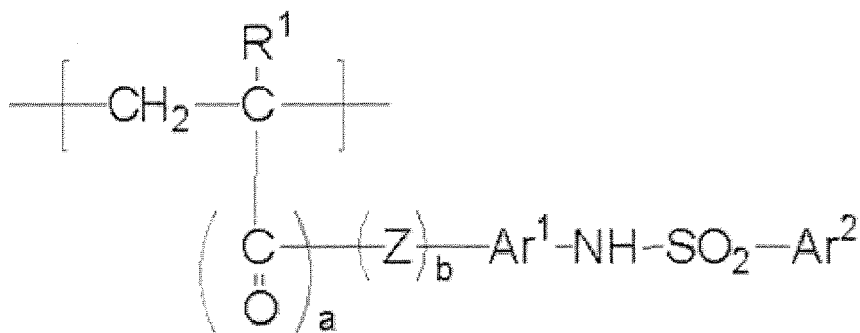
The specific acrylic resin according to the invention is a polymer having at least one repeating unit selected from a structural unit represented by the following Formula (I) or a structural unit represented by the following Formula (II).

It is thought that the specific acrylic resin having a side chain structure represented by Formula (I) or (II), which includes bulky aromatic groups at both sides of the sulfonamide linking group in which at least one of the bulky aromatic groups is a heteroaromatic group, provides both excellent burning durability and chemical resistance.

[0053]



Formula (I)



Formula (II)

[0054] In Formulae (I) and (II), R¹ represents a hydrogen atom or an alkyl group; z represents -O- or -NR²- wherein R² represents a hydrogen atom, an alkyl group, an alkenyl group or an alkynyl group; Ar¹ and Ar² each independently represent an aromatic group, and at least one of Ar¹ or Ar² represents a heteroaromatic group; and a and b each independently represent 0 or 1.

[0055] In Formula (I), R¹ represents a hydrogen atom or an alkyl group, wherein the alkyl group is a substituted or unsubstituted alkyl group, and is preferably an unsubstituted alkyl group. Examples of the alkyl group represented by R¹ include lower alkyl groups, such as a methyl group, an ethyl group, a propyl group and a butyl group. It is preferable that R¹ is a hydrogen atom or a methyl group.

[0056] Z represents -O- or -NR²-, and is preferably -NR²-. Herein, R² represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, or a substituted or unsubstituted alkynyl group. R² is preferably a hydrogen atom or an unsubstituted alkyl group, and more preferably a hydrogen atom.

[0057] a and b each independently represent 0 or 1. It is preferable that a represents 0 and b represents 1; both a and b represent 0; or both a and b represent 1. It is more preferable that both a and b represent 1.

More specifically, it is preferable that Z represents -O- when a represents 0 and b represents 1; and that Z represents -NR²- when both a and b represent 1 wherein R² preferably represents a hydrogen atom.

[0058] Ar¹ and Ar² each independently represent an aromatic group, and at least one of Ar¹ or Ar² represents a heteroaromatic group. Ar¹ represents a divalent aromatic group, and Ar² represents a monovalent aromatic group. The aromatic group represented by Ar¹ or Ar² is a substituent formed by substituting one or two linkage groups for one or two hydrogen atoms of the corresponding aromatic ring.

The aromatic ring may be selected from among hydrocarbon aromatic rings such as benzene, naphthalene and anthracene, or may be selected from heteroaromatic rings such as furan, thiophene, pyrrole, imidazole, 1, 2, 3- triazole, 1, 2, 4- triazole, tetrazole, oxazole, isooxazole, thiazole, isothiazole, thiadiazole, oxadiazole, pyridine, pyridazine, pyrimidine, pyrazine, 1, 3, 5- triazine, 1, 2, 4- triazine and 1, 2, 3- triazine.

The aromatic ring may be a fused ring formed by fusing two or more of the above rings together, such as benzofuran, benzothiophene, indole, indazole, benzoxazole, quinoline, quinazoline, benzimidazole or benzotriazole.

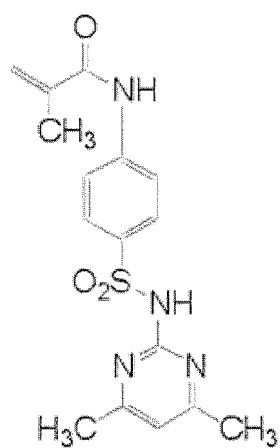
[0059] The aromatic and hetero-aromatic group may have an additional substituent, and examples of the additional substituent that can be introduced into the aromatic or hetero-aromatic group include an alkyl group, a cycloalkyl group, an alkenyl group, a cycloalkenyl group, an aryl group, a heteroaryl group, a hydroxy group, -SH, a carboxylic acid group or alkyl esters thereof, a sulfonic acid group and alkyl esters thereof, a phosphinic acid group and alkyl esters thereof, an amino group, a sulfonamide group, an amido group, a nitro group, a halogen atom, and substituents formed by two or more of these groups being linked together. The additional substituent may further have a substituent listed as the additional substituent.

[0060] Ar² preferably represents a heteroaromatic group optionally having a substituent. It is more preferable that Ar² represents a nitrogen-containing heteroaromatic ring selected from pyridine, pyridazine, pyrimidine, pyrazine, 1, 3, 5- triazine, 1, 2, 4- triazine, 1, 2, 3- triazine, tetrazole, oxazole, isooxazole, thiazole, isothiazole, thiadiazole, oxadiazole and the like.

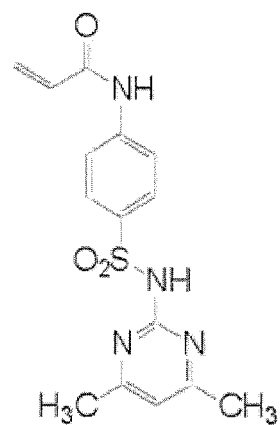
[0061] Examples of a monomer capable of forming the structural unit represented by Formula (I) or Formula (II) (Exemplified monomers (1) to (27)) are illustrated below, but these examples should not be construed as limiting the scope of the invention. Of the exemplified monomers illustrated below, a monomer having the linkage group -SO₂-NH- from the main chain side (e.g., Monomer (1)) corresponds to the structural unit represented by Formula (I), and a monomer having the linkage group -NH-SO₂- from the main chain side (e.g., Monomer (12)) corresponds to the structural unit represented by Formula (II).

[0062]

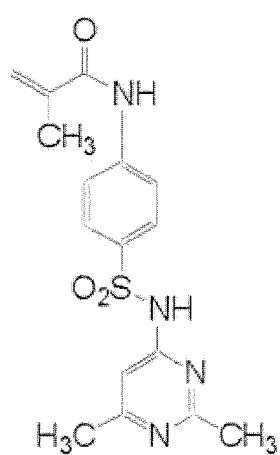
Monomer (1)



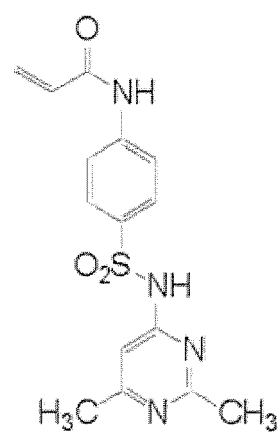
Monomer (2)



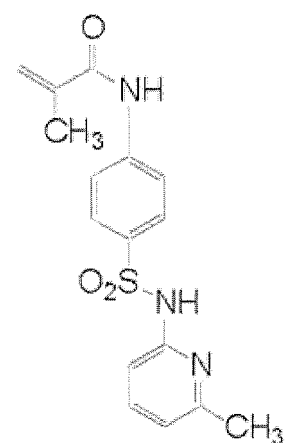
Monomer (3)



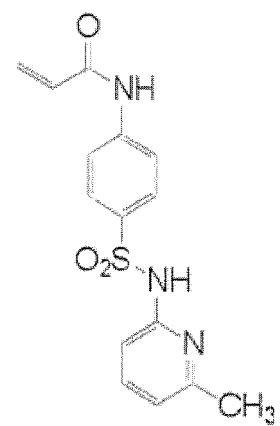
Monomer (4)



Monomer (5)

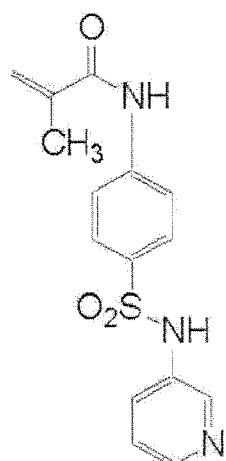


Monomer (6)

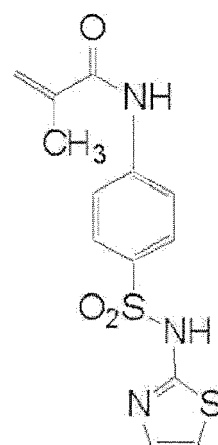


[0063]

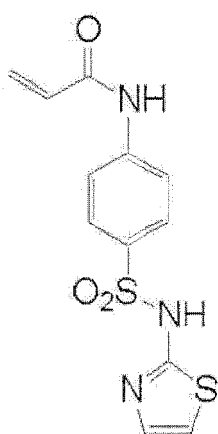
Monomer (7)



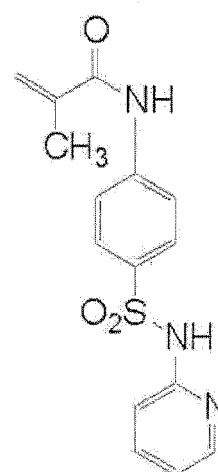
Monomer (8)



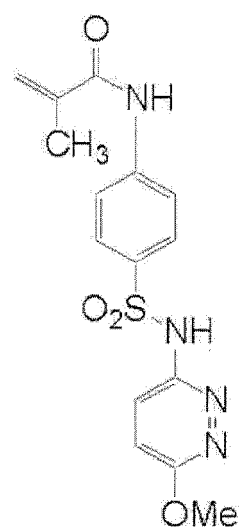
Monomer (9)



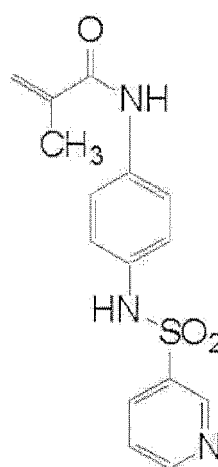
Monomer (10)



Monomer (11)

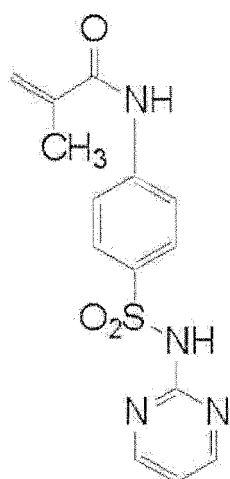


Monomer (12)

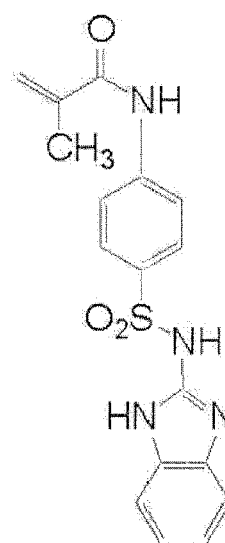


[0064]

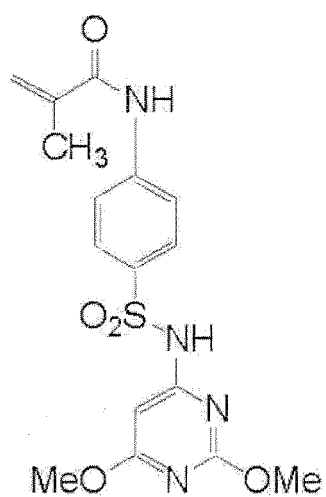
Monomer (13)



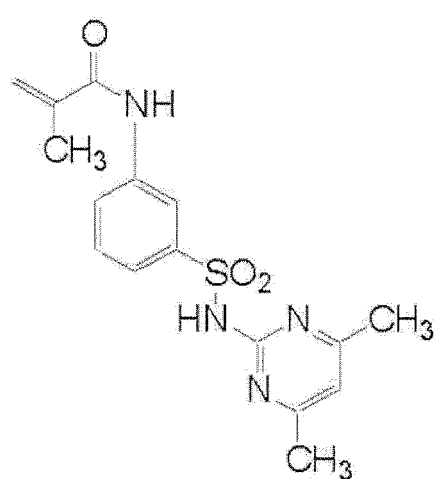
Monomer (14)



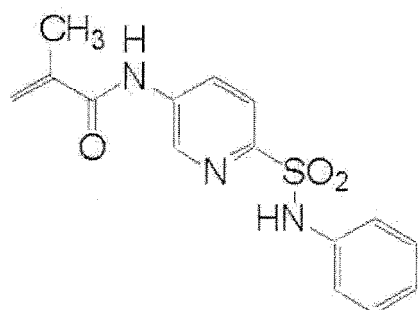
Monomer (15)



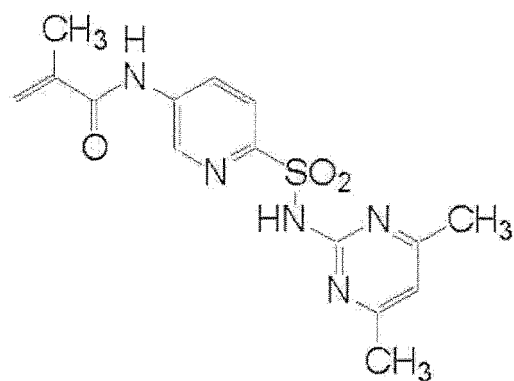
Monomer (16)



Monomer (17)

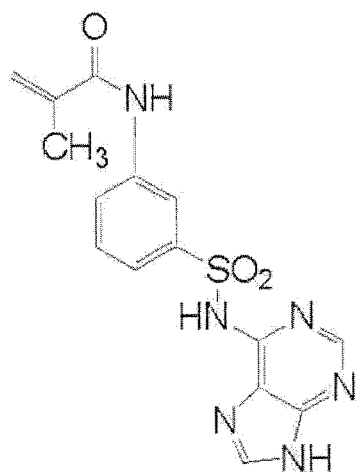


Monomer (18)

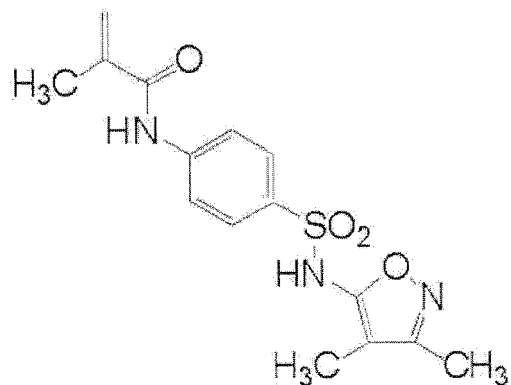


[0065]

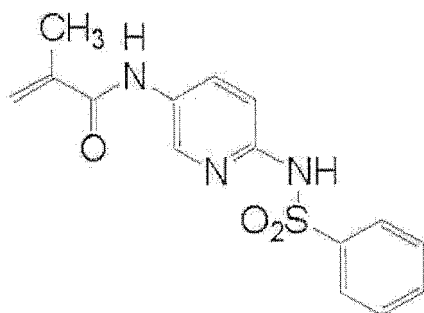
Monomer (19)



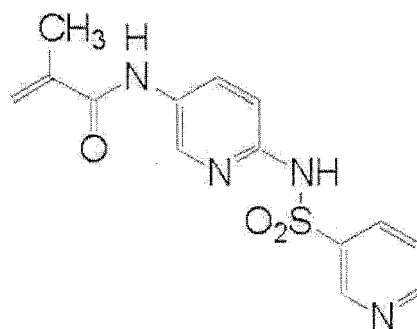
Monomer (20)



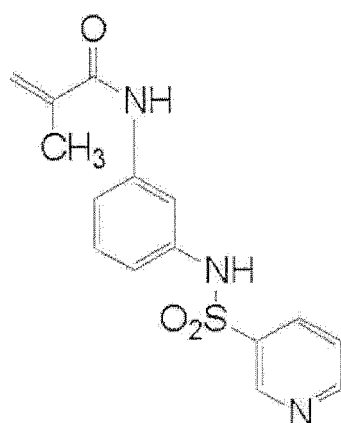
Monomer (21)



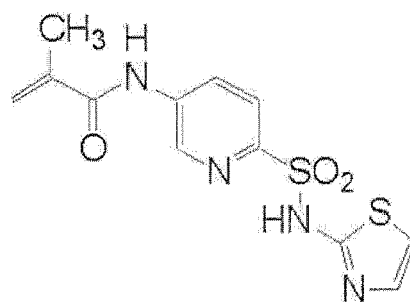
Monomer (22)



Monomer (23)

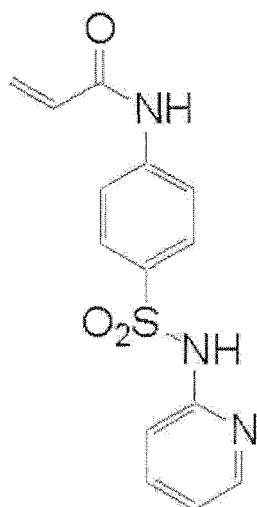


Monomer (24)

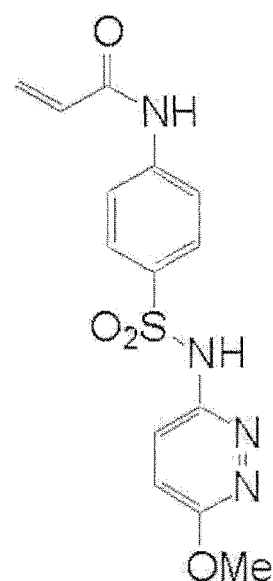


[0066]

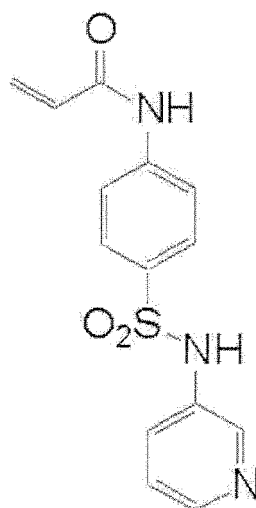
Monomer (25)



Monomer (26)



Monomer (27)



[0067] The specific acrylic resin is an alkali-soluble polymer containing a structural unit represented by Formula (I) and/or a structural unit represented by Formula (II). In the specific acrylic resin, the structural unit represented by Formula (I) may be used singly or in combination of two or more kinds thereof, and the structural unit represented by Formula (II) may be used singly or in combination of two or more kinds thereof.

The total content of the structural unit represented by Formula (I) and the structural unit represented by Formula (II) in the specific acrylic resin is preferably from 10% by mole to 100% by mole, more preferably from 20% by mole to 90% by mole, still more preferably from 30% by mole to 80% by mole, and yet more preferably from 30% by mole to 70% by mole.

[0068] The specific acrylic resin containing the above structural unit may be a copolymer containing another structural unit in addition to the structural unit represented by Formula (I) and/or the structural unit represented by Formula (II).

Examples of the another structural unit include a structural unit derived from a hydrophobic monomer having in a side chain thereof a substituent such as an alkyl group or an aryl group, and a structural unit derived from a hydrophilic monomer having in a side chain thereof a substituent such as an acidic group, an amido group, a hydroxy group or an ethylene oxide group. Although the another monomer to be copolymerized can be appropriately selected from these monomers in accordance with the intended use, the type of the monomer for copolymerization is required to be selected within the extent that alkali solubility of the specific acrylic resin is not impaired.

[0069] Examples of the another structural unit that can be used for the specific acrylic resin according to the invention

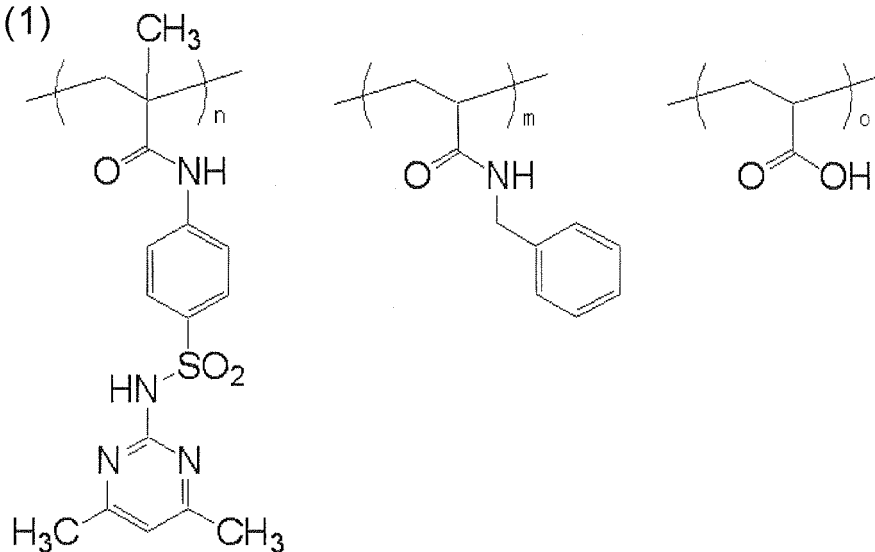
include (meth) acrylamide, N- substituted (meth) acrylamides, N- substituted maleimides, (meth) acrylic esters, a (meth) acrylic ester having a polyoxyethylene chain, 2- hydroxyethyl (meth) acrylate, styrene, styrenesulfonic acid, o-, p- or m- vinylbenzene acid, vinylpyridine, N- vinylcaprolactam, N- vinylpyrrolidine, (meth) acrylic acid, itaconic acid, maleic acid, glycidyl (meth) acrylate, a hydrolyzable vinyl acetate and vinylphosphonic acid. Among these, N- benzyl (meth) acrylamide and (meth) acrylic acid can be used as preferable copolymerization components.

[0070] The number-average molecular weight (M_n) of the specific acrylic resin is preferably from 10,000 to 500,000, more preferably from 10,000 to 200,000, and still more preferably from 10,000 to 100,000. The weight-average molecular weight (M_w) of the specific acrylic resin is preferably from 10,000 to 1000,000, more preferably from 20,000 to 500,000, and still more preferably from 20,000 to 200,000. The methods for measuring the molecular weights are described in detail in Examples below.

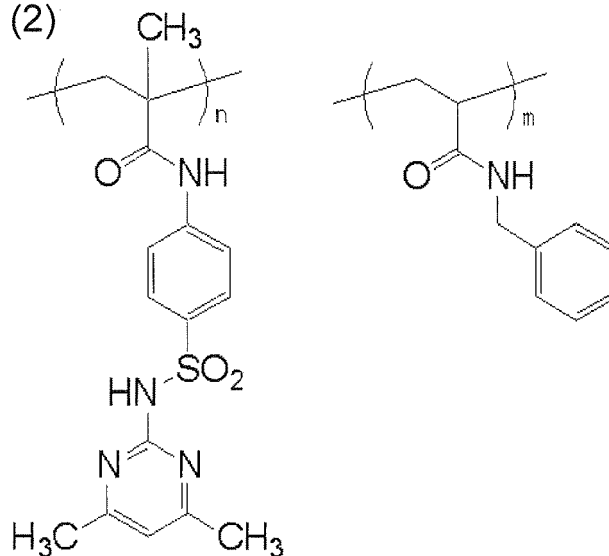
[0071] Examples of the structure of the specific acrylic resin that can be suitably used in the invention are listed below with their individual combinations of structural units.

[0072]

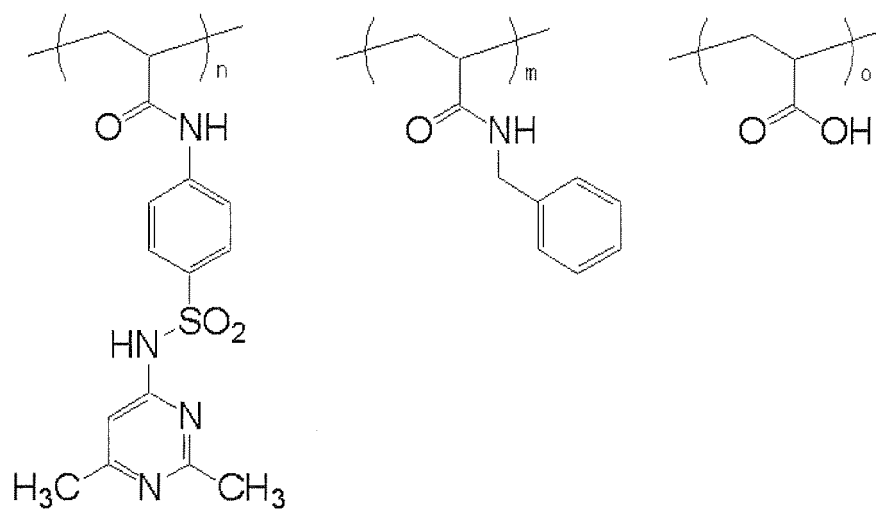
Copolymer (1)



Copolymer (2)

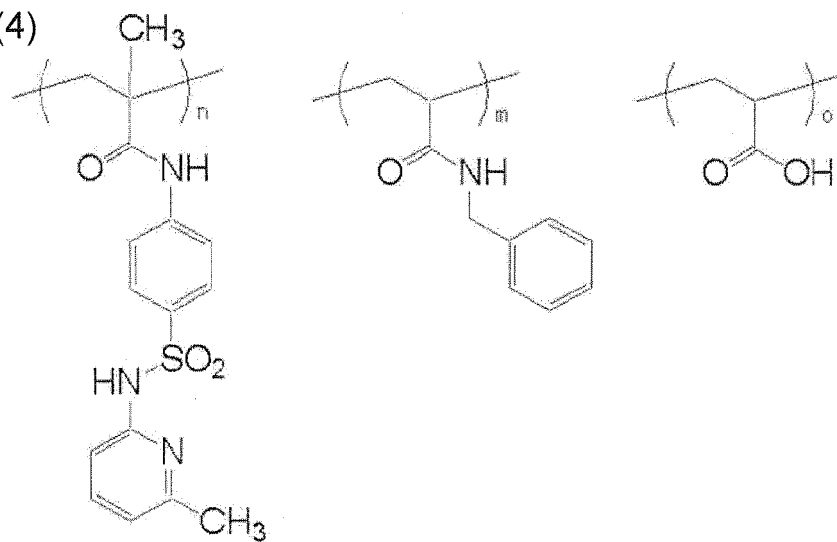


Copolymer (3)

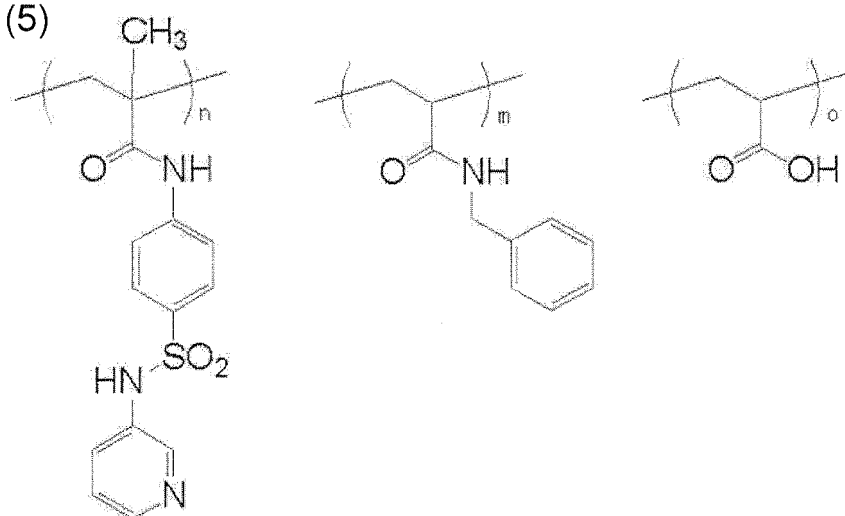


[0073]

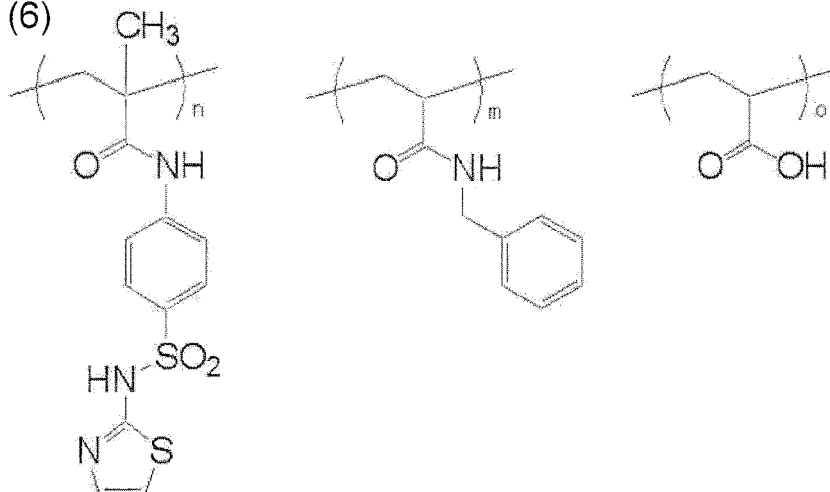
Copolymer (4)



Copolymer (5)

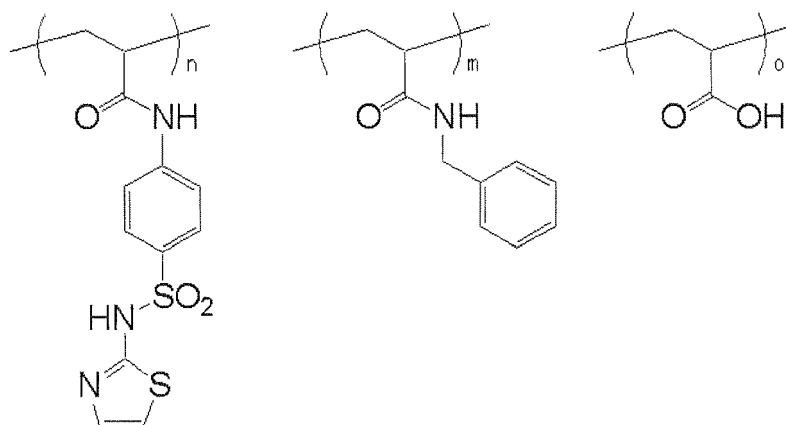


Copolymer (6)

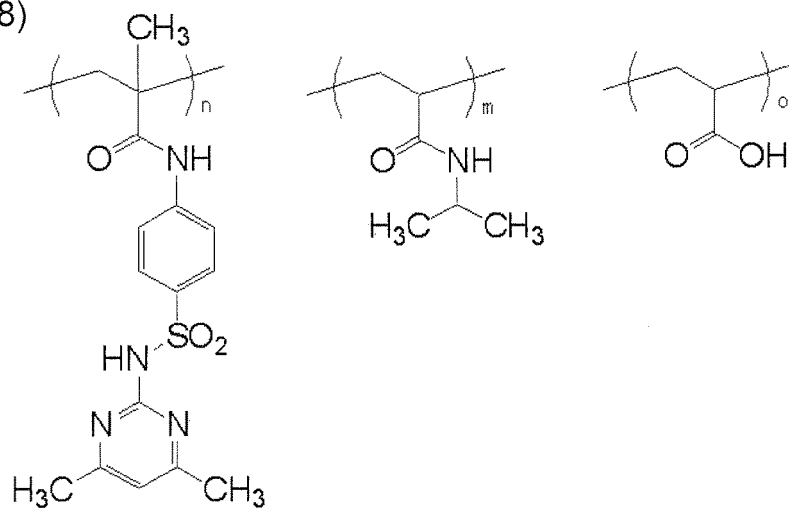


[0074]

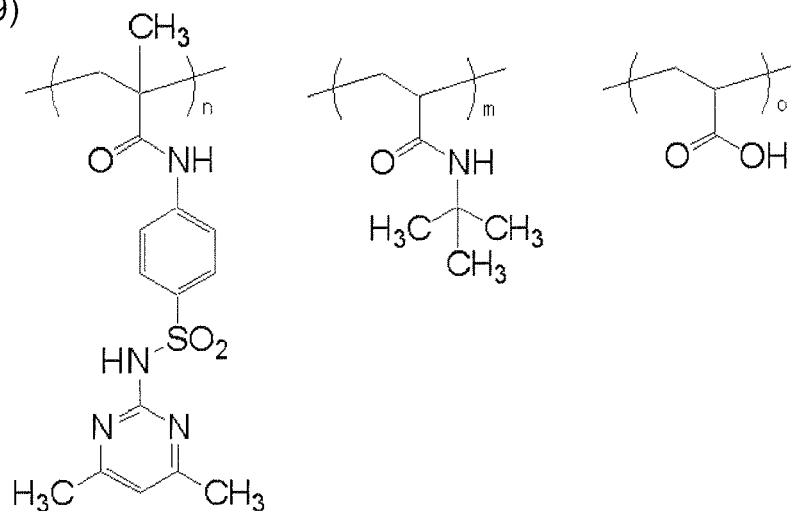
Copolymer (7)



Copolymer (8)

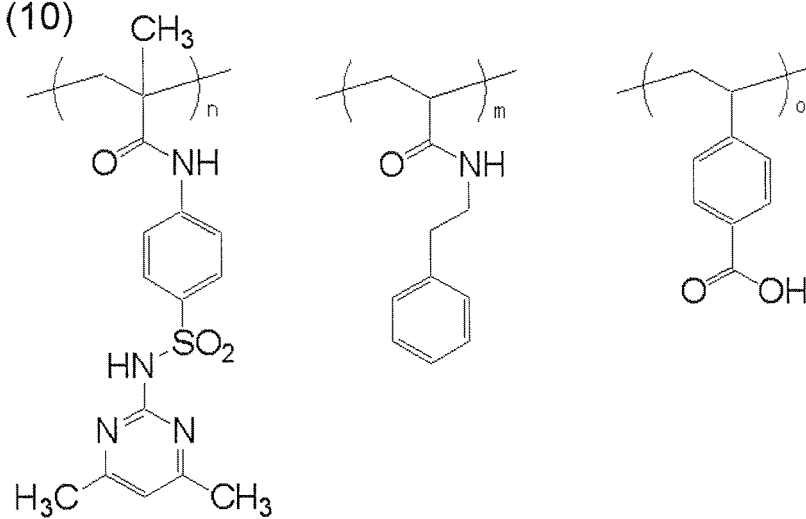


Copolymer (9)

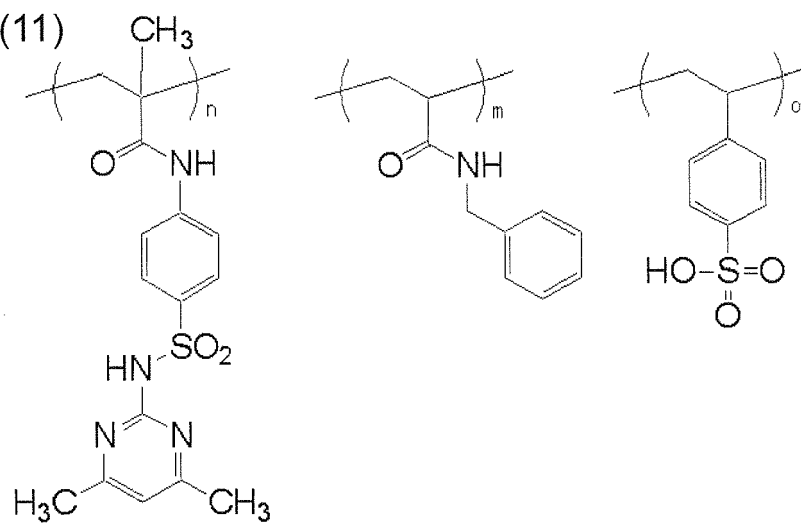


[0075]

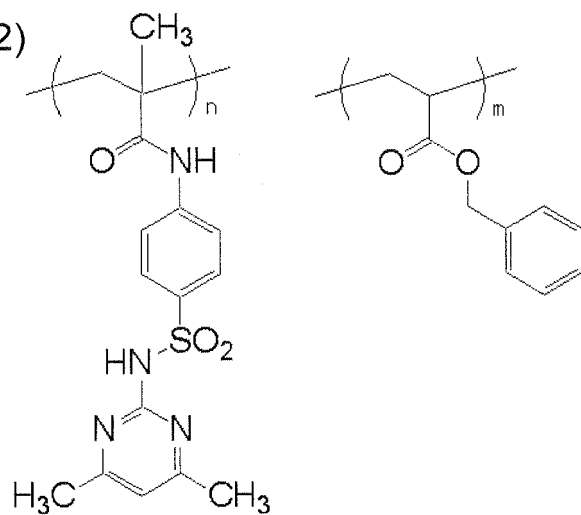
Copolymer (10)



Copolymer (11)

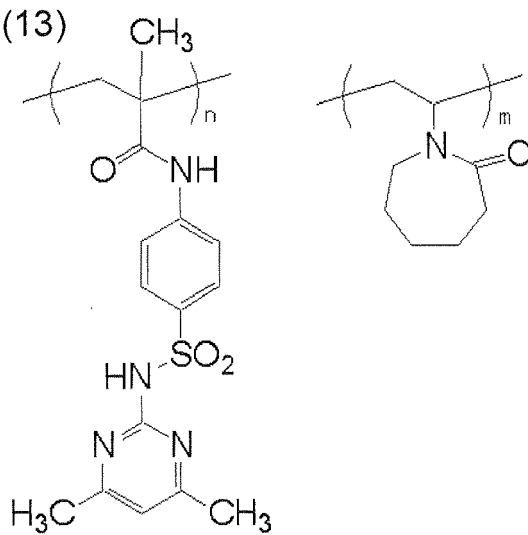


Copolymer (12)

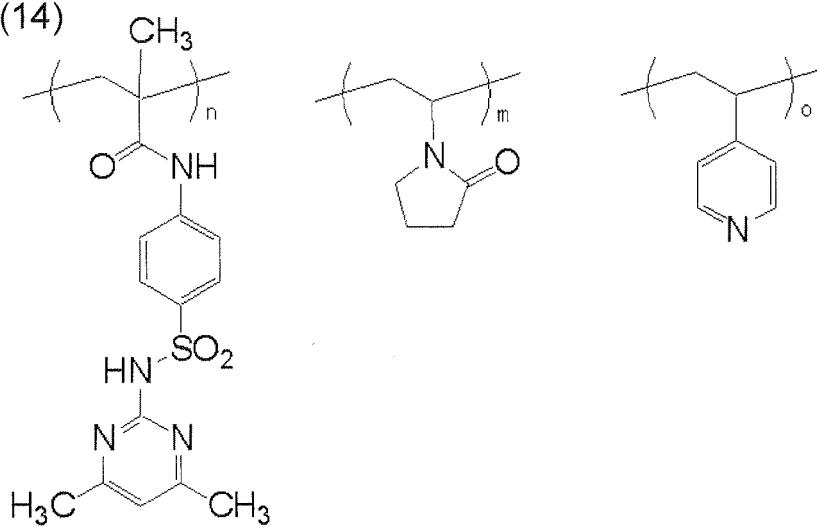


[0076]

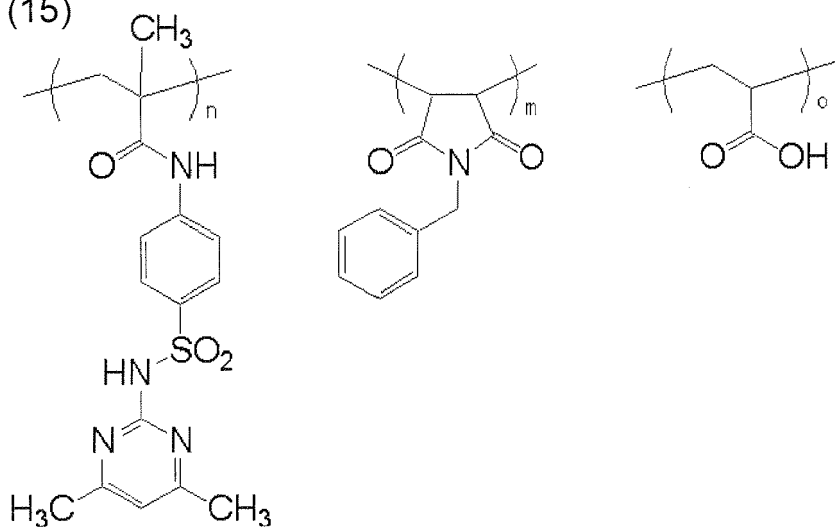
Copolymer (13)



Copolymer (14)

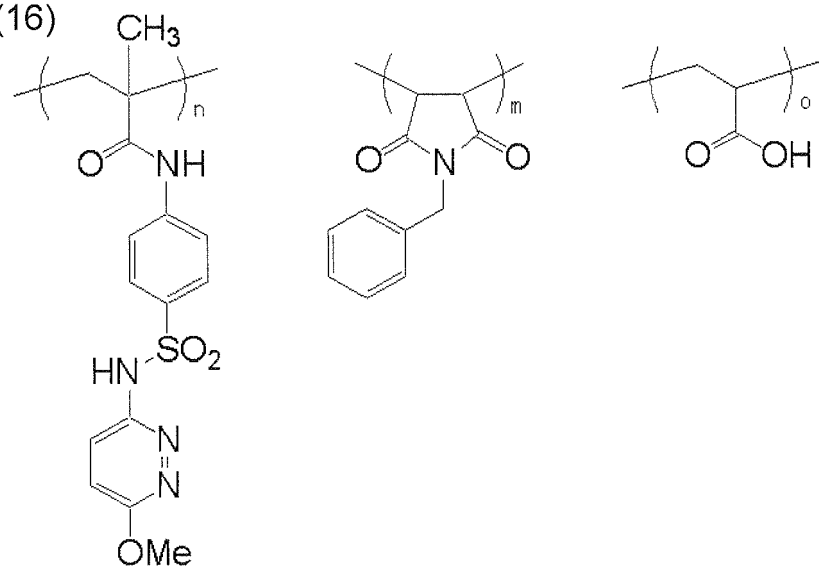


Copolymer (15)

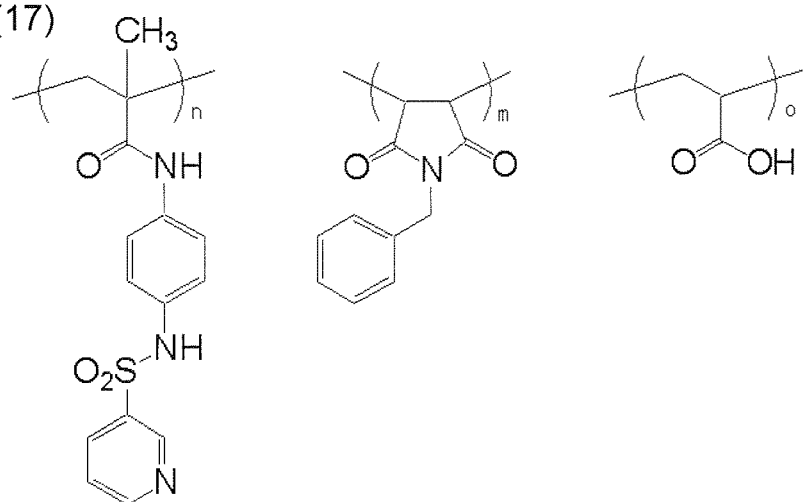


[0077]

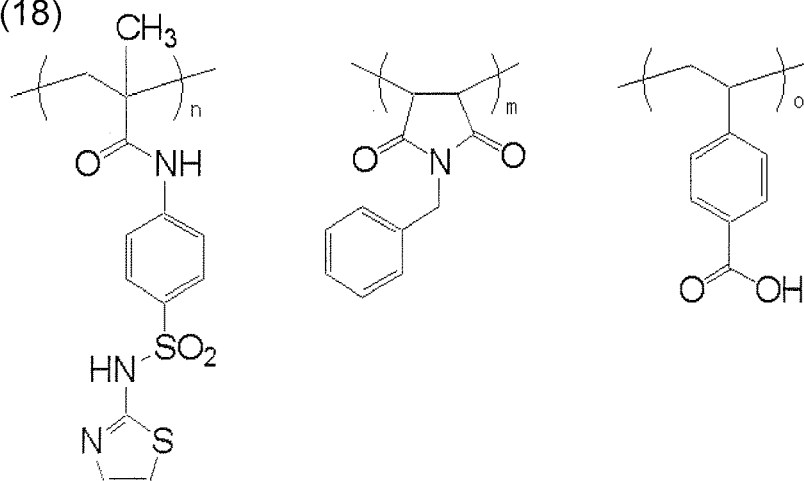
Copolymer (16)



Copolymer (17)

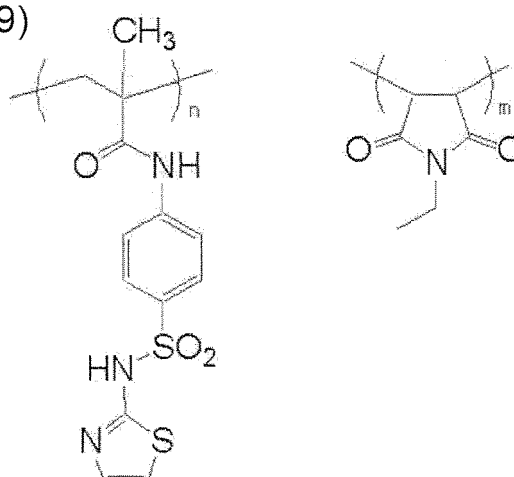


Copolymer (18)

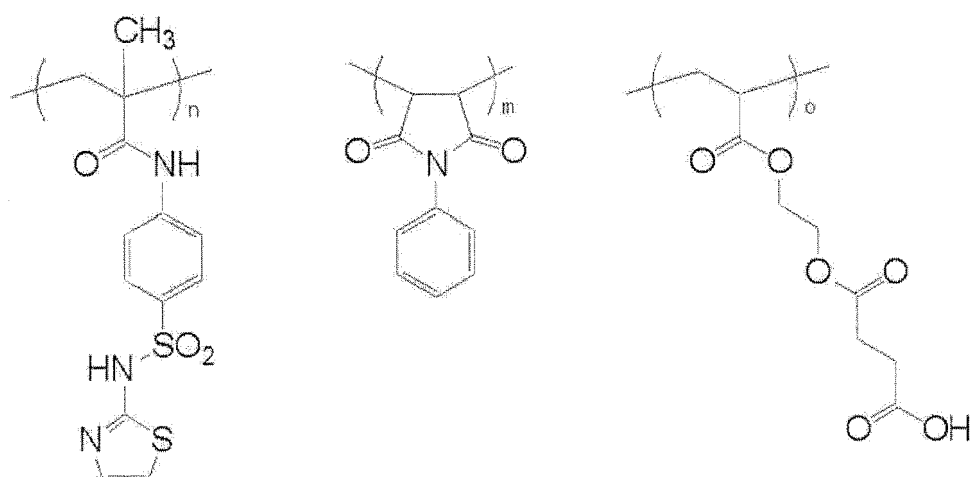


[0078]

Copolymer (19)



Copolymer (20)



[0079] Copolymer (21) : a copolymer in which a structural unit derived from N- (4- hydroxy- 3, 5- dimethyl- benzylacrylamide) is used instead of the structural unit derived from acrylic acid in Copolymer (15) .

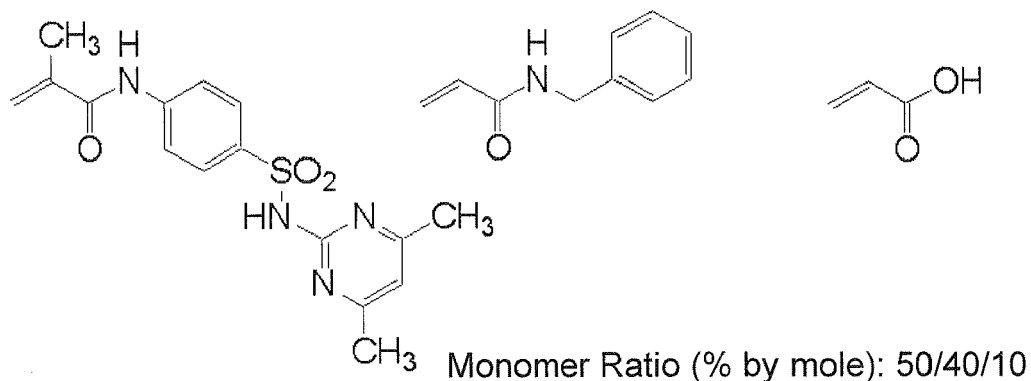
In each of Copolymers (1) to (21), each of m, n and o represent a molar ratio of the corresponding structural unit for

polymerization, and it is preferable that n represents from 10% by mole to 90% by mole; m represents from 5% by mole to 80 % by mole; and o represents from 0% by mole to 50 % by mole, provided that $n + m + o = 100$.

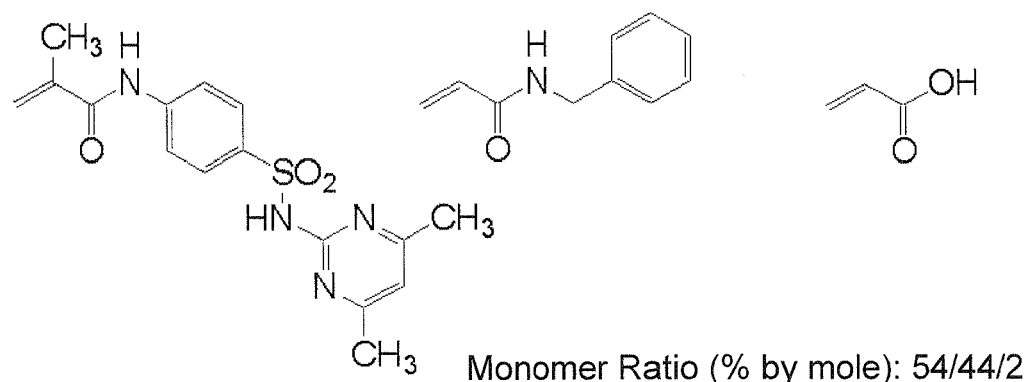
Specific examples of the specific acrylic resin according to the invention are illustrated below in terms of the monomers as starting materials (monomers for specific acrylic resins) and their molar ratio for polymerization, but the invention is not limited to these examples. Here, the specific acrylic resins according to the invention formed from these monomers are referred to as specific acrylic resins (1) to (8) .

[0080]

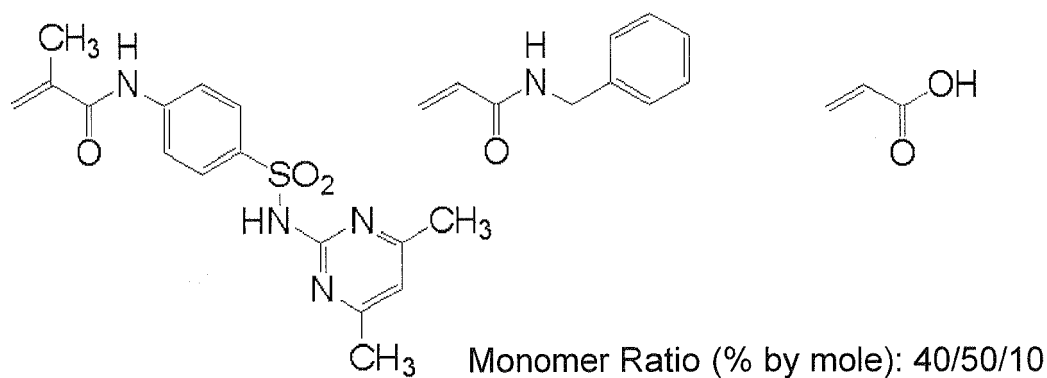
Monomers for Specific Acrylic Resin (1)



Monomers for Specific Acrylic Resin (2)

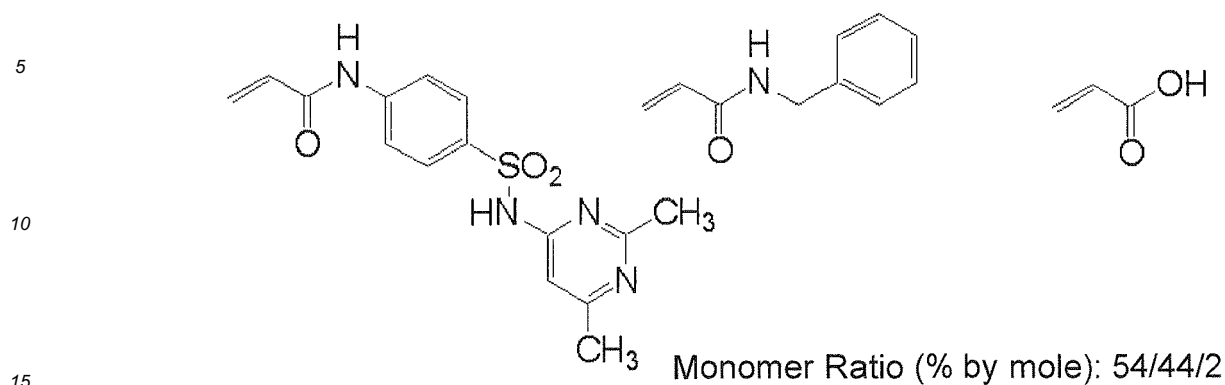


Monomers for Specific Acrylic Resin (3)

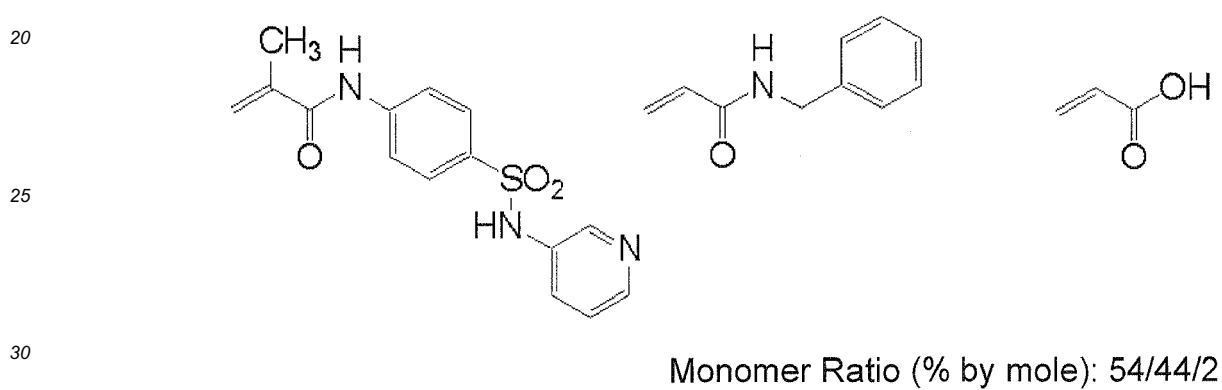


[0081]

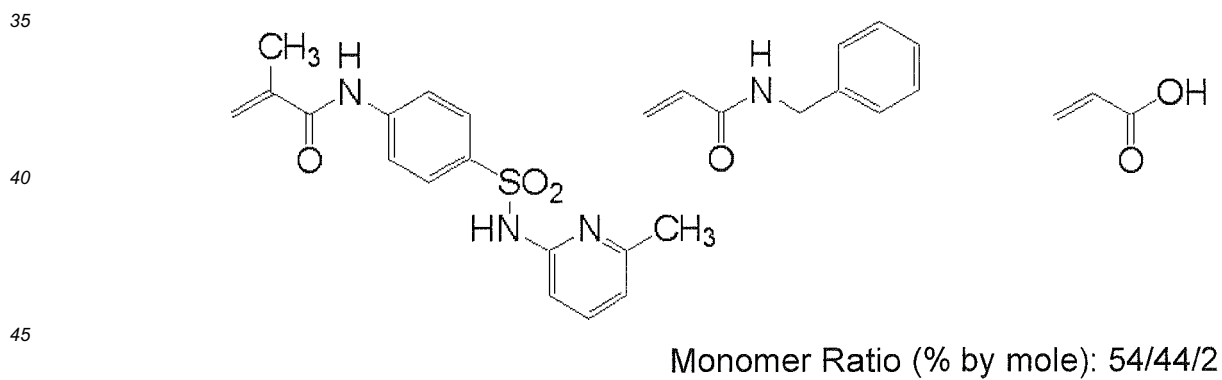
Monomers for Specific Acrylic Resin (4)



Monomers for Specific Acrylic Resin (5)



Monomers for Specific Acrylic Resin (6)

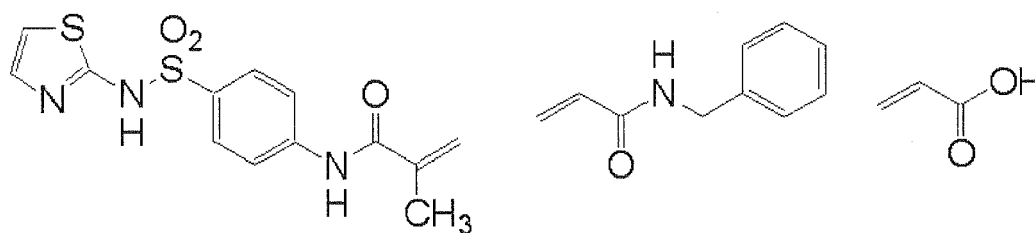


[0082]

Monomers for Specific Acrylic Resin (7)

50

55



Monomer Ratio (% by mole): 40/50/10

[0083] Monomers for specific acrylic resin (8):

Monomer (1) exemplified

above/ N- (4- hydroxy- 3, 5- dimethyl- benzylacrylamide) /N- benzyl maleimide monomer; ratio of monomers (% by mole) : 33.8/35/31.2

[0084] The specific acrylic resin (B) is added in an amount of preferably from 1% by mass to 99% by mass, more preferably from 5% by mass to 70% by mass, and most preferably from 10% by mass to 50% by mass, with respect to a total solid content of the recording layer provided in closest proximity to the substrate. When the amount of the specific acrylic resin (B) to be added is 1% by mass or more, the strength of image areas in the recording layer is high, and when the amount thereof is 99% by mass or less, both the strength of image areas and the developability of non-image areas are further improved.

[0085] The recording layer provided in closest proximity to the substrate in the invention is required to include the two types of resins, namely, the resin (A) having an onium salt structure and the (meth)acrylic resin (B) having at least one repeating unit selected from the structural unit represented by Formula (I) or the structural unit represented by Formula (II). The mixing ratio of resins (A) to (B) (the onium-containing resin (A):the specific acrylic resin (B)) in terms of mass ratio is preferably 1.0:0.1 to 1.0:8.0, and more preferably 1.0:0.2 to 1.0:7.0.

[0086] The constitutional elements of the invention will be described in more detail. The positive-working recording layer is first explained. The positive-working recording layer contains a resin and an infrared absorber (that is, a water-insoluble and alkali-soluble polymer compound and a compound for suppressing the alkali solubility of the water-insoluble and alkali-soluble polymer compound), and the solubility-suppressing capability thereof in exposed areas is cancelled by the exposure to an infrared laser beam, thereby increasing the solubility with respect to the alkaline developer and forming an image.

[0087] In the invention, the water-insoluble and alkali-soluble polymer compound (hereinafter also referred to as an "alkali-soluble resin" as required) used in the two or more recording layers may be a homopolymer having an acidic group on the main chain and/or a side chain thereof, a copolymer having an acidic group on the main chain and/or a side chain thereof, or a mixture of these polymers. Accordingly, the recording layer according to the invention has the properties for being dissolved when comes into contact with an alkali developer.

While the lower-recording layer in the planographic printing plate according to the invention includes, as the alkali-soluble resin, the above-described onium-containing resin (A) and specific acrylic resin (B) as essential components, the lower-recording layer may contain another alkali-soluble resin described below in addition to the onium-containing resin (A) and the specific acrylic resin (B), within the extent that the effects of the invention are not impaired.

Second Alkali-Soluble Polymer

[0088] The another alkali-soluble resin (hereinafter also referred to as a "second alkali-soluble polymer") that is used in the recording layer other than the lower recording layer (hereinafter also referred to as a "upper recording layer") in the invention and may be included in the lower recording layer if necessary is not specifically limited, as long as it is a conventionally known polymer. The polymer is preferably a polymer compound having in a molecule thereof at least one functional group selected from the group consisting of (1) a phenolic hydroxy group, (2) a sulfonamide group, and (3) an active imide group. Examples of the polymer compound include, but not limited to, those described below. Here, an alkali-soluble polymer compound (2) having a sulfonamide group described below encompassed in the "second alkali-soluble polymer" is a polymer having a structure different from that of the onium-containing resin (A).

[0089] Examples of the alkali-soluble polymer compound (1) having a phenolic hydroxy group include novolac resins such as a phenol formaldehyde resin, a m-cresol formaldehyde resin, a p-cresol formaldehyde resin, a mixed m-/p-cresol formaldehyde resin, and a mixed phenol/cresol (any of m-, p-, or mixed m-/p-) formaldehyde resin, and a pyrogallol-acetone resin. In addition, a polymer compound having a phenolic hydroxy group in a side chain thereof can be preferably

used as the polymer compound having a phenolic hydroxy group. Examples of the polymer compound having a phenolic hydroxy group in a side chain thereof include a polymer compound obtained by homopolymerizing a polymerizable monomer (a low-molecular weight compound) having, in one molecule thereof, at least one phenolic hydroxy group and at least one polymerizable unsaturated bond; and a polymer compound obtained by copolymerizing this polymerizable monomer with another polymerizable monomer.

[0090] Examples of the polymerizable monomer having at least one phenolic hydroxy group and at least one polymerizable unsaturated bond include an acrylamide having a phenolic hydroxy group, a methacrylamide having a phenolic hydroxy group, an acrylic ester having a phenolic hydroxy group, a methacrylic ester having a phenolic hydroxy group, and a hydroxystyrene having a phenolic hydroxy group. Specific examples of the polymerizable monomer that may be preferably used include N- (2- hydroxyphenyl) acrylamide, N- (3- hydroxyphenyl) acrylamide, N- (4- hydroxyphenyl) acrylamide, N- (2- hydroxyphenyl) methacrylamide, N- (3- hydroxyphenyl) methacrylamide, N- (4- hydroxyphenyl) methacrylamide, o- hydroxyphenylacrylate, m- hydroxyphenylacrylate, p- hydroxyphenylacrylate, o- hydroxyphenylmethacrylate, in- hydroxyphenylmethacrylate, p- hydroxyphenylmethacrylate, o- hydroxystyrene, m- hydroxystyrene, p- hydroxystyrene, 2- (2- hydroxyphenyl) ethylacrylate, 2- (3- hydroxyphenyl) ethylacrylate, 2- (4- hydroxyphenyl) ethylacrylate, 2- (2- hydroxyphenyl) ethylmethacrylate, 2- (3- hydroxyphenyl) ethylmethacrylate and 2- (4- hydroxyphenyl) ethylmethacrylate. In addition, a condensation polymer of phenol and formaldehyde having an alkyl group having 3 to 8 carbon atoms as a substituent, such as a t- butylphenol formaldehyde resin or an octylphenol formaldehyde resin as described in U.S. Patent No. 4, 123, 279 may be used in combination.

[0091] Examples of the alkali-soluble polymer compound (2) having a sulfonamide group include a polymer compound obtained by homopolymerizing a polymerizable monomer having a sulfonamide group; and a polymer compound obtained by copolymerizing this polymerizable monomer with another polymerizable monomer (but does not include the resin including a structural unit represented by Formula (I) and/or a structural unit represented by Formula (II)). Examples of the polymerizable monomer having a sulfonamide group include a polymerizable monomer (a low-molecular weight compound) having, in one molecule thereof, at least one polymerizable unsaturated bond and at least one sulfonamide group -NH-SO₂- in which at least one hydrogen atom is bonded to the nitrogen atom. Among these, a low-molecular weight compound having an acryloyl, aryl or vinyloxy group and a substituted or mono-substituted aminosulfonyl or substituted sulfonyl imino group is preferable.

[0092] The alkali- soluble polymer compound (3) having an active imide group is preferably those having an active imide group in the molecule thereof, and examples thereof include a polymer compound obtained by homopolymerizing a polymerizable monomer (a low- molecular weight compound) having, in one molecule thereof, at least one active imide group and at least one polymerizable unsaturated bond; and a polymer compound obtained by copolymerizing this polymerizable monomer with other polymerizable monomers. Specific examples of the polymer compound that can be preferably used include N- (p- toluenesulfonyl) methacrylamide, and N- (p- toluenesulfonyl) acrylamide.

[0093] Examples of the second alkali-soluble polymer that can be preferably used in the invention further include a polymer compound obtained by polymerizing two or more of polymerizable monomers selected from the group consisting of a polymerizable monomer having a phenolic hydroxy group, a polymerizable monomer having a sulfonamide group, and a polymerizable monomer having an active imide group; and a polymer compound obtained by copolymerizing two or more of these polymerizable monomers with another polymerizable monomer. When the polymerizable monomer having a sulfonamide group and/or the polymerizable monomer having an active imide group is copolymerized with the polymerizable monomer having a phenolic hydroxy group, the mass ratio of these components to be compounded is preferably in a range from 50:50 to 5:95, and more preferably in a range from 40:60 to 10:90.

[0094] In the invention, when the second alkali-soluble polymer is a copolymer of the polymerizable monomer having a phenolic hydroxy group, polymerizable monomer having a sulfonamide group and/or polymerizable monomer having an active imide group with another polymerizable monomer, such polymer contains an alkali-solubility-imparting monomer preferably in an amount of 10% by mole or more and, more preferably 20% by mole or more, in view of improving the alkali-solubility and development latitude of the precursor.

[0095] Examples of the another polymerizable monomer to be copolymerized with the polymerizable monomer having a phenolic hydroxy group, the polymerizable monomer having a sulfonamide group and/or the polymerizable monomer having an active imide group may include, but not limited to, compounds listed as the following (m1) to (m12)

(m1) (meth)acrylic esters having aliphatic hydroxy groups, such as 2-hydroxyethyl acrylate or 2-hydroxyethyl methacrylate;

(m2) alkyl acrylates, 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 methacrylates, 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) (meth) acrylamides, such as acrylamide, methacrylamide, N- methylol acrylamide, N- ethylacrylamide, N- hexylmethacrylamide, N- cyclohexylacrylamide, N- hydroxyethylacrylamide, N- phenylacrylamide, N- nitrophenylacrylamide and N- ethyl- N- phenylacrylamide;

[0096]

(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 butylate 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-vinylpyrrolidones, acrylonitriles and methacrylonitriles;

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

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

[0097] The second alkali-soluble polymer preferably has a phenolic hydroxy group in order to achieve excellent image formability by infrared laser exposure or the like. Examples the alkali-soluble polymer compound having a phenolic hydroxy group include a condensed copolymer of phenol and formaldehyde having an alkyl group having 3 to 8 carbon atoms as a substituent, such as a t-butylphenol formaldehyde resin or an octylphenol formaldehyde resin as described in US Patent No. 4,123,279.

[0098] As a method of copolymerizing the second alkali-soluble polymer, for example, a conventionally known graft copolymerization method, block copolymerization method or random copolymerization method may be used.

The second alkali-soluble polymer used in the upper recording layer is preferably a resin having a phenolic hydroxy group since it provides a strong hydrogen-bonding property in unexposed areas and easily releases a part of hydrogen bonds in exposed areas. The alkali-soluble polymer is more preferably a novolac resin. The alkali-soluble polymer preferably has a weight-average molecular weight of 500 to 20,000, and a number-average molecular weight of 200 to 10,000.

[0099] Examples of the alkali- soluble novolac resin used as the second alkali soluble polymer in the invention include alkali- soluble novolac resins such as a phenol formaldehyde resin, a xlenol cresol formaldehyde resin (3, 5-, 2, 3-, 2, 4-, or 2, 5- xlenol), a m- cresol formaldehyde resin, a p- cresol formaldehyde resin, a mixed m- /p- cresol formaldehyde resin and a mixed phenol/ cresol (any of m-, p- or mixed m- / p-) formaldehyde resin. The alkali- soluble novolac resins having a weight- average molecular weight of 500 to 20, 000 and a number- average molecular weight of 200 to 10, 000 can be used. Further, a condensation polymer of phenol and formaldehyde having an alkyl group having 3 to 8 carbon atoms as a substituent, such as a t- butylphenol formaldehyde resin or an octylphenol formaldehyde resin as described in U.S. Patent No. 4, 123, 279 may be used in combination.

[0100] It is preferable that the alkali-soluble novolac resin contains high proportion of a high-ortho novolac resin such as a xlenol cresol formaldehyde resin, a m-cresol formaldehyde resin or a p-cresol formaldehyde resin. More specifically, the alkali-soluble novolac resin contains the high-ortho novolac resin at an amount of preferably 10% by mass or more, and more preferably 30% by mass or more, with respect to a total mass of the whole novolac resin used in the alkali-soluble novolac resin.

[0101] Hereinbelow, respective compounds contained in the lower recording layer are explained.

Acid generator

The lower recording layer may contain an acid generator that is decomposed by the action of light or heat to generate an acid in order to improve the alkali solubility of the alkali- soluble resin in exposed areas.

Here, the "acid generator" indicates a compound that generates an acid by irradiation with light having a wavelength of 200 nm to 500 nm or by heating at 100°C or higher. Examples of the acid generator include known compounds that generate an acid by thermal decomposition, such as a photo initiator for photo- cationic polymerization, a photo initiator for photo- radical polymerization, a photo- achromatizing agent for dyes, a photo- discoloring agent and known acid generators used for micro- resist, and mixtures of these compounds. The acid generated from the acid generator is preferably a strong acid having a pKa of 2 or lower such as sulfonic acid and hydrochloric acid.

Preferable examples of the acid generator include triazine compounds such as those described in JP- A No. 11- 95415, and latent Bronsted acids such as those described in JP- A No. 7- 20629. Here, the latent Bronsted acid means a precursor that generates a Bronsted acid by decomposition. It is believed that the Bronsted acid can catalyze a matrix generating reaction between a resol resin and a novolac resin. Typical examples of the Bronsted acid suitable for this purpose include trifluoromethanesulfonic acid and hexafluorophosphonic acid.

[0102] Preferable examples of the acid generator further include ionic latent Bronsted acids, and examples thereof

include onium salts such as iodonium, sulfonium, phosphonium, selenonium, diazonium and arsonium salts. More specifically, preferable examples of the onium salt include diphenyliodonium hexafluorophosphate, triphenylsulfonium hexafluoroantimonate, phenylmethyl- ortho- cyanobenzylsulfonium trifluoromethane sulfonate and 2- methoxy- 4- aminophenyldiazonium hexafluorophosphate.

[0103] Preferable examples of the acid generator in the invention also include nonionic latent Bronsted acids, and examples thereof include compounds represented by the following formulae: RCH_2X , RCHX_2 , RCX_3 , $\text{R}(\text{CH}_2\text{X})_2$ and $\text{R}(\text{CH}_2\text{X})_3$ (wherein X represents Cl, Br, F or CF_3SO_3 ; and R represents an aromatic group, an aliphatic group or a combination of an aromatic group and an aliphatic group).

Examples of the useful ionic latent Bronsted acids include those represented by the following formula.

[0104]



[0105] In the above formula, when X represents iodine, R^3 and R^4 respectively represent a lone electron pair; and R^1 and R^2 each independently represent a unsubstituted aryl or group or a substituted aryl group. When X represents S or Se, R^4 represents a lone electron pair; and R^1 , R^2 and R^3 each independently represent a unsubstituted aryl group, a substituted aryl group, a unsubstituted aliphatic group, or a substituted aliphatic group. When X represents P or As, R^4 represent a unsubstituted aryl group, a substituted aryl group, a unsubstituted aliphatic group, or a substituted aliphatic group. W represents BF_4 , CF_3SO_3 , SbF_6 , CCl_3CO_2 , ClO_4 , AsF_6 , PF_6 or any corresponding acid having a pH value of less than 3. Any of the onium salts described in U.S. patent No. 4,708,925 may be used as the latent Bronsted acid used in the invention. Examples of these onium salts include iodonium, sulfonium, phosphonium, bromonium, chloronium, oxysulfoxonium, oxysulfonium, sulfoxonium, selenonium, telluronium and arsonium salts.

[0106] In the invention, a diazonium salt is preferably used as the latent Bronsted acid. The diazonium salt provides a sensitivity equivalent to that of other latent Bronsted acids in the infrared region and a higher sensitivity than that of the other latent Bronsted acids in the ultraviolet region.

[0107] From the viewpoint of image formability and in order to prevent scumming in non-image areas, the acid generator in the invention may be added to the lower recording layer at an amount of from 0.01% by mass to 50% by mass, preferably from 0.1% by mass to 2% by mass, and more preferably from 0.5% by mass to 20% by mass, with respect to a total solid content of the lower recording layer.

Infrared absorber

[0108] The positive-working recording layer in the invention contains an infrared absorber as a structural component having a light-to-heat converting function. The infrared absorber functions to convert absorbed infrared rays into heat and induce weakening of the interaction between binder molecules, decomposition of a developing inhibitor and generation of an acid upon scanning of the positive-working recording layer with laser, thereby significantly improving the solubility of the positive-working recording layer with respect to developer. Further, the infrared absorber itself may interact with the alkali-soluble resin to suppress the alkali-solubility.

When the infrared absorber is contained in the lower recording layer, it is thought that the infrared absorber is to be uniformly dispersed in a phase containing the homogeneously-mixed onium-containing resin (A) and specific acrylic resin (B), whereby the ability to cancel interaction is improved and, when an acid generator is contained, the ability to decompose the acid generator is improved.

The infrared absorber may also be added to the upper recording layer.

The infrared absorber used in the invention is a dye or pigment that efficiently absorbs infrared rays having a wavelength from 760 nm to 1,200 nm and preferably has an absorption maximum in a wavelength range from 760 nm to 1,200 nm.

[0109] Hereinbelow, the infrared absorber that can be preferably used for the planographic printing plate precursor of the invention is explained in detail.

Examples of dyes that can be used as the infrared absorber include commercially available dyes, and known dyes such as those described in "Dye Handbook" (edited by the Society of Synthesis Organic Chemistry, Japan, and published in 1970). Specific examples thereof include azo dyes, metal complex azo dyes, pyrazolone azo dyes, naphthoquinone dyes, anthraquinone dyes, phthalocyanine dyes, carbonium dyes, quinoneimine dyes, methine dyes, cyanine dyes, squarylium dyes, pyrylium dyes, and metal thiolate complexes.

[0110] Preferable examples of the dye include cyanine dyes such as those described in JP-A Nos. 58-125246, 59-84356, 59-202829, and 60-78787; methine dyes such as those described in JP-A Nos. 58-173696, 58-181690, and 58-194595; naphthoquinone dyes such as those described in JP-A Nos. 58-112793, 58-224793, 59-48187, 59-73996, 60-52940, and 60-63744; squarylium dyes such as those described in JP-A No. 58-112792; and cyanine dyes such as those described in GB Patent No. 434,875.

[0111] Other preferable examples of the dye include near infrared absorbing sensitizers such as those described in

U.S. Patent No. 5, 156, 938; substituted arylbenzo (thio) pyrylium salts such as those described in U.S. Patent No. 3, 881, 924; trimethinethiapyrylium salts such as those described in JP- A No. 57- 142645 (corresponding to U.S. Patent No. 4, 327, 169) ; pyrylium- base compounds such as those described in JP- A Nos. 58- 181051, 58- 220143, 59- 41363, 59- 84248, 59- 84249, 59- 146063, and 59- 146061; cyanine dyes such as those described in JP- A No. 59- 216146; pentamethinethiopyrylium salts such as those described in U.S. Patent No. 4, 283, 475; and pyrylium compounds such as those described in Japanese Patent Application Publication (JP- B) Nos. 5- 13514 and 5- 19702.

[0112] Preferable examples of the dye further include near infrared absorbing dyes represented by formula (I) or (II) in U.S. Patent No. 4,756,993.

Among these dyes, cyanine dyes, squarylium dyes, pyrylium salts, and nickel thiolate complexes are preferable.

[0113] The pigment used in the invention may be commercially available pigments and pigments such as those described in Color Index (C.I.) Handbook, "Latest Pigment Handbook" (edited by Japan Pigment Technique Association, and published in 1977), "Latest Pigment Application Technique" (by CMC Publishing Co., Ltd. in 1986), and "Printing Ink Technique" (by CMC Publishing Co., Ltd. in 1984).

[0114] 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. Specific examples of the pigment that can be used include insoluble azo pigments, azo lake pigments, condensed azo pigments, chelate azo pigments, phthalocyanine pigments, anthraquinone pigments, perylene and perynone pigments, thioindigo pigments, quinacridone pigments, dioxazine pigments, isoindolinone pigments, quinophthalone pigments, dyeing lake pigments, azine pigments, nitroso pigments, nitro pigments, natural pigments, fluorescent pigments, inorganic pigments, and carbon black.

[0115] These pigments may be used with or without surface treatment of the pigment particles. Examples of a method of the surface treatment include a method of coating the surface of the pigment particles with resin or wax; a method of adhering a surfactant onto the surface of the pigment particles; and a method of bonding a reactive material (such as a silane coupling agent, an epoxy compound, or a polyisocyanate) to the surface of the pigment particles. These 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 Application Technique" (by CMC Publishing Co., Ltd. in 1986).

[0116] The particle size of the pigment is preferably from 0.01 μm to 10 μm , more preferably from 0.05 μm to 1 μm , and even more preferably from 0.1 μm to 1 μm from the viewpoint of the stability of a recording layer coating liquid and the uniformity of the recording layer to be formed.

[0117] As the method of dispersing pigment, any known dispersing techniques used to produce ink or toner can be used. Examples of a machine that can be used for the dispersing pigment 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 Application Technique" (published by CMC Publishing Co., Ltd. in 1986).

[0118] Since the planographic printing plate precursor of the invention is a positive-working recording layer, it is preferable to use an infrared absorber that can interact with a binder polymer having a specific functional group to exert positive-working functions (that is, functions to inhibit the dissolution of unexposed areas in an alkali developer and cancel the dissolution inhibiting effect in exposed areas) to the recording layer. To this end, it is preferable that the infrared absorber has an onium salt structure. More specifically, among these infrared absorbers, cyanine dyes and pyrylium salts are more preferable. The details of the cyanine dye and pyrylium salt are described above.

[0119] In addition, an anionic infrared absorber as described in JP- A No. 11- 338131 can also be preferably used. This anionic infrared absorber has, as the mother nucleus thereof that substantially absorbs infrared rays, an anionic structure but not has a cationic structure.

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

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

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

Examples of the infrared absorber further include anionic infrared absorbers represented by the formula $[\text{Ga}^- - \text{M} - \text{Gb}]_m \text{X}^{m+}$ wherein Ga^- represents an anionic substituent, Gb represents a neutral substituent, and X^{m+} represents a cation having a valence of 1 to m (where m represents an integer of from 1 to 6) including a proton, as described in paragraphs [0014] to [0105] of JP- A No. 11- 338131.

[0120] The infrared absorber is preferably a dye, and preferable examples thereof include a dye having an onium salt structure as described in paragraphs [0018] to [0034] of JP-A No. 11-291652.

[0121] For the purpose of further improving the sensitivity and developing latitude, the above described infrared absorber exhibiting dissolution inhibiting effect, such as the cyanine dye, pyrylium salt dye or anionic dye, may be used in combination with another dye or pigment in the recording layer of the planographic printing plate precursor.

[0122] From the viewpoint of the image formability and in order to prevent scumming in non-image areas, the content

of the infrared absorber in the lower recording layer is preferably from 0.01% by mass to 50% by mass, more preferably from 0.1% by mass to 20% by mass, and still more preferably from 0.5% by mass to 15% by mass, with respect to a total solid content of the lower recording layer. From the viewpoint of the image formability and in order to prevent scumming in non-image areas, the content of the infrared absorber in the upper recording layer is preferably from 0.01

% by mass to 50% by mass, more preferably from 0.1% by mass to 20% by mass, and still more preferably from 0.5% by mass to 15% by mass, with respect to a total solid content of the another recording layer.

[0123] The recording layer of the planographic printing plate precursor of the invention is required to have abrasion resistance in relation to an infrared laser irradiation system. From the viewpoint of preventing abrasion, any polymer material may be used as a binder contained in the upper recording layer that functions as a light-receiving surface, as long as its solubility to an aqueous alkali (i.e., an alkali developer) is changed by thermal energy imparted thereto. From the viewpoint of availability and abrasion resistance, it is preferable to use a polymer that is insoluble in water but soluble in aqueous alkali solution.

[0124] The ceiling temperature of the polymer is given as an example of an index of the abrasion resistance. This ceiling temperature is a temperature at which, in a polymerization reaction of a vinyl compound or the like, the rate of a polymerization reaction is equal to the rate of a depolymerization reaction. It is preferable to select a polymer having a high ceiling temperature to obtain high abrasion resistance. As a simple method, a proper polymer may be selected using the decomposition temperature thereof as an index.

In the invention, the polymer that is a component of the recording layer may be a polymer having a decomposition temperature of preferably 150°C or higher, and more preferably 200°C or higher. The decomposition temperature 150°C or higher is preferable since the possibility of abrasion is decreased. It is preferable that each component other than the polymer compound contained in the recording layer has a decomposition temperature of 150°C or higher. However, a small amount of a component having a decomposition temperature lower than 150°C may also be contained as long as it does not cause substantial problem.

[0125] In addition to the components described above, a wide variety of known additives can be used in the positive-working recording layer of the planographic printing plate precursor of the invention in accordance with the intended use. Among plural recording layers, when the lower recording layer contains an infrared absorber, the lower recording layer is required to contain the onium-containing resin (A) and the specific acrylic resin (B) together with the infrared absorber. However, with regard to other additives, the additives similar to those to be added to the upper recording layer can be used for the lower recording layer.

Other additive

[0126] It is preferable to add a fluorine-containing polymer to each of the recording layers of the invention for the purpose of improving the developer resistance in image areas. Examples of the fluorine-containing polymer to be added to the recording layer include copolymers formed from fluorine-containing monomers such as those described in JP-A Nos. 11-288093 and 2000-187318.

[0127] Preferable examples of the fluorine-containing polymer include fluorine-containing acryl polymers P-1 to P-13 described in JP-A No. 11-288093; and fluorine-containing polymers obtained by copolymerizing any of fluorine-containing acryl monomers A-1 to A-33 described in JP-A No. 2000-187318 with any acryl monomers.

[0128] The fluorine-containing polymer exemplified above preferably has a weight-average molecular weight of 2,000 or more and a number-average molecular weight of 1,000 or more. It is more preferable that fluorine-containing polymer has a weight-average molecular weight of 5,000 to 300,000 and a number-average molecular weight of 2,000 to 250,000.

[0129] Commercially available fluorine surfactants having the preferable molecular weight may be used as the fluorine-containing polymer. Specific examples of such surfactants include MEGAFACE F-171, F-173, F-176, F-183, F-184, F-780 and F-781 (all are trade names, manufactured by DIC Corporation).

[0130] The fluorine-containing polymer may be used singly or in combination of two or more kinds thereof.

The amount of the fluorine-containing polymer to be added is 1.4% by mass or more, with respect to a solid content of the recording layer. The amount is preferably from 1.4% by mass to 5.0% by mass. When the amount is 1.4% by mass or more, the effect of improving the development latitude of the recording layer, which is the purpose of the addition of the fluorine-containing polymer, can be obtained. Even if the fluorine-containing polymer is added in an amount exceeding 5.0% by mass, the effect of improving the development latitude cannot be fully exerted, and there is a possibility that the surface of the recording layer may become hardly-soluble under the influence of the fluorine-containing polymer, thereby decreasing the sensitivity of the recording layer.

Dissolution Inhibitor

[0131] A thermally decomposable material (dissolution inhibitor) capable of substantially decreasing the solubility of the alkali-soluble polymer compound in the undecomposed state may be added to the lower recording layer or the upper

recording layer of the planographic printing plate precursor of the invention if necessary. Examples of the dissolution inhibitor include a low molecular weight onium salt compound, o-quinonediazide compound, aromatic sulfone compound and aromatic sulfonate compound. The addition of the dissolution inhibitor improves the dissolution inhibiting property of the image area in a developer, and allows the use, as an infrared absorber, of a compound that does not interact with the alkali-soluble resin. Examples of the onium salt used as an infrared absorber of the invention includes onium salt compounds having a lower molecular weight than that of the onium-containing resin (A), and specific examples thereof include diazonium salts (other than the onium-containing resin (A)) having a molecular weight of 1,000 or less, ammonium salts, phosphonium salts, iodonium salts, sulfonium salts, selenonium salts, arsonium salts and azinium salts.

[0132] Preferable examples of the low-molecular-weight onium salt used in the invention include diazonium salts such as those described in S. 1. Schlesinger, *Photogr. Sci. Eng.*, 18, 387 (1974), T. S. Bal et al., *Polymer*, 21, 423 (1980), and JP-A No. 5-158230; ammonium salts such as those described in U.S. Patent Nos. 4,069,055 and 4,069,056, and JP-A No. 3-140140; phosphonium salts such as those described in D. C. Necker et al., *Macromolecules*, 17, 2468 (1984), C. S. Wen et al., *Tech. Proc. Conf. Rad. Curing ASIA*, pp478 Tokyo, Oct (1988), and U.S. Patent Nos. 4,069,055 and 4,069,056; and iodonium salts such as those described in J. V. Crivello et al., *Macromolecules*, 10 (6), 1307 (1977), *Chem. & Eng. News*, Nov. 28, pp31 (1988), EP No. 104,143, U.S. Patent Nos. 5,041,358 and 4,491,628, and JP-A Nos. 2-150848 and 2-296514.

[0133] Preferable examples of the low-molecular-weight onium salt further include sulfonium salts such as those described in J. V. Crivello et al., *Polymer J.* 17, 73 (1985), J. V. Crivello et al., *J. Org. Chem.*, 43, 3055 (1978), W. R. Watt et al., *J. Polymer Sci., Polymer Chem. Ed.*, 22, 1789 (1984), J. V. Crivello et al., *Polymer Bull.*, 14, 279 (1985), J. V. Crivello et al., *Macromolecules*, 14 (5), 1141 (1981), J. V. Crivello et al., *J. Polymer Sci., Polymer Chem. Ed.*, 17, 2877 (1979), EP Nos. 370,693, 233,567, 297,443 and 297,442, U.S. Patent Nos. 4,933,377, 3,902,114, 4,491,628, 5,041,358, 4,760,013, 4,734,444 and 2,833,827, and DE Patent Nos. 2,904,626, 3,604,580 and 3,604,581; selenonium salts such as those described in J. V. Crivello et al., *Macromolecules*, 10 (6), 1307 (1977), and J. V. Crivello et al., *J. Polymer Sci., Polymer Chem. Ed.*, 17, 1047 (1979); and arsonium salts such as those described in C. S. Wen et al., and *The Proc. Conf. Rad. Curing ASIA*, pp478, Tokyo, Oct (1988).

[0134] A diazonium salt is preferably used as the dissolution inhibitor, and specific examples of the diazonium salt include those described in JP-A No. 5-158230.

Preferable examples of a counter ion of the onium salt include tetrafluoroboric acid, hexafluorophosphoric acid, triisopropylphenylsulfonic 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 triisopropylphenylsulfonic acid and 2,5-dimethylbenzenesulfonic acid are preferable.

[0135] Preferable examples of the quinonediazide include an o-quinonediazide compound. The o-quinonediazide compound used in the invention is a compound having at least one o-quinonediazide group, whose alkali-solubility is increased by thermal decomposition, and compounds having various structures may be used as the o-quinonediazide compound. In other words, the o-quinonediazide compound increases the solubility of the photosensitive system both by being thermally decomposed to lose the dissolution inhibiting ability with respect to a binder and by itself being changed to an alkali-soluble material.

The o-quinonediazide compound used in the invention is preferably a compound described in J. Koser, "Light-Sensitive Systems" (John Wiley & Sons, Inc.), pp. 339-352, and more preferably a sulfonic acid ester or sulfonamide of o-quinonediazide formed by reacting with an aromatic polyhydroxylate compound or with an aromatic amino compound. Preferable examples of the o-quinonediazide compound further include an ester of benzoquinone-(1,2)-diazidesulfonic acid chloride or naphthoquinone-(1,2)-diazide-5-sulfonic acid chloride and a pyrogallol-acetone resin, as described in JP-B No. 43-28403; and an ester of benzoquinone-(1,2)-diazidesulfonic acid chloride or naphthoquinone-(1,2)-diazide-5-sulfonic acid chloride and a phenol-formaldehyde resin such as those described in US Patent Nos. 3,046,120 and 3,188,210.

[0136] Preferable examples of the o-quinonediazide compound further include an ester of naphthoquinone-(1,2)-diazide-4-sulfonic acid chloride and a phenol-formaldehyde resin or cresol-formaldehyde resin; and an ester of naphthoquinone-(1,2)-diazide-4-sulfonic acid chloride and a pyrogallol-acetone resin. Other useful o-quinonediazide compounds are reported in unexamined or examined patent documents, examples of which include JP-A Nos. 47-5303, 48-63802, 48-63803, 48-96575, 49-38701 and 48-13354, JP-B Nos. 41-11222, 45-9610 and 49-17481, U.S. Patent Nos. 2,797,213, 3,454,400, 3,544,323, 3,573,917, 3,674,495 and 3,785,825, GB Patent Nos. 1,227,602, 1,251,345, 1,267,005, 1,329,888 and 1,330,932, and DE Patent No. 854,890.

[0137] The addition amount of the o-quinonediazide compound is preferably from 1% by mass to 50% by mass, more preferably from 5% by mass to 30% by mass, and still more preferably from 10% by mass to 30% by mass, with respect to a total solid content of each recording layer. These compounds may be used singly or in combination of two or more

kinds thereof.

The addition amount of the additives other than the o-quinonediazide compound is preferably from 1% by mass to 50% by mass, more preferably from 5% by mass to 30% by mass, and particularly preferably from 10% by mass to 30% by mass. The additives and the alkali-soluble resin used in the invention are preferably contained in the same layer.

Cyclic Acid Anhydride, Phenolic Compound, Organic Acid

[0138] In order to further increase the sensitivity, the recording layer may further contain a cyclic acid anhydride, a phenolic compound, an organic acid or the like.

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

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

Examples of the organic acid include sulfonic acids, sulfonic acids, alkylsulfuric acids, phosphonic acids, phosphates, and carboxylic acids, such as those described in JP- A Nos. 60- 88942 and 2- 96755. Specific examples thereof include p- toluenesulfonic acid, dodecylbenzenesulfonic acid, p- toluenesulfonic acid, ethylsulfuric acid, phenylphosphonic acid, phenylphosphinic acid, phenyl phosphate, diphenyl phosphate, benzoic acid, isophthalic acid, adipic acid, p- toluic acid, 3, 4- dimethoxybenzoic acid, phthalic acid, terephthalic acid, 4- cyclohexene- 1, 2- dicarboxylic acid, erucic acid, lauric acid, n- undecanoic acid and ascorbic acid.

The total content of the cyclic acid anhydrides, the phenols or the organic acids in the recording layer of the planographic printing plate precursor is preferably from 0.05% by mass to 20% by mass, more preferably from 0.1% by mass to 15% by mass, and still more preferably from 0.1% by mass to 10% by mass, with respect to a total solid content of the recording layer.

Colorant

[0139] A dye having a strong absorption in the visible region of the spectrum may be added to each recording layer according to the invention as a colorant for an image. Specific examples of the dye include Oil Yellow #101, Oil Yellow #103, Oil Pink #312, Oil Green BG, Oil Blue BOS, Oil Blue #603, Oil Black BY, Oil Black BS and Oil Black T- 505 (all manufactured by Orient Chemical Industries, Ltd.), Victoria Pure Blue, Crystal Violet (CI42555), Methyl Violet (CI42535), Ethyl Violet, Rhodamine B (CI145170B), Malachite Green (CI42000), Methylene Blue (CI52015), AIZEN SPILON BLUE C- RH (manufactured by Hodogaya Chemical Co., Ltd.), and dyes such as those described in JP- A No. 62- 293247.

[0140] The addition of dyes is preferable since image areas can be clearly discriminated from non-image areas after image formation. The amount of the dye to be added is preferably from 0.01% by mass to 10% by mass, with respect to a total solid content of the recording layer.

Surfactant

[0141] In order to broaden the latitude of the processing stability in development, the recording layer of the invention may contain a surfactant, and examples thereof include nonionic surfactants such as those described in JP-A Nos. 62-251740 and 3-208514, amphoteric surfactants such as those described in JP-A Nos. 59-121044 and 4-13149, siloxane compounds such as those described in EP No. 950517, and copolymers of fluorine-containing monomers such as those described in JP-A No. 11-288093.

[0142] Specific examples of nonionic surfactants include sorbitan tristearate, sorbitan monopalmitate, sorbitan trioleate, stearyl monoglyceride and polyoxyethylene nonyl phenyl ether. Specific examples of amphoteric surfactants include an alkylid (arninoethyl) glycine, an alkylpolyaminoethylglycine hydrochloride, 2- alkyl- N- carboxyethyl- N- hydroxyethylimidazolium betaine and N- tetradecyl- N, N- betaine type surfactants (such as AMOGEN K; trade name, manufactured by Dai- ichi Kogyo Seiyaku Co., Ltd.) . The siloxane compound is preferably a block copolymer of dimethylsiloxane and a polyalkylene oxide. Specific examples thereof include polyalkylene oxide modified silicones such as DBE- 224, DBE- 621, DBE- 712, DBP- 732 and DBP- 534 (all manufactured by Chisso Corporation) or TEGO GLIDE 100 (manufactured by Evonik Tego Chemie GmbH, Germany) .

The total content of the nonionic surfactant and the amphoteric surfactant is preferably from 0.05% by mass to 15% by mass, and more preferably from 0.1% by mass to 5% by mass, with respect to a total solid content of the recording layer.

Printing-out Agent

[0143] The planographic printing plate precursor of the invention may further contain a printing-out agent to immediately form a visible image after the heating caused by exposure, and/or a dye or pigment for coloring images. Typical examples of the printing-out agent include a combination of a compound (photo-acid generator) that releases an acid as a result of heating caused by exposure and an organic dye that can form a salt with the photo-acid generator.

[0144] Specific examples the combination include a combination of an o- naphthoquinonediazide- 4- sulfonic acid halogenide with a salt- formable organic dye, as described in JP- A Nos. 50- 36209 and 53- 8128; and a combination of a trihalomethyl compound with a salt- formable organic dye, as described in each of JP- A Nos. 53- 36223, 54- 74728, 60- 3626, 61- 143748, 61- 151644 and 63- 58440. The trihalomethyl compound includes an oxazole compound and a triazine compound, and both compounds have an excellent temporal stability and produce a clear print- out image. Examples of the photo- acid releasing agent further include various o- naphthoquinonediazide compounds such as those described in JP- A No. 55- 62444, 2- trihalomethyl- 5- aryl- 1, 3, 4- oxadiazole compound such as those described in JP- A No. 55- 77742, and diazonium salts.

Plasticizer

[0145] A plasticizer may be added to a recording layer coating liquid of the invention in order to impart flexibility or the like to a coated film. Examples thereof include butyl phthalyl, polyethylene glycol, tributyl citrate, diethyl phthalate, dibutyl phthalate, dihexyl phthalate, dioctyl phthalate, tricresyl phosphate, tributyl phosphate, trioctyl phosphate, tetrahydrofurfuryl oleate, oligomers and polymers of acrylic acid or methacrylic acid.

Method of Producing Planographic Printing Plate Precursor

[0146] Hereinbelow, the method of producing the planographic printing plate precursor of the invention is described. In the invention, the lower recording layer is first formed on a hydrophilic substrate. The lower recording layer may be suitably formed by dissolving and dispersing the onium- containing resin (A) and the specific acrylic resin (B), and optionally the infrared absorber and another component, in an appropriate solvent to prepare a lower recording layer coating composition, and coating the substrate therewith and dried.

[0147] Examples of the solvent suitably used for coating a recording layer include, but not limited to, ethylene dichloride, cyclohexanone, methyl ethyl ketone, methanol, ethanol, propanol, ethylene glycol monomethyl ether, 1- methoxy- 2- propanol, 2- methoxyethyl acetate, 1- methoxy- 2- propyl acetate, dimethoxyethane, methyl lactate, ethyl lactate, N, N- dimethylacetamide, N, N- dimethylformamide, tetramethyl urea, N- methylpyrrolidone, dimethylsulfoxide, sulfolane, γ - butyrolactone and toluene. These solvents may be used singly or in a combination of two or more kinds thereof. The concentration of the above components (total solid content including additives) in the solvent is preferably from 1% by mass to 50% by mass.

[0148] The lower recording layer and the upper recording layer (another recording layer) are in principle preferably formed as respective separate layers.

[0149] Examples of a method for forming two separate layers include, but not limited to, a method in which a difference in solvent solubility between components contained in the lower recording layer and components contained in the upper recording layer is utilized; and a method in which, after an upper recording layer is applied, the solvent is rapidly removed by drying. The latter method is a method in which a solvent contained in the upper recording layer is rapidly removed before the solvent exerts any influence such as by dissolving a part of the lower recording layer that has already been formed, thereby suppressing dissolution of the interface between the layers.

[0150] As the method in which a difference in solvent solubility between components contained in the lower recording layer and components contained in the upper recording layer is utilized, a solvent system in which all of the components contained in the lower recording layer are insoluble is used when applying an upper recording layer coating solution. This enables each layer to be formed in a clearly separated manner even when carrying out two- layer coating.

For example, as a component for a lower recording layer, a component insoluble for a solvent that can dissolve an alkali- soluble resin (upper layer component) such as methyl ethyl ketone, diethyl ketone, or 1- methoxy- 2- propanol is selected. Two layers may be formed by coating a lower recording layer using a solvent system that can dissolve a component in the lower recording layer and drying the resultant, and then coating an upper recording layer component mainly containing an alkali- soluble resin and being dissolved in methyl ethyl ketone, diethyl ketone, 1- methoxy- 2- propanol, or the like, and drying the resultant.

[0151] When a method of using a solvent that does not dissolve an alkali-soluble resin in the lower recording layer is used for applying a upper recording layer coating liquid, a mixed solvent of the solvent that does not dissolve an alkali-soluble resin and a solvent that can dissolve an alkali-soluble resin in the lower recording layer may be used as the upper recording layer coating liquid. The interlayer mixing between the upper recording layer and the lower recording

layer can be arbitrarily controlled by changing the mixing ratio of the both solvents. When the proportion of the solvent that can dissolve an alkali-soluble resin in the lower recording layer is increased, a part of the lower recording layer is dissolved upon application of the upper recording layer to form a particle-shape component that will be contained in the upper recording layer after being dried. The particle-shape component forms projections on the surface of the upper recording layer, thereby improving scratch resistance. On the other hand, components in the lower recording layer eluted into the upper recording layer tend to deteriorate the layer quality and chemical resistance of the lower recording layer. Thus, by controlling of the mixing ratio in consideration of physical properties for each layer, various characteristics can be exhibited, and further, partial compatibility between the layers can be achieved as described hereinafter.

[0152] In view of the effect of the invention, when the mixed solvent as described above is used as a solvent for the upper recording layer coating liquid, the amount of a solvent that can dissolve the onium containing resin (A) and the specific acrylic resin (B) in the lower recording layer is preferably 80% by mass or less with respect to a total mass of a solvent used to the upper recording layer coating liquid from the viewpoint of chemical resistance, and more preferably from 10% by mass to 60% by mass by taking into account of scratch resistance.

[0153] The method of drying a solvent extremely rapidly after application of a second layer (i.e., an upper recording layer) may be performed by blowing a high-pressure air through a slit nozzle provided in the direction approximately perpendicular to the running direction of a web; or by applying a heat energy as a conductive heat to a web from the under surface of the web using a roll (heating roll) in which a heating medium such as steam is provided; or by a combination of these methods.

As a method for applying a recording layer coating solution, various methods may be used, and examples thereof include bar coater coating, spin coating, spray coating, curtain coating, dip coating, air knife coating, blade coating, and roll coating. In particular, the upper recording layer coating method is preferably a non-contact method since it can prevent damage to the lower recording layer when applying the upper recording layer. Furthermore, although it is a contact method, it is possible to use bar coater coating as a method that is normally used for solvent system coating, and it is preferable to carry out coating in direct roll drive mode in order to prevent damage to the lower recording layer.

[0154] The dry coat weight of the lower recording layer in the planographic printing plate precursor is preferably from 0.5 g/m² to 2.0 g/m², and more preferably from 0.7 g/m² to 1.5 g/m², in order to obtain sufficient printing durability and improve the dissolution discrimination in the development.

[0155] The dry coat weight of the another recording layer (the upper recording layer) is preferably from 0.05 g/m² to 1.0 g/m², and more preferably from 0.07 g/m² to 0.7 g/m². When the upper recording layer is formed by two or more layers, the coating amount is the total coating amount thereof.

[0156] A surfactant such as a fluorine-based surfactant as described in JP-A No. 62-170950 may be added to a upper recording layer coating liquid and/or the upper recording layer in the invention to improve coating characteristics. The amount of the surfactant is preferably from 0.01% by mass to 1% by mass, and more preferably from 0.05% by mass to 0.5% by mass, with respect to a total solid content of the coating liquid.

Substrate

[0157] The substrate is not particularly limited as long as it is a plate-shaped material having dimensional stability, and examples thereof include paper, paper laminated with a plastic (e.g. polyethylene, polypropylene, polystyrene, etc.), a metal plate (e.g. aluminum, zinc, copper, etc.), a plastic film (e.g. cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose butyrate, cellulose acetate butyrate, cellulose nitrate, polyethylene terephthalate, polyethylene, polystyrene, polypropylene, polycarbonate, polyvinyl acetal, etc.), and paper or plastic film laminated or vapor-deposited with the above-mentioned metal.

[0158] The substrate that can be used in the invention is preferably a polyester film or an aluminum plate, and more preferably an aluminum plate since it has a favorable dimension stability and is relatively inexpensive. Examples of a suitable aluminum plate include a pure aluminum plate, and an alloy plate containing aluminum as a main component and a trace amount of another element; and a plastic film laminated or vapor-deposited with aluminum. Examples of other elements that may be contained in the aluminum alloy include silicon, iron, manganese, copper, magnesium, chromium, zinc, bismuth, nickel, and titanium. The content of other elements in the alloy is preferably 10% by mass or less.

A particularly preferable aluminum in the invention is pure aluminum, but since it is difficult to produce a completely pure aluminum in terms of refining techniques, it may contain a trace amount of another element.

Such an aluminum plate applied to the invention is not specified in terms of composition, and an aluminum plate formed from a conventionally known, widely used material may appropriately be used. The aluminum plate used in the invention preferably has a thickness of from 0.1 mm to 0.6 mm, more preferably from 0.15 mm to 0.4 mm, and still more preferably from 0.2 mm to 0.3 mm.

Here, in the invention, at least a surface of the substrate on which a recording layer is to be formed is require to be hydrophilic. Since an aluminum substrate whose surface has been roughened has a relatively high hydrophilicity, a surface hydrophilization treatment thereof does not necessarily required. However, it is preferable to conduct an appro-

appropriate surface hydrophilization treatment as described below even when any of the above described substrate (i.e., the aluminum substrate) is used, from the view point of improving the quality of printed material.

[0159] When an aluminum plate is used as the substrate, it is preferable to conduct a surface treatment such as a surface roughening treatment or an anodizing process.

Prior to roughening the surface of the aluminum plate, if desired, a degreasing treatment with, for example, a surfactant, an organic solvent, or an aqueous alkaline solution is carried out in order to remove rolling oil from the surface. The treatment to roughen the surface of the aluminum plate may be carried out by various methods such as, for example, a method involving mechanical roughening, a method involving electrochemical dissolution-roughening of the surface, and a method involving selective chemical dissolution of the surface. As the mechanical method, a known method such as a ball grinding method, a brush grinding method, a blast grinding method, or a buff grinding method can be employed. With regard to the electrochemical roughening method, there is a method in which alternating current or direct current is used in a hydrochloric acid or nitric acid electrolytic solution. As disclosed in JP-A-54-63902, a method in which the two methods are combined can also be employed.

The aluminum plate whose surface has been roughened is optionally subjected to an alkali etching treatment and a neutralizing treatment if necessary, and then, if desired, to an anodizing treatment in order to improve the water retention and the abrasion resistance of the surface. As the electrolyte used for the anodizing treatment of the aluminum plate, various electrolytes for forming a porous anodized film can be used, and in general, sulfuric acid, phosphoric acid, oxalic acid, chromic acid, or a mixture of these acids is used. The concentration of the electrolyte is determined appropriately according to the type of the electrolyte.

[0160] The conditions for anodizing treatment depend on the type of electrolyte used and cannot, as a rule, be fixed but in general an electrolyte concentration of from 1% by mass to 80% by mass, a solution temperature of from 5°C to 70°C, a current density of from 5 A/dm² to 60 A/dm², a voltage of from 1 V to 100 V, and an electrolysis time of from 10 seconds to 5 minutes are preferable. The amount of anodized coating is preferably 1.0 g/m² or more. When the amount of anodized coating is 1.0 g/m² or more, the printing durability is excellent, the non-image areas of the lithographic printing plate become resistant to scratching, and the so-called "scratch staining", which is caused by ink becoming attached to scratched areas during printing, can be suppressed.

[0161] After being subjected to the anodizing treatment, the surface of the aluminum is subjected to a hydrophilization treatment, if necessary. With regard to the hydrophilization treatment employed in the invention, there are methods employing an alkali metal silicate (for example, an aqueous solution of sodium silicate) as disclosed in U.S. Patent Nos. 2,714,066, 3,181,461, 3,280,734 and 3,902,734. In these methods, the substrate is immersed in an aqueous solution of sodium silicate or subjected to electrolysis. It is also possible to employ a method involving treatment with potassium fluorozirconate as disclosed in JP-B No. 36-22063, or with polyvinyl phosphonic acid as disclosed in U.S. Patent Nos. 3,276,868, 4,153,461 and 4,689,272.

[0162] The planographic printing plate precursor of the invention is provided on a substrate at least two layer of the lower recording layer and another recording layer (the upper recording layer), and an undercoat layer may be provided if necessary between the substrate and the lower recording layer.

[0163] As undercoat layer components, various organic compounds may be used, and it may be selected among carboxymethylcellulose; dextrin; gum arabic; an amino group-containing phosphonic acid such as 2-aminoethylphosphonic acid; substituted or unsubstituted organic phosphonic acids such as phenyl phosphonic acid, naphthylphosphonic acid, an alkylphosphonic acid, glycerophosphonic acid, methylenediphosphonic acid, and ethylenediphosphonic acid; substituted or unsubstituted organic phosphoric acids such as phenylphosphoric acid, naphthylphosphoric acid, an alkylphosphoric acid, and glycerophosphoric acid; substituted or unsubstituted organic phosphinic acids such as phenylphosphinic acid, naphthylphosphinic acid, an alkylphosphinic acid, and glycerophosphinic acid; amino acids such as glycine and β -alanine; and a hydroxy group-containing amine hydrochloride such as triethanolamine hydrochloride. These undercoat layer components may be used singly or in combination of two or more kinds thereof.

[0164] The organic undercoat layer may be provided by the following method. That is, there is a method in which a solution formed by dissolving the above-mentioned organic compound in water, an organic solvent such as methanol, ethanol or methyl ethyl ketone, or a mixed solvent thereof is applied onto an aluminum plate and dried; or a method in which an aluminum plate is immersed in a solution formed by dissolving the above-mentioned organic compound in water, an organic solvent such as methanol, ethanol, methyl ethyl ketone, or a mixed solvent thereof so as to make the above-mentioned compound adsorb thereon, followed by washing with water or the like and drying to provide an organic undercoat layer. In the former method, a solution of the organic compound at a concentration of from 0.005% by mass to 10% by mass may be applied by various methods. In the latter method, the concentration of the solution is preferably from 0.01% by mass to 20% by mass, more preferably from 0.05% by mass to 5% by mass, the immersion temperature is preferably from 20°C to 90°C, more preferably from 25°C to 50°C, and the immersion time is preferably from 0.1 second to 20 minutes, more preferably from 2 seconds to 1 minute.

The pH of the solution used therefor can be adjusted by a basic substance such as ammonia, triethylamine, or potassium hydroxide, or an acidic substance such as hydrochloric acid or phosphoric acid so that the pH is in the range of 1 to 12.

A yellow dye may be added to the solution, in order to improve the tone reproduction properties of the image recording material.

[0165] The coverage of the organic undercoat layer is suitably from 2 mg/m² to 200 mg/m², and is preferably from 5 mg/m² to 100 mg/m², from the view point of the printing durability. When the coverage is in the above range, sufficient printing durability can be obtained.

[0166] The positive-working planographic printing plate precursor produced as described above is usually subjected to an imagewise exposure and a development treatment.

In the invention, the planographic printing plate precursor is exposed to light from a light source that preferably has an emitting wavelength in the near-infrared region to the infrared region. Specifically, a light source used for image-wise exposure of the planographic printing plate precursor is preferably a solid laser or a semiconductor laser having an emission wavelength in the near-infrared region of from 760 nm to 1,200 nm.

[0167] The planographic printing plate precursor of the invention is subjected to a development treatment using water or an alkali developer after exposure. The development treatment may be carried out immediately after exposure, and a heat treatment may be carried out between an exposure step and a development step. When the heat treatment is carried out, the heating is preferably carried out at 60°C to 150°C for 5 seconds to 5 minutes. As the heating method, conventionally known various methods may be used. Examples of the heating method include a method in which a recording material is heated with being in contact with a panel heater or ceramic heater; and a non-contact method by means of a lamp or hot air. This heat treatment enables the energy required for recording to be reduced at the time when the laser is irradiated.

[0168] The planographic printing plate precursor of the invention has excellent post-exposure stability and thus deterioration in developability over a certain period of time after exposure is suppressed. Accordingly, the plate precursor after exposure may be subjected to a development step after the storing step of storing it for a certain period of time after the exposure.

The plate precursor after exposure may be accumulated until a predetermined amount is obtained, and then the accumulated and stored plates after exposure may be sequentially subjected to the development process.

In the storing step of storing the exposed planographic printing plate precursor, the plate may be stored for 1 to 3 hours after exposure. In the planographic printing plate precursor of the invention, even after being subject to the storing step in these conditions, a practically problematic deterioration in developability is scarcely observed.

[0169] Any conventionally known aqueous alkali solution may be used as a developer and replenisher to be used for platemaking from the planographic printing plate precursor of the invention.

The developer that can be used for the development treatment of the planographic printing plate precursor of the invention is a developer having a pH of from 9.0 to 14.0, preferably a pH of from 12.0 to 13.5. A conventionally known aqueous alkali solution may be used as the developer (hereinafter the developer and the replenisher are collectively referred to as the "developer"). Examples of the developer include inorganic alkali salts such as sodium silicate, potassium silicate, trisodium phosphate, tripotassium phosphate, triammonium phosphate, disodium hydrogenphosphate, dipotassium hydrogenphosphate, diammonium hydrogenphosphate, sodium carbonate, potassium carbonate, ammonium carbonate, sodium hydrogencarbonate, potassium hydrogencarbonate, ammonium hydrogen carbonate, sodium borate, potassium borate, ammonium borate, sodium hydroxide, ammonium hydroxide, potassium hydroxide and lithium hydroxide; and organic alkali agents such as monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, triisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethyleneimine, ethylenediamine, and pyridine.

These alkali solutions may be used singly or in combination of two or more kinds thereof.

[0170] Examples of the developer that can be used in the invention further include an aqueous alkali solution containing a non-reducing sugar and a base. The non-reducing sugars referred to herein the sugars having no free aldehyde and ketone groups and exhibiting no reductive property, and classified into trehalose type oligosaccharides where reducing groups are bound one another, glycosides where the reducing group of the sugar is bound to a non-sugar, and sugar alcohol where the sugar is reduced by hydrogenation. Any of these non-reducing sugars may be preferably used.

Examples of the trehalose type oligosaccharides include saccharose and trehalose. Examples of the glucosides include alkyl glucosides, phenol glucosides, and mustard oil glucosides. 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 allostulcitol. Preferable examples of the sugar alcohols include maltitol obtained by hydrogenation of disaccharide, and a reduced bodies (reduced starch syrup) obtained by hydrogenation of oligosaccharides. Among these non-reduced sugars, the sugar alcohol and saccharose are preferable. More specifically, D-sorbitol, saccharose, and reduced starch syrup are preferable since they exhibit a buffer effect within an appropriate pH range and are inexpensive.

[0171] These non-reducing sugars may be used singly or in combination of two or more kinds thereof. The content of the non-reducing sugar in the developer is preferably from 0.1 % by mass to 30% by mass, more preferably from 1% by mass to 20% by mass, with respect to a total amount of the developer.

As the base used in combination with the non-reducing sugar(s), conventionally known alkali agents may be employed. Examples thereof include inorganic alkali agents such as sodium hydroxide, potassium hydroxide, lithium hydroxide, trisodium phosphate, tripotassium phosphate, triammonium phosphate, disodium phosphate, dipotassium phosphate, diammonium phosphate, sodium carbonate, potassium carbonate, ammonium carbonate, sodium hydrogencarbonate, potassium hydrogencarbonate, ammonium hydrogencarbonate, sodium borate, potassium borate and ammonium borate; and organic alkali agents such as monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, triisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethyleneimine, ethylenediamine, and pyridine.

[0172] These alkali agents may be used singly or in combination of two or more kinds thereof. Among these alkali agents, sodium hydroxide and potassium hydroxide are preferable, since it enables pH adjustment over a wide range of pH values by regulating the addition amount thereof against the non-reducing sugar. Furthermore, trisodium phosphate, sodium carbonate, potassium carbonate and the like are preferable because of its buffering action.

[0173] When the development is carried out by means of an automatic development processor, an aqueous solution (or, replenisher) having a higher alkali strength than that of the developer can be added to the developer. It is known that this enables a great number of photosensitive plates to be processed without replacing the developer in the development tank over a long period of time. This replenishing manner is preferably used in the invention.

If necessary, various surfactants or organic solvents can be added to the developer and/or the replenisher in order to promote or suppress developability, disperse development scum, and enhance the ink-affinity of image areas of the printing plate.

As the replenisher, a solution having similar formulation with that of the developer may be used, or an aqueous alkaline solution having a higher pH value than that of the developer may be used.

Preferable examples of the surfactant that can be used in the developer and/or the replenisher include an anionic surfactant, a cationic surfactant, a nonionic surfactant and an amphoteric surfactant. Among these surfactants, an anionic surfactant, a nonionic surfactant and an amphoteric surfactant are preferable, and an anionic surfactant is more preferable. The anionic surfactant is preferably an anionic surfactant having a sulfonate structure, a carboxylate structure, or a phosphate structure, more preferably at least one selected from an anionic surfactant having a sulfonate structure or an anionic surfactant having a carboxylate structure, and still more preferably an anionic surfactant having a sulfonate structure.

Specific examples of the anionic surfactant include potassium cocoate, an alkyl sulfate, an alkyl ether sulfate, an alkyl sulfonate, an alkyl benzene sulfonate, an alkyl diphenylether disulfonate, an alkyl naphthalene sulfonate, a naphthalene sulfonate formaldehyde condensate, an alkyl phosphate, an alkyl ether phosphate, and lauryl-imino-dipropionate. Among these, an alkyl diphenylether disulfonate and lauryl-imino-dipropionate are preferable.

As the anionic surfactant, any of commercially available products may be used, and examples thereof include PIONINE C-158-G (trade name, manufactured by Takemoto Oil & Fat Co., Ltd.); ELEMNOR MON-2 (trade name, manufactured by Sanyo Chemical Industries, Ltd.); and CRAFTOL AP261 (trade name, manufactured by Cognis).

[0174] If necessary, the developer and the replenisher may contain a reducing agent (such as hydroquinone, resorcin, a sodium or potassium salt of an inorganic acid such as sulfurous acid or hydrogen sulfite acid), an organic carboxylic acid, a defoaming agent and/or a water softener. The printing plate developed with the developer and replenisher described above is subsequently subjected to post-development treatments with washing water, a rinse solution containing a surfactant and the like, and a desensitizing solution containing gum arabic and a starch derivative. Various combinations of these treatments may be employed for the post-treatment when the planographic printing plate precursor of the invention is used for forming a planographic printing plate.

[0175] In recent years, automatic development processors for plate precursors have been widely used in order to rationalize and standardize platemaking processes in the platemaking and printing industries. These automatic development processors are generally made up of a developing section and a post-development treatment section, and include a device for conveying printing plate precursors, various treating solution tanks, and spray devices.

These machines are machines for spraying respective treating solutions, which are pumped up, onto an exposed printing plate precursor through spray nozzles, for development, while the printing plate is being transported horizontally.

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

A so-called disposable processing method can also be used, in which treatments are conducted with the use of substantially fresh treating solutions.

Method of Producing Planographic Printing Plate

[0176] A method for producing a planographic printing plate according to the invention is explained.

The planographic printing plate precursor of the invention exhibits favorable dissolution discrimination and thus is applied to various methods for producing planographic printing plates. The planographic printing plate precursor has excellent post-exposure stability, and examples of the appropriate planographic printing platemaking method include a method of producing a planographic printing plate including, in this order, an exposure step of image-wise exposing a planographic printing plate precursor; a storing step of storing the planographic printing plate precursor after the exposure; and a development step of developing the planographic printing plate precursor after the store using an aqueous alkaline solution.

The storing step is performed if necessary. Since the planographic printing plate precursor of the invention exhibits favorable dissolution discrimination and wide latitude for a developer activity or the like, a high quality planographic printing plate can be obtained using any kinds of developer. In particular, since the planographic printing plate precursor of the invention has the excellent post-exposure stability, significant advantageous effects can be obtained when it is employed in a platemaking method requiring the storing step. In the storing step, the plate precursor of the invention has an excellent advantageous effect that a practically problematic deterioration in developability is scarcely observed, even after being stored, for example, for 1 to 3 hours in an atmosphere having a temperature of from 15°C to 30°C.

The developer used in the invention is as described above, and is preferably an alkaline developer containing, as a surfactant, at least one surfactant selected from an anionic surfactant having a sulfonate structure or an anionic surfactant having a carboxylate structure.

[0177] Since the planographic printing plate precursor of the invention exhibits favorable dissolution discrimination, the development step can be performed using a known developer under gentle conditions of developer temperature of 20°C to 25°C and development time of 5 sec to 20 sec.

After the development process, a washing treatment with water, a rinsing treatment and the like may be carried out.

In a case where unnecessary image portions (for example, a film edge mark of an original picture film) are present on a planographic printing plate obtained after the development treatment, the unnecessary image portions can be erased. The erasing is preferably performed by applying an erasing solution to unnecessary image portions, leaving the printing plate as it is for a given time, and washing the plate with water, as described in, for example, JP-B No. 2-13293. This erasing may also be performed by a method of radiating active rays introduced through an optical fiber onto the unnecessary image portions, and then developing the plate, as described in JP-A No. 5-174842.

[0178] The planographic printing plate thus obtained is, if desired, coated with a desensitizing gum, and subsequently the plate can be made available for printing. When it is desired to make a planographic printing plate with a higher degree of printing durability, a burning treatment can be applied to the planographic printing plate.

When the planographic printing plate is subjected to the burning treatment, it is preferable that the plate is pre-treated with a counter-etching solution before the burning treatment is conducted as described in JP-B Nos. 61-2518 and 55-28062, and JP-A Nos. 62-31859 and 61-159655.

Examples of the method of the counter-etching treatment include: a method of applying the counter-etching solution onto the planographic printing plate with a sponge or absorbent cotton infiltrated with the counter-etching solution; a method of immersing the planographic printing plate in a vat filled with the counter-etching solution; and a method of applying the counter-etching solution to the planographic printing plate with an automatic coater. In addition, achieving the uniformity in coating amount by using a squeegee or a squeegee roller after application leads to further preferable results.

[0179] In general, the amount of the counter-etching solution applied is suitably from 0.03 g/m² to 0.8 g/m² (dry mass). If necessary, the planographic printing plate onto which the counter-etching solution is applied may be dried, and then the plate is heated to a high temperature by means of a burning processor (for example, a burning processor BP-1300 (trade name) available from FUJIFILM Corporation) or the like. In this case, the heating temperature and the heating time, which may depend on the kind of components forming the image, are preferably from 180°C to 300°C and from 1 minute to 20 minutes, respectively.

When the planographic printing plate precursor according to the invention is subjected to the burning treatment after platemaking, strength of the recording layer is improved and thus high printing durability is achieved.

The planographic printing plate after the burning treatment may be further subjected if necessary to treatment known in the art such as a water washing treatment and a gumming treatment. However, when a counter-etching solution containing a water-soluble polymer compound or the like is used, so-called desensitizing treatment such as gumming may be omitted.

The planographic printing plate obtained by such treatments are then applied to an offset printing machine or the like to be used for printing on a great number of sheets.

EXAMPLES

[0180] The present invention is explained below by reference to Examples, but the scope of the present invention is not limited to these Examples.

Preparation of Exemplified Monomers used for synthesizing Specific Acrylic Resin (B)

[0181] Exemplified Monomers (1), (2), (8), (9) and (13) for forming the specific acrylic resins (B) according to the invention can be synthesized using the method described in Hofmann et al., *Markromolekulare Chemie*, vol. 177, pp. 1791-1813 (1976), and those skilled in the art would be able to easily obtain similar monomers by selecting several different starting materials.

Synthesis of Exemplified Monomer (11)

[0182] Exemplified Monomer (11) can be synthesized using a method similar to the method described in Kang and Bae, *Journal of Controlled Release*, vol. 80, pp. 145- 155. Details of the synthesis method are as follows. 4- amino- N- (6- methoxy- 3- pyridaziny)- benzosulfonamide in an amount of 10 g (35.6 mmol) was dispersed and dissolved in 120 ml of acetonitrile, and thereto was added a solution prepared by dissolving 1.42 g (35.6 mmol) of sodium hydroxide in 30 mL of water. The reactant solution thus prepared was cooled to - 10°C, and the reaction was allowed to continue for 1 hour in a reaction vessel at ordinary temperatures. To the reaction solution obtained, 10 mg of 2, 6- di- tert- butyl- 4- methylphenol (BHT) was added. The resulting mixture was then dried under normal atmospheric pressure. The oily residue thus obtained was dissolved in a mixture of 150 mL of methylene chloride and 100 mL of 2N HCl, and the resultant was separated by using 50 mL of methylene chloride, 520 mL of 2N HCl and 100 mL of water, dried over $MgSO_4$ and then refluxed under normal atmospheric pressure. The obtained synthesis product was purified by column chromatography, thereby obtaining 2.39 g (yield: 19%) of Exemplified Monomer (11) .

Synthesis of Exemplified Monomer (4)

[0183] Exemplified Monomer (4) can be synthesized by a method similar to the method by which Exemplified Monomer (11) is synthesized, except that acryloyl chloride is used in place of methacryloyl chloride. 4- amino- N- (2, 6- dimethyl- 4- pyrimidinyl)- benzosulfonamide in an amount of 24.9 g (89.5 mmol) was dispersed and dissolved in 500 mL of acetonitrile, and thereto was added a solution prepared by dissolving 8.10 g (89.5 mmol) of potassium hydroxide in 75 mL of water. The reactant solution thus prepared was cooled to 0°C, and the reaction was allowed to continue for 14 hours in a reaction vessel at ordinary temperatures. A small amount of precipitate formed was filtered off. The resulting reaction solution was mixed with 25 mg of BHT, and dried under normal atmospheric pressure. The residue thus obtained was dissolved in 350 mL of refluxing methanol. After cooling to room temperature, the methanol solution was added to 1.6 liter of a 1: 1 mixture of hexane and methyl- t- butyl ester. The resulting mixture was filtered and dried. The synthesis product thus obtained was purified by column chromatography to give Exemplified Monomer (4) .

Synthesis of Exemplified Monomer (10)

1. Synthesis of 4-Amino-N-2-pyrimidylbenzenesulfonamide as Intermediate

[0184] 4- acetoamino- benzosulfonyl chloride in an amount of 288.75 g (1.21 mol) and 2- aminopyrimidine in an amount of 113.8 g (1.21 mol) were dispersed and dissolved in 1350 mL of acetonitrile. Thereto, was added 105.2 g (1.33 mol) of pyridine over at least 5 minutes. The temperature of the resulting mixture was raised to 60°C. Reaction was allowed to continue for 2 hours at 60°C. Thereafter, the reaction solution was cooled. Then, N- {4- [(2- pyrimidinylamino) sulfonyl] phenyl} acetamide precipitated in part out of the intermediate was filtered off. A second product was subjected to filtration under reduced pressure, and isolated by evaporation. The synthesis product obtained was treated with 1, 500 mL of ice- cold water. The second product was treated with 1, 500 mL of water at 40°C. N- {4- [(2- pyrimidinylamino) sulfonyl] phenyl} acetamide thus produced was filtered off. Thus, 155.9 g of N- {4- [(2- pyrimidinylamino) sulfonyl] phenyl} acetamide was obtained (yield: 55%) .

[0185] The isolated N- {4- [(2- pyrimidinylamino) sulfonyl] phenyl} acetamide was dissolved in 2.5 liter of a 1: 1 mixture of ethanol and 1- methoxy- 2- propanol. Thereto, was added an aqueous solution of 105 g (2.66 moles) of sodium hydroxide, and the resulting mixture was refluxed for one hour. Then, the mixture was cooled to room temperature, and the solvents were removed under reduced pressure. The reaction product was dissolved in 1, 300 mL of water, and adjusted to the acidity of pH 1 by addition of concentrated hydrochloric acid. The resulting solution was cooled to 0°C.

The insoluble substance was removed by filtration. The water phase was extracted with 450 mL of methylene chloride three times, and adjusted to a neutral region of pH 7 by use of a 10N sodium hydroxide solution. The intermediate 4-amino- N- 2- pyrimidylbenzenesulfonamide precipitated out of the resulting water phase was filtered off and dried. Thus, 93.4 g of 4- amino- N- 2- pyrimidylbenzenesulfonamide was obtained (yield: 70.7%) .

2. Syntheses of Exemplified Monomer (10)

[0186] To 24.9 g (0.1 mol) of the thus obtained 4- amino- N- 2- pyrimidylbenzenesulfonamide, was added 0.25 g of BHT dissolved in 400 mL of pyridine. The resulting mixture was cooled to 0°C. Thereto, was added dropwise 12.54 g (0.12 mol) of methacryloyl chloride. The reaction was allowed to continue for 1 hour under the temperature condition of 0°C to 5°C. Thereafter, the reaction was allowed to continue overnight at ordinary temperature. The solvent was removed under reduced pressure, and the product was added to a 1: 1 mixture of ethanol and water.

This crude product was filtered off and dried. The residue obtained was refluxed in a 1: 1 mixture of acetone and water. These operations were repeated twice, and the product was filtered off and dried. Thus, 16.3 g of Exemplified Monomer (10) was obtained (yield: 49%) .

Exemplified Monomers (5), (6) and (7) can also be synthesized under the reaction scheme similar to the above.

Synthesis of Specific Acrylic Resin (1)

[0187] In a 250- mL reaction vessel, were placed 160 mmol of Exemplified Monomer (1) having a sulfonamide group, 20.6 g (132 mmol) of benzylacetamide, 2.31 g (32 mmol) of acrylic acid and 104 g of γ - butyrolactone, and the resulting mixture was heated up to 140°C while being stirred at 200 rpm. This reaction was conducted under a circulating current of nitrogen. After the solid substance was dissolved, the temperature of the reaction vessel was lowered to 100°C. Thereto, were added in sequence 0.37 mL of TRIGONOX DC50 (trade name, manufactured by Akzo Nobel Corporate) and a solution prepared by dissolving 1.48 mL of TRIGONOX 141 (trade name, manufactured by Akzo Nobel Corporate) in 3.66 mL of butyrolactone. After the initiation of reaction, the reaction vessel temperature was raised to 143°C, and thereto was added 1.87 mL of TRIGONOX DC50 over at least two hours. The reaction of the mixture of the reactants was conducted for 2 hours at 140°C while being stirred at 400 rpm. The temperature of the resulting reaction mixture was lowered to 120°C, and the stirring rate was increased to 500 rpm. Thereto, was added 86.8 mL of 1- methyl- 2- propanol, and the temperature of the resulting solution was cooled to room temperature.

The polymer structure is confirmed by ¹H- NMR spectrography and by size exclusion chromatography using dimethyl- acetamide/ 0.21 % LiCl as a mark and a mixed column (polystyrene equivalent) .

With respect to the molecular weight of specific acrylic resin (1), Mn was found to be 20, 500, Mw 66, 000, and PD 3.05.

Syntheses of Specific Acrylic Resins (2), (4), (5) and (6)

[0188] In the following synthesis method, Exemplified Monomer (1) as a starting material was used for synthesizing specific acrylic resin (2), Exemplified Monomer (3) as a starting material was used for synthesizing specific acrylic resin (4), Exemplified Monomer (7) as a starting material was used for synthesizing specific acrylic resin (5), and Exemplified Monomer (5) as a starting material was used for synthesizing specific acrylic resin (6), respectively.

In a 250- mL reaction vessel, were placed 162 mmol of the monomer specified above as a starting material, 21.3 g (132 mmol) of benzylacetamide, 0.43 g (6 mmol) of acrylic acid and 103 g of γ - butyrolactone, and the resulting mixture was heated up to 140°C while being stirred at 200 rpm. This reaction was conducted under a circulating current of nitrogen. After the solid matter was dissolved, the temperature of the reaction vessel was lowered to 100°C. Thereto, were added in sequence 0.35 mL of TRIGONOX DC50 (trade name, manufactured by Akzo Nobel Corporate) and a solution prepared by dissolving 1.39 mL of TRIGONOX 141 (trade name, manufactured by Akzo Nobel Corporate) in 3.43 mL of butyrolactone. After the initiation of reaction, the temperature of the reaction vessel was raised to 140°C, and thereto was added 1.75 mL of TRIGONOX DC50 over at least two hours. The reaction of the mixture of reactants was conducted for 2 hours at 145°C while being stirred at 400 rpm. The temperature of the resulting reaction mixture was lowered to 120°C, and the stirring rate was increased to 500 rpm. Thereto, was added 85.7 mL of 1- methyl- 2- propanol, and the temperature of the resulting solution was cooled to room temperature.

The structure of each polymer was ascertained by the same techniques as that of specific acrylic resin (1) . Results obtained are shown below.

Specific acrylic resin (2): Mn: 28,000, Mw: 66,000, PD: 2.84
 Specific acrylic resin (4): Mn: 34,000, Mw: 162,000, PD: 4.76
 Specific acrylic resin (5): Mn: 22,000, Mw: 44,000, PD: 1.91
 Specific acrylic resin (6): Mn: 23,500, Mw: 55,000, PD: 2.24

Syntheses of Specific Acrylic Resins (3) and (7)

[0189] In the following synthetic method, Exemplified Monomer (1) as a starting material was used for synthesizing specific acrylic resin (3), and Exemplified Monomer (8) as a starting material was used for synthesizing specific acrylic resin (7), respectively.

In a 250- mL reaction vessel, were placed 132 mmol of the monomer specified above as a starting material, 25.0 g (160 mmol) of benzylacetamide, 2.31 g (32 mmol) of acrylic acid and 104 g of γ - butyrolactone, and the resulting mixture was heated up to 140°C while being stirred at 200 rpm. This reaction was conducted under a circulating current of nitrogen. After the solid substance was dissolved, the temperature of the reaction vessel was lowered to 100°C. Thereto, were added in sequence 0.37 mL of TRIGONOX DC50 (trade name, manufactured by Akzo Nobel Corporate) and a solution prepared by dissolving 1.87 mL of TRIGONOX 141 (trade name, manufactured by Akzo Nobel Corporate) in 3.43 mL of butyrolactone. After the initiation of reaction, the temperature of the reaction vessel was raised to 140°C, and thereto was added 1.48 mL of TRIGONOX DC50 over at least two hours. The reaction of the mixture of reactants was conducted for 2 hours at 140°C while being stirred at 400 rpm. The temperature of the resulting reaction mixture was decreased to 120°C, and the stirring rate was increased to 500 rpm. Thereto, was added 86.8 mL of 1- methyl- 2- propanol, and the temperature of the resulting solution was cooled to room temperature.

The structure of each polymer was ascertained by the same techniques as that of specific acrylic resin (1) . Results obtained are shown below.

Specific acrylic resin (3): Mn: 30,000, Mw: 85,000, PD: 2.78

Specific acrylic resin (7): Mn: 17,000, Mw: 29,000, PD: 1.67

Syntheses of Specific Acrylic Resin (8)

[0190] In a 1- L reaction vessel, were placed 38.1 g (110 mmol) of Exemplified Monomer (1), 23.4 g (114 mmol) of N-(4- hydroxy- 3, 5- dimethyl) benzylacrylamide, 18.9 g (101 mmol) of N- benzyl maleimide and 241 g of γ - butyrolactone, and the resulting mixture was heated up to 140°C while being stirred at 200 rpm. This reaction was conducted under a circulating current of nitrogen. After the solid matter was dissolved, the temperature of the reaction vessel was lowered to 100°C. Thereto, were added in sequence 0.74 mL of TRIGONOX DC50 (trade name, manufactured by Akzo Nobel Corporate) and a solution prepared by dissolving 3.74 mL of TRIGONOX 141 (trade name, manufactured by Akzo Nobel Corporate) in 6.86 mL of butyrolactone. After the initiation of reaction, the temperature of the reaction vessel was raised to 140°C, and thereto was added 2.96 mL of TRIGONOX DC50 over at least two hours. The reaction of the mixture of reactants was conducted for 2 hours at 140°C while being stirred at 400 rpm. The temperature of the resulting reaction mixture was lowered to 120°C, and the stirring rate was increased to 500 rpm. Thereto, was added 200 mL of 1- methyl- 2- propanol, and the temperature of the resulting solution was cooled to room temperature.

The structure of each polymer was ascertained by the same techniques as that of specific acrylic resin (1) . Results obtained are shown below.

Specific acrylic resin (8): Mn: 33,000, Mw: 93,000, PD: 2.82

*Synthesis Example of Onium-Containing Resin (A)**Method for Obtaining Onium-Containing Monomer*

[0191] An onium-containing monomer necessary for the synthesis of an onium-containing resin can be synthesized using the method described in "J. Goethz J. Polym. Sci., 25, 201 (1957)", and those skilled in the art would be able to easily obtain similar monomers by selecting several different starting materials. Alternatively, there may be used products commercially available from Sigma-Aldrich Co., Ltd., Tokyo Chemical Industry Co. Ltd., and the like.

Synthesis of Onium-Containing Resin (A-1)

[0192] In a 2- L three- necked flask, were placed 221.7 g (1.0 mol) of trimethyl- (4- vinylbenzyl) ammonium chloride and 106.0 g of methanol, and the mixture solution was heated while stirring under nitrogen flow to be maintained at 60°C. Thereto, was added 2.3 g (10 mmol) of dimethyl 2, 2'- azobis (isobutyrate), and keep stirring for 30 minutes. Thereto, were added dropwise a solution prepared by dissolving 317.6 g of trimethyl- (4- vinylbenzyl) ammonium chloride and 3.5 g of dimethyl 2, 2'- azobis (isobutyrate) in 250.0 g of methanol over two hours. After completion of the dropwise addition, the temperature of the resultant was raised to 65°C and keep stirring under nitrogen flow for 10 hours. After completion of the reaction, the temperature of the resulting reaction solution was cooled to room temperature. The

obtained reaction solution was poured into 12 L of ethyl acetate. The precipitated solid was filtered off and dried to obtain a yield of 485.5 g. The molecular weight of the obtained solid was determined by a light scattering method, giving a weight- average molecular weight (Mw) of 25, 000.

5 *Synthesis of Onium-Containing Resin (A-2)*

[0193] A polymer having a weight- average molecular weight (Mw) of 30, 000 was synthesized by a method similar to the method by which Onium- containing resin (A- 1) is synthesized, except that 4- methyl- 4- (4- vinylbenzyl) morpholin- 4- ium chloride was used in place of trimethyl- (4- vinylbenzyl) ammonium chloride.

10 *Synthesis of Onium- Containing Resin (A- 3)*

A polymer having a weight- average molecular weight (Mw) of 40, 000 was synthesized by a method similar to the method by which Onium- containing resin (A- 1) is synthesized, except that triethyl- (4- vinylbenzyl) ammonium chloride was used in place of trimethyl- (4- vinylbenzyl) ammonium chloride.

Synthesis of Onium- Containing Resin (A- 4)

15 A polymer having a weight- average molecular weight (Mw) of 18, 000 was synthesized by a method similar to the method by which Onium- containing resin (A- 1) is synthesized, except that 1- (4- vinylbenzyl) pyridin- 1- ium chloride was used in place of trimethyl- (4- vinylbenzyl) ammonium chloride.

Synthesis of Onium- Containing Resin (A- 5)

20 A polymer having a weight- average molecular weight (Mw) of 30, 000 was synthesized by a method similar to the method by which Onium- containing resin (A- 1) is synthesized, except that dimethylethyl- (4- vinylbenzyl) ammonium chloride was used in place of trimethyl- (4- vinylbenzyl) ammonium chloride.

Synthesis of Onium-Containing Resin (A-6)

25 **[0194]** A polymer having a weight- average molecular weight (Mw) of 60, 000 was synthesized by a method similar to the method by which Onium- containing resin (A- 1) is synthesized, except that tris (2'- hydroxyethyl)- (4- vinylbenzyl) ammonium chloride was used in place of trimethyl- (4- vinylbenzyl) ammonium chloride.

Synthesis of Onium- Containing Resin (A- 7)

30 A polymer having a weight- average molecular weight (Mw) of 40, 000 was synthesized by a method similar to the method by which Onium- containing resin (A- 1) is synthesized, except that tributyl- (4- vinylbenzyl) phosphonium chloride was used in place of trimethyl- (4- vinylbenzyl) ammonium chloride.

Synthesis of Onium- Containing Resin (A- 8)

A polymer having a weight- average molecular weight (Mw) of 25, 000 was synthesized by a method similar to the method by which Onium- containing resin (A- 1) is synthesized, except that triethyl- (4- vinylbenzyl) ammonium bromide was used in place of trimethyl- (4- vinylbenzyl) ammonium chloride.

35 *Synthesis of Onium- Containing Resin (A- 9)*

A polymer having a weight- average molecular weight (Mw) of 20, 000 was synthesized by a method similar to the method by which Onium- containing resin (A- 1) is synthesized, except that triethyl- 4- (1'- propenyl benzyl) ammonium chloride was used in place of trimethyl- (4- vinylbenzyl) ammonium chloride.

40 *Synthesis of Onium-Containing Resin (A-10)*

[0195] A polymer having a weight- average molecular weight (Mw) of 30, 000 was synthesized by a method similar to the method by which Onium- containing resin (A- 1) is synthesized, except that triethyl- (4- vinylbenzyl) ammonium hexafluorophosphate was used in place of trimethyl- (4- vinylbenzyl) ammonium chloride.

45 *Synthesis of Onium- Containing Resin (A- 11)*

A polymer having a weight- average molecular weight (Mw) of 30, 000 was synthesized by a method similar to the method by which Onium- containing resin (A- 1) is synthesized, except that triethyl- (4- vinylbenzyl) ammonium tetrafluoroborate was used in place of trimethyl- (4- vinylbenzyl) ammonium chloride.

50 *Synthesis of Onium- Containing Resin (A- 12)*

A polymer having a weight- average molecular weight (Mw) of 40, 000 was synthesized by a method similar to the method by which Onium- containing resin (A- 1) is synthesized, except that triethyl- (4- vinylbenzyl) ammonium mesylate was used in place of trimethyl- (4- vinylbenzyl) ammonium chloride.

Synthesis of Onium- Containing Resin (A- 13)

55 A polymer having a weight- average molecular weight (Mw) of 55, 000 was synthesized by a method similar to the method by which Onium- containing resin (A- 1) is synthesized, except that [2- (methacryloyloxy) ethyl] trimethylammonium chloride was used in place of trimethyl- (4- vinylbenzyl) ammonium chloride.

Synthesis of Onium-Containing Resin (A-14)

[0196] A polymer having a weight- average molecular weight (Mw) of 40, 000 was synthesized by a method similar to the method by which Onium- containing resin (A- 1) is synthesized, except that trimethyl- [2- (methacryloyl amino) ethyl] aminium chloride was used in place of trimethyl- (4- vinylbenzyl) ammonium chloride.

Synthesis of Onium- Containing Resin (A- 15)

A polymer having a weight- average molecular weight (Mw) of 18, 000 was synthesized by a method similar to the method by which Onium- containing resin (A- 1) is synthesized, except that [2- (methacryloyloxy) ethyl] dimethylammonium chloride was used in place of trimethyl- (4- vinylbenzyl) ammonium chloride.

Synthesis of Onium- Containing Resin (A- 16)

A polymer having a weight- average molecular weight (Mw) of 20, 000 was synthesized by a method similar to the method by which Onium- containing resin (A- 1) is synthesized, except that 2- hydroxytrimethyl [3- (methacryloyl amino) propyl] aminium chloride was used in place of trimethyl- (4- vinylbenzyl) ammonium chloride.

Synthesis of Onium- Containing Resin (A- 17)

A polymer having a weight- average molecular weight (Mw) of 18, 000 was synthesized by a method similar to the method by which Onium- containing resin (A- 1) is synthesized, except that diethyl- (4- vinylbenzyl) sulfonium nitrate was used in place of trimethyl- (4- vinylbenzyl) ammonium chloride.

Synthesis of Onium- Containing Resin (A- 18)

A polymer having a weight- average molecular weight (Mw) of 20, 000 was synthesized by a method similar to the method by which Onium- containing resin (A- 1) is synthesized, except that 1- (4- vinylbenzyl) tetrahydro- 1H- thiophen- 1- ium chloride was used in place of trimethyl- (4- vinylbenzyl) ammonium chloride.

Synthesis of Onium- Containing Resin (A- 19)

A polymer having a weight- average molecular weight (Mw) of 30, 000 was synthesized by a method similar to the method by which Onium- containing resin (A- 1) is synthesized, except that [2- (acryloyloxy) ethyl] tributyl phosphonium chloride was used in place of trimethyl- (4- vinylbenzyl) ammonium chloride.

Synthesis of Onium-Containing Resin (A-20)

[0197] A polymer having a weight- average molecular weight (Mw) of 40, 000 was synthesized by a method similar to the method by which Onium- containing resin (A- 1) is synthesized, except that 2- (2, 5- dioxo- 2, 5- dihydro- 1H- pyrrol- 1- yl)- N, N, N- triethylethanaminium chloride was used in place of trimethyl- (4- vinylbenzyl) ammonium chloride.

Synthesis of Onium- Containing Resin (A- 21)

A polymer having a weight- average molecular weight (Mw) of 50, 000 was synthesized by a method similar to the method by which Onium- containing resin (A- 1) is synthesized, except that 1- [4- (2, 5- dioxo- 2, 5- dihydro- 1H- pyrrol- 1- yl) phenyl]- N, N, N- triethylethanaminium chloride was used in place of trimethyl- (4- vinylbenzyl) ammonium chloride.

Synthesis of Onium- Containing Resin (A- 22)

A polymer having a weight- average molecular weight (Mw) of 40, 000 was synthesized by a method similar to the method by which Onium- containing resin (A- 1) is synthesized, except that 1- [4- (2, 5- dioxo- 2, 5- dihydro- 1H- pyrrol- 1- yl) methylphenyl]- N, N, N- triethylethanaminium bromide was used in place of trimethyl- (4- vinylbenzyl) ammonium chloride.

*Examples 1 to 35 and Comparative Examples 1 and 2**Preparation of Substrate*

[0198] The surface of an aluminium plate (JIS A 1050) having a thickness of 0.3 mm was subject to graining treatment by use of an aqueous pumice suspension as an abrasive with the aid of a rotary nylon brush. The surface roughness (center line average roughness) was 0.5 μm . After washing with water, the plate was dipped in a 10% aqueous solution of sodium hydroxide maintained at 70°C and etched so that the amount of aluminum dissolved became 6 g/m³. After washing with water, the plate was dipped in a 30% aqueous solution of nitric acid for 1 min to be neutralized, and then sufficiently washed with water. Thereafter, electrolytic surface roughening of the plate was carried out in a 0.7% aqueous solution of nitric acid for 20 sec by use of a rectangular wave alternating waveform voltage of an anode voltage of 13 V and a cathode voltage of 6 V, the plate was dipped in a 20% sulfuric acid solution having a temperature of 50°C to wash the surface thereof, and then washed with water. The aluminum sheet after the surface roughening was subjected to a porous anodized film-forming treatment in a 20% sulfuric acid solution by use of a direct current. The electrolysis was carried out in a current density of 5 A/dm² to prepare a substrate having an anodized film of 4.0 g/m² on the surface by controlling the electrolysis time. The resulting substrate was treated in a saturated steam chamber at 100°C and 1 atm for 10 sec to obtain a substrate (a) having a sealing ratio of 60%. The substrate (a) was subjected to a hydrophilic

surface-forming treatment in a 2.5% by mass aqueous solution of sodium silicate at 30°C for 10 sec.

Formation of Undercoat Layer

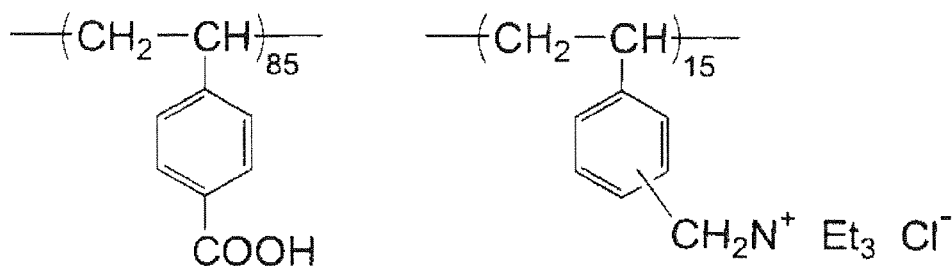
[0199] After the alkali metal silicate treatment, the resulting aluminum substrate was coated with the following undercoat layer coating liquid, and then dried at 80 °C for 15 sec to prepare a substrate [A]. The amount of the coated film (undercoat layer) was 15 mg/m² after drying.

[0200] Formulation of Undercoat Layer Coating Liquid

Polymer compound 1 as described below	0.3 g
Methanol	100 g
Water	1 g

[0201]

Polymer Compound 1



Weight-average Molecular Weight: 28,000

Formation of Positive-working Recording Layer

[0202] The obtained substrate [A] was coated with the following lower recording layer coating liquid by using a wire bar so as to become 1.3 g/m² in coat amount, and dried in a dryer oven at 150°C for 40 sec to form a lower recording layer. Thereafter, the substrate [A] having the lower recording layer was coated with the following upper recording layer coating liquid by using a wire bar to form an upper recording layer, and dried at 150°C for 40 sec such that a total coat amount of the lower recording layer and the upper recording layer become 1.7 g/m², thereby obtaining each of planographic printing plate precursors of Examples 1 to 35 and planographic printing plate precursors of Comparative Examples 1 and 2.

[0203]

Formulation of Lower Recording Layer Coating Liquid

Onium-containing resin [resin (A): resins shown in Table 1]	amounts shown in Table 1
Specific acrylic resin [resin (B): resin shown in Table 1]	amounts shown in Table 1
Naphthalene sulfonic acid salt of Crystal Violet	0.10 g
Fluorine-based surfactant F-780-F (manufactured by DIC Corporation)	0.01 g
Methyl ethyl ketone	5.00 g
1-Methoxy-2-propanol	5.00 g
N,N-dimethylformamide	10.00 g

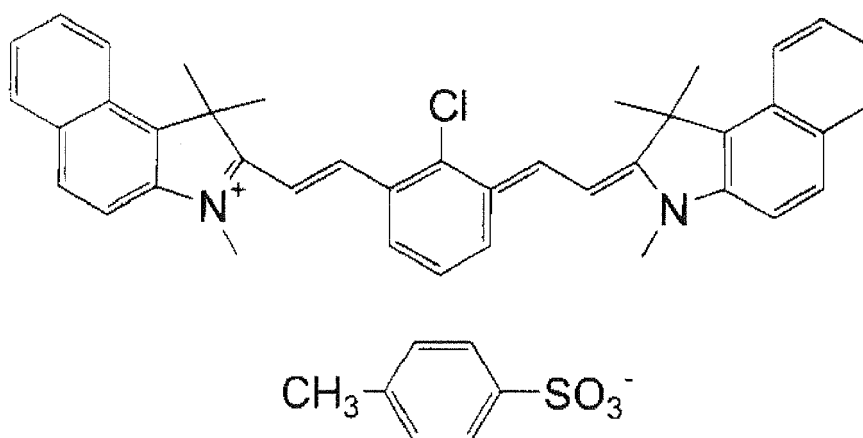
[0204]

Formulation of Upper Recording Layer Coating Liquid

Novolac resin (phenol/m-cresol/p-cresol = 50/30/20 (molar ratio); weight-average molecular weight: 8,000)	0.80 g
Cyanine dye A (the following structure)	0.10 g
Fluorine-based surfactant (a surfactant for improving surface property) [MEGAFAC F781F, manufactured by DIC, Inc.]	0.022 g
Fluorine-based surfactant (a surfactant for improving image formability) [MEGAFAC F780 (30%) manufactured by DIC, Inc.]	0.120 g
Methyl ethyl ketone	15.1 g
1-Methoxy-2-propanol	7.7 g

[0205]

Cyanine Dye A



[0206]

Table 1

	Onium-containing resin (A)		Specific acrylic resin (B)		Evaluation results		
	Compound	Amount (g)	Compound	Amount (g)	Development latitude	Sensitivity (W)	Post-exposure stability (W)
Example 1	A-1	0.3	(1)	0.7	6	4.8	5.1
Example 2	A-1	0.3	(1)	1.0	7	4.8	5.0
Example 3	A-1	0.6	(1)	0.7	7	4.9	5.2
Example 4	A-1	0.6	(1)	0.3	6	4.9	5.2
Example 5	A-1	0.2	(1)	0.7	6	4.8	5.1
Example 6	A-1	0.3	(2)	0.7	7	4.8	5.1
Example 7	A-1	0.3	(4)	0.7	7	4.8	5.1
Example 8	A-3	0.3	(5)	0.7	7	4.7	5.0
Example 9	A-3	0.3	(7)	0.7	7	4.8	5.1
Example 10	A-3	0.3	(2)	0.7	7	4.7	4.9

(continued)

	Onium-containing resin (A)		Specific acrylic resin (B)		Evaluation results		
	Compound	Amount (g)	Compound	Amount (g)	Development latitude	Sensitivity (W)	Post-exposure stability (W)
Example 11	A-5	0.3	(2)	0.7	7	4.7	4.9
Example 12	A-12	0.3	(4)	0.7	7	4.7	4.9
Example 13	A-13	0.3	(6)	0.7	6	5.1	5.4
Example 14	A-14	0.3	(6)	0.7	6	5.2	5.5
Example 15	A-13	0.3	(8)	0.7	6	5.3	5.6
Example 16	A-14	0.3	(8)	0.7	6	5.2	5.6
Example 17	A-2	0.3	(3)	0.7	7	4.8	5.1
Example 18	A-4	0.3	(5)	0.7	7	4.8	5.1
Example 19	A-6	0.3	(5)	0.7	7	4.8	5.1
Example 20	A-7	0.3	(7)	0.7	6	4.8	5.2
Example 21	A-8	0.3	(7)	0.7	6	4.8	5.2
Example 22	A-9	0.3	(7)	0.7	6	4.8	5.1
Example 23	A-10	0.3	(6)	0.7	7	4.9	5.3
Example 24	A-11	0.3	(8)	0.7	6	4.9	5.3
Example 25	A-17	0.3	(8)	0.7	6	4.9	5.3
Example 26	A-13	0.3	(8)	0.7	6	5.4	5.7
Example 27	A-19	0.3	(8)	0.7	6	5.3	5.6
Example 28	A-18	0.3	(1)	0.7	6	4.8	5.1
Example 29	A-13	0.3	(6)	0.7	6	5.2	5.5
Example 30	A-14	0.3	(6)	0.7	6	5.2	5.6
Example 31	A-15	0.3	(8)	0.7	6	5.1	5.5
Example 32	A-16	0.3	(8)	0.7	6	5.1	5.5
Example 33	A-20	0.3	(1)	0.7	6	5.3	5.6
Example 34	A-21	0.3	(1)	0.7	6	5.2	5.5
Example 35	A-22	0.3	(1)	0.7	6	5.2	5.6
Comparative Example 1	None	-	(1)	1.0	3	5.9	6.8
Comparative Example 2	A-1	1.0	None	-	2	6.5	7.0

[0207] Details of the respective polymers shown in Table 1 are as follows:

Onium-containing resin (A): the exemplary compounds (A-1) to (A-22) above Specific acrylic resin (B): the specific acrylic resins (1) to (8) synthesized as above.

Evaluation of Planographic Printing Plate Precursor

[0208] On each of the obtained planographic printing plate precursors of Examples 1 to 35 and Comparative Examples 1 and 2, the following evaluations were conducted. The results are shown in Table 1 above.

Each planographic printing plate precursor obtained was kept under conditions of a temperature of 25°C and a relative humidity of 50% for 5 days, and a test pattern was formed imagewise on the planographic printing plate precursor in Trendsetter 3244 manufactured by Creo at a beam intensity of 9.0 W and a drum rotational velocity of 150 rpm.

Then, the planographic printing plate precursor was developed at a constant liquid temperature of 29°C and a development period of 24 sec in PS PROCESSOR 900H (manufactured by Fuji Photo Film Co. Ltd.) that contained a diluted solution of alkaline developer A or B having the compositions as described below, of which the electrical conductivity was modified by changing the content of water and thus the dilution rate in the alkaline developer.

[0209] *Composition of Alkaline Developer A*

SiO ₂ · K ₂ O [K ₂ O/SiO ₂ = 1/1 (molar ratio)]	4.0% by mass
Citric acid	0.5% by mass
Polyethylene glycol lauryl ether (weight-average molecular weight: 1,000)	0.5% by mass
Water	95.0% by mass

[0210] *Composition of Alkaline Developer B*

D-sorbit	2.5% by mass
Sodium hydroxide	0.85% by mass
Polyethylene glycol lauryl ether (weight-average molecular weight: 1,000)	0.5% by mass
Water	96.15% by mass

[0211] The development latitude, sensitivity, and post-exposure stability respectively of the positive-working planographic printing plate precursors obtained were evaluated. The details of respective evaluation methods are as follows.

1. Evaluation of development latitude

[0212] The difference between the maximum and minimum values of electrical conductivity of the developers, which were able to develop successfully without causing the reduction in density of the image areas and scum or discoloration stemming from persistent residual films of the recording layer owing to inferior development, was assumed to be a development latitude.

2. Evaluation of sensitivity

[0213] The planographic printing plate precursors obtained were exposed to various exposing energies, a test pattern was formed imagewise using TRENDSETTER 3244 manufactured by Creo. Subsequently, the patterns were developed using an alkaline developer having an intermediate (average) value in electrical conductivity between the maximum and minimum values of the electrical conductivity of the developer that were able to develop successfully without causing the reduction in density of the image areas and scum or discoloration stemming from persistent residual films of the recording layer owing to inferior development during evaluation of the development latitude above. The exposure quantity (beam strength at a drum-rotational speed of 150 rpm) that allowed development of non-image areas using this developer was determined and assumed as the sensitivity. A smaller value indicates a higher sensitivity.

3. Evaluation of post-exposure stability

[0214] The planographic printing plate precursors after exposure were stored for 1 hour under an environment of 25°C and a relative humidity of 70%, and then the sensitivity thereof was evaluated in a manner similar to the sensitivity evaluation method above. The degree of decrease in sensitivity from that immediately after exposure was used as an indicator for post-exposure stability. The values represent the sensitivity 1 hour after exposure, and a value closer to the sensitivity immediately after exposure indicates more favorable post-exposure stability.

[0215] Results of Table 1 reveal that the difference (dissolution discrimination) between the dissolution resistance of unexposed areas (image areas) in the developer and the solubility of exposed areas (non-image areas) is increased and post-exposure stability was improved when the onium-containing resin (A) and the specific acrylic resin (B) according

to the invention are used.

On the other hand, in Comparative Examples 1 and 2, which do not contain either of the onium-containing resin (A) or the specific acrylic resin (B), both the dissolution discrimination and the post-exposure stability were insufficient as compared with Examples.

Comparative Examples 36 to 70 and Comparative Examples 3 and 4

[0216] The obtained substrate [A] was coated with the following lower recording layer coating liquid by using a wire bar so as to become 1.3 g/m² in coat amount, and dried in a dryer oven at 150°C for 40 sec to form a lower recording layer. Thereafter, the substrate [A] having the lower recording layer was coated with the following upper recording layer coating liquid by using a wire bar to form an upper recording layer, and dried at 150°C for 40 sec such that a total coat amount of the lower recording layer and the upper recording layer become 1.7 g/m², thereby obtaining each of planographic printing plate precursors of Examples 36 to 70 and planographic printing plate precursors of Comparative Examples 3 and 4.

[0217]

Formulation of Lower Recording Layer Coating Liquid

Onium-containing resin [resin (A): resins shown in Table 1]	amounts shown in Table 2
Specific acrylic resin [resin (B): resin shown in Table 1]	amounts shown in Table 2
Naphthalene sulfonic acid salt of Crystal Violet	0.10 g
Fluorine-based surfactant F-780-F (manufactured by DIC Corporation)	0.01 g
Methyl ethyl ketone	5.00 g
1-Methoxy-2-propanol	5.00 g
N,N-dimethylformamide	10.00 g

[0218]

Formulation of Upper Recording Layer Coating Liquid

Specific acrylic resin [resin (B): resin shown in Table 2]	0.80 g
Novolac resin (phenol/m-cresol/p-cresol = 50/30/20 (molar ratio); weight-average molecular weight: 8,000)	0.60 g
Cyanine dye A (the above structure)	0.10 g
Fluorine-based surfactant (a surfactant for improving surface property) [MEGAFAC F781F, manufactured by DIC, Inc.]	0.022 g
Fluorine-based surfactant (a surfactant for improving image formability) [MEGAFAC F780 (30%) manufactured by DIC, Inc.]	0.120 g
Methyl ethyl ketone	15.1 g
1-Methoxy-2-propanol	7.7 g

[0219]

Table 2

	Onium-containing resin (A)		Specific acrylic resin (B)		Evaluation results		
	Compound	Amount (g)	Compound	Amount (g)	Development latitude	Sensitivity (W)	Post-exposure stability (W)
Example 36	A-1	0.2	(1)	0.4	6	4.8	5.0
Example 37	A-1	0.2	(1)	0.5	7	4.8	5.0
Example 38	A-1	0.3	(1)	0.4	7	4.9	5.1
Example 39	A-1	0.3	(1)	0.1	6	4.8	5.1

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(continued)

5		Onium-containing resin (A)		Specific acrylic resin (B)		Evaluation results		
		Compound	Amount (g)	Compound	Amount (g)	Development latitude	Sensitivity (W)	Post-exposure stability (W)
10	Example 40	A-1	0.1	(1)	0.4	7	4.8	5.1
	Example 41	A-1	0.2	(2)	0.4	7	4.7	5.1
	Example 42	A-1	0.2	(4)	0.4	7	4.7	5.1
	Example 43	A-3	0.2	(5)	0.4	7	4.7	5.0
15	Example 44	A-3	0.2	(7)	0.4	7	4.8	5.1
	Example 45	A-3	0.2	(2)	0.4	7	4.7	4.9
	Example 46	A-5	0.2	(2)	0.4	7	4.7	4.9
20	Example 47	A-12	0.2	(4)	0.4	7	4.7	4.9
	Example 48	A-13	0.2	(6)	0.4	6	5.1	5.4
	Example 49	A-14	0.2	(6)	0.4	6	5.1	5.4
	Example 50	A-13	0.2	(8)	0.4	6	5.2	5.6
25	Example 51	A-14	0.2	(8)	0.4	6	5.2	5.6
	Example 52	A-2	0.2	(3)	0.4	7	4.8	5.1
	Example 53	A-4	0.2	(5)	0.4	7	4.8	5.1
30	Example 54	A-6	0.2	(5)	0.4	7	4.8	5.1
	Example 55	A-7	0.2	(7)	0.4	6	4.8	5.1
	Example 56	A-8	0.2	(7)	0.4	6	4.8	5.1
	Example 57	A-9	0.2	(7)	0.4	6	4.8	5.1
35	Example 58	A-10	0.2	(6)	0.4	7	4.9	5.2
	Example 59	A-11	0.2	(8)	0.4	6	4.8	5.2
	Example 60	A-17	0.2	(8)	0.4	6	4.8	5.3
40	Example 61	A-13	0.2	(8)	0.4	6	5.3	5.6
	Example 62	A-19	0.2	(8)	0.4	6	5.3	5.6
	Example 63	A-18	0.2	(1)	0.4	6	4.8	5.1
	Example 64	A-13	0.2	(6)	0.4	6	5.2	5.5
45	Example 65	A-14	0.2	(6)	0.4	6	5.2	5.6
	Example 66	A-15	0.2	(8)	0.4	6	5.1	5.5
	Example 67	A-16	0.2	(8)	0.4	6	5.1	5.5
50	Example 68	A-20	0.2	(1)	0.4	6	5.2	5.5
	Example 69	A-21	0.2	(1)	0.4	6	5.1	5.4
	Example 70	A-22	0.2	(1)	0.4	6	5.1	5.4
55	Comparative Example 3	None	-	(1)	0.4	2	6.2	6.9
	Comparative Example 4	A-1	0.4	None	-	2	7.0	7.5

[0220] Results of Table 2 revealed that the planographic printing plate precursors having the upper recording layer containing the onium-containing resin (A) and the specific acrylic resin (B) exhibit improved dissolution discrimination and high post-exposure stability.

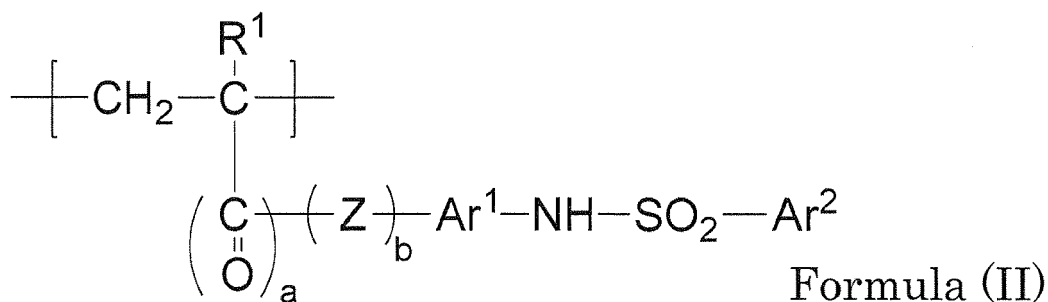
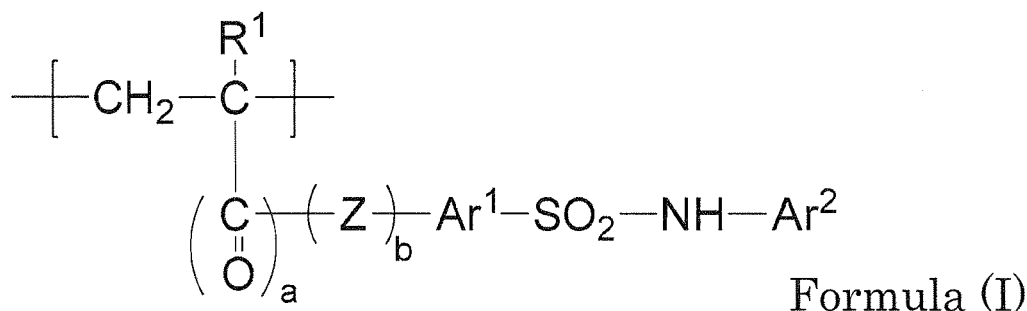
On the other hand, in both Comparative Example 3 that does not contains the onium-containing resin (A) and Comparative Example 4 that does not contains the specific acrylic resin (B) the dissolution discrimination was insufficient and the post-exposure stability did not improved.

[0221] According to the invention, there is provided a planographic printing plate precursor having a sufficient difference between the dissolution resistance of unexposed areas in a developer and the solubility of exposed areas, in which deterioration in developability is suppressed when it is not developed immediately after exposure but is developed after a certain period of time.

The invention also provide a method for producing a planographic printing plate precursor, which can produce a high quality planographic printing plate in which deterioration in developability of exposed areas is suppressed even when the exposed planographic printing plate precursor is not developed immediately after exposure but is developed after a certain period of time (i.e., developed after so-called "post-exposure storage").

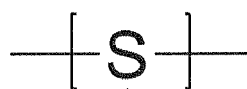
Claims

1. A planographic printing plate precursor, comprising: a substrate having a hydrophilic surface; and two or more recording layers provided on the substrate and each containing an alkali-soluble resin, wherein at least one of the two or more recording layers is a positive-working recording layer including an infrared absorbing agent, and wherein, of the two or more recording layers, a recording layer provided in closest proximity to the substrate includes a resin (A) having an onium salt structure and a (meth)acrylic resin (B) having at least one repeating unit selected from a structural unit represented by the following Formula (I) or a structural unit represented by the following Formula (II):



wherein, in Formulae (I) and (II), R¹ represents a hydrogen atom or an alkyl group; Z represents -O- or -N(R²)- wherein R² represents a hydrogen atom, an alkyl group, an alkenyl group, or an alkynyl group; Ar¹ and Ar² each independently represent an aromatic group, and at least one of Ar¹ or Ar² is a heteroaromatic group; and a and b each independently represent 0 or 1.

2. The planographic printing plate precursor according to claim 1, wherein the resin (A) having an onium salt structure is a resin including a repeating unit represented by the following Formula (III):

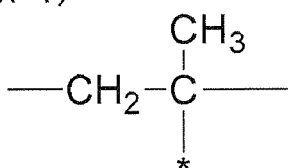


Formula (III)

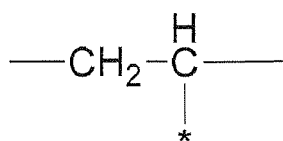
wherein, in Formula (III), S represents a linking group forming the polymer main chain; T represents a single bond linking S and M or a di- or higher-valent linking group; M represents a substituent including an onium structure; Z represents a substituent including an anion structure; and M⁺ and Z⁻ together form an onium salt structure.

3. The planographic printing plate precursor according to claim 2, wherein S in Formula (III) is represented by the following Formula (X-1), (X-2) or (X-3):

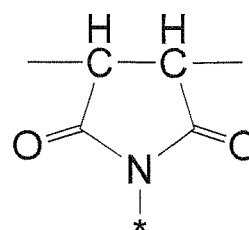
(X-1)



(X-2)

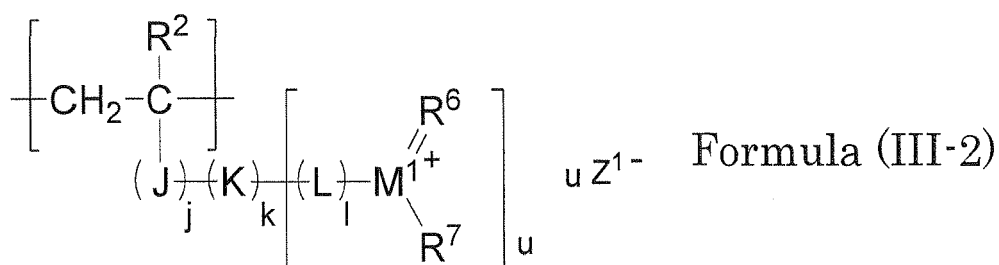
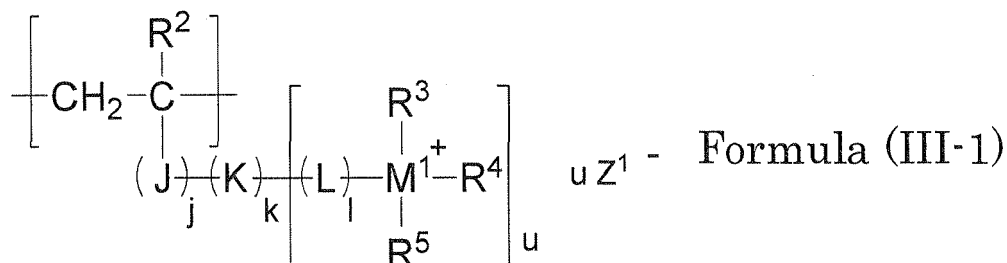


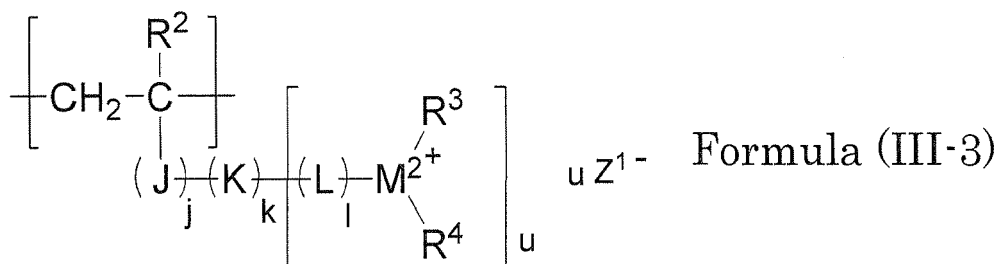
(X-3)



wherein, in Formulae (X-1) to (X-3), the symbol "*" represents a position at which S is linked with T.

4. The planographic printing plate precursor according to claim 2, wherein the repeating unit represented by Formula (III) is a repeating unit represented by the following Formula (III-1), (III-2), or (III-3):





wherein, in Formula (III-1), R² represents a hydrogen atom, an alkyl group, or a halogen atom; J represents a divalent linking group; K represents an aromatic group; L represents a divalent linking group; M¹ represents an atom belonging to group 15 of the periodic table; Z¹⁻ represents a counter anion; R³, R⁴, and R⁵ each independently represent a hydrogen atom, an alkyl group, an aromatic group, or an aralkyl group, at least one R³ and R⁴ may be linked to each other to form a ring, and R⁴ and R⁵ may be linked to each other to form a ring; j, k, and l each independently represent 0 or 1 provided that j and k are not 0 at the same time; and u represents an integer of 1 to 3; wherein, in Formula (III-2), R², J, K, L, M¹, Z¹⁻, j, k, l, and u have the same definitions as R², J, K, L, M¹, Z¹⁻, j, k, l, and u in Formula (III-1), respectively; R⁶ represents an alkylidyne group; R⁷ represents a hydrogen atom, an alkyl group, an aromatic group, or an aralkyl group; and R⁶ and R⁷ may be linked to each other to form a ring; and wherein, in Formula (III-3), R², J, K, L, Z¹⁻, j, k, l, and u have the same definitions as R², J, K, L, Z¹⁻, j, k, l, and u in Formula (III-1), respectively; R³ and R⁴ each independently represent a hydrogen atom, an alkyl group, an aromatic group, or an aralkyl group, and R³ and R⁴ may be linked to each other to form a ring; and M² represents a sulfur atom.

5. The planographic printing plate precursor according to claim 2, wherein M⁺ Z⁻ in Formula (III) forms a structure including an iodonium salt or a pyridinium salt.
6. The planographic printing plate precursor according to any one of claims 1 to 5, wherein the resin (A) having an onium salt structure has a weight-average molecular weight (M_w) of from 5,000 to 1,000,000.
7. The planographic printing plate precursor according to any one of claims 1 to 6, wherein the (meth)acrylic resin (B) further comprises at least one of a structural unit derived from a hydrophobic monomer having, in a side chain thereof, an alkyl group or an aryl group, or a structural unit derived from a hydrophilic monomer having, in a side chain thereof, an acidic group, an amido group, a hydroxy group or an ethylene oxide group.
8. The planographic printing plate precursor according to any one of claims 1 to 7, wherein a content ratio (A:B) of the resin (A) having an onium salt structure and the (meth)acrylic resin (B) having at least one repeating unit selected from the structural unit represented by Formula (I) or the structural unit represented by Formula (II) in the recording layer provided in closest proximity to the substrate is from 1.0:0.1 to 1.0:8.0 in terms of mass.
9. A method for producing a planographic printing plate, the method comprising, in this order:
 - image-wise exposing the planographic printing plate precursor according to any one of claims 1 to 8;
 - storing the planographic printing plate precursor after the exposure; and
 - developing the planographic printing plate precursor after the storage, using an aqueous alkaline solution.

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