



RADIATION SENSITIVE RESIN COMPOSITION

Detailed Description of the Invention

The present invention relates to a radiation sensitive
5 resin composition. More specifically, it relates to a
radiation sensitive resin composition which is useful as a
chemically amplifying positive resist suitable for
lithography using various types of radiation such as
ultraviolet rays from a KrF excimer laser or the like, far
10 ultraviolet rays, X-rays and charged corpuscular rays.

In the field of lithography typically used for the
production of integrated circuit elements, while the reduction
of the design rule of lithography is in rapid progress for
the purpose of obtaining more highly integrated circuits,
15 the development of a lithography process capable of stably
forming a highly accurate fine pattern having a line width
of 0.5 μm or less is now actively under way.

However, it is difficult to form such a fine pattern
very accurately with a prior art method using visible radiation
20 (wavelength of 700 to 400 nm) or near ultraviolet radiation
(wavelength of 400 to 300 nm). Therefore, lithography
processes are proposed which can achieve wider focusing depth
and use radiation having a short wavelength (300 nm or less)
effective in reducing the design rule.

25 The above lithography processes using radiation having
such a short wavelength are processes which use far ultraviolet
rays from a KrF excimer laser (wavelength of 248 nm) or ArF
excimer laser (wavelength of 193 nm), X-rays such as
synchrotron radiation or charged corpuscular rays such as
30 electron rays. As a high-resolution resist for use with the
above radiation having a short wavelength, a "chemically
amplified resist" is proposed by International Business
Machine Co., Ltd., and efforts are now being made energetically
to improve this chemically amplified resist.



This chemically amplified resist causes a radiation sensitive acid-generating agent contained therein to generate an acid through exposure to radiation (to be referred to as "exposure" hereinafter), a chemical reaction (for example, change of polarity, cleavage of a chemical bond, crosslinking reaction or the like) is caused in a resist film by the catalytic function of this acid, and a pattern is formed by making use of a phenomenon that the solubility in a developer of an exposed portion changes.

Of conventional chemically amplified resists, there are known the following resists which exhibit relatively good resist performance: one comprising a resin in which an alkali affinity group contained in an alkali soluble resin is protected by a t-butyl ester group or t-butoxycarbonyl group (JP-B 2-27660) (the term "JP-B" as used herein means an "examined Japanese patent publication"), one comprising a resin in which an alkali affinity group contained in an alkali soluble resin is protected by a ketal group (JP-A 7-140666) (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), one comprising a resin in which an alkali affinity group contained in an alkali soluble resin is protected by an acetal group such as an ethoxyethyl group or tetrahydropyranyl group (JP-A 2-161436 and JP-A 5-249682), and one comprising a combination of a resin in which an alkali affinity group contained in an alkali soluble resin is protected by a t-butoxycarbonyl group and a resin in which an alkali affinity group contained in an alkali soluble resin is protected by an acetal group (JP-A 8-15864 and JP-A 10-31309).

However, it is said that the practical use of these chemically amplified resists in a lithography process with a design rule of 0.26 μm or less in particular is attended with difficulties because the chemically amplified resists have their own problems.

For example, a resist comprising a resin in which an alkali affinity group contained in an alkali soluble resin is protected by a t-butyl ester group has such a problem that, if it is not heated at a temperature of 130°C or more after exposure, it is difficult to secure sufficient stability against changes in post exposure time delay (to be abbreviated as PED hereinafter) from exposure to a heat treatment, which is industrially disadvantageous. A resist comprising a resin in which an alkali affinity group contained in an alkali soluble resin is protected by a t-butoxycarbonyl group is unsatisfactory in terms of resolution and a resist comprising a resin in which an alkali affinity group contained in an alkali soluble resin is protected by a silyl group involves such a problem that it is difficult to peel the resist from a substrate.

Meanwhile, it can be said that a resist comprising a resin in which an alkali affinity group contained in an alkali soluble resin is protected by an ethoxyethyl group or tetrahydropyranyl group has high potential because the same process conditions as a novolak resin-naphthoquinonediazide-based i-ray resist, such as heating temperature and developing conditions, can be used. However, the top surface and side surface of a formed pattern are significantly uneven and impede the fine control of the line width of a fine pattern as the first problem to be solved. The second problem is that the influence of a so-called optical proximity effect is large, whereby size differences or the rounding or recessing phenomenon of pattern edge portions readily occurs due to the nonuniform density of a pattern. If size differences caused by the nonuniform density of a pattern are large, when an isolated pattern is exposed to the optimum quantity of light for a line-and-space pattern, the isolated pattern cannot have its design size and satisfy needs for one-chip logic circuits and one-chip memory circuits

due to the recent popularization of multi media. Further,
the third problem is that a sufficient focus latitude cannot
be obtained due to unsatisfactory resolution when a fine
contact hole having a high aspect ratio (resist film
5 thickness/aperture size) whose needs are growing due to the
recent use of a demascene process is to be formed.

Under the above circumstances, there has been growing
demand for a resist which is excellent in the resolution of
a line-and-space pattern, pattern shape and the resolution
10 of an isolated pattern with a small optical proximity effect,
has a sufficient focus latitude when a contact hole having
a high aspect ratio is to be formed and has small unevenness,
that is, small surface roughness of the top surface and side
surface of a pattern.

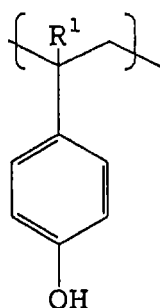
15 It is an object of the present invention to provide a
radiation sensitive resin composition which is sensitive to
various types of radiation effectively, is excellent in terms
of resolution and pattern form, has small film surface roughness
and a small optical proximity effect, and is useful as a
20 chemically amplifying positive resist capable of forming a
fine pattern, such as a line-and-space pattern, isolated
pattern or contact hole pattern, with stability and high
accuracy.

Other objects and advantages of the present invention
25 will become apparent from the following description.

According to the present invention, the above objects
and advantages of the present invention are attained by a
radiation sensitive resin composition comprising:

(A) a copolymer containing a recurring unit represented
30 by the following formula (1):

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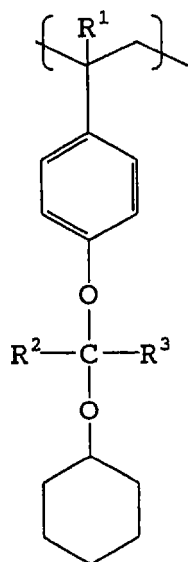


... (1)

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wherein R¹ is a hydrogen atom or a methyl group,
and a recurring unit represented by the following formula
(2):

15



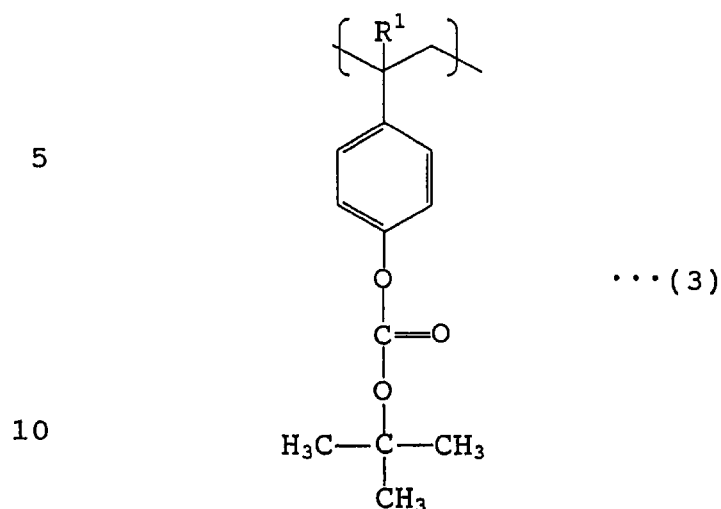
... (2)

20

25

wherein R¹ is the same as defined above, R² is a hydrogen atom or a methyl group, and R³ is a methyl group or an ethyl group;

(B) a copolymer containing a recurring unit represented by the above formula (1) and a recurring unit represented by the following formula (3):



wherein R¹ is the same as defined above; and

(C) a radiation sensitive acid generating agent.

15 Fig. 1 is a sectional view of a resist pattern for explaining a film surface roughness evaluation method.

The present invention will be described in detail hereunder.

20 Copolymer (A)

The copolymer (A) used in the present invention contains a recurring unit represented by the above formula (1) (to be referred to as "recurring unit (1)" hereinafter) and a recurring unit represented by the above formula (2) (to be referred to as "recurring unit (2)" hereinafter). In the copolymer (A), the total content of the recurring units (1) and (2) is preferably 70 mol% or more based on the total of all the recurring units. The content of the recurring unit (1) is preferably more than 40 mol% and less than 90 mol% based on the total of all the recurring units and the content of the recurring unit (2) is preferably more than 3 mol% and less than 40 mol% based on the total of all the recurring units. The total content of the recurring units (1) and (2) is more preferably 75 mol% or more based on the total of all

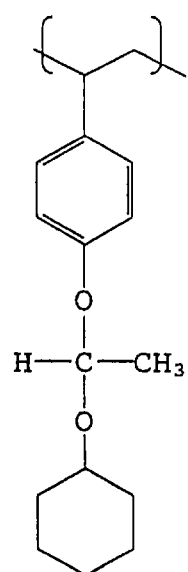
the recurring units. The content of the recurring unit (1) is more preferably more than 50 mol% and less than 80 mol% based on the total of all the recurring units and the content of the recurring unit (2) is more preferably more than 5 mol% and less than 30 mol% based on the total of all the recurring units.

When the total content of the recurring units (1) and (2) is less than 70 mol% based on the total of all the recurring units, the resolution of a line-and-space pattern and the focus latitude of a contact hole tend to lower. When the content of the recurring unit (1) is 40 mol% or less based on the total of all the recurring units, the heat resistance of the obtained resist is liable to lower. On the other hand, when the content is 80 mol% or more, the solubility in an alkali developer of the obtained copolymer is apt to become too high and the resolution of a line-and-space pattern is apt to lower. Further, when the content of the recurring unit (2) is 3 mol% or less based on the total of all the recurring units, the focus latitude of a contact hole tends to lower, while when the content is 40 mol% or more, the optical proximity effect is liable to become large and the film surface roughness of a pattern is also liable to become large.

Recurring units represented by the following formulas (4) to (6) can be enumerated as examples of the recurring unit (2) in the copolymer (A).

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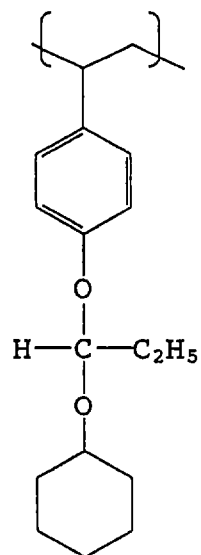
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... (4)

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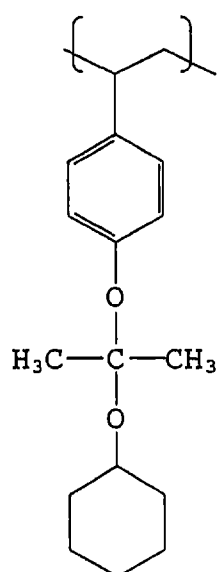
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... (5)

20

25



... (6)

30

Of the above recurring units, the recurring unit represented by the formula (4) is particularly preferable.

Although the detailed mechanism that can explain why the skeleton represented by the above formula (2) exhibits
5 more excellent performance than other acetal skeletons is unknown, it is assumed that the excellent performance is exhibited in the following points (1) to (3):

(1) Sufficiently high resolution can be obtained for the formation of a fine contact hole due to a large difference
10 in dissolution speed between an exposed portion and an unexposed portion (dissolution contrast) after a deprotection reaction because the above skeleton has a larger dissolution suppression effect than an acetal protecting group having
7 or less carbon atoms, such as a 1-ethoxyethyl group or
15 1-ethoxypropyl group, due to its larger number of carbon atoms than the acetal protecting group.

(2) An alcohol by-produced at the time of removing an acetal protecting group has a higher boiling point than that of the acetal protecting group having less than 7 carbon atoms, such
20 as an 1-ethoxyethyl group or 1-ethoxypropyl group, and partially remains in the film at the time of PEB to promote the diffusion of an acid. As a result, an abnormal local deprotection reaction does not proceed and a deprotection reaction proceeds uniformly in an exposed portion, thereby
25 preventing the film surface from being roughened.

(3) When an acetal having 10 or more carbon atoms, specifically an acetal having a long-chain alkyl group or long-chain ether skeleton, such as a dodecyl skeleton or triethylene glycol, is used, a dissolution suppression effect
30 becomes high while heat resistance greatly deteriorates due to the large movement of a side-chain segment. Meanwhile, the acetal protecting group having 7 to 9 carbon atoms and a cyclohexane skeleton in the present invention is more rigid than a straight-chain skeleton due to its alicyclic skeleton

and can retain heat resistance required for a resist.

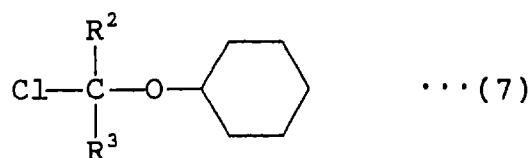
The copolymer (A) can contain at least one recurring unit (to be referred to as "other recurring unit" hereinafter) other than the above recurring units (1) and (2) as the case
5 may be.

Monomers which give the other recurring unit include styrenes such as styrene, α -methylstyrene, 4-methylstyrene, 4-methoxystyrene, 4-t-butoxystyrene, 4-(1-ethoxyethoxystyrene), 4-(1-ethoxypropoxystyrene),
10 4-(1-t-butoxyethoxystyrene), 4-(1-n-butoxyethoxystyrene), 4-tetrahydropyranyloxystyrene, 4-acetoxystyrene, 4-t-butoxycarbonylmethoxystyrene, 2-hydroxystyrene, 3-hydroxystyrene and 3-methyl-4-hydroxystyrene; unsaturated carboxylic acids and acid anhydrides thereof such as
15 (meth)acrylic acid, maleic acid, fumaric acid, crotonic acid, mesaconic acid, citraconic acid, itaconic acid, maleic anhydride and methyl maleic anhydride; esters such as methyl esters, ethyl esters, n-propyl esters, i-propyl esters, n-butyl esters, i-butyl esters, sec-butyl esters, t-butyl
20 esters, n-amyl esters, 2-hydroxyethyl esters, 2,2-dimethyl-3-hydroxypropyl esters, benzyl esters, isobornyl esters, adamantyl esters, tricyclodecanyl esters and tetracyclodecanyl esters of the above unsaturated carboxylic acids; unsaturated nitriles such as
25 (meth)acrylonitrile, maleinnitrile, fumaronitrile, mesaconitrile, citraconitrile and itaconitrile; unsaturated amides such as (meth)acrylamide, crotonamide, maleinamide, fumaramide, mesaconamide, citraconamide and itaconamide; unsaturated imides such as maleimide and N-phenyl
30 maleimide; unsaturated alcohols such as (meth)allyl alcohols; vinylanilines; vinylpyridines; and other vinyl compounds such as N-vinyl- ϵ -caprolactam, N-vinylpyrrolidone, N-vinylimidazole and N-vinylcarbazole. These monomers may be used alone or in admixture of two or more.

Of the above monomers which give the other recurring unit, styrene, 4-methylstyrene, 4-methoxystyrene, 4-t-butoxystyrene, 4-t-butoxycarbonyloxystyrene, 4-(1-ethoxyethoxystyrene), 4-(1-ethoxypropoxystyrene), 4-tetrahydropyranyloxystyrene, 4-acetoxystyrene, 4-t-butoxycarbonylmethoxystyrene, 2-hydroxystyrene, 3-hydroxystyrene, 3-methyl-4-hydroxystyrene, t-butyl (meth)acrylate, isobornyl (meth)acrylate, adamantyl (meth)acrylate, tricyclodecanyl (meth)acrylate and (meth)acrylonitrile are preferable.

The content of the other recurring unit derived from any one of the above monomers is preferably 30 mol% or less, more preferably 25 mol% or less, based on the total of all the recurring units contained in the copolymer (A).

The copolymer (A) can be produced by the following methods (a) to (c), for example.
method (a): Some of the phenolic hydroxyl groups of a hydroxystyrene polymer produced by radical polymerization, anionic polymerization or cationic polymerization, such as a sodium phenoxide derivative exemplified by poly(4-hydroxystyrene) or poly(4-hydroxystyrene-co-styrene), are converted into acetal groups by reacting the polymer with a compound represented by the following formula (7):



wherein R^2 and R^3 are the same as defined in the above formula (2),

such as 1-cyclohexyloxy-1-chloroethane.

method (b): Some of the phenolic hydroxyl groups of a hydroxystyrene polymer produced by radical polymerization,

anionic polymerization or cationic polymerization, such as poly(4-hydroxystyrene), poly(4-hydroxystyrene-co-styrene), poly(4-hydroxystyrene-co-4-t-butoxystyrene), poly(4-hydroxystyrene-co-4-acetoxystyrene),
5 poly(4-hydroxystyrene-co-2-hydroxystyrene), poly(4-hydroxystyrene-co-3-hydroxystyrene), poly(4-hydroxystyrene-co-3-methyl-4-hydroxystyrene), poly(t-butyl 4-hydroxystyrene-co-(meth)acrylate), poly(isobornyl 4-hydroxystyrene-co-(meth)acrylate),
10 poly(adamantyl 4-hydroxystyrene-co-(meth)acrylate), poly(tricyclodecanyl 4-hydroxystyrene-co-(meth)acrylate) or poly(4-hydroxystyrene-co-(meth)acrylonitrile) are converted into acetal groups by addition-reacting the polymer with an unsaturated ether compound represented by the above
15 formula (2) such as cyclohexyl vinyl ether, cyclohexyl propenyl ether or 2-cyclohexyloxy propene and, as required, other unsaturated ether compound such as ethyl vinyl ether, ethyl-1-propenyl ether or 2,3-dihydropyran in the presence of a weak acidic catalyst.

20 method (c): 4-hydroxystyrene and a monomer corresponding to the recurring unit (2) are copolymerized, together with a monomer corresponding to the other recurring unit as required, in the presence of a suitably selected radical polymerization initiator or the like by block polymerization, solution
25 polymerization, precipitation polymerization, emulsion polymerization, suspension polymerization or block-suspension polymerization.

The weight average molecular weight (to be abbreviated as "Mw" hereinafter) in terms of polystyrene measured by gel
30 permeation chromatography (to be abbreviated as "GPC" hereinafter) of the copolymer (A) is generally 1,000 to 100,000, preferably 3,000 to 40,000, more preferably 3,000 to 30,000. When the Mw of the copolymer (A) is less than 1,000, the sensitivity and heat resistance of the obtained resist tend

to lower, while when the Mw is more than 100,000, the solubility in a developer of the resist tends to lower.

The ratio (Mw/Mn) of the Mw to the number average molecular weight (to be abbreviated as "Mn" hereinafter) in terms of polystyrene measured by GPC of the copolymer (A) is generally 1.0 to 10.0, preferably 1.0 to 5.0.

In the present invention, the above copolymers (A) may be used alone or in admixture of two or more.

10 Copolymer (B)

The copolymer (B) used in the present invention contains the above recurring unit (1) and a recurring unit represented by the above formula (3) (to be referred to as "recurring unit (3)" hereinafter). In the copolymer (B), the total content of the recurring units (1) and (3) is preferably 70 mol% or more based on the total of all the recurring units. The content of the recurring unit (1) is preferably more than 40 mol% and less than 90 mol% based on the total of all the recurring units and the content of the recurring unit (3) is preferably more than 3 mol% and less than 40 mol% based on the total of all the recurring units. The total content of the recurring units (1) and (3) is more preferably 75 mol% or more based on the total of all the recurring units. The content of the recurring unit (1) is more preferably more than 50 mol% and less than 80 mol% based on the total of all the recurring units and the content of the recurring unit (3) is more preferably more than 5 mol% and less than 30 mol% based on the total of all the recurring units.

When the total content of the recurring units (1) and (3) is less than 70 mol% based on the total of all the recurring units, the resolution of a line-and-space pattern and the focus latitude of a contact hole tend to lower. When the content of the recurring unit (1) is 40 mol% or less based on the total of all the recurring units, the heat resistance

of the obtained resist is liable to lower. When the content is 80 mol% or more, on the other hand, the solubility in an alkali developer of the obtained copolymer is apt to become too high and the resolution of a line-and-space pattern is apt to lower. Further, when the content of the recurring unit (3) is 3 mol% or less based on the total of all the recurring units, the focus latitude of a contact hole tends to lower, while when the content is 40 mol% or more, the optical proximity effect is liable to become large and the film surface roughness of a pattern is also liable to become large.

Although the detailed mechanism that explains why the skeleton represented by the above formula (3) exhibits more excellent performance than other acetal skeletons is unknown, it is assumed that the skeleton of the formula (3) exhibits excellent performance for the same reasons as (1) to (3) given for the above formula (2).

The copolymer (B) may contain at least one recurring unit (to be referred to as "other recurring unit" hereinafter) other than the above recurring units (1) and (3) as the case may be.

Monomers which give the other recurring unit and preferable monomers out of these are the same as those listed for the copolymer (A).

The content of the other recurring unit derived from any one of the monomers is preferably 30 mol% or less, more preferably 25 mol% or less based on the total of all the recurring units contained in the copolymer (B).

The copolymer (B) may be produced by the following methods (d) and (e).

method (d): Some of the phenolic hydroxyl groups of a hydroxystyrene polymer produced by radical polymerization, anionic polymerization or cationic polymerization, such as poly(4-hydroxystyrene), poly(4-hydroxystyrene-co-styrene), poly(4-hydroxystyrene-co-4-t-butoxystyrene),

poly(4-hydroxystyrene-co-4-acetoxystyrene),
poly(4-hydroxystyrene-co-2-hydroxystyrene),
poly(4-hydroxystyrene-co-3-hydroxystyrene),
poly(4-hydroxystyrene-co-3-methyl-4-hydroxystyrene),
5 poly(t-butyl 4-hydroxystyrene-co-(meth)acrylate),
poly(isobornyl 4-hydroxystyrene-co-(meth)acrylate),
poly(adamantyl 4-hydroxystyrene-co-(meth)acrylate),
poly(tricyclodecanyl 4-hydroxystyrene-co-(meth)acrylate)
or poly(4-hydroxystyrene-co-(meth)acrylonitrile), are
10 converted into t-butoxycarbonate groups by reacting the
polymer with di-t-butyl carbonate in the presence of a basic
catalyst such as triethylamine.
method (e): 4-hydroxystyrene and a monomer corresponding to
the recurring unit (3) are copolymerized, together with a
15 monomer corresponding to the other recurring unit as required,
in the presence of a suitably selected radical polymerization
initiator or the like by block polymerization, solution
polymerization, precipitation polymerization, emulsion
polymerization, suspension polymerization or
20 block-suspension polymerization.

The Mw in terms of polystyrene measured by GPC of the
copolymer (B) is generally 1,000 to 100,000, preferably 3,000
to 40,000, more preferably 3,000 to 30,000. When the Mw of
the copolymer (B) is less than 1,000, the sensitivity and
25 heat resistance of the obtained resist tend to lower, while
when the Mw is more than 100,000, the solubility in a developer
of the resist tends to lower.

The ratio (Mw/Mn) of the Mw to the Mn in terms of
polystyrene measured by GPC of the copolymer (B) is generally
30 1.0 to 10.0, preferably 1.0 to 5.0.

In the present invention, the copolymer (A) and the
copolymer (B) may be optionally blended with a resin and a
low-molecular weight compound which do not impair the
uniformity of a coating film when the resulting solution is

applied to a substrate and which have excellent compatibility with the copolymer (A) and the copolymer (B). In this case, the total amount of the resin and low-molecular weight compound to be blended is preferably 100 parts or less by weight based on 100 parts by weight of the total of the copolymer (A) and the copolymer (B).

Radiation sensitive acid-generating agent (C)

The radiation sensitive acid-generating agent (C) (to be referred to as "acid generating agent" hereinafter) used in the present invention is a compound which generates an acid through exposure.

The acid-generating agent is an (1) onium salt, (2) sulfone compound, (3) sulfonate compound, (4) sulfonylimide compound, (5) diazomethane compound or (6) disulfonylmethane compound.

Illustrative examples of the acid-generating agent are given below.

(1) onium salt such as an iodonium salt, sulfonium salt, phosphonium salt, diazonium salt, ammonium salt or pyridinium salt.

Illustrative examples of the onium salt compound include bis(4-t-butylphenyl)iodonium nonafluorobutanesulfonate, bis(4-t-butylphenyl)iodonium trifluoromethanesulfonate, bis(4-t-butylphenyl)iodonium pyrenesulfonate, bis(4-t-butylphenyl)iodonium dodecylbenzenesulfonate, bis(4-t-butylphenyl)iodonium p-toluenesulfonate, bis(4-t-butylphenyl)iodonium benzenesulfonate, bis(4-t-butylphenyl)iodonium 10-camphorsulfonate, bis(4-t-butylphenyl)iodonium octanesulfonate, bis(4-t-butylphenyl)iodonium 2-trifluoromethylbenzenesulfonate, diphenyl iodonium nonafluorobutanesulfonate, diphenyl iodonium trifluoromethanesulfonate, diphenyl iodonium

- pyrenesulfonate, diphenyl iodonium dodecylbenzenesulfonate,
diphenyl iodonium p-toluenesulfonate, diphenyl iodonium
benzenesulfonate, diphenyl iodonium 10-camphorsulfonate,
diphenyl iodonium octanesulfonate, diphenyl iodonium
5 2-trifluoromethylbenzenesulfonate, triphenylsulfonium
nonafluorobutanesulfonate, triphenylsulfonium
trifluoromethanesulfonate, triphenylsulfonium
pyrenesulfonate, triphenylsulfonium
dodecylbenzenesulfonate, triphenylsulfonium
10 p-toluenesulfonate, triphenylsulfonium benzenesulfonate,
triphenylsulfonium 10-camphorsulfonate, triphenylsulfonium
octanesulfonate, triphenylsulfonium
2-trifluoromethylbenzenesulfonate, triphenylsulfonium
hexafluoroantimonate, triphenylsulfonium
15 naphthalenesulfonate, 4-t-butylphenyl·diphenylsulfonium
nonafluorobutanesulfonate,
4-t-butylphenyl·diphenylsulfonium
trifluoromethanesulfonate,
4-t-butylphenyl·diphenylsulfonium pyrenesulfonate,
20 4-t-butylphenyl·diphenylsulfonium dodecylbenzenesulfonate,
4-t-butylphenyl·diphenylsulfonium p-toluenesulfonate,
4-t-butylphenyl·diphenylsulfonium benzenesulfonate,
4-t-butylphenyl·diphenylsulfonium 10-camphorsulfonate,
4-t-butylphenyl·diphenylsulfonium octanesulfonate,
25 4-t-butylphenyl·diphenylsulfonium
2-trifluoromethylbenzenesulfonate,
4-t-butoxyphenyl·diphenylsulfonium
nonafluorobutanesulfonate and
4-hydroxyphenyl·benzyl·methylsulfonium
30 p-toluenesulfonate.

(2) sulfone compound such as a β -ketosulfone,
 β -sulfonylsulfone or α -diazo compound thereof.

Illustrative examples of the sulfone compound include
phenacylphenylsulfone, mesitylphenacylsulfone,

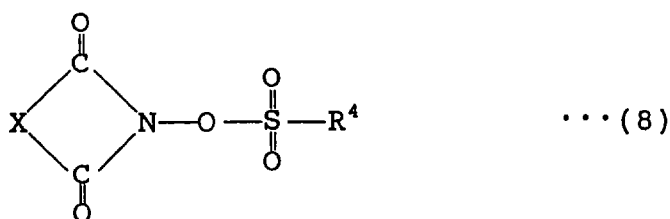
bis(phenylsulfonyl)methane and 4-trisphenacylsulfone.

(3) sulfonate compound such as an alkyl sulfonate, haloalkyl sulfonate, aryl sulfonate or iminosulfonate.

Illustrative examples of the sulfonate compound include
 5 benzoin tosylate, pyrogallol tristrifluoromethane sulfonate,
 pyrogallol trisnonafluorobutane sulfonate, pyrogallol
 methane trisulfonate,
 nitrobenzyl-9,10-diethoxyanthracene-2-sulfonate,
 α-methylolbenzoin tosylate, α-methylolbenzoin
 10 octanesulfonate, α-methylolbenzoin trifluoromethane
 sulfonate and α-methylolbenzoin dodecylsulfonate.

(4) sulfonimide compound represented by the following
 formula (8):

15



20 wherein X is a divalent group such as an alkylene group,
 arylene group or alkoxy group, and R⁴ is a monovalent
 group such as an alkyl group, aryl group,
 halogen-substituted alkyl group or halogen-substituted
 aryl group.

25 Illustrative examples of the sulfonimide compound
 include N-(trifluoromethylsulfonyloxy)succinimide,
 N-(trifluoromethylsulfonyloxy)phthalimide,
 N-(trifluoromethylsulfonyloxy)diphenyl maleimide,
 N-(trifluoromethylsulfonyloxy)bicyclo[2.2.1]hept-5-ene-2
 30 ,3-dicarboxyimide,
 N-(trifluoromethylsulfonyloxy)-7-oxabicyclo[2.2.1]hept-5
 -ene-2,3-dicarboxyimide,
 N-(trifluoromethylsulfonyloxy)bicyclo[2.2.1]heptane-5,6-
 oxy-2,3-dicarboxyimide,

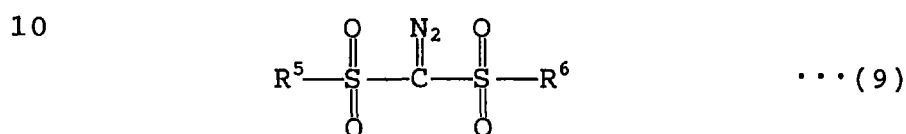
- N-(trifluoromethylsulfonyloxy)naphthylimide,
 N-(10-camphorsulfonyloxy)succinimide,
 N-(10-camphorsulfonyloxy)phthalimide,
 N-(10-camphorsulfonyloxy)diphenyl maleimide,
 5 N-(10-camphorsulfonyloxy)bicyclo[2.2.1]hept-5-ene-2,3-
 dicarboxyimide,
 N-(10-camphorsulfonyloxy)-7-oxabicyclo[2.2.1]hept-5-ene-
 2,3-dicarboxyimide,
 N-(10-camphorsulfonyloxy)bicyclo[2.2.1]heptane-5,6-oxy-2
 10 ,3-dicarboxyimide, N-(10-camphorsulfonyloxy)naphthylimide,
 N-(p-toluenesulfonyloxy)succinimide,
 N-(p-toluenesulfonyloxy)phthalimide,
 N-(p-toluenesulfonyloxy)diphenyl maleimide,
 N-(p-toluenesulfonyloxy)bicyclo[2.2.1]hept-5-ene-2,3-
 15 dicarboxyimide,
 N-(p-toluenesulfonyloxy)-7-oxabicyclo[2.2.1]hept-5-ene-2
 ,3-dicarboxyimide,
 N-(p-toluenesulfonyloxy)bicyclo[2.2.1]heptane-5,6-oxy-2,
 3-dicarboxyimide, N-(p-toluenesulfonyloxy)naphthylimide,
 20 N-(2-trifluoromethylbenzenesulfonyloxy)succinimide,
 N-(2-trifluoromethylbenzenesulfonyloxy)phthalimide,
 N-(2-trifluoromethylbenzenesulfonyloxy)diphenyl maleimide,
 N-(2-trifluoromethylbenzenesulfonyloxy)bicyclo[2.2.1]
 hept-5-ene-2,3-dicarboxyimide,
 25 N-(2-trifluoromethylbenzenesulfonyloxy)-7-oxabicyclo[2.2
 .1]hept-5-ene-2,3-dicarboxyimide,
 N-(2-trifluoromethylbenzenesulfonyloxy)bicyclo[2.2.1]
 heptane-5,6-oxy-2,3-dicarboxyimide,
 N-(2-trifluoromethylbenzenesulfonyloxy)naphthylimide,
 30 N-(nonafluorobutylsulfonyloxy)succinimide,
 N-(nonafluorobutylsulfonyloxy)phthalimide,
 N-(nonafluorobutylsulfonyloxy)diphenyl maleimide,
 N-(nonafluorobutylsulfonyloxy)bicyclo[2.2.1]hept-5-ene-2
 ,3-dicarboxyimide,

N-(nonafluorobutylsulfonyloxy)-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide,

N-(nonafluorobutylsulfonyloxy)bicyclo[2.2.1]heptane-5,6-oxy-2,3-dicarboxyimide and

5 N-(nonafluorobutylsulfonyloxy)naphthylimide.

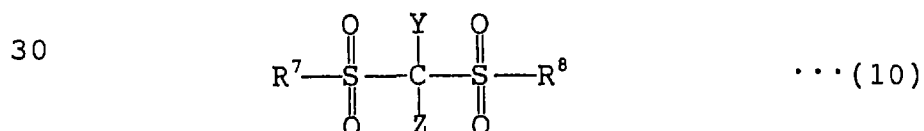
(5) diazomethane compound represented by the following formula (9):



wherein R⁵ and R⁶ may be the same or different and are each
 15 a monovalent group such as an alkyl group, aryl group, halogen-substituted alkyl group or halogen-substituted aryl group.

Illustrative examples of the diazomethane compound include bis(trifluoromethylsulfonyl)diazomethane,
 20 bis(cyclohexylsulfonyl)diazomethane, bis(phenylsulfonyl)diazomethane, bis(p-toluenesulfonyl)diazomethane, methylsulfonyl-p-toluenesulfonyl diazomethane, 1-cyclohexylsulfonyl-1-(1,1-dimethylethylsulfonyl)
 25 diazomethane and bis(1,1-dimethylethylsulfonyl)diazomethane.

(6) disulfonylmethane compound represented by the following formula (10):



wherein R⁷ and R⁸ may be the same or different and are each a monovalent linear or branched aliphatic hydrocarbon group,

cycloalkyl group, aryl group, aralkyl group or other monovalent organic group having a hetero atom, and Y and Z may be the same or different and are each an aryl group, hydrogen atom, monovalent linear or branched aliphatic hydrocarbon group or other monovalent organic group having a hetero atom, with the proviso that at least one of Y and Z is an aryl group, or Y and Z are connected to each other to form a monocyclic or polycyclic structure having at least one unsaturated bond or to form a group represented by the following formula (11):



wherein Y' and Z' may be the same or different, Y's may be the same as or different from one another, Z's may be the same as or different from one another, and Y's and Z's are each a hydrogen atom, halogen atom, alkyl group, cycloalkyl group, aryl group or aralkyl group, or Y' and Z' bonded to the same carbon atom or different carbon atoms are connected to each other to form a carbon monocyclic structure, and n is an integer of 2 to 10.

The above acid-generating agents may be used alone or in admixture of two or more.

In the present invention, the amount of the acid-generating agent is preferably 0.1 to 20 parts by weight, more preferably 0.5 to 15 parts by weight based on 100 parts by weight of the total of the copolymer (A) and the copolymer (B).

Acid diffusion control agent

In the present invention, an acid diffusion control agent having the function of controlling such a phenomenon that

an acid generated from an acid generating agent by exposure is dispersed in a resist film and the function of suppressing an unfavorable chemical reaction in an unexposed area is preferably further blended.

5 By using this acid diffusion control agent, the storage stability of a composition and the resolution of a resist can be improved and changes in the line width of a resist pattern caused by fluctuations in PED can be suppressed, thereby making it possible to obtain very excellent process
10 stability.

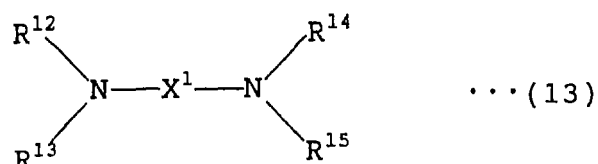
The acid diffusion control agent is preferably a nitrogen-containing organic compound whose basicity is not changed by exposure or a heat treatment in the formation process of a resist pattern.

15 The nitrogen-containing organic compound is a compound represented by the following formula (12):



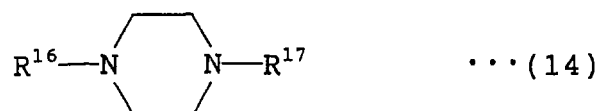
20 wherein R^9 , R^{10} and R^{11} may be the same or different and are each a hydrogen atom, alkyl group, aryl group or a alkyl group (to be referred to as "nitrogen-containing compound (I)" hereinafter), diamino compound having two nitrogen atoms in the molecule (to be referred to as
25 "nitrogen-containing compound (II)" hereinafter), diamino polymer having three or more nitrogen atoms (to be referred to as "nitrogen-containing compound (III)" hereinafter),

a compound represented by the following formula (13) (to be
30 referred to as "nitrogen-containing compound (IV)" hereinafter):



wherein X^1 is a polymethylene chain having 2 to 8 main chain carbon atoms, R^{12} , R^{13} , R^{14} and R^{15} are independently a linear, branched or cyclic alkyl group having 1 to 12 carbon atoms, aryl group having 6 to 12 carbon atoms or aralkyl group having 7 to 12 carbon atoms, or R^{12} and R^{13} or R^{14} and R^{15} are bonded together to form a 5- to 8-membered heterocyclic structure together with one nitrogen atom in the formula (13) and the rest of R^{12} to R^{15} are independently a linear, branched or cyclic alkyl group having 1 to 12 carbon atoms, aryl group having 6 to 12 carbon atoms or aralkyl group having 7 to 12 carbon atoms, and at least one of the polymethylene chain, alkyl group, aryl group, aralkyl group and heterocyclic structure has at least one hydroxyl group bonded to a carbon atom, with the proviso that the polymethylene chain, alkyl group, aryl group, aralkyl group and heterocyclic structure can have an oxygen atom, sulfur atom or carbonyl group between the carbon atoms of any carbon-to-carbon bond and that a hydrogen atom bonded to any one of the carbon atoms may be substituted with at least one substituent other than a hydroxyl group such as an alkoxy group or phenoxy group,

a compound represented by the following formula (14) (to be referred to as "nitrogen-containing compound (V)" hereinafter):

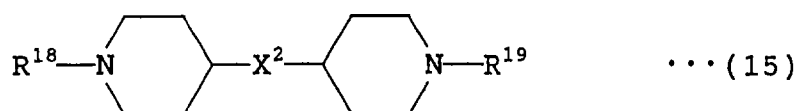


wherein R^{16} and R^{17} are independently a linear, branched or cyclic alkyl group having 1 to 12 carbon atoms, aryl group having 6 to 12 carbon atoms or aralkyl group having 7 to 12 carbon atoms, and at least one of the alkyl group, aryl group, aralkyl group and a piperazine ring in the formula (14) has at least one hydroxyl group bonded to

a carbon atom, with the proviso that the alkyl group, aryl group and aralkyl group can have an oxygen atom, sulfur atom or carbonyl group between the carbon atoms of any carbon-to-carbon bond and that a hydrogen atom bonded to any one of the carbon atoms may be substituted with at least one substituent other than a hydroxyl group such as an alkoxyl group or phenoxy group,

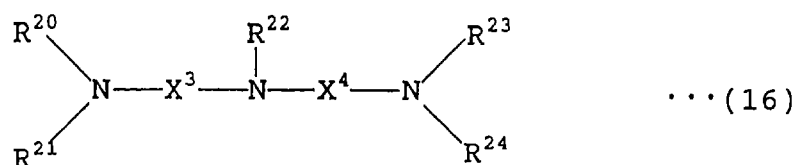
a compound represented by the following formula (15) (to be referred to as "nitrogen-containing compound (VI)"

hereinafter):



wherein X^2 is a polymethylene chain having 2 to 8 main chain carbon atoms, R^{18} and R^{19} are independently a linear, branched or cyclic alkyl group having 1 to 12 carbon atoms, aryl group having 6 to 12 carbon atoms or aralkyl group having 7 to 12 carbon atoms, and at least one of the polymethylene chain, alkyl group, aryl group, aralkyl group and one or two piperidine rings in the formula (15) has at least one hydroxyl group bonded to a carbon atom, with the proviso that the polymethylene chain, alkyl group, aryl group and aralkyl group can have an oxygen atom, sulfur atom or carbonyl group between the carbon atoms of any carbon-to-carbon bond and that a hydrogen atom bonded to any one of the carbon atoms may be substituted with at least one substituent other than a hydroxyl group such as an alkoxyl group or phenoxy group,

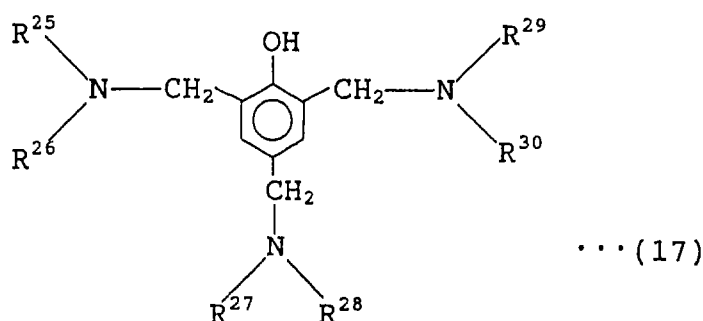
a compound represented by the following formula (16) (to be referred to as "nitrogen-containing compound (VII)" hereinafter):



5

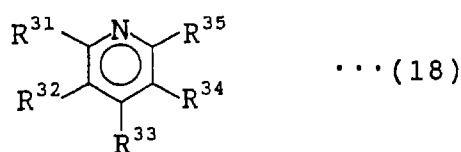
wherein X^3 and X^4 are independently a polymethylene chain having 2 to 8 main chain carbon atoms, R^{20} , R^{21} , R^{22} , R^{23} and R^{24} are a linear, branched or cyclic alkyl group having 1 to 12 carbon atoms, aryl group having 6 to 12 carbon atoms or aralkyl group having 7 to 12 carbon atoms, or R^{20} and R^{21} or R^{23} and R^{24} are bonded together to form a 5- to 8-membered heterocyclic structure together with one nitrogen atom in the formula (16) and the rest of R^{20} to R^{24} are independently a linear, branched or cyclic alkyl group having 1 to 12 carbon atoms, aryl group having 6 to 12 carbon atoms or aralkyl group having 7 to 12 carbon atoms, and at least one of the polymethylene chain, alkyl group, aryl group, aralkyl group and heterocyclic structure has at least one hydroxyl group bonded to a carbon atom, with the proviso that the polymethylene chain, alkyl group, aryl group, aralkyl group and heterocyclic structure can have an oxygen atom, sulfur atom or carbonyl group between the carbon atoms of any carbon-to-carbon bond and that a hydrogen atom bonded to any one of the carbon atoms may be substituted with at least one substituent other than a hydroxyl group such as an alkoxyl group or phenoxy group, a compound represented by the following formula (17) (to be referred to as "nitrogen-containing compound (VIII)" hereinafter):

25



wherein R^{25} , R^{26} , R^{27} , R^{28} , R^{29} and R^{30} are independently a
 linear, branched or cyclic alkyl group having 1 to 12 carbon
 atoms, aryl group having 6 to 12 carbon atoms or aralkyl
 group having 7 to 12 carbon atoms, or R^{25} and R^{26} , R^{27} and
 R^{28} , or R^{29} and R^{30} are bonded together to form a 5- to
 8-membered heterocyclic structure together with one
 nitrogen atom in the formula (17) and the rest of R^{25} to
 R^{30} are independently a linear, branched or cyclic alkyl
 group having 1 to 12 carbon atoms, aryl group having 6
 to 12 carbon atoms or aralkyl having 7 to 12 carbon atoms,
 with the proviso that at least one of the alkyl group,
 aryl group, aralkyl group and heterocyclic structure can
 have at least one hydroxyl group bonded to a carbon atom
 and have an oxygen atom, sulfur atom or carbonyl group
 between the carbon atoms of any carbon-to-carbon bond and
 that a hydrogen atom bonded to any one of the carbon atoms
 may be substituted with at least one substituent other
 than a hydroxyl group such as an alkoxyl group or phenoxy
 group,

a compound represented by the following formula (18) (to be
 referred to as "nitrogen-containing compound (IX)"
 hereinafter):



wherein R^{31} , R^{32} , R^{33} , R^{34} and R^{35} are independently a hydrogen

atom, hydroxyl group, linear, branched or cyclic alkyl group having 1 to 12 carbon atoms, aryl group having 6 to 12 carbon atoms or aralkyl group having 7 to 12 carbon atoms, or R^{31} and R^{32} , R^{32} and R^{33} , R^{33} and R^{34} , or R^{34} and R^{35} are bonded together to form a 6-membered aromatic ring structure together with two carbon atoms in the formula (18) and the rest of R^{31} to R^{35} are independently a hydrogen atom, hydroxyl group, linear, branched or cyclic alkyl group having 1 to 12 carbon atoms, aryl group having 6 to 12 carbon atoms or aralkyl group having 7 to 12 carbon atoms, and at least one of R^{31} to R^{35} is a hydroxyl group, or at least one of the alkyl group, aryl group, aralkyl group and aromatic ring structure has at least one hydroxyl group bonded to a carbon atom, with the proviso that when at least one of R^{31} to R^{35} is a hydroxyl group, at least one of the alkyl group, aryl group, aralkyl group and aromatic ring structure represented by R^{31} to R^{35} can have at least one hydroxyl group, that the alkyl group, aryl group aralkyl group and aromatic ring structure can have an oxygen atom, sulfur atom or carbonyl group between the carbon atoms of any carbon-to-carbon bond and that a hydrogen atom bonded to any one of the carbon atoms may be substituted with at least one substituent other than a hydroxyl group such as an alkoxyl group, phenoxy group or pyridyl group,

amide group-containing compound, urea compound or nitrogen-containing heterocyclic compound.

Illustrative examples of the nitrogen-containing compound (I) include monoalkylamines such as n-hexylamine, n-heptylamine, n-octylamine, n-nonylamine and n-decylamine; dialkylamines such as di-n-butylamine, di-n-pentylamine, di-n-hexylamine, di-n-heptylamine, di-n-octylamine, di-n-nonylamine and di-n-decylamine; trialkylamines such as triethylamine, tri-n-propylamine, tri-n-butylamine,

tri-n-pentylamine, tri-n-hexylamine, tri-n-heptylamine, tri-n-octylamine, tri-n-nonylamine and tri-n-decylamine; aromatic amines such as aniline, N-methylaniline, N,N-dimethylaniline, 2-methylaniline, 3-methylaniline, 4-methylaniline, 4-nitroaniline, diphenylamine, triphenylamine and 1-naphthylamine; and the like.

Illustrative examples of the nitrogen-containing compound (II) include ethylenediamine, N,N,N',N'-tetramethylethylenediamine, tetramethylenediamine, hexamethylenediamine, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl ether, 4,4'-diaminobenzophenone, 4,4'-diaminodiphenylamine, 2,2'-bis(4-aminophenyl)propane, 2-(3-aminophenyl)-2-(4-aminophenyl)propane, 2-(4-aminophenyl)-2-(3-hydroxyphenyl)propane, 2-(4-aminophenyl)-2-(4-hydroxyphenyl)propane, 1,4-bis[1-(4-aminophenyl)-1-methylethyl]benzene, 1,3-bis[1-(4-aminophenyl)-1-methylethyl]benzene and the like.

Illustrative examples of the nitrogen-containing compound (III) include polymers such as polyethylene-imine, polyallylamine and dimethylaminoethyl acrylamide.

Illustrative examples of the nitrogen-containing compound (IV) include compounds having one hydroxyl group such as

N,N,N'-trimethyl-N'-(2-hydroxyethyl)ethylenediamine,
 N,N,N'-triethyl-N'-(2-hydroxyethyl)ethylenediamine,
 N,N,N'-trimethyl-N'-(2-hydroxypropyl)ethylenediamine,
 N,N,N'-triethyl-N'-(2-hydroxypropyl)ethylenediamine,
 N,N,N'-triphenyl-N'-(2-hydroxyethyl)ethylenediamine,
 N,N,N'-tribenzyl-N'-(2-hydroxyethyl)ethylenediamine,
 N,N,N'-tribenzyl-N'-(2-hydroxypropyl)ethylenediamine,
 N,N,N'-trimethyl-N'-(4-hydroxyphenyl)ethylenediamine,
 N,N,N'-trimethyl-N'-(4-hydroxybenzyl)ethylenediamine,

- N,N,N'-trimethyl-N'-(2-hydroxyethyl)trimethylenediamine,
 N,N,N'-trimethyl-N'-(2-hydroxyethyl)
 tetramethylenediamine,
 N,N,N'-trimethyl-N'-(2-hydroxyethyl)
 5 pentamethylenediamine,
 N,N,N'-trimethyl-N'-(2-hydroxyethyl)hexamethylenediamine,
 N,N,N'-trimethyl-N'-(2-hydroxyethyl)
 heptamethylenediamine,
 N,N,N'-trimethyl-N'-(2-hydroxyethyl)octamethylenediamine,
 10 1,3-bis(dimethylamino)-2-propanol,
 1,3-bis(diethylamino)-2-propanol,
 1-dimethylamino-2-(3'-hydroxypyrrolidino)ethane,
 1-dimethylamino-2-(3'-hydroxymethylpyrrolidino)ethane,
 1-dimethylamino-2-{3'-(2''-hydroxyethyl)pyrrolidino}
 15 ethane and 1-dimethylamino-2-(4'-hydroxypiperidino)ethane;
 compounds having two hydroxyl groups such as
 N,N'-dimethyl-N,N'-bis(2-hydroxyethyl)ethylenediamine,
 N,N'-diethyl-N,N'-bis(2-hydroxyethyl)ethylenediamine,
 N,N'-dimethyl-N,N'-bis(2-hydroxypropyl)ethylenediamine,
 20 N,N'-diethyl-N,N'-bis(2-hydroxypropyl)ethylenediamine,
 N,N'-dimethyl-N,N'-bis(4-hydroxyphenyl)ethylenediamine,
 N,N'-dimethyl-N,N'-bis(4-hydroxybenzyl)ethylenediamine,
 1,2-bis(3'-hydroxypyrrolidino)ethane,
 1,2-bis(3'-hydroxymethylpyrrolidino)ethane,
 25 1,2-bis{3'-(2''-hydroxyethyl)pyrrolidino}ethane,
 1,2-bis(4'-hydroxypiperidino)ethane,
 1,2-bis(4'-hydroxymethylpiperidino)ethane,
 1,2-bis{4'-(2''-hydroxyethyl)piperidino}ethane and
 1-morpholino-2-{bis(2'-hydroxyethyl)amino}ethane;
 30 compounds having three hydroxyl groups such as
 N-methyl-N,N',N'-tris(2-hydroxyethyl)ethylenediamine,
 N-n-dodecyl-N,N',N'-tris(2-hydroxyethyl)ethylenediamine,
 N-methyl-N,N',N'-tris(4-hydroxyphenyl)ethylenediamine,
 N-methyl-N,N',N'-tris(4-hydroxybenzyl)ethylenediamine,

1-(3'-hydroxypyrrolidino)-2-{bis(2'-hydroxyethyl)amino}
ethane, and

1-(4'-hydroxypiperidino)-2-{bis(2'-hydroxyethyl)amino}
ethane; and compounds having four or more hydroxyl groups

- 5 such as N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine,
N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine,
N,N,N',N'-tetrakis(4-hydroxyphenyl)ethylenediamine,
N,N,N',N'-tetrakis(4-hydroxybenzyl)ethylenediamine,
N,N,N',N'-tetrakis(2-hydroxy-3-methoxypropyl)
10 ethylenediamine,
N,N,N',N'-tetrakis(2-hydroxy-3-ethoxypropyl)
ethylenediamine,
N,N,N',N'-tetrakis(2-hydroxy-3-n-propoxypropyl)
ethylenediamine,
15 N,N,N',N'-tetrakis(2-hydroxy-3-phenoxypropyl)
ethylenediamine,
N,N'-dimethyl-N,N'-bis(2,3-dihydroxypropyl)
ethylenediamine,
N,N'-diethyl-N,N'-bis(2,3-dihydroxypropyl)
20 ethylenediamine,
N-methyl-N,N',N'-tris(2,3-dihydroxypropyl)
ethylenediamine and
N,N,N',N'-tetrakis(2,3-dihydroxypropyl)ethylenediamine.

- Illustrative examples of the nitrogen-containing
25 compound (V) include compounds having one hydroxyl group such
as N-methyl-N'-(2-hydroxyethyl)piperazine,
N-ethyl-N'-(2-hydroxyethyl)piperazine,
N-n-propyl-N'-(2-hydroxyethyl)piperazine,
N-n-butyl-N'-(2-hydroxyethyl)piperazine,
30 N-n-hexyl-N'-(2-hydroxyethyl)piperazine,
N-n-octyl-N'-(2-hydroxyethyl)piperazine,
N-n-decyl-N'-(2-hydroxyethyl)piperazine,
N-n-dodecyl-N'-(2-hydroxyethyl)piperazine,
N-methyl-N'-(2-hydroxypropyl)piperazine,

- N-methyl-N'-(3-hydroxypropyl)piperazine,
 N-phenyl-N'-(2-hydroxyethyl)piperazine,
 N-benzyl-N'-(2-hydroxyethyl)piperazine,
 N-methyl-N'-(4-hydroxyphenyl)piperazine and
 5 N-methyl-N'-(4-hydroxybenzyl)piperazine; compounds having
 two hydroxyl groups such as
 N,N'-bis(2-hydroxyethyl)piperazine,
 N,N'-bis(2-hydroxypropyl)piperazine,
 N,N'-bis(4-hydroxyphenyl)piperazine,
 10 N,N'-bis(4-hydroxybenzyl)piperazine,
 N-methyl-N'-(2,3-dihydroxypropyl)piperazine and
 N-ethyl-N'-(2,3-dihydroxypropyl)piperazine; compounds
 having three hydroxyl groups such as
 N-(2-hydroxyethyl)-N'-(2,3-dihydroxypropyl)piperazine,
 15 N-(2-hydroxypropyl)-N'-(2,3-dihydroxypropyl)piperazine,
 N-(4-hydroxyphenyl)-N'-(2,3-dihydroxypropyl)piperazine
 and N-(4-hydroxybenzyl)-N'-(2,3-
 dihydroxypropyl)piperazine; and compounds having four or more
 hydroxyl groups such as
 20 N,N'-bis(2,3-dihydroxypropyl)piperazine,
 N,N'-bis(3,4-dihydroxyphenyl)piperazine,
 N,N'-bis(3,4,5-trihydroxyphenyl)piperazine,
 N,N'-bis(3,4-dihydroxybenzyl)piperazine and
 N,N'-bis(3,4,5-trihydroxybenzyl)piperazine.
 25 Illustrative examples of the nitrogen-containing
 compound (VI) include compounds having one hydroxyl group
 such as
 1-{4'-(N-methylpiperidinyl)}-2-[4'-{N-(2''-hydroxyethyl)
 piperidinyl}]ethane,
 30 1-{4'-(N-n-dodecylpiperidinyl)}-2-[4'-{N-(2''-
 hydroxyethyl)piperidinyl}]ethane,
 1-{4'-(N-benzylpiperidinyl)}-2-[4'-{N-(2''-hydroxyethyl)
 piperidinyl}]ethane,
 1,3-bis{4'-(N-methylpiperidinyl)}-2-propanol,

- 1-{4'-(N-methylpiperidinyl)}-3-[4'-(N-(2''-hydroxyethyl)piperidinyl)]propane,
 1-{4'-(N-methylpiperidinyl)}-6-[4'-(N-(2''-hydroxyethyl)piperidinyl)]hexane and
 5 1-{4'-(N-methylpiperidinyl)}-8-[4'-(N-(2''-hydroxyethyl)piperidinyl)]octane; compounds having two hydroxyl groups such as
 1,2-bis[4'-(N-(2''-hydroxyethyl)piperidinyl)]ethane,
 1,2-bis[4'-(N-(2''-hydroxypropyl)piperidinyl)]ethane,
 10 1,2-bis[4'-(N-(2''-hydroxyethyl)piperidinyl)]propane and
 1,2-bis[4'-(N-(2''-hydroxypropyl)piperidinyl)]propane;
 compounds having three hydroxyl groups such as
 1-[4'-(N-(2''-hydroxyethyl)piperidinyl)]-2-[4'-(N'-(2'',
 3''-dihydroxypropyl)piperidinyl)]ethane,
 15 1-[4'-(N-(2''-hydroxypropyl)piperidinyl)]-2-[4'-(N'-(2'',
 ,3''-dihydroxypropyl)piperidinyl)]ethane,
 1-[4'-(N-(2''-hydroxyethyl)piperidinyl)]-2-[4'-(N'-(2'',
 ,3''-dihydroxypropyl)piperidinyl)]propane and
 1-[4'-(N-(2''-hydroxypropyl)piperidinyl)]-2-[4'-(N'-(2'',
 ,3''-dihydroxypropyl)piperidinyl)]propane; and compounds
 20 having four or more hydroxyl groups such as
 1,2-bis{N-(2',3'-dihydroxypropyl)piperazinyl}ethane,
 1,2-bis{N-(3',4'-dihydroxyphenyl)piperazinyl}ethane,
 1,2-bis{N-(3',4',5'-trihydroxyphenyl)piperazinyl}ethane,
 25 1,2-bis{N-(3',4'-dihydroxybenzyl)piperazinyl}ethane and
 1,2-bis{N-(3',4',5'-trihydroxybenzyl)piperazinyl}ethane.

Illustrative examples of the nitrogen-containing compound (VII) include compounds having one hydroxyl group such as bis(2-dimethylaminoethyl)·2-hydroxyethylamine,
 30 bis(2-dimethylaminoethyl)·2-hydroxypropylamine,
 N,N,N'-trimethyl-N'-{2-(3'-hydroxypyrrolidino)ethyl}
 ethylenediamine,
 bis(2-pyrrolidinoethyl)·2-hydroxyethylamine,
 bis(2-pyrrolidinoethyl)·2-hydroxypropylamine,

- methyl·2-pyrrolidinoethyl·2-(3'-hydroxypyrrolidino)ethylamine,
 N,N,N'-trimethyl-N'-{2-(4'-hydroxypiperidino)ethyl}ethylenediamine and
- 5 N,N-dimethyl-N'-(2-piperidinoethyl)-N'-(2-hydroxyethyl)ethylenediamine; compounds having two hydroxyl groups such as N,N',N''-trimethyl-N,N''-bis(2-hydroxyethyl)diethylenetriamine,
 N,N,N'',N''-tetramethyl-N'-(2,3-dihydroxypropyl)
- 10 diethylenetriamine,
 N-methyl-N-(2-pyrrolidinoethyl)-N',N'-bis(2-hydroxyethyl)ethylenediamine,
 methyl·bis{2-(3'-hydroxypyrrolidino)ethyl}amine,
 bis(2-pyrrolidinoethyl)·2,3-dihydroxypropylamine,
- 15 N-methyl-N-(2-piperidinoethyl)-N',N'-bis(2-hydroxyethyl)ethylenediamine,
 methyl·bis{2-(4'-hydroxypiperidino)ethyl}amine and
 bis(2-morpholinoethyl)·2,3-dihydroxypropylamine;
 compounds having three hydroxyl groups such as
- 20 N,N''-dimethyl-N,N',N''-tris(2-hydroxyethyl)diethylenetriamine,
 N,N''-dimethyl-N,N',N''-tris(2-hydroxypropyl)diethylenetriamine,
 N-(2-pyrrolidinoethyl)-N,N',N''-tris(2-hydroxyethyl)
- 25 ethylenediamine,
 N-(2-piperidinoethyl)-N,N',N''-tris(2-hydroxyethyl)ethylenediamine, bis{2-(3'-hydroxypyrrolidino)ethyl}·2-hydroxyethylamine and
 bis{2-(4'-hydroxypiperidino)ethyl}·2-hydroxyethylamine;
- 30 and compounds having four or more hydroxyl groups such as N'-methyl-N,N,N'',N''-tetrakis(2-hydroxyethyl)diethylenetriamine,
 N'-ethyl-N,N,N'',N''-tetrakis(2-hydroxyethyl)diethylenetriamine,

- N'-n-butyl-N,N,N'',N''-tetrakis(2-hydroxyethyl)
 diethylenetriamine,
 N'-n-hexyl-N,N,N'',N''-tetrakis(2-hydroxyethyl)
 diethylenetriamine,
 5 N'-n-octyl-N,N,N'',N''-tetrakis(2-hydroxyethyl)
 diethylenetriamine,
 N'-n-decyl-N,N,N'',N''-tetrakis(2-hydroxyethyl)
 diethylenetriamine,
 N'-n-dodecyl-N,N,N'',N''-tetrakis(2-hydroxyethyl)
 10 diethylenetriamine,
 N'-phenyl-N,N,N'',N''-tetrakis(2-hydroxyethyl)
 diethylenetriamine,
 N'-benzyl-N,N,N'',N''-tetrakis(2-hydroxyethyl)
 diethylenetriamine,
 15 N,N,N',N'',N''-pentakis(2-hydroxyethyl)
 diethylenetriamine,
 N,N,N',N'',N''-pentakis(2-hydroxypropyl)
 diethylenetriamine,
 N,N,N',N'',N''-pentakis(4-hydroxyphenyl)
 20 diethylenetriamine,
 N,N,N',N'',N''-pentakis(4-hydroxybenzyl)
 diethylenetriamine,
 N,N,N',N'',N''-pentakis(2-hydroxy-3-methoxypropyl)
 diethylenetriamine,
 25 N,N,N',N'',N''-pentakis(2-hydroxy-3-ethoxypropyl)
 diethylenetriamine,
 N,N,N',N'',N''-pentakis(2-hydroxy-3-n-propoxypropyl)
 diethylenetriamine,
 N,N,N',N'',N''-pentakis(2-hydroxy-3-phenoxypropyl)
 30 diethylenetriamine,
 N, N''-dimethyl-N,N',N''-tris(2,3-dihydroxypropyl)
 diethylenetriamine,
 N'-methyl-N,N,N'',N''-tetrakis(2,3-dihydroxypropyl)
 diethylenetriamine and

N,N,N',N'',N''-pentakis(2,3-dihydroxypropyl)
diethylenetriamine.

Illustrative examples of the nitrogen-containing compound (VIII) include compounds having one hydroxyl group
 5 such as 2,4,6-tris(dimethylaminomethyl)phenol,
 2,4,6-tris(diethylaminomethyl)phenol,
 2,4,6-tris(diphenylaminomethyl)phenol,
 2,4,6-tris(dibenzylaminomethyl)phenol,
 2,4,6-tris(pyrrolidinomethyl)phenol,
 10 2,4,6-tris(piperidinomethyl)phenol,
 4-morpholinomethyl-2,6-bis(dimethylaminomethyl)phenol and
 2,4,6-tris(morpholinomethyl)phenol; compounds having two
 hydroxyl groups such as
 2,6-bis(dimethylaminomethyl)-4-[(methyl(2'-
 15 hydroxyethyl)amino)methyl]phenol,
 2,6-bis(dimethylaminomethyl)-4-[(methyl(2'-
 hydroxypropyl)amino)methyl]phenol,
 2,6-bis(dimethylaminomethyl)-4-(3'-
 hydroxypyrrolidinomethyl)phenol and
 20 2,6-bis(dimethylaminomethyl)-4-(4'-
 hydroxypiperidinomethyl)phenol; compounds having three
 hydroxyl groups such as
 2,6-bis(dimethylaminomethyl)-4-[(bis(2'-hydroxyethyl)
 amino)methyl]phenol,
 25 2,6-bis(dimethylaminomethyl)-4-[(bis(2'-hydroxypropyl)
 amino)methyl]phenol, 4-(dimethylaminomethyl)-2,6-bis(3'-
 hydroxypyrrolidinomethyl)phenol,
 4-(dimethylaminomethyl)-2,6-bis(4'-
 hydroxypiperidinomethyl)phenol,
 30 2,6-bis(pyrrolidinomethyl)-4-[(bis(2'-hydroxyethyl)amino
)methyl]phenol and
 2,6-bis(piperidinomethyl)-4-[(bis(2'-hydroxyethyl)amino)
 methyl]phenol; and compounds having four or more hydroxyl
 groups such as

4-dimethylaminomethyl-2,6-bis[$\{$ bis(2'-hydroxyethyl)amino
 }methyl]phenol,
 4-dimethylaminomethyl-2,6-bis[$\{$ bis(2'-hydroxypropyl)
 amino}methyl]phenol,
 5 2,4,6-tris[$\{$ bis(2'-hydroxyethyl)amino}methyl]phenol,
 2,4,6-tris[$\{$ bis(2'-hydroxypropyl)amino}methyl]phenol,
 2,4,6-tris(3'-hydroxypyrrolidinomethyl)phenol,
 2,4,6-tris(3'-hydroxymethylpyrrolidinomethyl)phenol,
 2,4,6-tris[$\{$ 3'-(2''-hydroxyethyl)pyrrolidino}methyl]
 10 phenol, 2,4,6-tris(4'-hydroxypiperidinomethyl)phenol,
 2,4,6-tris(4'-hydroxymethylpiperidinomethyl)phenol,
 2,4,6-tris[$\{$ 4'-(2''-hydroxyethyl)piperidino}methyl]
 phenol and
 2,4,6-tris[$\{$ 4'-(2'',3''-dihydroxypropyl)piperidino}
 15 methyl]phenol.

Illustrative examples of the nitrogen-containing
 compound (IX) include compounds having one hydroxyl group
 such as 2-hydroxypyridine, 3-hydroxypyridine,
 4-hydroxypyridine, 2-hydroxy-3-methylpyridine,
 20 2-hydroxy-4-methylpyridine, 2-hydroxy-5-methylpyridine,
 2-hydroxy-6-methylpyridine, 3-hydroxy-2-methylpyridine,
 3-hydroxy-4-methylpyridine, 3-hydroxy-5-methylpyridine,
 3-hydroxy-6-methylpyridine, 4-hydroxy-2-methylpyridine,
 4-hydroxy-3-methylpyridine, 2-hydroxy-4-ethylpyridine,
 25 2-hydroxy-4-n-propylpyridine,
 2-hydroxy-4-1-propylpyridine, 2-hydroxy-4-n-butylpyridine,
 2-hydroxy-4-n-dodecylpyridine, 2-hydroxy-4-phenylpyridine,
 2-hydroxy-4-benzylpyridine, 2-hydroxymethylpyridine,
 3-hydroxymethylpyridine, 4-hydroxymethylpyridine,
 30 2-(2'-hydroxyethyl)pyridine, 3-(2'-hydroxyethyl)pyridine,
 4-(2'-hydroxyethyl)pyridine, 2-(2'-hydroxypropyl)pyridine,
 3-(2'-hydroxypropyl)pyridine,
 4-(2'-hydroxypropyl)pyridine,
 4-(4'-hydroxyphenyl)pyridine,

- 4-(4'-hydroxybenzyl)pyridine, 2-quinolinol, 3-quinolinol,
 4-quinolinol, 1-isoquinolinol, 3-isoquinolinol,
 4-isoquinolinol and α -pyridoin; compounds having two hydroxyl
 groups such as 2,3-dihydroxypyridine, 2,4-dihydroxypyridine,
 5 2,5-dihydroxypyridine, 2,6-dihydroxypyridine,
 3,4-dihydroxypyridine, 3,5-dihydroxypyridine,
 2-hydroxy-3-hydroxymethylpyridine,
 2-hydroxy-4-hydroxymethylpyridine,
 2-hydroxy-5-hydroxymethylpyridine,
 10 2-hydroxy-6-hydroxymethylpyridine,
 3-hydroxy-4-hydroxymethylpyridine,
 3-hydroxy-5-hydroxymethylpyridine,
 2-hydroxy-3-(2'-hydroxyethyl)pyridine,
 2-hydroxy-4-(2'-hydroxyethyl)pyridine,
 15 2-hydroxy-5-(2'-hydroxyethyl)pyridine,
 2-hydroxy-6-(2'-hydroxyethyl)pyridine,
 3-hydroxy-4-(2'-hydroxyethyl)pyridine,
 3-hydroxy-5-(2'-hydroxyethyl)pyridine,
 2,3-bis(hydroxymethyl)pyridine,
 20 2,4-bis(hydroxymethyl)pyridine,
 2,5-bis(hydroxymethyl)pyridine,
 2,6-bis(hydroxymethyl)pyridine,
 3,4-bis(hydroxymethyl)pyridine,
 3,5-di(hydroxymethyl)pyridine,
 25 2,3-bis(2'-hydroxyethyl)pyridine,
 2,4-bis(2'-hydroxyethyl)pyridine,
 2,5-bis(2'-hydroxyethyl)pyridine,
 2,6-bis(2'-hydroxyethyl)pyridine,
 3,4-bis(2'-hydroxyethyl)pyridine,
 30 3,5-bis(2'-hydroxyethyl)pyridine,
 3-(2'-pyridyl)-1,2-propanediol,
 3-(3'-pyridyl)-1,2-propanediol,
 3-(4'-pyridyl)-1,2-propanediol,
 2-(2'-pyridyl)-1,3-propanediol,

- 2-(3'-pyridyl)-1,3-propanediol,
 2-(4'-pyridyl)-1,3-propanediol,
 2-(2'-pyridyl)-1,4-butanediol,
 2-(3'-pyridyl)-1,4-butanediol,
 5 2-(4'-pyridyl)-1,4-butanediol,
 2-(2'-pyridyl)-2,3-butanediol,
 2-(3'-pyridyl)-2,3-butanediol,
 2-(4'-pyridyl)-2,3-butanediol,
 2,3-di(2'-pyridyl)-1,4-butanediol,
 10 2,3-di(3'-pyridyl)-1,4-butanediol,
 2,3-bis(4'-pyridyl)-1,4-butanediol,
 2,3-bis(2'-pyridyl)-2,3-butanediol,
 2,3-bis(3'-pyridyl)-2,3-butanediol and
 2,3-bis(4'-pyridyl)-2,3-butanediol; compounds having three
 15 hydroxyl groups such as
 2,6-dihydroxy-4-hydroxymethylpyridine,
 3,5-dihydroxy-4-hydroxymethylpyridine,
 2,6-dihydroxy-4-(2'-hydroxyethyl)pyridine,
 3,5-dihydroxy-4-(2'-hydroxyethyl)pyridine,
 20 4-hydroxy-2,6-bis(hydroxymethyl)pyridine,
 4-hydroxy-3,5-bis(hydroxymethyl)pyridine,
 4-hydroxy-2,6-bis(2'-hydroxyethyl)pyridine,
 4-hydroxy-3,5-bis(2'-hydroxyethyl)pyridine,
 2,4,6-tris(hydroxymethyl)pyridine,
 25 3,4,5-tris(hydroxymethyl)pyridine,
 2,4,6-tris(2'-hydroxyethyl)pyridine and
 3,4,5-tris(2'-hydroxyethyl)pyridine; and compounds having
 four or more hydroxyl groups such as
 2,6-bis(2'-hydroxyethyl)-4-(2',3'-dihydroxypropyl)
 30 pyridine, 2,6-bis(2',3'-dihydroxypropyl)pyridine,
 2,6-bis(2',3'-dihydroxypropyl)-4-(2'-hydroxyethyl)
 pyridine,
 2,6-bis(2',3'-dihydroxypropyl)-4-(2'-hydroxypropyl)
 pyridine, 2,4,6-tris(2',3'-dihydroxypropyl)pyridine and

3,4,5-tris(2',3'-dihydroxypropyl)pyridine.

Illustrative examples of the amide group-containing compound include formamide, N-methylformamide,

N,N-dimethylformamide, acetamide, N-methylacetamide,

5 N,N-dimethylacetamide, propionamide, benzamide, pyrrolidone, N-methylpyrrolidone and the like.

Illustrative examples of the urea compound include urea, methylurea, 1,1-dimethylurea, 1,3-dimethylurea,

1,1,3,3-tetramethylurea, 1,3-diphenylurea,

10 tributylthiourea and the like.

Illustrative examples of the nitrogen-containing heterocyclic compound include imidazoles such as imidazole, benzimidazole, 4-methylimidazole and

4-methyl-2-phenylimidazole; pyridines such as pyridine,

15 2-methylpyridine, 4-methylpyridine, 2-ethylpyridine,

4-ethylpyridine, 2-phenylpyridine, 4-phenylpyridine,

N-methyl-4-phenylpyridine, nicotine, nicotinic acid,

nicotinic acid amide, quinoline, 8-oxyquinoline and acridine;

pyrazine, pyrazole, pyridazine, quinoxaline, purine,

20 pyrrolidine, piperidine, morpholine, 4-methylmorpholine,

piperazine, 1,4-dimethylpiperazine,

1,4-diazabicyclo[2.2.2]octane and the like.

Of the above nitrogen-containing organic compounds, the nitrogen-containing compounds (I) and the

25 nitrogen-containing heterocyclic compounds are preferable.

Of the nitrogen-containing compounds (I), trialkylamines are particularly preferable and, of the nitrogen-containing heterocyclic compounds, pyridines are particularly preferable.

30 The above acid diffusion control agents may be used alone or in admixture of two or more.

The amount of the acid diffusion control agent is preferably 15 parts or less by weight, more preferably 0.001 to 10 parts by weight, much more preferably 0.005 to 5 parts

by weight, based on 100 parts by weight of the total of the copolymer (A) and the copolymer (B). When the amount of the acid diffusion control agent is larger than 15 parts by weight, the sensitivity of a resist and the developability of an exposed portion tend to lower. When the amount is smaller than 0.001 part by weight, the pattern shape and dimensional accuracy of a resist may lower according to process conditions.

Other additives

The radiation sensitive resin composition of the present invention may comprise a surfactant which has the function of improving the coating properties and striation of a composition and the developability of a resist.

Illustrative examples of the surfactant include polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene octylphenol ether, polyoxyethylene nonylphenol ether, polyethylene glycol dilaurate, polyethyleneglycol distearate and the like. Commercial products of the surfactant include F Top EF301, EF303 and EF352 (Tokem Products Co., Ltd.), Megafac F171 and F173 (Dainippon Ink and Chemicals, Inc.), Florade FC430 and FC431 (Sumitomo 3M Limited), Asahi Guard AG710 and Surflon S-382, SC101, SC102, SC103, SC104, SC105 and SC106 (Asahi Glass Co., Ltd.), KP341 (Shin-Etsu Chemical Co., Ltd.), Polyflow No. 75 and No. 95 (Kyo-eisha Kagaku Co., Ltd.) and the like.

The amount of the surfactant is generally 2 parts or less by weight based on 100 parts by weight of the total of the copolymer (A) and the copolymer (B).

The radiation sensitive resin composition of the present invention may further comprise a sensitizer which exhibits the function of increasing the amount of a generated acid by absorbing the energy of radiation and transmitting it to the acid generating agent and has the effect of improving

the apparent sensitivity of a resist.

Preferable examples of the sensitizer include benzophenones, Rose Bengales, anthracenes and the like.

5 The amount of the sensitizer is generally 50 parts or less by weight based on 100 parts by weight of the total of the copolymer (A) and the copolymer (B).

10 The latent image of an exposed portion is visualized and the influence of halation at the time of exposure can be alleviated by blending a dye and/or pigment, and adhesion to a substrate can be further improved by blending an adhesive aid.

15 A halation-preventing agent such as 4-hydroxy-4'-methylchalcone, shape-improving agent, storage stabilizer, anti-foaming agent and the like may also be blended as other additives.

Solvent

20 A solution of the radiation sensitive resin composition of the present invention is prepared by uniformly dissolving the composition in a solvent to ensure that the total solid content should become 1 to 50 wt%, preferably 5 to 40 wt% when used, and filtering the resulting solution with a filter having a pore diameter of about 0.2 μm .

25 Illustrative examples of the solvent used to prepare the above composition solution include ethylene glycol monoalkyl ether acetates such as ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, ethylene glycol mono-n-propyl ether acetate and ethylene glycol mono-n-butyl ether acetate; propylene glycol monoalkyl
30 ethers such as propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol mono-n-propyl ether and propylene glycol mono-n-butyl ether; propylene glycol dialkyl ethers such as propylene glycol dimethyl ether, propylene glycol diethyl ether, propylene glycol di-n-propyl

ether and propylene glycol di-n-butyl ether; propylene glycol monoalkyl ether acetates such as propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol mono-n-propyl ether acetate and propylene glycol mono-n-butyl ether acetate; lactates such as methyl lactate, ethyl lactate, n-propyl lactate and i-propyl lactate; aliphatic carboxylates such as n-amyl formate, i-amyl formate, ethyl acetate, n-propyl acetate, i-propyl acetate, n-butyl acetate, i-butyl acetate, n-amyl acetate, i-amyl acetate, i-propyl propionate, n-butyl propionate and i-butyl propionate; other esters such as ethyl hydroxyacetate, ethyl 2-hydroxy-2-methylpropionate, methyl 2-hydroxy-3-methylbutyrate, ethyl methoxyacetate, ethyl ethoxyacetate, methyl 3-methoxypropionate, ethyl 3-methoxypropionate, methyl 3-ethoxypropionate, ethyl 3-ethoxypropionate, 3-methoxybutyl acetate, 3-methyl-3-methoxybutyl acetate, 3-methyl-3-methoxybutyl propionate, 3-methyl-3-methoxybutyl butyrate, methyl acetoacetate, ethyl acetoacetate, methyl pyruvate and ethyl pyruvate; aromatic hydrocarbons such as toluene and xylene; ketones such as methyl ethyl ketone, methyl propyl ketone, methyl butyl ketone, 2-heptanone, 3-heptanone, 4-heptanone and cyclohexanone; amides such as N-methylformamide, N,N-dimethylformamide, N-methylacetamide, N,N-dimethylacetamide and N-methylpyrrolidone; and lactones such as γ -butyrolactone.

These solvents may be used alone or in admixture of two or more.

30 Formation of resist pattern

To form a resist pattern from the radiation sensitive resin composition of the present invention, the composition solution prepared as described above is coated on a substrate such as a silicon wafer or a wafer coated with aluminum by

suitable coating means such as rotation coating, cast coating, roll coating or the like to form a resist film, which is prebaked at a temperature of 70 to 160°C as the case may be before exposed through a predetermined mask pattern. The radiation
5 used herein is suitably selected from ultraviolet rays such as i-rays (wavelength of 365 nm), far ultraviolet rays from an ArF excimer laser (wavelength of 193 nm) or KrF excimer laser (wavelength of 248 nm), X-rays such as synchrotron radiation and charged corpuscular rays such as electron rays
10 according to the type of acid-generating agent. Exposure conditions such as the amount of exposure are suitably selected according to the composition of the radiation sensitive resin composition and the types of additives.

To form a highly accurate fine pattern stably in the
15 present invention, postbaking is preferably carried out at a temperature of 70 to 160°C for 30 seconds or more after exposure. In this case, when the temperature of postbaking after exposure is lower than 70°C, differences in sensitivity according to the type of substrate may spread.

20 Thereafter, the exposed resist film is developed with an alkali developer at 10 to 50°C for 30 to 200 seconds to form a predetermined resist pattern.

The alkali developer is an alkaline aqueous solution prepared by dissolving an alkaline compound such as an alkali
25 metal hydroxide, ammonia water, mono-, di- or tri-alkyl amine, mono-, di- or tri-alkanol amine, heterocyclic amine, tetraalkyl ammonium hydroxide, choline, 1,8-diazabicyclo[5.4.0]-7-undecene or 1,5-diazabicyclo[4.3.0]-5-nonene to a concentration of 1 to
30 10 wt%, preferably 1 to 5 wt%.

The developer which is the above alkaline aqueous solution may contain a water-soluble organic solvent such as methanol or ethanol, and a surfactant in a suitable amount.

When an alkaline aqueous solution is used as the

developer, the film is generally rinsed with water after developed.

To prevent the influence of basic impurities contained in an environmental atmosphere upon the formation of a resist pattern, a protective film may be formed on the resist film.

Examples

The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting. The measurement of Mw and Mn and the evaluation of each resist were carried out in accordance with the following methods.

Mw and Mn

GPC columns (G2000H_{XL} x 2 + G3000H_{XL} x 1 + G4000H_{XL} x 1) manufactured by Toso Co., Ltd. are used to measure Mw and Mn by GPC using monodisperse polystyrene as the standard under the following analytical conditions.

flow rate: 1.0 ml/minute

eluting solvent: tetrahydrofuran

column temperature: 40°C

Resolution (1L1S)

The amount of exposure for forming a line-and-space pattern (1L1S) having a design size of 0.26 μm at a line/space width ratio of 1:1 is taken as the optimum amount of exposure and the minimum size (μm) of a line-and-space pattern (1L1S) which is resolved with this optimum amount of exposure is taken as resolution (1L1S).

Resolution (1L3S)

The resolution at which the line width of a semi-isolated pattern (1L3S) with a design size of 0.26 μm resolved with the above optimum amount of exposure is in the range of (design

size $\pm 10\%$) is taken as the resolution (1L3S) of the semi-isolated pattern (1L3S).

Focus Latitude (1H1S)

5 The focusing depth is changed at an amount of exposure with which the aperture of a resolved contact hole pattern having a design size of $0.22\text{ }\mu\text{m}$ and a contact hole (1H1S) pitch of $0.44\text{ }\mu\text{m}$ becomes a design size of $0.22\text{ }\mu\text{m}$ and the size of the focusing depth at which the aperture of the hole
10 patter is in the range of (design size $\pm 10\%$) is taken as DOF of a 1H1S pattern. As DOF increases, the process margin becomes larger and the production yield of actual devices becomes higher.

15 film surface roughness

 The sectional size of a line-and-space pattern (1L1S) having a design size of $0.26\text{ }\mu\text{m}$ is measured with a scanning electron microscope and the film surface roughness is evaluated based on the following criteria from the value of
20 Ld which is obtained by subtracting Lin (minimum size) from Lout (maximum size). The surface unevenness of Fig. 1 is exaggerated.

Ld is less than $0.01\text{ }\mu\text{m}$: good

Ld is $0.01\text{ }\mu\text{m}$ or more: not good

25

Synthesis of copolymer (A)

Synthesis Example 1

 The anionic polymerization of 176 g of 4-t-butoxystyrene was carried out in 500 ml of tetrahydrofuran in the presence
30 of sec-butyl lithium at -78°C . After the polymerization reaction, the obtained resin solution was solidified in methanol to obtain 150 g of white poly(4-t-butoxystyrene). This solid was dissolved in 600 g of dioxane, diluted hydrochloric acid was added to carry out hydrolysis at 70°C

for 12 hours, and the obtained product was solidified in a large amount of water to obtain a white solid. Thereafter, this resin was dissolved in acetone and solidified in a large amount of water repeatedly to form white powder which was
5 then filtered and dried overnight at 50° C under reduced pressure. The obtained poly(4-hydroxystyrene) had an Mw of 11,400 and an Mw/Mn of 1.01. Thereafter, 24 g of the poly(4-hydroxystyrene) was dissolved in 100 g of butyl acetate and bubbling was carried out with nitrogen gas for 30 minutes.
10 Subsequently, 8 g of cyclohexylvinyl ether was added to this solution, and 1 g of pyridinium p-toluenesulfonate was added as a catalyst to carry out a reaction at room temperature for 12 hours. Thereafter, the reaction solution was added dropwise to a 1 wt% ammonia aqueous solution to precipitate
15 a polymer which was then filtered and dried overnight in a vacuum drier at 50° C. This polymer had an Mw of 13,000 and an Mw/Mn of 1.01. When analyzed by ¹³C-NMR, it had such a structure that 23 % of the hydrogen atoms of the phenolic hydroxyl groups contained in the poly(4-hydroxystyrene) were
20 substituted by a 1-cyclohexyloxyethyl group. This polymer is designated as copolymer (A-1).

Synthesis Example 2

300 Grams of 4-t-butoxystyrene and 2.0 g of
25 azobisisobutyronitrile were dissolved in 300 g of dioxane, and this solution was heated in a nitrogen atmosphere at 60° C for 16 hours to polymerize the 4-t-butoxystyrene. The obtained reaction solution was added dropwise to a large amount of methanol to solidify the formed poly(4-t-butoxystyrene)
30 resin. This solidified resin was re-dissolved in dioxane, diluted sulfuric acid was added to this solution, and the solution was heated at 60° C for 12 hours to carry out hydrolysis.

This resin solution was transferred to a separation funnel, a large amount of ethyl acetate and a large amount

of water were added to this resin solution, the resulting solution was mixed by shaking and left to stand so as to separate an ethyl acetate layer (upper layer) and a water layer (lower layer) which was discarded. This operation was repeated until
5 the discarded water layer became completely neutral, the resin solution was dried under reduced pressure, and the obtained resin was re-dissolved in acetone. This resin solution was added dropwise to a large amount of water to solidify the resin, and the formed white powdery resin was filtered and
10 heated overnight at 50° C under reduced pressure to be dried.

The obtained resin was poly(4-hydroxystyrene) having an Mw of 11,000 and an Mw/Mn of 1.6.

After 24 g of this poly(4-hydroxystyrene) was dissolved in 100 g of butyl acetate, bubbling was carried out with nitrogen
15 gas for 30 minutes. Thereafter, 6 g of cyclohexyl vinyl ether, 4 g of ethyl vinyl ether and 1 g of pyridinium p-toluenesulfonate as a catalyst were added to this solution to carry out a reaction at room temperature for 12 hours. This reaction solution was then added dropwise to a 1 wt% ammonia aqueous solution to
20 precipitate a polymer which was then filtered and dried overnight in a vacuum drier at 50° C. This polymer had an Mw of 13,500 and an Mw/Mn of 1.6. When analyzed by ¹³C-NMR, it had such a structure that 15 % of the hydrogen atoms of the phenolic hydroxyl groups contained in the
25 poly(4-hydroxystyrene) were substituted by a 1-cyclohexyloxyethyl group and 7 % of the hydrogen atoms were substituted by a 1-ethoxyethyl group. This polymer is designated as copolymer (A-2).

30 Synthesis Example 3

108 Grams of 4-vinylphenol and 10 g of styrene were dissolved in 1,000 ml of acetonitrile purified by distillation, a slight amount of methanol was added to the solution, the resulting solution was cooled to -10° C in a dry ice-acetone

bath, and 3,000 g (0.1 mol/l) of an acetonitrile solution of $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ as a cationic polymerization initiator was added dropwise under agitation. After 1 hour of agitation, the obtained product was added to a large amount of water and the precipitated white solid was dried overnight at 40°C under reduced pressure. This resin had an Mw of 11,800 and an Mw/Mn of 1.3. When the obtained resin was analyzed by ^1H -NMR and ^{13}C -NMR, it was a copolymer of 4-hydroxystyrene and styrene in a ratio of 9:1. After 24 g of this copolymer was dissolved in 100 g of butyl acetate, bubbling was carried out with nitrogen gas for 30 minutes. Thereafter, 7 g of cyclohexyl vinyl ether was added to this solution and 1 g of pyridinium p-toluenesulfonate was added as a catalyst to carry out a reaction at room temperature for 12 hours. The reaction solution was then added dropwise to a 1 wt% ammonia aqueous solution to precipitate a polymer which was then filtered and dried overnight in a vacuum drier at 50°C. This polymer had an Mw of 12,700 and an Mw/Mn of 1.3. When analyzed by ^{13}C -NMR, it had such a structure that 15 % of the hydrogen atoms of the phenolic hydroxyl groups contained in the 4-hydroxystyrene-styrene copolymer were substituted by a 1-cyclohexyloxyethoxy group. This polymer is designated as copolymer (A-3).

25 Synthesis Example 4

180 Grams of 4-acetoxystyrene, 10 g of t-butyl acrylate, 6.0 g of azobisisobutyronitrile and 1.5 g of t-dodecylmercaptan were dissolved in 200 g of propylene glycol monomethyl ether and polymerized in a nitrogen atmosphere for 16 hours with the reaction temperature maintained at 70°C. After polymerization, the reaction solution was added dropwise to a large amount of hexane to solidify and purify and the formed resin. Thereafter, 500 g of propylene glycol monomethyl ether was added to the purified resin again, and

additionally, 300 g of methanol, 100 g of triethylamine and 20 g of water were added to carry out hydrolysis under reflux at a boiling point for 8 hours. After the reaction, the solvent and triethylamine were distilled off under reduced pressure, the obtained resin was dissolved in acetone and added dropwise to a large amount of water to be solidified, and the formed white powder was filtered and dried overnight at 50°C under reduced pressure.

This resin had an Mw of 12,000 and an Mw/Mn of 1.7. When analyzed by ¹³C-NMR, it was a copolymer of 4-hydroxystyrene and t-butyl acrylate in a molar ratio of 92:8. 24 Grams of this resin was dissolved in 200 g of distilled butyl acetate, 6 g of cyclohexylvinyl ether was added, 1 g of pyridinium p-toluenesulfonate was added as a catalyst to carry out a reaction at room temperature for 12 hours. The reaction solution was then added dropwise to a 1 wt% ammonia aqueous solution to precipitate a polymer which was then filtered and dried overnight in a vacuum drier at 50°C. This polymer had an Mw of 13,200 and an Mw/Mn of 1.7. When analyzed by ¹³C-NMR, it had such a structure that 16 % of the hydrogen atoms of the phenolic hydroxyl groups contained in the poly(4-hydroxystyrene-t-butyl acrylate) copolymer were substituted by a 1-cyclohexyloxyethoxy group. This polymer is designated as copolymer (A-4).

Synthesis Example 5

20 Grams of di-t-butyl carbonate was added under agitation to a solution of 36 g of the poly(p-t-hydroxystyrene) produced in Synthesis Example 1 and having an Mw of 11,400 and an Mw/Mn of 1.01 and 15 g of triethylamine dissolved in 500 g of dioxane, the resulting mixture was further stirred at room temperature for 6 hours, and oxalic acid was added to neutralize the triethylamine. Thereafter, the reaction solution was added dropwise to a large amount of water to

solidify a polymer which was then washed with pure water several times, filtered and dried overnight in a vacuum drier at 50° C.

The obtained polymer had an Mw of 13,000 and an Mw/Mn of 1.03. When analyzed by ¹³C-NMR, it has such a structure that 24 % of the hydrogen atoms of the phenolic hydroxyl groups contained in the poly(4-hydroxystyrene) were substituted by a t-butoxycarbonyl group. This resin is designated as copolymer (B-1).

10 Synthesis Example 6

170 Grams of 4-t-butoxystyrene, 15 g of acrylonitrile and 7 g of azobisisobutyronitrile were dissolved in 400 g of dioxane, and this solution was heated in a nitrogen atmosphere at 75° C for 16 hours to carry out polymerization. The obtained reaction solution was added dropwise to a large amount of methanol to solidify the formed copolymer resin of poly-4-t-butoxystyrene and acrylonitrile. This solidified resin was re-dissolved in dioxane, diluted sulfuric acid was added to this solution, and the resulting solution was heated at 40° C for 12 hours to carry out hydrolysis.

This resin solution was transferred to a separation funnel, a large amount of ethyl acetate and a large amount of water were added, the resulting solution was mixed by shaking and left to stand to separate an ethyl acetate layer (upper layer) and a water layer (lower layer), which was discarded. This operation was repeated until the discarded water layer became completely neutral, the resin solution was dried under reduced pressure, and the obtained resin was re-dissolved in acetone. This resin solution was added dropwise to a large amount of water to solidify the resin, and the formed white powdery resin was filtered and heated overnight at 50° C under reduced pressure to be dried.

The obtained resin had an Mw of 8,900 and an Mw/Mn of 1.8. When analyzed by ¹H-NMR and ¹³C-NMR, the hydrolysis of

nitrile hardly proceeded and the resin was a copolymer of 4-hydroxystyrene and acrylonitrile in a ratio of 95:5. Thereafter, 18 g of di-t-butyl carbonate was added under agitation to a solution of 36 g of this resin and 15 g of triethylamine dissolved in 500 g of dioxane, the resulting mixture was further stirred at room temperature for 6 hours, and oxalic acid was added to neutralize the triethylamine. Thereafter, the reaction solution was added dropwise to a large amount of water to solidify a polymer which was then washed with pure water several times, filtered and dried overnight in a vacuum drier at 50°C.

The obtained polymer had an Mw of 9,300 and an Mw/Mn of 1.8. When analyzed by ¹H-NMR and ¹³C-NMR, it had such a structure that 21 % of the hydrogen atoms of the phenolic hydroxyl groups contained in the poly(4-hydroxystyrene-acrylonitrile)copolymer were substituted by a t-butoxycarbonyl group. This resin is designated as copolymer (B-2).

Comparative Synthesis Example 1

After 24 g of poly(4-hydroxystyrene) having an Mw of 12,000 was dissolved in 100 g of dioxane, bubbling was carried out with nitrogen gas for 30 minutes. Thereafter, 5 g of ethylvinyl ether and 1 g of pyridinium p-toluenesulfonate as a catalyst were added to this solution to carry out a reaction at room temperature for 12 hours. The reaction solution was then added dropwise to a 1 wt% ammonia aqueous solution to precipitate a polymer which was then filtered and dried overnight in a vacuum drier at 50°C.

This polymer had an Mw of 13,000 and an Mw/Mn of 1.7. When analyzed by ¹³C-NMR, it had such a structure that 34 % of the hydrogen atoms of the phenolic hydroxyl groups contained in the poly(p-hydroxystyrene) were substituted by a 1-ethoxyethyl group. This polymer is designated as copolymer

(α -1).

Examples 1 to 13 and Comparative Examples 1 to 3

Homogeneous solutions were prepared by mixing the
5 components shown in Table 1 (parts are based on weight) and
filtered with a membrane filter having a pore diameter of
0.2 μm to prepare composition solutions. Thereafter, each
of the composition solutions was spin-coated on a silicon
wafer and prebaked under the conditions shown in Table 2 to
10 form a resist film having a thickness of 0.7 μm .

Thereafter, the resist film was exposed using the
NSR2205EX12B stepper of Nikon Co., Ltd. ($\text{NA} = 0.55$) in Examples
1 to 10, 12 and 13 and Comparative Examples 1 and 2 of the
present invention and the direct drawing electron-beam
15 exposure tools of Hitachi Keisokuki Co., Ltd. (acceleration
voltage of 50 KeV) in Example 11 and postbaked under the
conditions shown in Table 2. The postbaked resist film was
then developed with a 2.38 wt% aqueous solution of tetramethyl
ammonium hydroxide by a puddling method at 23° C for 1 minute,
20 washed with pure water and dried to form a resist pattern.

The evaluation results of the obtained resist films are
shown in Table 3.

Table 1

	resin (A) (parts)	resin (B) (parts)	acid-generating agent (C) (parts)	acid diffusion control agent (D) (parts)	additive (E) (parts)	solvent (F) (parts)
Ex. 1	A-1 50	B-1 50	C-1 2	D-1 0.10 D-2 0.05		F-1 300 F-2 150
Ex. 2	A-2 60	B-1 40	C-2 2	D-2 0.10 D-3 0.04		F-1 300 F-2 150
Ex. 3	A-3 60	B-1 40	C-3 0.5 C-4 6	D-2 0.15 D-3 0.03		F-1 300 F-2 150
Ex. 4	A-3 50	B-2 50	C-4 5	D-2 0.12 D-3 0.05		F-3 450
Ex. 5	A-1 40	B-2 60	C-3 1 C-5 8	D-1 0.10 D-4 0.05		F-1 300 F-2 150
Ex. 6	A-1 50	B-1 50	C-6 6 C-1 0.5	D-1 0.07 D-4 0.05		F-1 300 F-2 150
Ex. 7	A-4 60	B-1 40	C-4 6	D-1 0.10 D-2 0.05		F-4 450
Ex. 8	A-1 70	B-1 30	C-1 0.5 C-7 6	D-2 0.15 D-3 0.03		F-1 150 F-3 300
Ex. 9	A-2 30	B-1 70	C-4 6 C-2	D-1 0.10 D-2 0.05		F-1 350 F-3 100
Ex. 10	A-2 50	B-1 50	C-4 4 C-7 2	D-1 0.10 D-2 0.05	E-1 10	F-1 300 F-4 100
Ex. 11	A-2 20	B-1 80	C-4 6	D-1 0.15 D-2 0.05	E-2 10	F-2 450
Ex. 12	A-2 80	B-1 20	C-5 6	D-4 0.15		F-1 300 F-2 100
Ex. 13	A-1 50	B-1 50	C-2 1 C-3 1	D-1 0.10 D-2 0.05	E-3 5	F-1 100 F-2 300
C.Ex. 1		B-1 100	C-1 3	D-1 0.10 D-2 0.05		F-1 300 F-2 100
C.Ex. 2	α -1 50	B-1 50	C-4 6	D-1 0.10 D-2 0.05		F-1 300 F-2 100

Table 2

	PB temperature (°C)	PB time (sec)	light source	PEB temperature (°C)	PEB time (sec)
Ex.1	90	60	KrF excimer laser	90	60
Ex.2	90	60	KrF excimer laser	100	60
Ex.3	100	60	KrF excimer laser	100	90
Ex.4	100	60	KrF excimer laser	110	60
Ex.5	110	60	KrF excimer laser	100	60
Ex.6	90	60	KrF excimer laser	110	60
Ex.7	80	60	KrF excimer laser	100	60
Ex.8	90	60	KrF excimer laser	100	60
Ex.9	90	60	KrF excimer laser	90	60
Ex.10	100	60	KrF excimer laser	115	60
Ex.11	105	60	electron rays (acceleration voltage of 50 KeV)	90	60
Ex.12	110	60	KrF excimer laser	100	60
Ex.13	95	90	KrF excimer laser	110	90
C.Ex.1	90	60	KrF excimer laser	100	60
C.Ex.2	90	60	KrF excimer laser	100	60

Table 3

	sensitivity	1L1S resolution (μm)	1L3S resolution (μm)	hole DOF (μm)	film surface roughness
Ex.1	34mj/cm ²	0.18	0.18	1.2	satisfactory
Ex.2	27mj/cm ²	0.18	0.18	1.2	satisfactory
Ex.3	27mj/cm ²	0.18	0.19	1.2	satisfactory
Ex.4	27mj/cm ²	0.18	0.19	1.2	satisfactory
Ex.5	31mj/cm ²	0.18	0.18	1.2	satisfactory
Ex.6	20mj/cm ²	0.18	0.19	1.2	satisfactory
Ex.7	19mj/cm ²	0.18	0.19	1.2	satisfactory
Ex.8	24mj/cm ²	0.18	0.18	1.2	satisfactory
Ex.9	28mj/cm ²	0.18	0.19	1.2	satisfactory
Ex.10	36mj/cm ²	0.18	0.19	1.2	satisfactory
Ex.11	5pC/cm ²	0.18	0.19	1.2	satisfactory
Ex.12	25mj/cm ²	0.18	0.18	1.2	satisfactory
Ex.13	33mj/cm ²	0.18	0.18	1.2	satisfactory
C.Ex.1	28mj/cm ²	0.23	0.23	not resolved	not acceptable
C.Ex.2	25mj/cm ²	0.19	0.19	0.20	not acceptable

Note: The smaller the value of the resolution the better.

The larger the value of the DOF the better.

The acid-generating agents, acid diffusion control agents, additives and solvents used in Examples and Comparative Examples are as follows.

5 acid-generating agents

- C-1: triphenylsulfonium nonafluorobutanesulfonate
C-2: bis(4-t-butylphenyl)iodonium p-toluenesulfonate
C-3: 4-t-butoxyphenyl·diphenylsulfonium
 10-camphorsulfonate
10 C-4: bis(cyclohexylsulfonyl)diazomethane
C-5: N-(10-camphorsulfonyloxy)bicyclo[2.2.1]heptane-5,6
 -oxy-2,3-dicarboxyimide
C-6: 1,1-bis(phenylsulfonyl)cyclohexane
C-7: bis(1,4-dioxaspiro[4,5]decane-7-sulfonyl)
15 diazomethane

acid diffusion control agents

- D-1: nicotinic acid amide
D-2: tri-n-octylamine
20 D-3: triethanolamine
D-4: 2-phenylbenzimidazole

additives

- E-1: p-hydroxystyrene-styrene copolymer (molar ratio = 9:1,
25 Mw = 3,000)
E-2: 2,2-bis(4-t-butoxyphenyl)propane
E-3: diphenolic acid

solvent

- 30 F-1: ethyl lactate
F-2: ethyl 3-ethoxypropionate
F-3: propylene glycol monomethyl ether acetate
E-4: 2-heptanone

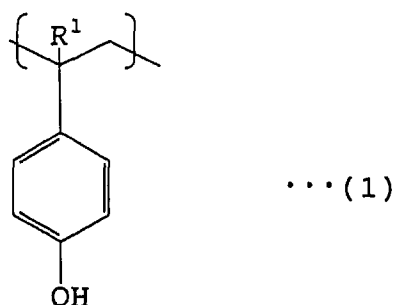
The radiation sensitive resin composition of the present invention is excellent in terms of resolution and pattern shape, has small film surface roughness and optical proximity effect, can form a fine line-and-space pattern and fine
5 isolated pattern with high accuracy and stability and has a wide focus latitude for the processing of a fine contact hole pattern with a high aspect ratio. In addition, the radiation sensitive resin composition of the present invention is effectively sensitive to various types of radiation such
10 as ultraviolet rays, far ultraviolet rays, X-rays and electron rays. Therefore, the radiation sensitive resin composition of the present invention can be extremely advantageously used as a chemically amplifying positive resist in the production of semiconductor devices whose design rule is expected to
15 be further reduced in the future.

What is claimed is:

1. A radiation sensitive resin composition comprising:

(A) a copolymer containing a recurring unit represented by the following formula (1):

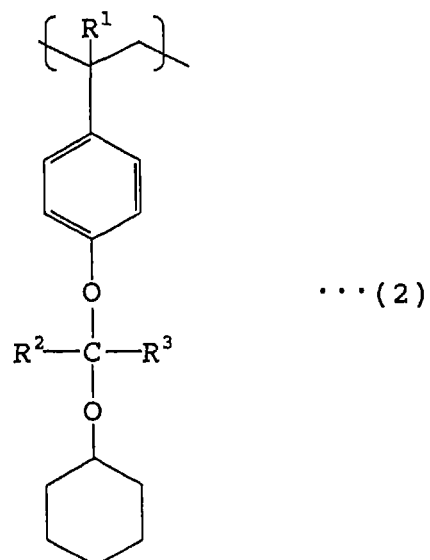
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wherein R^1 is a hydrogen atom or methyl group,
and a recurring unit represented by the following formula
(2):

15



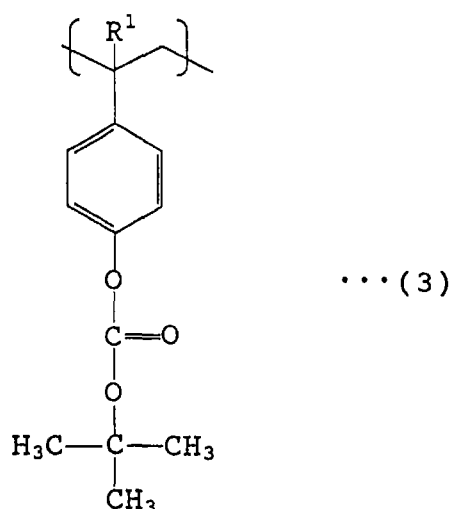
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wherein R^1 is the same as defined above, R^2 is a hydrogen atom or methyl group, and R^3 is a methyl group or ethyl group;

(B) a copolymer containing a recurring unit represented by the above formula (1) and a recurring unit represented by the following formula (3):

30

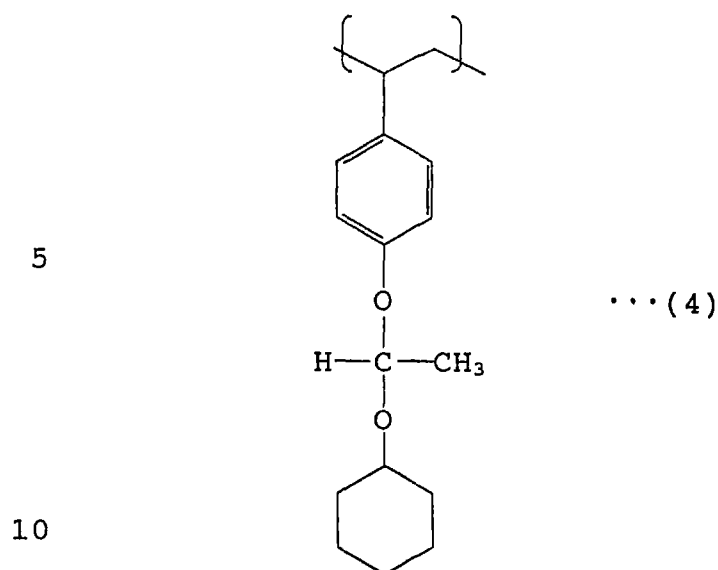


wherein R^1 is the same as defined above; and
 (C) a radiation sensitive acid-generating agent.

2. The radiation sensitive resin composition of claim 1,
 15 wherein the total content of the recurring units (1) and (2)
 in the copolymer (A) is 70 mol% or more based on the total
 of all the recurring units.

3. The radiation sensitive resin composition of claim 1,
 20 wherein the content of the recurring unit (1) in the copolymer
 (A) is more than 40 mol% and less than 90 mol% based on the
 total of all the recurring units and the content of the recurring
 unit (2) in the copolymer (A) is more than 3 mol% and less
 than 40 mol% based on the total of all the recurring units.

4. The radiation sensitive resin composition of claim 1,
 wherein the recurring unit (2) in the copolymer (A) is
 represented by the following formula (4):



5. The radiation sensitive resin composition of claim 1, wherein the total content of the recurring units (1) and (3) in the copolymer (B) is 70 mol% or more based on the total of all the recurring units.

6. The radiation sensitive resin composition of claim 1, wherein the content of the recurring unit (1) in the copolymer (B) is more than 40 mol% and less than 90 mol% based on the total of all the recurring units and the content of the recurring unit (3) in the copolymer (B) is more than 3 mol% and less than 40 mol% based on the total of all the recurring units.

7. The radiation sensitive resin composition of claim 1, wherein the copolymer (A) contains a recurring unit derived from at least one monomer selected from the group consisting of styrene, 4-methylstyrene, 4-methoxystyrene, 4-t-butoxystyrene, 4-t-butoxycarbonyloxystyrene, 4-(1-ethoxyethoxystyrene), 4-(1-ethoxypropoxystyrene), 4-tetrahydropyranyloxystyrene, 4-acetoxystyrene, 4-t-butoxycarbonylmethoxystyrene, 2-hydroxystyrene, 3-hydroxystyrene, 3-methyl-4-hydroxystyrene, t-butyl (meth)acrylate, isobornyl (meth)acrylate, adamantyl (meth)acrylate, tricyclodecanyl (meth)acrylate and

(meth)acrylonitrile, as a recurring unit other than the recurring units (1) and (2).

8. The radiation sensitive resin composition of claim 1,
5 wherein the copolymer (B) contains a recurring unit derived from at least one monomer selected from the group consisting of styrene, 4-methylstyrene, 4-methoxystyrene, 4-t-butoxystyrene, 4-t-butoxycarbonyloxystyrene, 4-(1-ethoxyethoxystyrene), 4-(1-ethoxypropoxystyrene),
10 4-tetrahydropyranyloxystyrene, 4-acetoxystyrene, 4-t-butoxycarbonylmethoxystyrene, 2-hydroxystyrene, 3-hydroxystyrene, 3-methyl-4-hydroxystyrene, t-butyl (meth)acrylate, isobornyl (meth)acrylate, adamantyl (meth)acrylate, tricyclodecanyl (meth)acrylate and
15 (meth)acrylonitrile, as a recurring unit other than the recurring units (1) and (3).

9. The radiation sensitive resin composition of claim 1, which contains at least one member selected from the group
20 consisting of an onium salt, sulfone compound, sulfonate compound, sulfonimide compound, diazomethane compound and disulfonylmethane compound, as the radiation sensitive acid-generating agent (C).

25 10. The radiation sensitive resin composition of claim 1, which further contains a nitrogen-containing organic compound as an acid diffusion control agent.