

METHODS FOR STABILIZING A PHOTOACID GENERATOR

FIELD OF THE INVENTION

5 [0001] The present application relates to methods for stabilizing a photoacid generator in a photoresist composition, photoresist compositions, and uses of photoresist compositions.

BACKGROUND OF THE INVENTION

10 [0002] When attempting to form a fine pattern by lithography method, a high resolution is required for the resist material. To meet such a demand, a chemically amplified resist composition comprising a base resin and a photoacid generator is used.

15 [0003] For example, a chemically amplified positive type resist composition comprises a resin component, solubility of which in an alkali aqueous solution increases by the action of an acid, and a photoacid generator which generates an acid when exposed to light. Upon forming a resist pattern, when the acid is generated by the photoacid generator, the exposed portion becomes alkali-soluble.

20 [0004] Patent Document 1 studies a process for producing a resist composition, comprising the steps of: preparing an organic solvent (S) using ethyl lactate that comprises an antioxidant, so that a concentration of said antioxidant within said organic solvent (S) is 10 ppm or greater, and
25 dissolving a base material component in said organic solvent (S).

[0005] Patent Document 2 studies a method, comprising:
providing a layered structure comprising a resist layer disposed on a surface
of a substrate, the resist layer comprising the PAG polymer of claim 13;
30 pattern-wise exposing the resist layer to radiation, thereby forming an exposed resist layer;

baking the exposed resist layer at about 90 degrees centigrade to about 130 degrees centigrade for at least 1 second, thereby forming a treated resist layer; and
selectively removing a region of the treated resist layer using a developer,
5 thereby forming a patterned resist layer.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0006] [Patent document 1] US 2009-155713 A
10 [Patent document 2] US 2018-044459 A

SUMMARY OF THE INVENTION

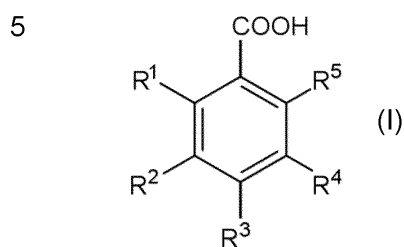
[0007] The inventors newly have found that there are still one or more of considerable problems for which improvement is desired, as listed below:
15 A photoacid generator in a photoresist composition is decomposed, a photoacid generator decomposes due to the reaction between a photoacid generator and a solvent; a photoacid generator decomposes due to the reaction between a photoacid generator and a solvent under the existence of an amine; when bottom anti-reflective coating is not formed, standing wave in
20 a resist pattern is reduced; a resist pattern width is not uniform; rectangularity of a resist pattern is insufficient; resolution of a resist pattern is insufficient; heat resistance of a resist pattern is insufficient; and efficiency of manufacturing process is insufficient.

25 [0008] The inventors have found that these problems can be solved by providing methods as disclosed and claimed hereinafter.

[0009] The invention relates to a method for stabilizing a photoacid generator in a photoresist composition comprising, essentially consisting of or
30 consisting of, step (a);

- 3 -

(a) mixing multiple compounds to form a photoresist composition, wherein the multiple compounds comprise a polymer, a photoacid generator, an amine and a compound A represented by formula (I);



wherein R^1 to R^5 are each independently H, C_{1-20} alkyl, C_{1-20} alkoxy, OH or NH_2 , preferably H, C_{1-10} alkyl or OH, more preferably H or OH;

when R^1 to R^5 are each independently an alkyl, one or more non-adjacent CH_2 -groups are optionally replaced by $-O-$, $-S-$, $-CO-$, $-CO-O-$, $-O-CO-$, $-O-CO-O-$, $-CR-CR-$ or $-C\equiv C-$.

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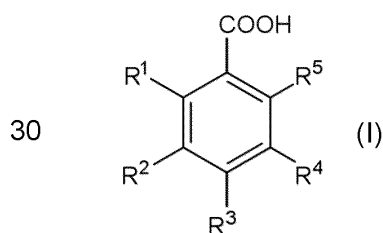
[0010] The invention further relates to a photoresist composition comprising, essentially consisting of or consisting of, a polymer, a photoacid generator, a compound A represented by formula (I) and an amine;

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wherein the molar ratio of the compound A to the amine is in the range from 0.1 to 10, preferably 0.2 to 8, more preferably 0.3 to 5, very preferably 0.5 to 3;

preferably the content of the amine is in the range from 0.1 to 1 mass parts, more preferably 0.2 to 0.9 mass parts, very preferably 0.3 to 0.8 mass parts based on 100 mass parts of the polymer;

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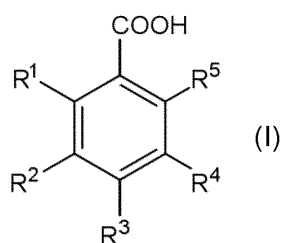


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wherein R^1 to R^5 are each independently H, C_{1-20} alkyl, C_{1-20} alkoxy, OH or NH_2 , preferably H, C_{1-10} alkyl, C_{1-10} alkoxy or OH, more preferably H or OH; when R^1 to R^5 are each independently an alkyl, one or more non-adjacent CH_2 -groups are optionally replaced by $-O-$, $-S-$, $-CO-$, $-CO-O-$,
 5 $-O-CO-$, $-O-CO-O-$, $-CR-CR-$ or $-C\equiv C-$.

[0011] The invention furthermore relates to use of a compound A represented by formula (I) for stabilizing a photoacid generator in a photoresist composition;

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wherein R^1 to R^5 are each independently H, C_{1-20} alkyl, C_{1-20} alkoxy, OH or NH_2 , preferably H, C_{1-10} alkyl or OH, more preferably H or OH; when R^1 to R^5 are each independently an alkyl, one or more non-adjacent CH_2 -groups are optionally replaced by $-O-$, $-S-$, $-CO-$, $-CO-O-$,
 20 $-O-CO-$, $-O-CO-O-$, $-CR-CR-$ or $-C\equiv C-$.

TECHNICAL EFFECTS OF THE INVENTION

[0012] The present invention may provide one or more of the following effects:
 25 Decomposition of a photoacid generator in a photoresist composition is suppressed, reaction between a photoacid generator and a solvent that results in a decomposition of the photoacid generator is suppressed; reaction between a photoacid generator and a solvent that results in decomposition of the photoacid generator under the existence of an amine is suppressed;
 30 reaction between a photoacid generator and a solvent that results in a decomposition of the photoacid generator under the existence of a tertiary

amine is suppressed; even when bottom anti-reflective coating is not formed, effect of reducing standing wave in a resist pattern is sufficient; a resist pattern width is uniform; rectangularity of a resist pattern is sufficient; resolution of a resist pattern is sufficient; heat resistance of the resist pattern is sufficient; and efficiency of manufacturing process is sufficient.

[0013] [Definition of the terms]

Unless otherwise specified in the present specification, the definitions and examples described in this paragraph are followed.

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[0014] The singular form includes the plural form and "one" or "that" means "at least one". An element of a concept can be expressed by a plurality of species, and when the amount (for example, mass % or mol%) is described, it means sum of the plurality of species. "And/or" includes a combination of all elements and also includes single use of the element.

15

[0015] When a numerical range is indicated using "to" or "-", it includes both endpoints and units thereof are common. For example, 5 to 25 mol% means 5 mol% or more and 25 mol% or less.

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[0016] The descriptions such as " C_{x-y} ", " C_x-C_y " and " C_x " mean the number of carbons in a molecule or substituent. For example, C_{1-6} alkyl means an alkyl chain having 1 or more and 6 or less carbons (methyl, ethyl, propyl, butyl, pentyl, hexyl etc.).

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[0017] When a polymer has a plural type of repeating units, these repeating units copolymerize. The copolymerization of these repeating units is any of alternating copolymerization, random copolymerization, block copolymerization, graft copolymerization, or a mixture thereof. When polymer or resin is represented by a structural formula, n, m or the like that is attached next to parentheses indicate the number of repetitions.

30

Celsius is used as the temperature unit. For example, 20 degrees means 20 degrees Celsius.

5 [0018] The additive refers to a compound itself having a function thereof (for example, in the case of a base generator, a compound itself that generates a base). An embodiment in which the compound is dissolved or dispersed in a solvent and added to a composition is also possible. As one embodiment of the present invention, it is preferable that such a solvent is contained in the composition according to the present invention as the solvent (C) or another
10 component.

DETAILED DESCRIPTION OF THE INVENTION

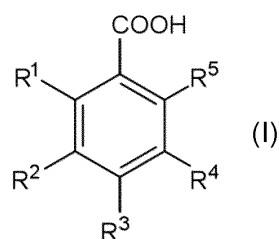
[0019] Hereinafter, embodiments of the present invention are described in detail.

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[0020] [Method for stabilizing a photoacid generator in a photoresist composition]

The method of stabilizing a photoacid generator in a photoresist composition according to the present invention (hereafter referred to as the method)
20 comprises, essentially consists of or consists of, step (a);
(a) mixing multiple compounds to form a photoresist composition, wherein the multiple compounds comprise a polymer, a photoacid generator, an amine and a compound A represented by formula (I);

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wherein R¹ to R⁵ are each independently H, C₁₋₂₀ alkyl, C₁₋₂₀ alkoxy, OH or NH₂, preferably H, C₁₋₁₀ alkyl or OH, more preferably H or OH;

when R¹ to R⁵ are each independently an alkyl, one or more non-adjacent CH₂-groups are optionally replaced by —O—, —S—, —CO—, —CO—O—, —O—CO—, —O—CO—O—, —CR—CR— or —C≡C—.

5 [0021] Step (a)

In step (a), the multiple compounds may be mixed without adhering to a specific order. The multiple compounds may be mixed with or without a solvent.

10 [0022] In some embodiments of the present invention, the step (a) contains, essentially consists of or consists of, the following steps in this order.

(a1) mixing the polymer with the photoacid generator to form a first mixture,
(a2) mixing the first mixture obtained in the step (a1) with the amine to form a second mixture, and

15 (a3) mixing the second mixture obtained in the step (a2) with the compound A represented by the formula (I).

[0023] In some embodiments of the present invention, the step (a) contains, essentially consists of or consists of, the following steps in this order.

20 (a1) mixing the polymer with the photoacid generator to form a first mixture,
(a2) mixing the first mixture obtained in the step (a1) with the compound A represented by the formula (I) to form a second mixture, and
(a3) mixing the second mixture obtained in the step (a2) with the amine.

25 [0024] In some embodiments of the present invention, the step (a) contains, essentially consists of or consists of, the following steps in this order.

(a1) mixing the polymer with the amine to form a first mixture,
(a2) mixing the first mixture obtained in the step (a1) with the photoacid generator to form a second mixture, and

30 (a3) mixing the second mixture obtained in the step (a2) with the compound A represented by the formula (I).

[0025] In some embodiments of the present invention, the step (a) contains, essentially consists of or consists of, the following steps in this order.

(a1) mixing the polymer with the amine to form a first mixture,

5 (a2) mixing the first mixture obtained in the step (a1) with the compound A represented by the formula (I) to form a second mixture, and

(a3) mixing the second mixture obtained in the step (a2) with the photoacid generator.

10 [0026] In some embodiments of the present invention, the step (a) contains, essentially consists of or consists of, the following steps in this order.

(a1) mixing the polymer with the compound A represented by the formula (I) to form a first mixture,

(a2) mixing the first mixture obtained in the step (a1) with the amine to form a second mixture, and

15 (a3) mixing the second mixture obtained in the step (a2) with the photoacid generator.

[0027] In some embodiments of the present invention, the step (a) contains, essentially consists of or consists of, the following steps in this order.

20 (a1) mixing the polymer with the compound A represented by the formula (I) to form a first mixture,

(a2) mixing the first mixture obtained in the step (a1) with the photoacid generator to form a second mixture, and

(a3) mixing the second mixture obtained in the step (a2) with the amine.

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[0028] In some embodiments of the present invention, the step (a) contains, essentially consists of or consists of, the following steps in this order.

(a1) mixing the photoacid generator with the amine to form a first mixture,

30 (a2) mixing the first mixture obtained in the step (a1) with the compound A represented by the formula (I) to form a second mixture, and

(a3) mixing the second mixture obtained in the step (a2) with the polymer.

[0029] In some embodiments of the present invention, the step (a) contains, essentially consists of or consists of, the following steps in this order.

(a1) mixing the photoacid generator with the amine to form a first mixture,

5 (a2) mixing the first mixture obtained in the step (a1) with the polymer to form a second mixture, and

(a3) mixing the second mixture obtained in the step (a2) with the compound A represented by the formula (I).

10 [0030] In some embodiments of the present invention, the step (a) contains, essentially consists of or consists of, the following steps in this order.

(a1) mixing the photoacid generator with the compound A represented by the formula (I) to form a first mixture,

(a2) mixing the first mixture obtained in the step (a1) with the polymer to form a second mixture, and

15 (a3) mixing the second mixture obtained in the step (a2) with the amine.

[0031] In some embodiments of the present invention, the step (a) contains, essentially consists of or consists of, the following steps in this order.

20 (a1) mixing the photoacid generator with the compound A represented by the formula (I) to form a first mixture,

(a2) mixing the first mixture obtained in the step (a1) with the amine to form a second mixture, and

(a3) mixing the second mixture obtained in the step (a2) with the polymer.

25 [0032] In some embodiments of the present invention, the step (a) contains, essentially consists of or consists of, the following steps in this order.

(a1) mixing the amine with the compound A represented by the formula (I) to form a first mixture,

30 (a2) mixing the first mixture obtained in the step (a1) with the polymer to form a second mixture, and

(a3) mixing the second mixture obtained in the step (a2) with the photoacid generator.

[0033] In some embodiments of the present invention, the step (a) contains, essentially consists of or consists of, the following steps in this order.

(a1) mixing the amine with the compound A represented by the formula (I) to form a first mixture,

5 (a2) mixing the first mixture obtained in the step (a1) with the polymer to form a second mixture, and

(a3) mixing the second mixture obtained in the step (a2) with the photoacid generator.

10 [0034] In some embodiments of the present invention, essentially consists of or consists of, the following steps in this order.

(a1) mixing the polymer, the photoacid generator and the amine at the same time to form a first mixture, and

(a2) mixing the first mixture obtained in the step (a1) with the compound A
15 represented by the formula (I).

[0035] In some embodiments of the present invention, the step (a) contains, essentially consists of or consists of, the following steps in this order.

(a1) mixing the polymer, the photoacid generator, and the compound A
20 represented by the formula (I) at the same time to form a first mixture, and

(a2) mixing the first mixture obtained in the step (a1) with the amine.

[0036] In some embodiments of the present invention, the step (a) contains, essentially consists of or consists of, the following steps in this order.

25 (a1) mixing the polymer, the amine, and the compound A represented by the formula (I) at the same time to form a first mixture, and

(a2) mixing the first mixture obtained in the step (a1) with the photoacid generator.

30 [0037] In some embodiments of the present invention, the step (a) contains, essentially consists of or consists of, the following steps in this order.

(a1) mixing the photoacid generator, the amine, and the compound A represented by the formula (I) at the same time to form a first mixture, and
(a2) mixing the first mixture obtained in the step (a1) with the polymer.

5 [0038] In some embodiments of the present invention, the step (a) contains, essentially consists of or consists of, the following step.

(a1) mixing the polymer, the photoacid generator, the compound A represented by the formula (I) and the amine at the same time.

10 [0039] According to the present invention, preferably at least the amine and the compound A are first mixed in the step (a1). In said preferable embodiment, the rest of the compounds may be mixed either together with or separately from the amine and the compound A without adhering to a specific order.

15 [0040] This is not bound by theory, but it is believed that by first mixing at least the amine and the compound A, the decomposition of the photoacid generator is more sufficiently suppressed.

20 [0041] In another preferable embodiment, at least the amine and the compound A may be first mixed with a solvent separately to form an amine solution and a compound A solution.

In another preferable embodiment, at least the amine and the compound A may be first mixed with a solvent at the same time to form a first mixture.

25 [0042] This is not bound by theory, but it is believed that by first mixing at least the amine and the compound A with a solvent, the amine and the compound A are more sufficiently mixed. Because of that, it is believed that the decomposition of the photoacid generator is more sufficiently suppressed.

30 [0043] Thus, the step (a1) may contain the following steps (a1') and (a2') or the following step (a1'').

(a1') mixing the amine and the compound A with a solvent separately to form an amine solution and a compound A solution, and

(a2') mixing the amine solution and the compound A solution to form a first mixture.

- 5 (a1'') mixing the amine and the compound A with a solvent at the same time to form a first mixture.

[0044] One or more compounds other than the polymer, the photoacid generator, the amine, and the compound A represented by the formula (I) (hereafter, referred to as other compounds) may be included in the multiple
10 compounds and mixed with the polymer, the photoacid generator, the amine, and the compound A represented by the formula (I). Other compounds may be mixed without adhering to a specific order.

15 [0045] The multiple compounds may be mixed by well-known processes such as stirring the multiple compounds with a rod or an agitator having a paddle, a propeller or a turbine. One or more compounds included in the multiple compounds may be added to another compound or a mixture of two or more compounds dropwise intermittently over a predetermined time at a
20 temperature in a certain range. The temperature while mixing may be raised or lowered at moderate timings.

[0046] The predetermined time is preferably in the range from 1 to 120 min, more preferably 1 to 90 min, very preferably 1 to 60 min, furthermore
25 preferably 1 to 30 min. The range of temperature is preferably from 1 to 90 °C, more preferably from 5 to 60 °C, very preferably from 10 to 40 °C, furthermore preferably from 15 to 30 °C.

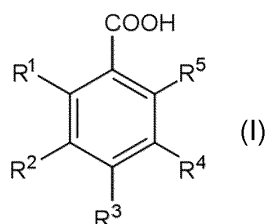
[0047] Compound A

30 The multiple compounds contain the compound A. This is not bound by theory, but it is considered that the compound A stabilizes a photoacid generator. It is considered that a photoacid generator decomposes under the existence of an

amine and that the compound A suppresses the photoacid generator's decomposition.

[0048] The compound A is represented by formula (I);

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wherein R^1 to R^5 are each independently H, C_{1-20} alkyl, C_{1-20} alkoxy, OH or NH_2 , preferably H, linear, branched or cyclic structure containing C_{1-20} alkyl, linear, branched or cyclic structure containing C_{1-20} alkoxy or OH, more preferably H, linear, branched or cyclic structure containing C_{1-10} alkyl, linear or branched or cyclic structure containing C_{1-10} alkoxy or OH, very preferably H or OH.

15

When R^1 to R^5 are each independently an alkyl, one or more non-adjacent CH_2 -groups are optionally replaced by $-O-$, $-S-$, $-CO-$, $-CO-O-$, $-O-CO-$, $-O-CO-O-$, $-CR-CR-$ or $-C\equiv C-$, preferably not replaced.

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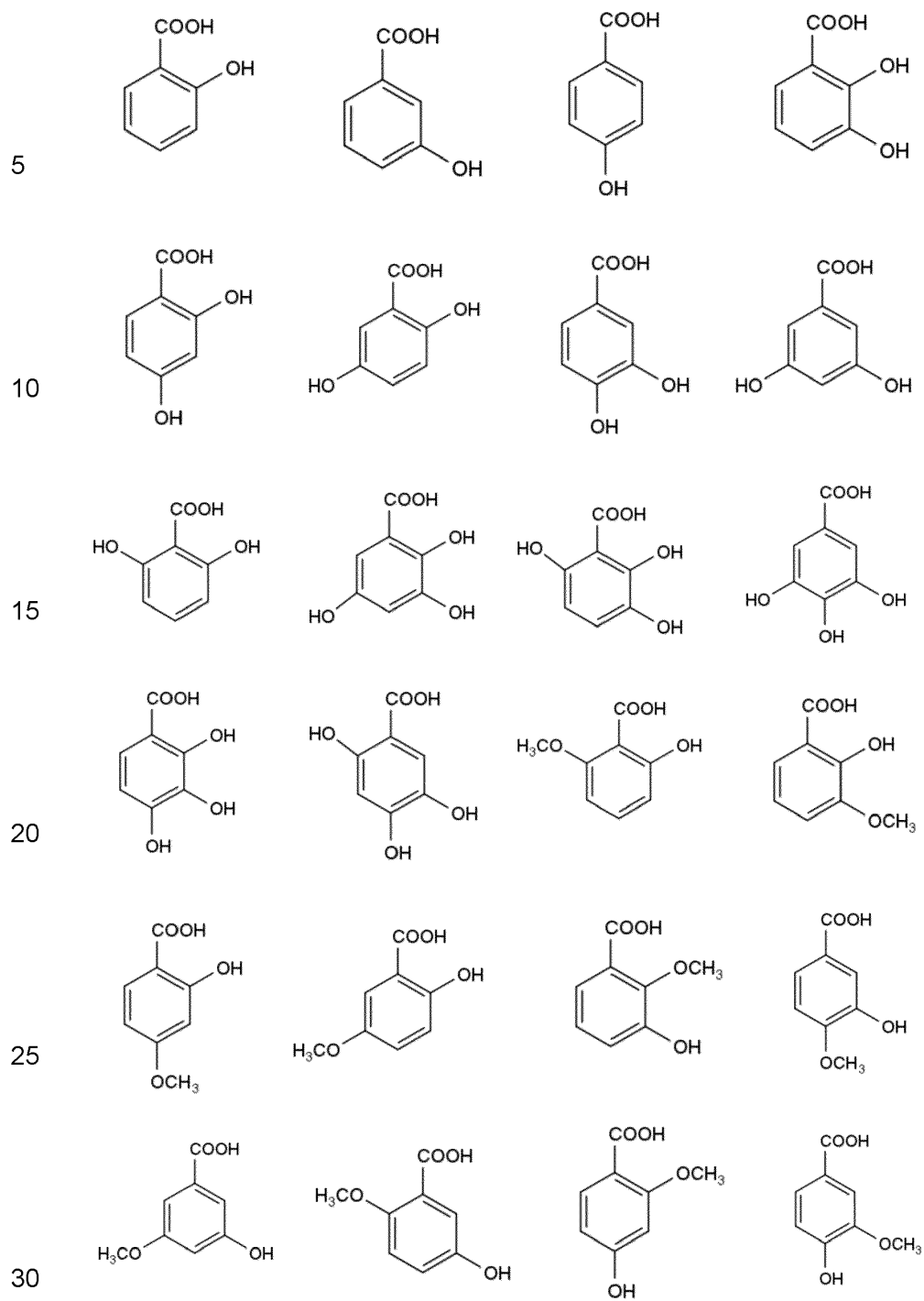
[0049] Preferably at least one of R^1 to R^5 is OH, more preferably at least one of R^1 and R^5 is OH, very preferably R^1 or R^5 is OH.

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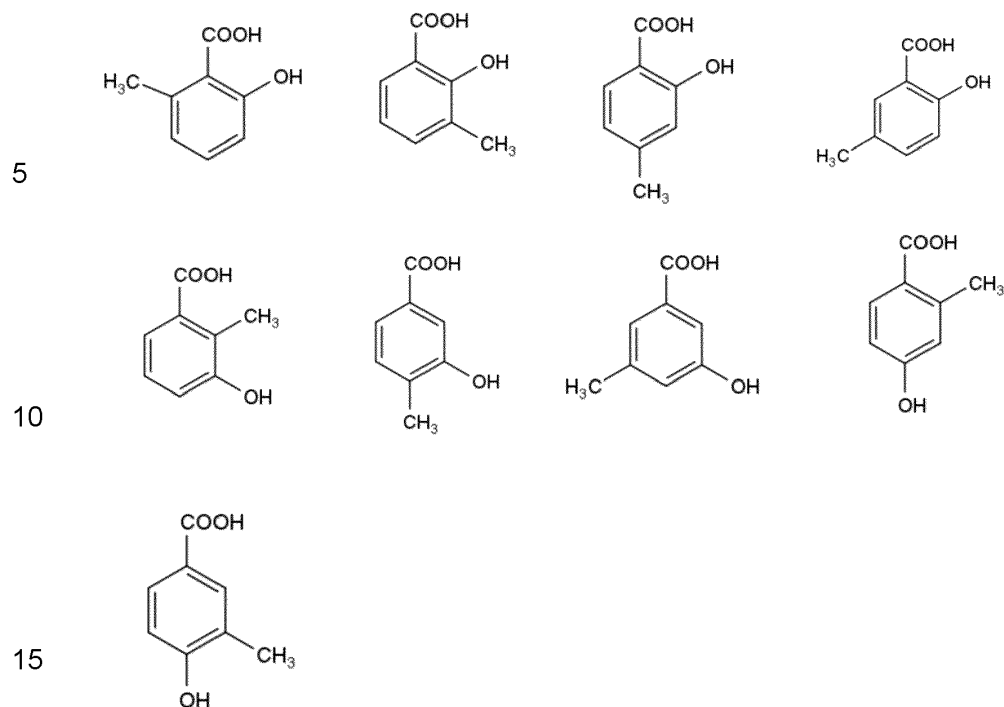
Preferably at least one of R^1 to R^5 is H, more preferably at least one of R^2 to R^4 is H, very preferably R^2 to R^4 are H.

[0050] Exemplified embodiments of the compound A are selected from one or more members of the following group consisting of:

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[0051] The molecular weight of the compound A is preferably in the range from 10 to 1,000, more preferably 30 to 800, very preferably 50 to 500, and most preferably 100 to 300. The molecular weight of the compound A can be measured by well-known methods such as freezing point depression method and vapor pressure depression method.

[0052] The content of the compound A is preferably 0.01 to 1 mass parts, more preferably 0.05 to 0.8 mass parts, very preferably 0.07 to 0.5 mass parts based on 100 mass parts of the polymer.

[0053] The molar ratio of the compound A to the amine is preferably in the range from 0.1 to 10, more preferably 0.2 to 8, very preferably 0.3 to 5 and most preferably 0.5 to 3.

[0054] This is not bound by theory, but it is considered that the compound A further sufficiently suppresses the decomposition of the photoacid generator when the molar ratio of the compound A to the amine is in the above-mentioned range.

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[0055] Amine

The multiple compounds contain an amine. In a preferred embodiment, the amine is selected from one or more members of the following group consisting of a primary amine, a secondary amine and a tertiary amine. More preferably said amine is a tertiary amine.

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[0056] The primary amine may be selected from one or more members of the following group consisting of ethylamine, propylamine, butylamine, 2-ethylhexylamine, octylamine, and dodecylamine, n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-hexadecylamine, n-octadecylamine and oleylamine.

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[0057] The secondary amine may be selected from one or more members of the following group consisting of dimethylamine, diethylamine, dipropylamine, dibutylamine, diamylamine, dihexylamine, diheptylamine, bis-2-ethylhexylamine, methylethylamine, ethylbutylamine, N-methyl-1-amino-cyclohexane, ethylamylamine, piperidine, piperazine and morpholine.

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[0058] The tertiary amine may be selected from one or more members of the following group consisting of trimethylamine, triethylamine, tri-n-propylamine, tri-n-butylamine, tri-n-hexylamine, tri-n-pentylamine, tri-n-heptylamine, tri-n-octylamine, tri-n-nonylamine, tri-n-decylamine and tri-n-dodecylamine, more preferably selected from one or more members of the following group consisting of the group consisting of tri-n-heptylamine, tri-n-octylamine and tri-n-nonylamine.

25

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[0059] The content of the amine is preferably in the range from 0.1 to 1 mass parts, more preferably 0.2 to 0.9 mass parts, very preferably 0.3 to 0.8 mass parts based on 100 mass parts of the polymer.

- 5 [0060] The molecular weight of the amine is preferably in the range from 30 to 1,000, more preferably 100 to 800, very preferably 150 to 600, most preferably 200 to 500.

[0061] Photoacid generator

- 10 The multiple compounds contain a photoacid generator. In a preferred embodiment, the photoacid generator is represented by formula (A-1).
 B^{n+} cation B^{n-} anion (A-1)
 wherein B^{n+} cation is preferably a cation represented by the formula (AC1), a cation represented by the formula (AC2), or a cation represented by the
 15 formula (AC3). B^{n+} cation is n valent as a whole. n is 1 to 3, preferably 1 or 2, more preferably 1.

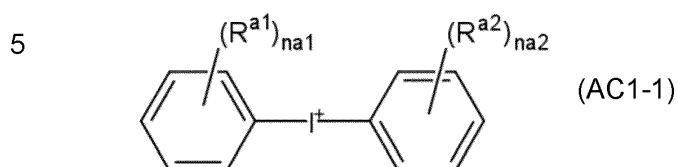
- [0062] B^{n-} anion is preferably an anion represented by the formula (AA1), an anion represented by the formula (AA2), or an anion represented by the
 20 formula (AA3). B^{n-} anion is n valent as a whole. n is 1 to 3, preferably 1 or 2, more preferably 1.

[0063] The formula (AC1) is as follows;

- 25 $R^1 - I^+ - R^2$ (AC1)

- wherein R^1 and R^2 are each independently C_{1-20} alkyl, C_{1-20} aryl or C_{1-20} aralkyl, preferably linear, branched or cyclic structure containing C_{1-20} alkyl, C_{1-20} aryl or C_{1-20} aralkyl, more preferably C_{1-15} aryl or C_{1-15} aralkyl, very
 30 preferably C_{1-10} aryl.

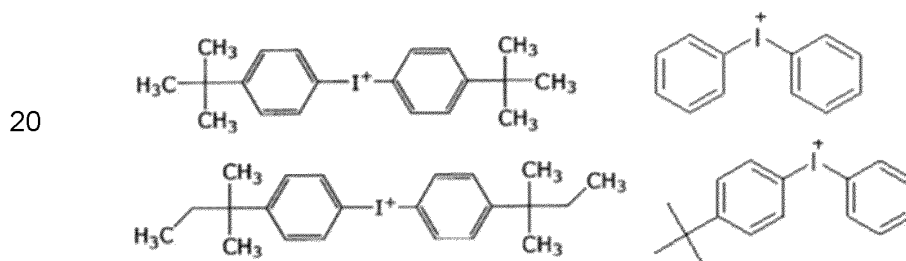
[0064] Preferably, a cation represented by the formula (AC1) may also be represented by formula (AC1-1);



10 wherein R^{a1} and R^{a2} are each independently linear, branched or cyclic structure containing C_{1-6} alkyl, linear, branched or cyclic structure containing C_{1-6} alkoxy or C_{6-12} aryl, preferably branched C_{4-6} alkyl, more preferably *t*-butyl or 1,1-dimethylpropyl, very preferably *t*-butyl. $na1$ and $na2$ are each independently 0, 1, 2 or 3, preferably each 1.

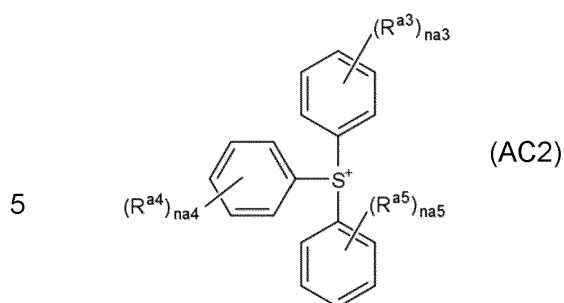
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[0065] Exemplified embodiments of the formula (AC1) are as follows.



25 [0066] The formula (AC2) is as follows;

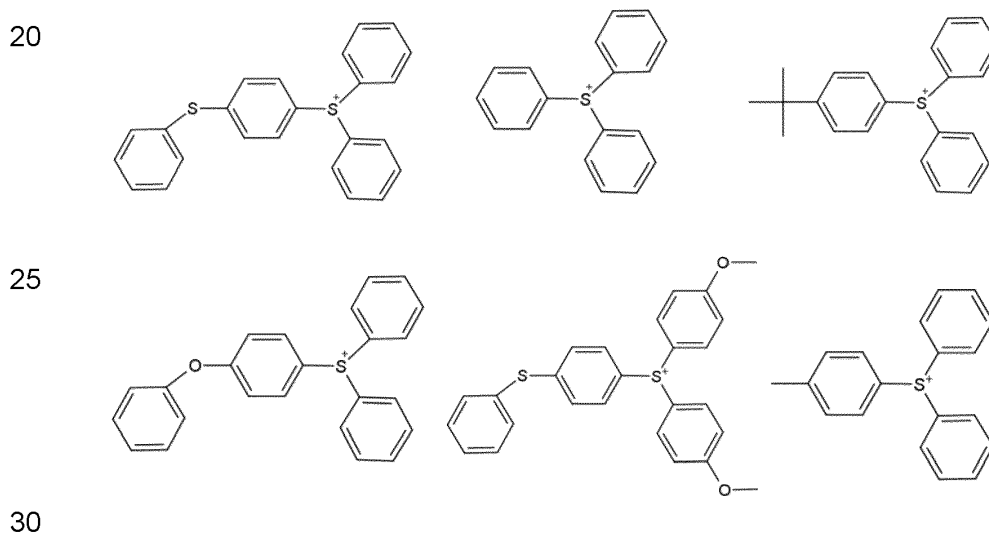
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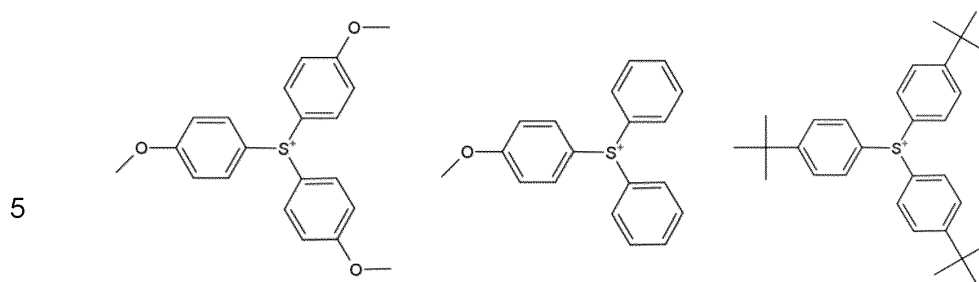
wherein R^{a3} to R^{a5} are each independently linear, branched or cyclic structure
 10 containing C_{1-6} alkyl, linear, branched or cyclic structure containing C_{1-6}
 alkoxy, C_{6-12} aryl, C_{6-12} arylthio or C_{6-12} aryloxy, preferably methyl, ethyl, t-
 butyl, methoxy, ethoxy, phenylthio or phenyloxy, more preferably t-butyl,
 methoxy, ethoxy, phenylthio or phenyloxy.

$na3$ to $na5$ are each independently 0, 1, 2 or 3. It is also a preferred
 15 embodiment that $na3$ to $na5$ are all 1 and R^{a3} to R^{a5} are all identical. It is also
 a preferred embodiment that $na3$ to $na5$ are all 0.

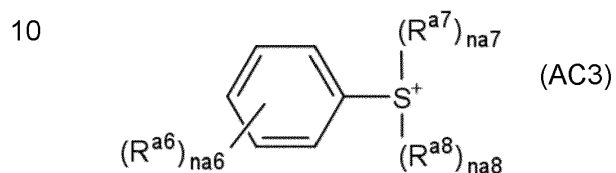
[0067] Exemplified embodiments of the formula (AC2) are as follows.



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[0068] The formula (AC3) is as follows;

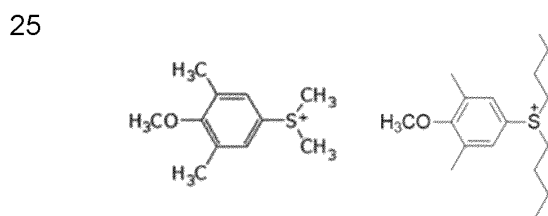


15 wherein R^{a6} is each independently linear, branched or cyclic structure containing C_{1-6} alkyl, linear, branched or cyclic structure containing C_{1-6} alkoxy or C_{6-12} aryl, preferably methyl, ethyl, methoxy or ethoxy, more preferably methyl or methoxy.

R^{a7} and R^{a8} are each independently linear, branched or cyclic structure containing C_{1-6} alkyl, preferably methyl, ethyl or linear butyl, more preferably methyl. $na6$ to $na8$ are each independently 0, 1, 2 or 3; more preferably 1 or 3.

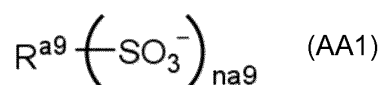
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[0069] Exemplified embodiment of the formula (AC3) are as follows.



30

[0070] The formula (AA1) is as follows:



5 wherein R^{a9} is linear, branched or cyclic structure containing C_{1-6} fluorine-substituted alkyl, linear, branched or cyclic structure containing C_{1-6} fluorine-substituted alkoxy, C_{6-12} fluorine-substituted aryl, C_{2-12} fluorine-substituted acyl or C_{6-12} fluorine-substituted alkoxyaryl, preferably linear, branched or cyclic structure containing C_{2-6} fluorine-substituted alkyl or C_{6-10} fluorine-substituted aryl, more preferably linear C_{2-4} fluorine-substituted alkyl or C_{6-8} fluorine-substituted aryl, very preferably linear C_4 fluorine-substituted alkyl or C_7 fluorine-substituted aryl. In the fluorine-substituted alkyl of R^{a9} , an embodiment in which all the hydrogen present in the alkyl moiety are substituted with fluorine is preferable (hereafter, the state where all the hydrogen of a group are substituted with fluorine is referred to as "fully fluorine-substituted").

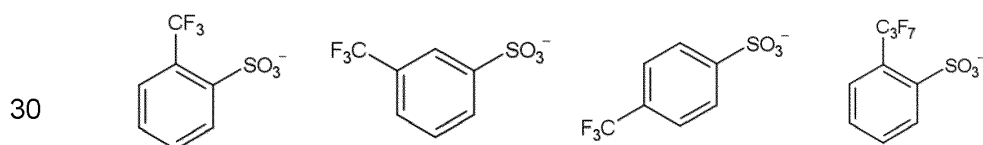
15 R^{a9} is preferably fully fluorine-substituted methyl, ethyl, propyl, butyl, pentyl or toluene where methyl is fully fluorine-substituted, more preferably fully fluorinated propyl, butyl, pentyl or toluene where methyl is fully fluorine-substituted, very preferably fully fluorinated butyl or toluene where methyl is fully fluorine-substituted.

20 $na9$ is 1 or 2, preferably 1. When $na9$ is 2, R^{a9} becomes divalent, and hydrogen or fluorine of R^{a9} becomes a single bond and is bonded to an S atom.

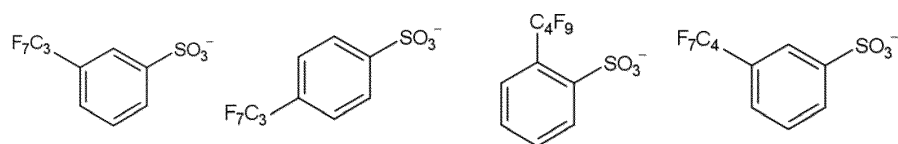
25

[0071] Exemplified embodiments of the formula (AA1) are as follows.

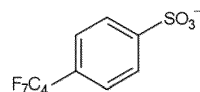
$CF_3SO_3^-$, $C_3F_7SO_3^-$, $C_4F_9SO_3^-$,



- 22 -

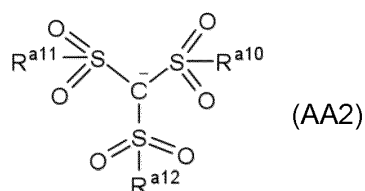


5



[0072] The formula (AA2) is as follows:

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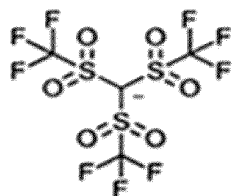


15

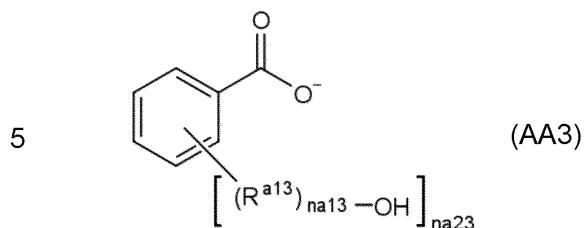
R^{a10} to R^{a12} are each independently linear, branched or cyclic structure containing C_{1-6} fluorine-substituted alkyl, linear, branched or cyclic structure containing C_{1-6} fluorine-substituted alkoxy, linear, branched or cyclic structure containing C_{1-6} alkyl, preferably linear, branched or cyclic structure containing C_{1-6} fully fluorine-substituted alkyl, more preferably linear or branched C_{1-6} fully fluorine-substituted alkyl, very preferably fully fluorine-substituted methyl, ethyl, or t-butyl, most preferably fully fluorine-substituted methyl.

[0073] An exemplified embodiment of the formula (AA2) is as follows.

30

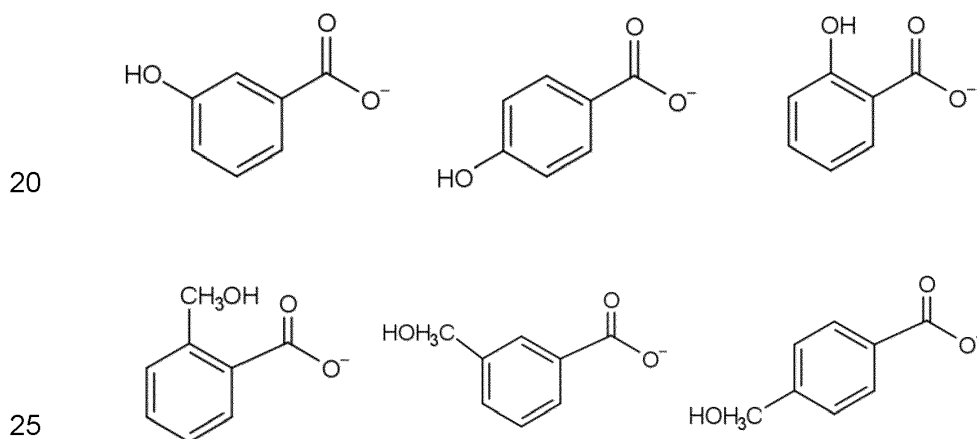


[0074] The formula (AA3) is as follows:

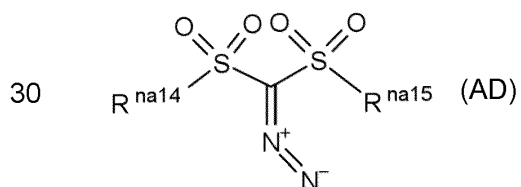


10 R^{a13} is linear, branched or cyclic structure containing C_{1-6} alkylene or C_{6-12} arylene, preferably methylene, ethylene, propylene or butylene, more preferably methylene or ethylene, very preferably methylene.
 $na13$ is 0 or 1, preferably 0.
 $na23$ is 1, 2 or 3, preferably 1 or 2, more preferably 1.

15 [0075] Exemplified embodiments of the formula (AA3) are as follows.



[0076] The photoacid generator may also be represented by formula (AD).

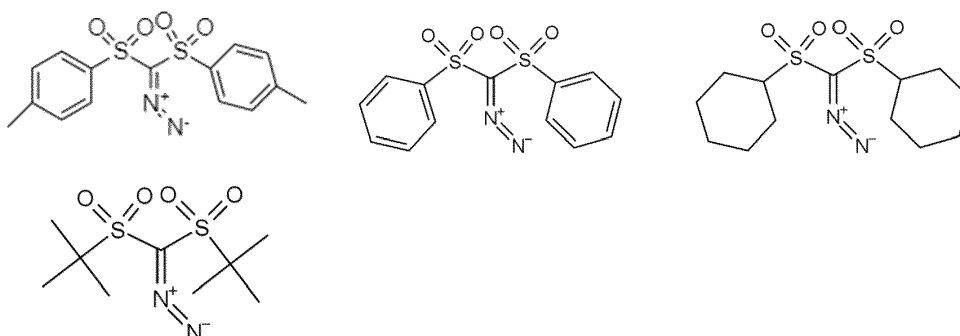


R^{na14} and R^{na15} are each independently linear, branched or cyclic structure containing C₁₋₆ alkyl or C₆₋₁₂ aryl, preferably linear, branched or cyclic structure containing C₂₋₆ alkyl or C₆₋₁₀ aryl, more preferably branched or cyclic structure containing C₄₋₆ alkyl or C₆₋₈ aryl.

5

[0077] Exemplified embodiments of the formula (AD) are as follows.

10



15

[0078] The photoacid generator preferably comprises a cation represented by the formula (AC1) or (AC2) and an anion represented by the formula (AA1) or (AA3).

20

[0079] The photoacid generator of the present invention may be selected from one or more members of the following group consisting of the photoacid generator consisting of the cation represented by the formula (AC1) and the anion represented by the formula (AA1), the photoacid generator consisting of the cation represented by the formula (AC1) and the anion represented by the formula (AA2), the photoacid generator consisting of the cation represented by the formula (AC1) and the anion represented by the formula (AA3), the photoacid generator consisting of the cation represented by the formula (AC2) and the anion represented by the formula (AA1), the photoacid generator consisting of the cation represented by the formula (AC2) and the anion represented by the formula (AA2), the photoacid generator consisting of the cation represented by the formula (AC2) and the anion represented by the formula (AA3), the photoacid generator consisting of the cation

25

30

represented by the formula (AC3) and the anion represented by the formula (AA1), the photoacid generator consisting of the cation represented by the formula (AC3) and the anion represented by the formula (AA2), the photoacid generator consisting of the cation represented by the formula (AC3) and the anion represented by the formula (AA3), and the photoacid generator represented by the formula (AD).

[0080] The content of the photoacid generator is preferably in the range from 1 to 10 mass parts, more preferably 2 to 7 mass parts, very preferably 2.5 to 5 mass parts based on 100 mass parts of the polymer..

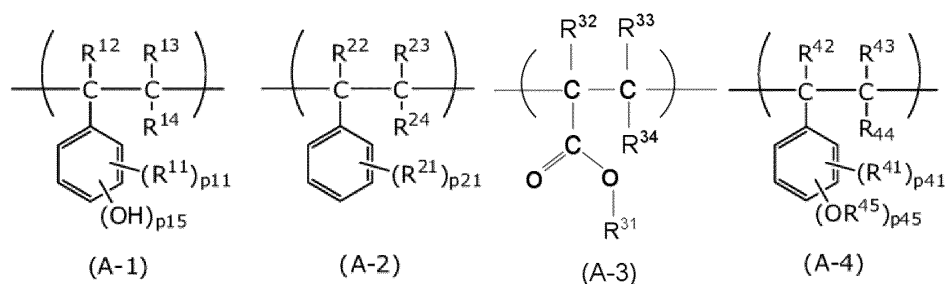
[0081] The weight average molecular weight of the photoacid generator is preferably in the range from 30 to 1,000, more preferably 100 to 800, very preferably 150 to 600, most preferably 200 to 500.

15

[0082] Polymer

The multiple compounds contain a polymer. the polymer comprises at least one of the following repeating units (A-1) to (A-4);

20



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wherein R^{11} , R^{21} , R^{41} and R^{45} are each independently C_{1-10} alkyl, preferably linear, branched or cyclic structure containing C_{1-10} alkyl, more preferably linear, branched or cyclic structure containing C_{1-6} alkyl, very preferably linear or branched C_{1-6} alkyl.

30

One or more of non-adjacent CH₂-groups of R¹¹, R²¹, R⁴¹ and R⁴⁵ are optionally replaced by -O-.

R¹², R¹³, R¹⁴, R²², R²³, R²⁴, R³¹, R³², R³³, R³⁴, R⁴², R⁴³ and R⁴⁴ are each independently H, C₁₋₅ alkyl, C₁₋₅ alkoxy or -COOH, preferably H, linear,
 5 branched or cyclic structure containing C₁₋₅ alkyl, linear, branched or cyclic structure containing C₁₋₅ alkoxy or -COOH, more preferably H, linear, branched or cyclic structure containing C₁₋₅ alkyl, very preferably H or tert-butyl.

p₁₁ is 0 to 4, preferably 0 to 2, more preferably 0.

10 p₁₅ is 0 to 2, preferably 1.

p₁₁ + p₁₅ ≤ 5 is satisfied.

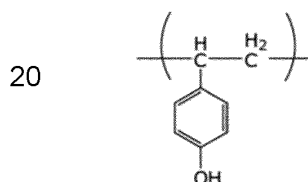
p₂₁ is 0 to 4, preferably 0 to 2, more preferably 0.

p₄₁ is 0 to 4, preferably 0 to 2, more preferably 0.

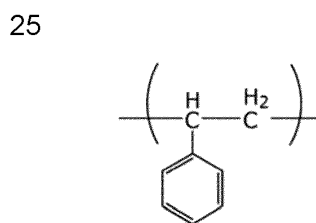
p₄₅ is 1 to 2, preferably 1.

15 p₄₁ + p₄₅ ≤ 5 is satisfied.

[0083] Exemplified embodiment of the formula (A-1) includes the following.

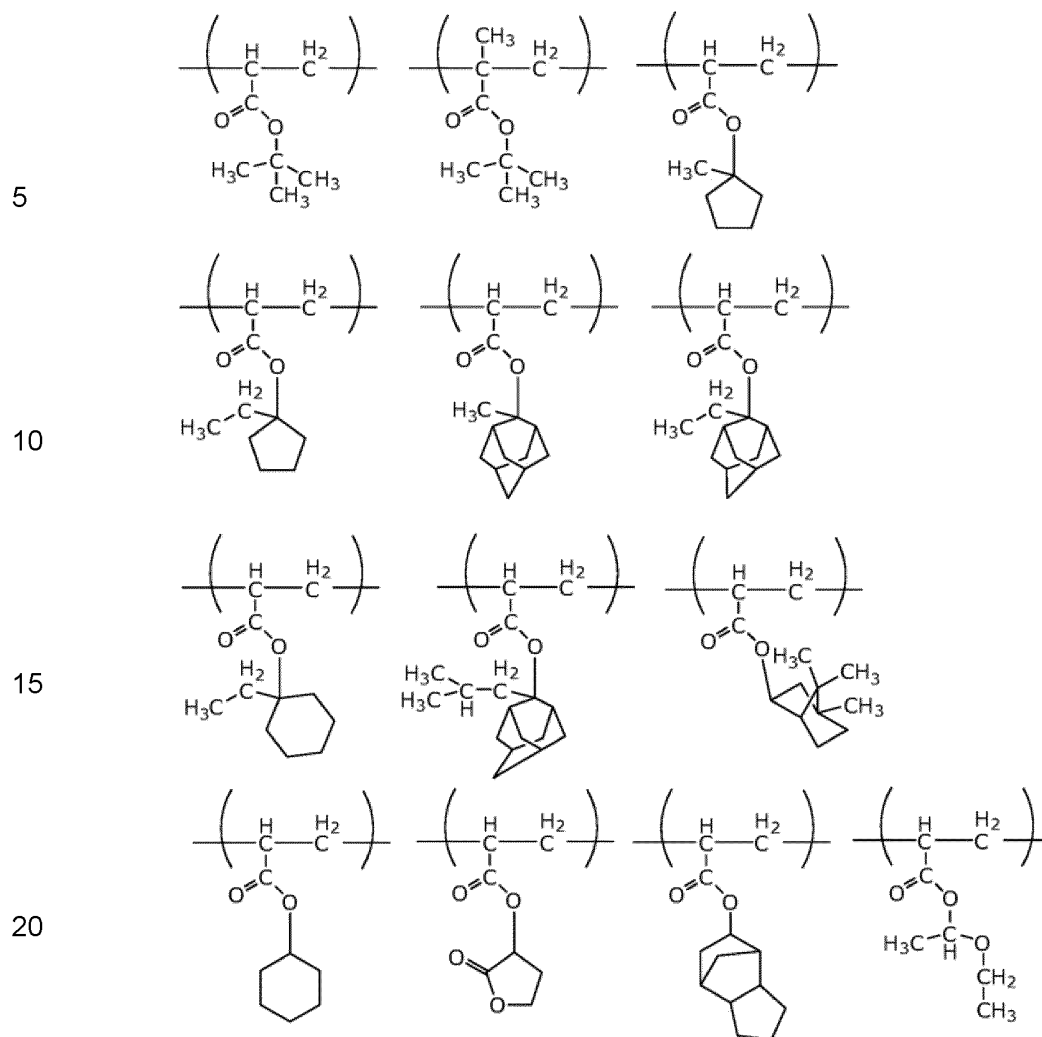


[0084] Exemplified embodiment of the formula (A-2) includes the following.

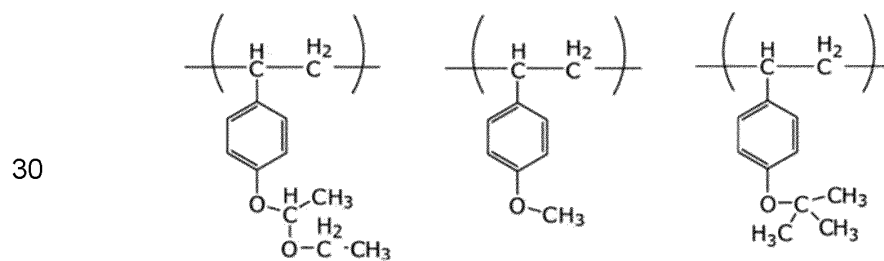


30

[0085] Exemplified embodiments of the formula (A-3) include the followings.



[0086] Exemplified embodiments of the formula (A-4) include the followings.



[0087] The polymer may comprise plural kinds of repeating units represented by the formula (A-1), (A-2), (A-3) or (A-4). For example, it is possible for the polymer to have a repeating unit (A-1) where $p_{15} = 1$ and a repeating unit (A-1) where $p_{15} = 2$ at a ratio of 1 : 1. In this case, it becomes $p_{15} = 1.5$ as a whole.

[0088] These structural units are appropriately blended according to the purpose. It is a preferred embodiment that the structural units are blended so that an increase rate of solubility in the alkaline aqueous solution becomes appropriate by the acid.

n_{A-1} , n_{A-2} , n_{A-3} and n_{A-4} , which are the numbers of repeating units represented by the formulae (A-1), (A-2), (A-3) and (A-4) in the polymer (A), are described below.

[0089] $n_{A-1}/(n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4})$ is preferably 40 to 80%; more preferably 45 to 75%, very preferably 50 to 70%; and most preferably 55 to 65%.

$n_{A-2}/(n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4})$ is preferably 0 to 40%; more preferably 0 to 35%; very preferably 5 to 35%; and most preferably 15 to 25%.

$n_{A-3}/(n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4})$ is preferably 0 to 40%; more preferably 10 to 40%; very preferably 15 to 30%; and most preferably 15 to 25%.

$n_{A-4}/(n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4})$ is preferably 0 to 40%; more preferably 10 to 40%; very preferably 15 to 30%; and most preferably 15 to 25%.

As an embodiment of the present invention, when $n_{A-3} > 0$, $n_{A-4} = 0$.

[0090] The polymer may be selected from one or more of the polymers comprising at least one of the repeating units (A-1) to (A-4).

The polymer may also comprise one or more additional repeating units other than the repeating units represented by the formulae (A-1), (A-2), (A-3) and (A-4).

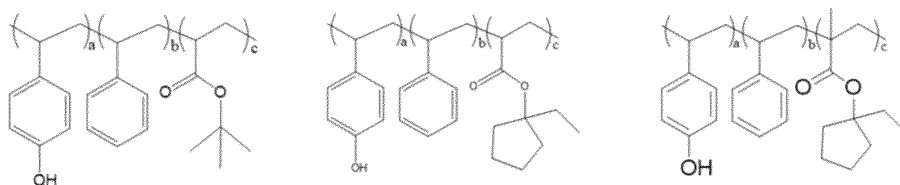
n_{total} , which is the total number of all repeating units included in the polymer, satisfies the following.

$(n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4})/n_{\text{total}}$ = preferably 80 to 100%, more preferably 90 to 100%, and very preferably 95 to 100%. It is also a preferred embodiment of the polymer to include no further repeating unit $((n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4})/n_{\text{total}} = 100\%)$.

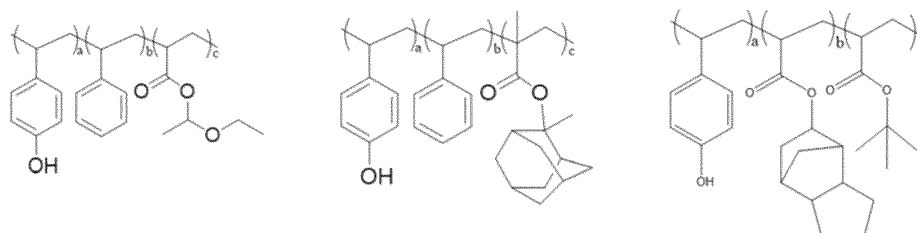
5

[0091] Exemplified embodiments of the polymer include the following.

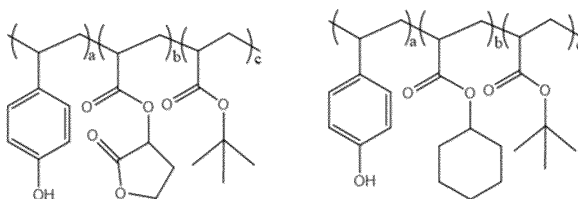
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[0092] The content of the polymer is preferably in the range from 40 to 99 mass %, more preferably 60 to 98 mass %, very preferably 70 to 97 mass %, and most preferably 80 to 96 mass % based on the content of the compounds other than the solvent.

30

The weight average molecular weight (hereinafter referred to as M_w in some cases) of the polymer is preferably in the range from 2,000 to 50,000; more preferably 4,000 to 40,000, very preferably 6,000 to 30,000; and most preferably 8,000 to 20,000.

[0093] In the present invention, Mw can be measured by gel permeation chromatography (GPC). In the measurement, it is a preferable example that a GPC column at 40 degrees Celsius, an elution solvent of tetrahydrofuran at 0.6 mL/min and monodisperse polystyrene as a standard are used.

5

[0094] The multiple compounds may include one or more additional polymers that do not comprise repeating units represented by the formulae (A-1), (A-2), (A-3) and (A-4). The content of the additional polymers is preferably in the range from 0 to 10 mass %, more preferably 0 to 5 mass %, very preferably 0 to 1 mass %, and most preferably 0 mass % (not included) based on the content of the compounds other than the solvent.

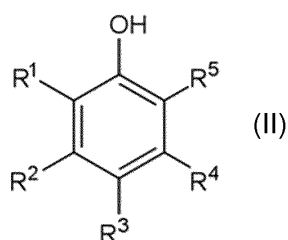
10

[0095] Compound B

15

The multiple compounds may contain the compound B. The compound B is represented by formula (II);

20



wherein R¹ and R⁵ are each independently C₁₋₂₀ alkyl or C₁₋₂₀ alkoxy, preferably linear, branched or cyclic structure containing C₁₋₂₀ alkyl or linear, branched or cyclic structure containing C₁₋₂₀ alkoxy, more preferably linear or branched C₁₋₁₀ alkyl, very preferably branched C₁₋₅ alkyl.

R² to R⁴ are each independently H, C₁₋₂₀ alkyl or C₁₋₂₀ alkoxy, preferably H, linear, branched or cyclic structure containing C₁₋₂₀ alkyl or linear, branched or cyclic structure containing C₁₋₂₀ alkoxy, more preferably H or linear or branched C₁₋₁₀ alkyl, very preferably H or linear C₁₋₅ alkyl, most preferably H or methyl.

25

30

When R¹ to R⁵ are each independently alkyl, then one or more of non-adjacent CH₂-groups are optionally replaced by —O—, —S—, —CO—, —CO—O—, —O—CO—, —O—CO—O—, —CR=CR— or —C≡C—.

5 R³ and R⁴ may form a mono- or polycyclic organic ring system with each other.

[0096] Preferably at least one of R¹, R³ and R⁵ is linear, branched or cyclic structure containing C₁₋₂₀ alkyl, more preferably at least one of R¹, R³ and R⁵ is linear or branched C₁₋₁₀ alkyl, very preferably R¹, R³ and R⁵ are linear or
10 branched C₁₋₅ alkyl.

[0097] Preferably at least one of R² and R⁴ is H, more preferably R² and R⁴ are H.

15 [0098] This is not bound by theory, but it is considered that the compound B suppressed the decomposition of the photoacid generator by capturing radicals that induces the decomposition.

[0099] The molar ratio of the compound B to the photoacid generator is in the
20 range from 0.01 to 3, preferably 0.03 to 1.5, more preferably 0.05 to 0.5.

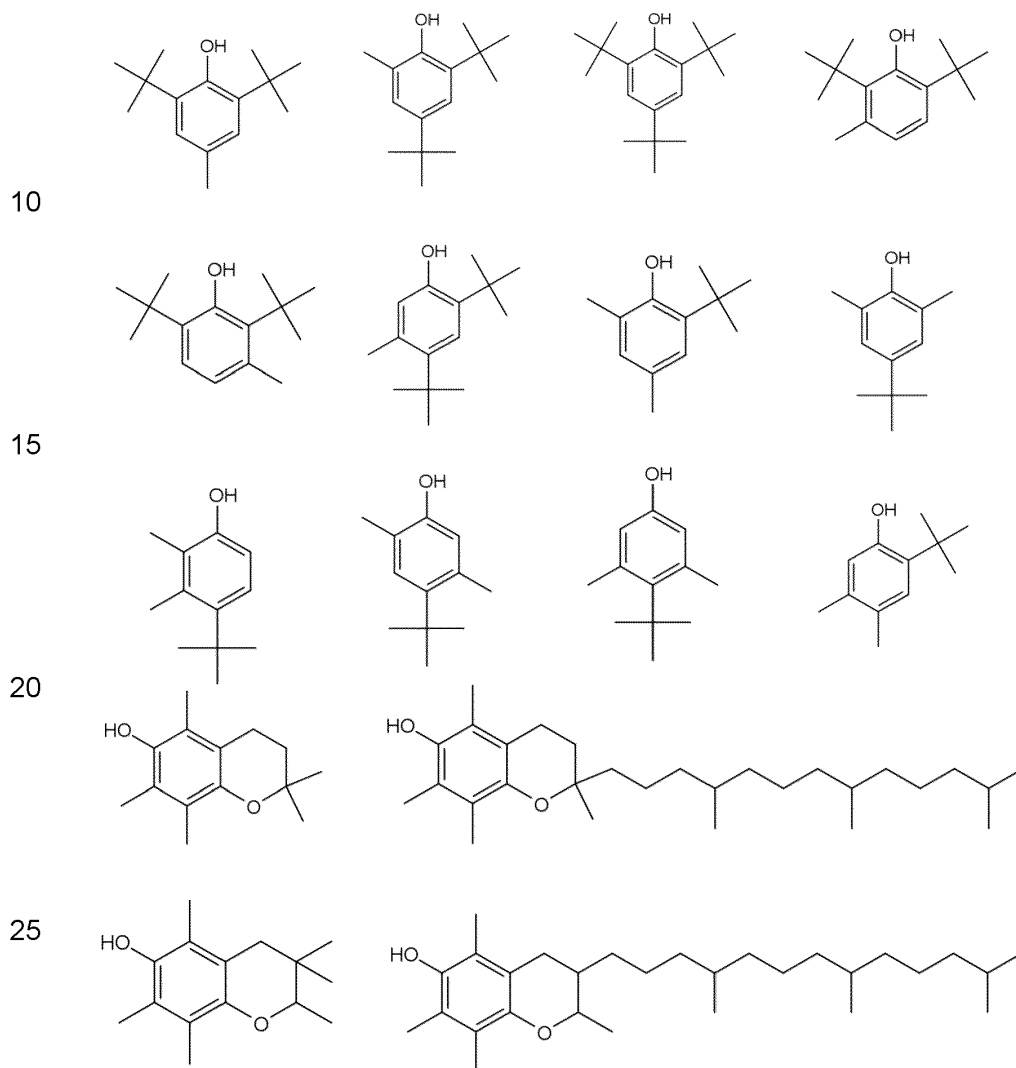
[0100] This is not bound by theory, but it is considered that the compound B further sufficiently suppresses the decomposition of the photoacid generator when the molar ratio of the compound B to the photoacid generator is in the
25 above-mentioned range.

[0101] The molecular weight of the compound B is preferably in the range from 10 to 1,000, more preferably 30 to 800, very preferably 50 to 500, and most preferably 100 to 300.

30

[0102] The content of the compound B is preferably in the range from 0.05 to 5 mass parts, more preferably 0.1 to 3 mass parts, very preferably 0.2 to 1.5 mass parts based on 100 mass parts of the polymer.

5 [0103] Exemplified embodiments of the polymer include the following.



[0104] Solvent

30 The multiple compounds may include a solvent.

The solvent may be selected from one or more members of the following group consisting of methanol, ethanol, n-propanol, i-propanol (isopropyl alcohol, IPA), n-butanol, i-butanol, sec-butanol, t-butanol, n-pentanol, i-pentanol, 2-methylbutanol, sec-pentanol, t-pentanol, 3-methoxybutanol, n-
5 hexanol, 2-methylpentanol, sec-hexanol, 2-ethylbutanol, sec-heptanol, heptanol-3, n-octanol, 2-ethylhexanol, sec-octanol, n-nonyl alcohol, 2,6-dimethylheptanol-4, n-decanol, sec-undecyl alcohol, trimethylnonyl alcohol, sec-tetradecyl alcohol, sec-heptadecyl alcohol, phenol, cyclohexanol, methylcyclohexanol, 3,3,5-trimethylcyclohexanol, benzyl alcohol,
10 phenylmethylcarbinol, diacetone alcohol, cresol, ethylene glycol, propylene glycol, 1,3-butylene glycol, pentanediol-2,4, 2-methylpentanediol-2,4, hexanediol-2,5, heptanediol-2,4, 2-ethyl-1,3-hexanediol, diethylene glycol, dipropylene glycol, triethylene glycol, tripropylene glycol, glycerin, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol
15 mono-n-butyl ether, ethylene glycol mono-n-hexyl ether, ethylene glycol monophenyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol mono-n-hexyl ether, ethoxytriglycol, propylene glycol monomethyl ether (PGME), propylene glycol monomethyl ether acetate (PGMEA), propylene
20 glycol monoethyl ether, propylene glycol monopropyl ether, propylene glycol monobutyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol mono propyl ether, dipropylene glycol monobutyl ether, tripropylene glycol monomethyl ether, 4-methyl-2-pentanol, 3-methyl-2-pentanol, 2-methyl-2-pentanol, 3-methyl-2-butanol, 2-methyl-2-
25 butanol, 4-methyl-2-hexanol, 5-methyl-2-hexanol, 3-methyl-2-hexanol, 2-methyl-2-hexanol, ethyl lactate (EL), propyl lactate, n-butyl lactate, n-amyl lactate, butyric acid, methyl 2-hydroxyisobutyrate, methyl 2-hydroxybutyrate, methyl 3-hydroxybutyrate, methyl 4-hydroxybutyrate, ethyl 2-
hydroxyisobutyrate, ethyl 2-hydroxybutyrate, ethyl 3-hydroxybutyric acid and
30 ethyl 4-hydroxybutyrate, preferably selected from one or more members of the following group consisting of i-propanol, PGME, PGMEA, EL, propylene glycol dimethyl ether and N-methylpyrrolidone, more preferably selected from

one or more members of the following group consisting of the group consisting of PGME, PGMEA and EL.

5 [0105] The boiling point of the solvent at 101,325 Pa is preferably 30 to 300°C, more preferably 40 to 250°C, and very preferably 50 to 200°C.

[0106] The content of the solvent is preferably in the range from 500 to 3,000 mass parts, more preferably 1,000 to 2,000 mass parts, very preferably 700 to 1,700 mass parts based on 100 mass parts of the polymer.

10

[0107] Photobase generator

The multiple compounds may contain a photobase generator. The photobase generator may be selected from one or more members of the following group consisting of 1,2-Dicyclohexyl-4,4,5,5-tetramethylbiguanidium n-butyltriphenylborate, nitrobenzyl capped 1,8-diazabicyclo-[5.4.0]undec-7-ene, benzyl capped 1,8-diazabicyclo-[5.4.0]undec-7-ene, 2-(9-Oxoxanthen-2-yl)propionic acid 1,5,7-triazabicyclo[4.4.0]dec-5-ene salt, 1,5,7-Triazabicyclo[4.4.0]dec-5-ene-HBPh4 and triphenylmethanol, preferably triphenylmethanol.

20

[0108] The content of the photobase generator is preferably in the range from 0.1 to 5 mass parts, more preferably 0.3 to 3 mass parts, very preferably 0.5 to 2 mass parts based on 100 mass parts of the polymer.

25 [0109] Surfactant

The multiple compounds may contain a surfactant. The surfactant may be a nonionic surfactant, an anionic surfactant or an amphoteric surfactant.

30 [0110] The nonionic surfactant may be selected from one or more members of the following group consisting of polyoxyethylene alkyl ethers such as polyoxyethylene lauryl ether, polyoxyethylene oleyl ether and polyoxyethylene cetyl ether, polyoxyethylene fatty acid diesters,

polyoxyethylene fatty acid monoesters, polyoxyethylene polyoxypropylene block polymer, acetylene alcohol, acetylene glycol, polyethoxylate of acetylene alcohol, acetylene glycol derivatives such as polyethoxylate of acetylene glycol, fluorine-containing surfactants such as FLUORAD (trade name, 3M Japan), MEGAFACE (trade name: DIC), SURFLON (trade name, AGC), organosiloxane surfactants such as KF-53 (trade name, Shin-Etsu Chemical), polyether-modified siloxane and BYK-333 (trade name, BYK). Examples of the acetylene glycol include 3-methyl-1-butyne-3-ol, 3-methyl-1-pentyn-3-ol, 3,6-dimethyl-4-octyne-3,6-diol, 2,4,7,9-tetramethyl- 5-decyne-4,7-diol, 3,5-dimethyl-1-hexyne-3-ol, 2,5-dimethyl-3-hexyne-2,5-diol, 2,5-dimethyl-2,5-hexanediol.

It is a preferred embodiment that the surfactant is a polyether-modified siloxane.

[0111] The content of the surfactant is in the range from 0.01 to 0.5 mass parts, more preferably 0.02 to 0.3 mass parts, very preferably 0.03 to 0.1 mass parts based on 100 mass parts of the polymer.

[0112] Other compounds

The multiple compounds may contain a compound other than the above-mentioned compound.

[0113] The other compound may be selected from one or more members of the following group consisting of a surface smoothing agent, a dye, a contrast enhancer, an acid, a radical generator, a substrate adhesion enhancer, a plasticizer and an antifoaming agent.

[0114] The dye may be an anthracene compound. It is a preferred embodiment that the anthracene compound is 9-(4-hydroxybenzil)-1-(4-hydroxyphenyl)anthracene.

[0115] The content of the other compound is preferably in the range from 0.1 to 5 mass parts, more preferably 0.3 to 3 mass parts, very preferably 0.5 to 2 mass parts based on 100 mass parts of the polymer.

5 [0116] [Photoresist composition]

In another aspect, the present invention also relates to the photoresist composition comprising a polymer, a photoacid generator, a compound A represented by formula (I) and an amine, wherein the molar ratio of the compound A to the amine is in the range from
10 0.1 to 10.

[0117] Compound A

The photoresist composition contains a compound A. The detail of the compound is described in the section of "Compound A" in "Method for
15 stabilizing a photoacid generator in a photoresist composition."

[0118] Amine

The photoresist composition contains an amine. The detail of the amine is described in the section of "Amine" in "Method for stabilizing a photoacid
20 generator in a photoresist composition."

[0119] Photoacid generator

The photoresist composition contains a photoacid generator. The detail of the photoacid generator is describe in the section of "Photoacid generator" in
25 "Method for stabilizing a photoacid generator in a photoresist composition."

[0120] Polymer

The photoresist composition contains a polymer. The detail of the polymer is described in the section of "Polymer" in "Method for stabilizing a photoacid
30 generator in a photoresist composition."

[0121] Compound B

[0121] The photoresist composition may contain compound B. The detail of the compound B is described in the section of "Compound B" in "Method for stabilizing a photoacid generator in a photoresist composition."

5 [0122] Solvent

The photoresist composition may include a solvent.

The detail of the solvent is described in the section of "Solvent" in "Method for stabilizing a photoacid generator in a photoresist composition."

10 [0123] Photobase generator

The photoresist composition may contain a photobase generator. The detail of the photobase generator is described in the section of "Photobase generator" in "Method for stabilizing a photoacid generator in a photoresist composition."

15

[0124] Surfactant

The photoresist composition may contain a surfactant. The detail of the surfactant is described in the section of "Surfactant" in "Method for stabilizing a photoacid generator in a photoresist composition."

20

[0125] Other compounds

The photoresist composition may contain a compound other than the above-mentioned compound. The detail of the other compound is described in the section of "Other compounds" in "Method for stabilizing a photoacid generator in a photoresist composition."

25

[0126] [Use of a compound A]

In another aspect, the present invention further relates to use of a compound A for stabilizing a photoacid generator in a photoresist composition.

30 The detail of the compound A is described in the section of "Compound A" in "Method for stabilizing a photoacid generator in a photoresist composition."

[0127] [Example]

The present invention is described below with reference to several examples.

The embodiment of the present invention is not limited only to these examples. Mass parts of every ingredient in the examples are all based on 100 mass parts of the polymers.

[0128] Preparation of photoresist composition

Example 1

0.29 mass parts of 2-hydroxybenzoic acid and 0.371 mass parts of tri-n-octylamine are added to 159.60 mass parts of PGME separately. The PGME solution of 2-hydroxybenzoic acid and the PGME solution of tri-n-octylamine are mixed. To the mixed solution, 792.98 mass parts of PGMEA and 319.52 mass parts of EL are added simultaneously. To the mixed solution, 30.0 mass parts of polymer (1) and 70.0 mass parts of polymer (2) are added simultaneously. To the mixed solution, 2.0 mass parts of bis(4-methylphenylsulfonyl)diazomethane, 0.6 mass parts of di(4-*t*-butyl)phenyliodonium 2-(trifluoromethyl)benzenesulfonate, and 1.5 mass parts of [4-(1,1-Dimethylethyl)phenyl]diphenylsulfonium perfluorobutanesulfonate and 0.232 mass parts of triphenylsulfonium 2-hydroxybenzoate are added simultaneously as photoacid generators. To the mixed solution, 0.812 mass parts of triphenylmethanol is added. To the mixed solution, 0.06 mass parts of polyether-modified polysiloxane and 0.84 mass parts of 9-(4-hydroxybenzil)-1-(4-hydroxyphenyl)anthracene are added simultaneously.

The mixed solution is stirred overnight at 25°C and the solution is filtrated by a 0.05μm thick filter to yield the photoresist composition.

[0129] Example 2

Except for the point that the amount of 2-hydroxybenzoic acid is changed from 0.29 mass parts to 0.1451 mass parts, the photoresist composition is yielded by the same manner as described by example 1.

[0130] Example 3

Except for the point that the amount of 2-hydroxybenzoic acid is changed from 0.29 mass parts to 0.0725 mass parts, the photoresist composition is yielded by the same manner as described by example 1.

5

[0131] Example 4

Except for the point that 0.4398 mass parts of 2,6-Di-tert-butyl-4-methylphenol is further added together with the polyether-modified polysiloxane and the 9-(4-hydroxybenzil)-1-(4-hydroxyphenyl)anthracene, the photoresist composition is yielded by the same manner as described by example 1.

10

[0132] Example 5

Except for the point that 0.2199 mass parts of 2,6-Di-tert-butyl-4-methylphenol is further added together with the polyether-modified polysiloxane and the 9-(4-hydroxybenzil)-1-(4-hydroxyphenyl)anthracene, the photoresist composition is yielded by the same manner as described by example 1.

15

[0133] Comparative Example 1

Except for the point that 2-hydroxybenzoic acid is not added, the photoresist composition is yielded by the same manner as described by example 1.

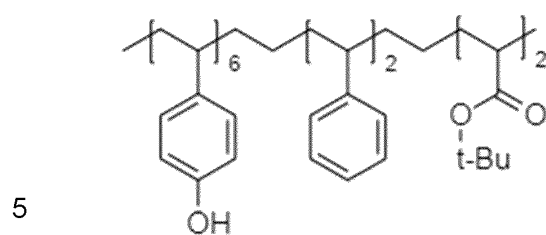
20

[0134] The structures of the polymers and the photoacid generators used in the Examples and the Comparative Example are the followings.

25

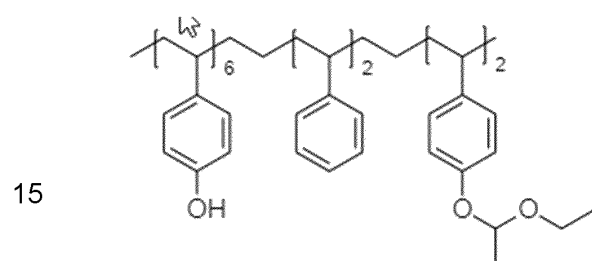
Polymer (1)

30



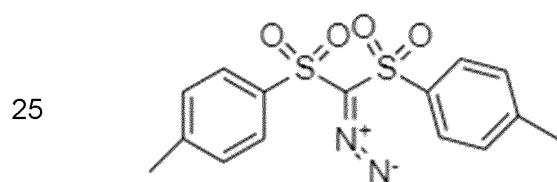
Mw: 12,000, PDI: 1.84

10 Polymer (2)



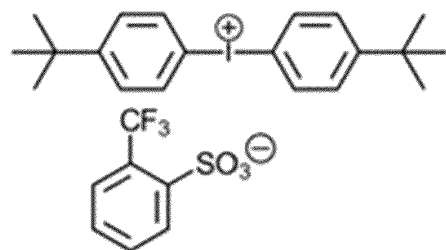
Mw: 13,000, PDL:1.92

20 Bis(4-methylphenylsulfonyl)diazomethane



30 Di(4-t-butyl)phenyliodonium 2-(trifluoromethyl)benzenesulfonate

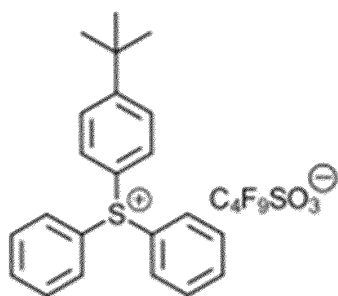
5



[4-(1,1-Dimethylethyl)phenyl]diphenylsulfonium perfluorobutanesulfonate

10

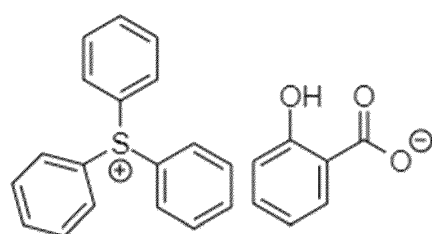
15



Triphenylsulfonium 2-hydroxybenzoate

20

25



[0135] The molar ratios of the compound A to the amine and the molar ratios of the compound B to the photoacid generators are shown on Table 1.

30

[Table 1]

5

	Example 1	Example 2	Example 3	Example 4
Molar ratio (Compound A/ Amine)	2	1	0.5	2
Molar ratio (Compound B/ Photoacid generators)	0	0	0	0.16

10

15

	Example 5	Comparative Example 1
Molar ratio (Compound A/ Amine)	2	0
Molar ratio (Compound B/ Photoacid generators)	0.08	0

20

[0136] Aging test

The photoresist compositions of Examples 1 to 5 and Comparative Example 1 are divided into two portions respectively and stored in brown glass bottles. One bottle is placed in a -20°C environment to serve as a reference sample. The other is subjected to an accelerated aging test by being kept in a 40°C environment for one week, simulating the effects of half a year's aging at room temperature.

[0137] Coating

The aged photoresist compositions are coated on 8-inch wafers respectively using MK-8 clean track (Tokyo Electron). The wafers are first placed in an

oven unit at 90°C for 35 seconds for Hexamethyldisilazan (HMDS) preprocessing. The spin speed is adjusted to approximately 1200 rpm to achieve a film thickness of 310 nm. Subsequently, the wafers coated with the photoresist compositions undergo a post-apply bake (PAB) process at 90°C
5 for 35 seconds. A 43nm top antireflective coating layer (TARC AZ Aquatar-VIII A30) is applied on top of the photoresist layer at a speed of approximately 780 rpm.

[0138] Lithography

10 The wafers are prepped for the lithography process. A KrF stepper FPS-300-EX5 (Canon) is utilized for the lithography processes. The stepper's numerical aperture is 0.63, and its sigma value is 0.65. IT&DT photo mask with CD size of 180nm is chosen for lithography. The size of the mask is fixed at the above size and a plurality of resist patterns is formed by changing
15 the exposure amount and implementing the development mentioned later. A calibration curve is prepared based on the exposure mount data. From this calibration curve, the exposure amount where the measured size of the resist pattern coincides with the mask size (a pattern of 1:1 line and space) is determined. The determined exposure amount is referred to as Eop. The Eop
20 values of the reference samples stored at -20°C are labeled as Eop1, while those of the aged samples maintained at 40°C are designated as Eop2.

[0139] Development

After the lithography, the wafers are returned to the clean track for further
25 development. The wafers undergo a post-exposure bake (PEB) at 135°C for 90 seconds. Thereafter, it is developed using a 2.38 wt.% tetramethylammonium hydroxide developer for 30 seconds to form the photoresist patterns on the wafers respectively.

30 [0140] Stability Assessment

The change rate between Eop1 and Eop2 is calculated based on the formula below.

$$\Delta Eop = (Eop1 - Eop2) / Eop1 \times 100 (\%)$$

5 [0141] The photoacid generator stability is assessed based on the following criteria.

A: $\Delta Eop < 9\%$

B: $9\% \leq \Delta Eop < 15\%$

10 C: $\Delta Eop \geq 15\%$

The result of the assessment is shown on Table 2.

[Table 2]

	Eop1 (mJ/cm ²)	Eop2 (mJ/cm ²)	ΔEop	Photoacid generator stability assessment
15 Example 1	18.18	16.81	7.54%	A
Example 2	17.87	16.20	9.35%	B
Example 3	18.15	15.96	12.07%	B
Example 4	18.59	17.93	3.55%	A
Example 5	19.11	17.77	7.01%	A
20 Comparative Example 1	17.44	13.77	21.44 %	C

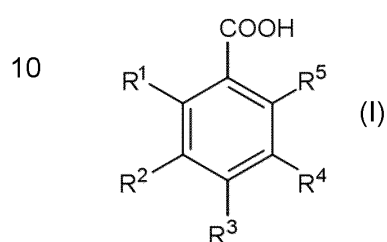
[0142] As shown in Table 2, Examples 1 to 5 show improved ΔEop values compering to the ΔEop value of Comparative Example 1.

25

30

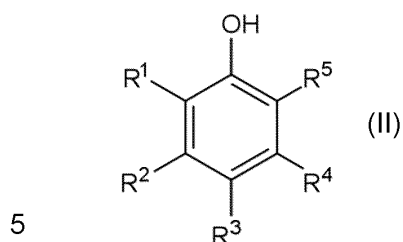
Claims

1. A method for stabilizing a photoacid generator in a photoresist composition comprising step (a);
 5 (a) mixing multiple compounds to form a photoresist composition, wherein the multiple compounds comprise a polymer, a photoacid generator, an amine and a compound A represented by formula (I);



- 15 wherein R¹ to R⁵ are each independently H, C₁₋₂₀ alkyl, C₁₋₂₀ alkoxy, OH or NH₂, preferably H, C₁₋₁₀ alkyl or OH, more preferably H or OH;
 when R¹ to R⁵ are each independently an alkyl, one or more non-adjacent CH₂-groups are optionally replaced by —O—, —S—, —CO—, —CO—O—,
 20 —O—CO—, —O—CO—O—, —CR=CR— or —C≡C—.

2. The method according to claim 1, wherein the molar ratio of the compound A to the amine is in the range from 0.1 to 10, preferably 0.2 to 8, more preferably 0.3 to 5, very preferably 0.5 to 3,
 25 preferably the content of the amine is in the range from 0.1 to 1 mass parts, more preferably 0.2 to 0.9 mass parts, very preferably 0.3 to 0.8 mass parts based on 100 mass parts of the polymer.
3. The method according to claims 1 or 2, wherein the multiple compounds
 30 further comprise a compound B represented by formula (II);



wherein R¹ and R⁵ are each independently C₁₋₂₀ alkyl or C₁₋₂₀ alkoxy,
preferably C₁₋₂₀ alkyl, more preferably C₁₋₁₀ alkyl;

wherein R² to R⁴ are each independently H, C₁₋₂₀ alkyl or C₁₋₂₀ alkoxy,
10 preferably H or C₁₋₂₀ alkyl, more preferably H or C₁₋₁₀ alkyl;

when R¹ to R⁵ are each independently an alkyl, then one or more of non-
adjacent CH₂-groups are optionally replaced by —O—, —S—, —CO—, —
CO—O—, —O—CO—, —O—CO—O—, —CR—CR— or —C≡C—;

wherein R³ and R⁴ may form a mono- or polycyclic organic ring system with
15 each other.

4. The method according to claim 3, wherein the molar ratio of the
compound B to the photoacid generator is in the range from 0.01 to 3,
preferably 0.03 to 1.5, more preferably 0.05 to 0.5.

20

5. The method according to any one of claims 1 to 4, wherein the amine
is a tertiary amine, preferably selected from one or more members of the
following group consisting of trimethylamine, triethylamine, tri-n-propylamine,
tri-n-butylamine, tri-n-hexylamine, tri-n-pentylamine, tri-n-heptylamine, tri-n-
25 octylamine, tri-n-nonylamine, tri-n-decylamine and tri-n-dodecylamine,
more preferably selected from one or more members of the following group
consisting of the group consisting of tri-n-heptylamine, tri-n-octylamine and
tri-n-nonylamine.

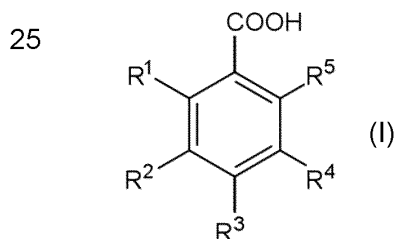
30 6. The method according to any one of claims of 1 to 5, wherein the
photoacid generator comprises a cation represented by formula (AC1);



wherein R^1 and R^2 are each independently C_{1-20} alkyl, C_{1-20} aryl or C_{1-20} aralkyl, preferably C_{1-15} aryl or C_{1-15} aralkyl, more preferably C_{1-10} aryl.

The method according to any one of claims 1 to 6, wherein the multiple compounds further comprise a solvent, preferably selected from one or more members of the following group consisting of i-propanol, propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, propylene glycol dimethyl ether, ethyl lactate and N-methylpyrrolidone, more preferably selected from one or more members of the following group consisting of propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate and ethyl lactate.

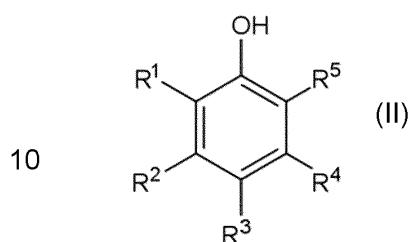
8. A photoresist composition comprising a polymer, a photoacid generator, a compound A represented by formula (I) and an amine, wherein the molar ratio of the compound A to the amine is in the range from 0.1 to 10, preferably 0.2 to 8, more preferably 0.3 to 5, very preferably 0.5 to 3, preferably the content of the amine is in the range from 0.1 to 1 mass parts, more preferably 0.2 to 0.9 mass parts, very preferably 0.3 to 0.8 mass parts based on 100 mass parts of the polymer;



wherein R^1 to R^5 are each independently H, C_{1-20} alkyl, C_{1-20} alkoxy, OH or NH_2 , preferably H, C_{1-10} alkyl or OH, more preferably H or OH;

when R¹ to R⁵ are each independently an alkyl, one or more non-adjacent CH₂-groups are optionally replaced by —O—, —S—, —CO—, —CO—O—, —O—CO—, —O—CO—O—, —CR—CR— or —C≡C—.

- 5 9. The photoresist composition according to claim 8, wherein the composition further comprises a compound B represented by formula (II);



wherein R¹ and R⁵ are each independently C₁₋₂₀ alkyl or C₁₋₂₀ alkoxy, preferably C₁₋₂₀ alkyl, more preferably C₁₋₁₀ alkyl;

- 15 R² to R⁴ are each independently H, C₁₋₂₀ alkyl or C₁₋₂₀ alkoxy, preferably H or C₁₋₂₀ alkyl, more preferably H or C₁₋₁₀ alkyl;

when R¹ to R⁵ are each independently an alkyl, then one or more of non-adjacent CH₂-groups are optionally replaced by —O—, —S—, —CO—, —CO—O—, —O—CO—, —O—CO—O—, —CR=CR— or —C≡C—;

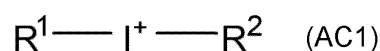
- 20 wherein R³ and R⁴ may form a mono- or polycyclic organic ring system with each other.

10. The photoresist composition according to claim 9, wherein the molar ratio of the compound B to the photoacid generator is in the range from 0.01 to 3, preferably 0.03 to 1.5, more preferably 0.05 to 0.5.

11. The photoresist composition according to any one of claims 8 to 10, wherein the amine is a tertiary amine, preferably selected from one or more members of the following group consisting of trimethylamine, triethylamine, tri-n-propylamine, tri-n-butylamine, tri-n-hexylamine, tri-n-pentylamine, tri-n-heptylamine, tri-n-octylamine, tri-n-nonylamine, tri-n-decylamine and tri-n-

dodecylamine, more preferably selected from one or more members of the following group consisting of tri-n-heptylamine, tri-n-octylamine and tri-n-nonylamine.

- 5 12. The photoresist composition according to any one of claims of 8 to 11, wherein the photo acid generator comprises a cation represented by formula (AC1);

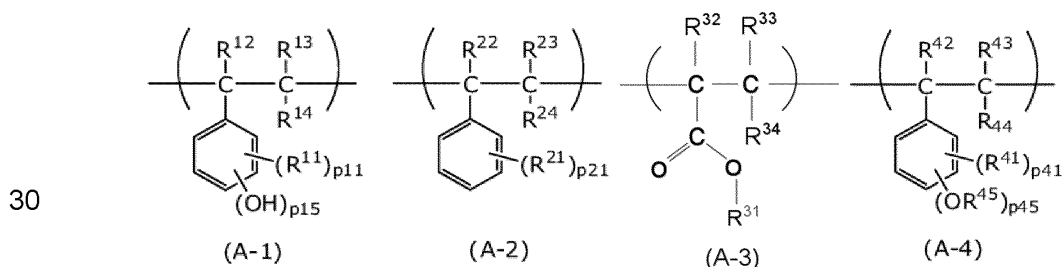


10

wherein R^1 to R^2 are each independently C_{1-20} alkyl, C_{1-20} aryl or C_{1-20} aralkyl, preferably C_{1-15} aryl or C_{1-15} aralkyl, more preferably C_{1-10} aryl.

13. The photoresist composition according to any one of claims 8 to 12, 15 wherein the photoresist composition further comprises a solvent, preferably selected from one or more members of the following group consisting of i-propanol, propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, propylene glycol dimethyl ether, ethyl lactate and N-methylpyrrolidone, more preferably selected from one or more members of 20 the following group consisting of propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate and ethyl lactate.

14. The photoresist composition according to any one of claims 8 to 13, 25 wherein the polymer comprises at least one of the following repeating units (A-1) to (A-4);



- 50 -

wherein R^{11} , R^{21} , R^{41} and R^{45} are each independently C_{1-10} alkyl;

one or more of non-adjacent CH_2 -groups of R^{11} , R^{21} , R^{41} and R^{45}

are optionally replaced by $-O-$;

wherein R^{12} , R^{13} , R^{14} , R^{22} , R^{23} , R^{24} , R^{31} , R^{32} , R^{33} , R^{34} , R^{42} , R^{43} and R^{44} are

5 each independently H, C_{1-5} alkyl, C_{1-5} alkoxy or $-COOH$;

p_{11} is 0 to 4, p_{15} is 0 to 2, and $p_{11} + p_{15} \leq 5$;

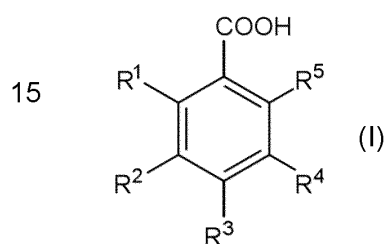
p_{21} is 0 to 4;

n_{21} is 0 to 1;

p_{41} is 0 to 4, p_{45} is 1 to 2, and $p_{41} + p_{45} \leq 5$.

10

15. Use of a compound A represented by formula (I) for stabilizing a photoacid generator in a photoresist composition;



20 wherein R^1 to R^5 are each independently H, C_{1-20} alkyl, C_{1-20} alkoxy, OH or NH_2 , preferably H, C_{1-10} alkyl or OH, more preferably H or OH;

when R^1 to R^5 are each independently an alkyl, one or more non-adjacent CH_2 -groups are optionally replaced by $-O-$, $-S-$, $-CO-$, $-CO-O-$, $-O-CO-$, $-O-CO-O-$, $-CR=CR-$ or $-C \equiv C-$.

25

30