

ADDITIVE FOR RESIST AND RESIST COMPOSITION COMPRISING SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention relates to an additive for resist which can suppress leaching caused by water at the time of an immersion lithographic process by increasing the hydrophobicity of the surface of a resist film, and can form a fine resist pattern having excellent
10 sensitivity and resolution, and to a resist composition containing the additive for resist.

2. Description of the Related Art

 Along with the recent trend of high integration of large scale integrated circuits (LSI) and an increase in
15 the processing speed, there is a demand for fine fabrication of photoresist patterns. As the exposure light to be used at the time of forming a resist pattern, g-line (436 nm), i-line (365 nm), or the like of a mercury lamp has been mainly used.

20 However, as the increase in the resolution that stems from the exposure wavelength approaches a substantial limit, a method of making the exposure wavelength shorter has been suggested as a means for forming a finer photoresist pattern. For example, in particular, a KrF
25 excimer laser (248 nm), an ArF excimer laser, and the like

of shorter wavelengths are used instead of the i-line (365 nm).

An ArF immersion lithographic method of using an ArF excimer laser as a light source is characterized by being
5 carried out by enclosing water between a projection lens and a wafer substrate. This method utilizes the refractive index of water at 193 nm, so that even if a lens having a numerical aperture of 1.0 or greater is used, pattern formation is possible, and this method is usually
10 referred to as an immersion exposure method. However, there is a problem that since a resist film is brought into direct contact with pure water, the acid generated by a photoacid generator, or the amine compound that is included in the resist film as a quencher is easily
15 dissolved in water, and thereby, a change in the shape of the resist pattern, pattern destruction caused by swelling, and various defects such as bubble defects and watermark defects occur.

Accordingly, for the purpose of blocking a resist
20 film from a medium such as water, there has been suggested a method of forming a protective film or an upper layer film between the resist film and water. Such a resist protective film is required to have characteristics that the protective film has a sufficient light transmittance
25 at the relevant wavelength so as not to interrupt exposure,

can be formed on a resist film without causing intermixing with the resist film, can form and maintain a stable film without being dissolved out in a medium such as water at the time of immersion exposure, and can be easily
5 dissolved in an alkali liquid or the like, which serves as a developing liquid at the time of development.

Patent Document 1: Korean Patent Application Laid-Open No. 2011-0084848 (published on July 27, 2011)

Patent Document 2: Korean Patent Application Laid-Open
10 No. 2008-0000522 (published on January 2, 2008)

Patent Document 3: Korean Patent Application Laid-Open No. 2011-0079649 (published on July 7, 2011)

SUMMARY OF THE INVENTION

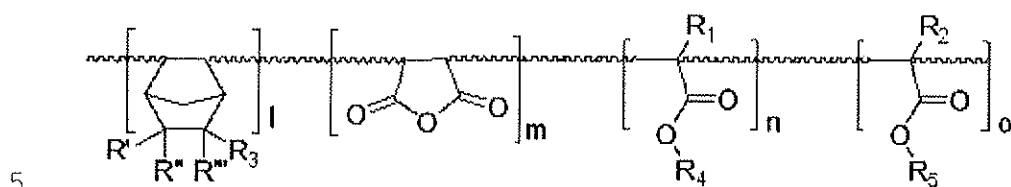
15 It is an object of the present invention to provide an additive for resist which can suppress leaching by water at the time of an immersion lithographic process by increasing the hydrophobicity of the surface of a resist film, and can form a fine resist pattern having excellent
20 sensitivity and resolution.

It is another object of the present invention to provide a resist composition containing the additive, and a method for forming a resist pattern by using the composition.

25 In order to achieve the objects described above, an

additive for resist according to an aspect of the present invention is a copolymer represented by the following formula (1):

[Chemical Formula 1]



wherein in the formula (1),

R' , R'' and R''' each independently represent a group selected from the group consisting of a hydrogen atom, a C_1 - C_4 alkyl group, a halogen atom, and a C_1 - C_4 haloalkyl group in which one of the hydrogen atoms of an alkyl group is substituted by a halogen atom;

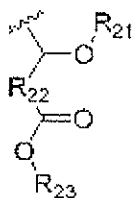
10

R_1 and R_2 each independently represent a hydrogen atom or a C_1 - C_8 alkyl group;

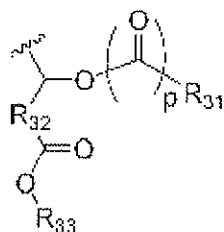
R_3 represents a group selected from the group consisting of a hydrogen atom and functional groups represented by the following formulas (2) and (3):

15

[Chemical Formula 2]



[Chemical Formula 3]

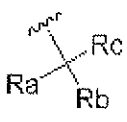
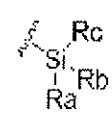


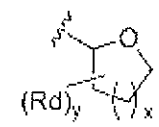
wherein in the formulas (2) and (3), R_{21} represents a hydrogen atom, or a hydroxyl-protecting group selected from the group consisting of a C_1 - C_{20} alkyl group, a (C_1 - C_{20} alkoxy)alkyl group, a C_3 - C_{30} cycloalkyl group, a formyl group, a (C_1 - C_{20} alkyl)carbonyl group, a (C_3 - C_{30} cycloalkyl)carbonyl group, a (C_1 - C_{20} alkyl)carboxyl group, and a (C_3 - C_{30} cycloalkyl)carboxyl group;

R_{31} represents a hydrophobic group selected from the group consisting of a C_1 - C_{20} haloalkyl group, an organosilicon group and a C_3 - C_{20} hydrocarbon group, such that if R_{31} represents an organosilicon group, p represents 0, while if R_{31} represents a C_1 - C_{20} haloalkyl group or a C_3 - C_{20} hydrocarbon group, p represents 1;

R_{22} and R_{32} each independently represent a group selected from the group consisting of a C_1 - C_{20} alkanediyl group, a C_2 - C_{20} alkenediyl group, a C_1 - C_{20} heteroalkanediyl group, a C_2 - C_{20} heteroalkenediyl group, a C_3 - C_{30} cycloalkanediyl group, a C_3 - C_{30} cycloalkenediyl group, a C_2 - C_{30} heterocycloalkanediyl group, and a C_3 - C_{30} heterocycloalkenediyl group;

R_{23} and R_{33} each independently represent an acid-labile

group selected from the group consisting of , ,

and , wherein R_a , R_b , R_c and R_d each independently represent a group selected from the group consisting of a C_1 - C_{20} alkyl group, a C_3 - C_{30} cycloalkyl group, a (C_1 - C_{10} alkyl)cycloalkyl group, a hydroxyalkyl group, a C_1 - C_{20} alkoxy group, a (C_1 - C_{10} alkoxy)alkyl group, an acetyl group, an acetylalkyl group, a carboxyl group, a (C_1 - C_{10} alkyl)carboxyl group, a (C_3 - C_{18} cycloalkyl)carboxyl group, and a C_3 - C_{30} heterocycloalkyl group, or adjacent groups may be bonded to each other to form a C_3 - C_{30} saturated or unsaturated hydrocarbon ring or a C_2 - C_{30} heterocyclic group;

x represents an integer from 0 to 3; y represents an integer from 0 to 10;

R_4 represents a hydrophobic group selected from the group consisting of a C_1 - C_{20} haloalkyl group, an organosilicon group, and a C_3 - C_{20} hydrocarbon group;

R_5 represents a group selected from the group consisting of a hydrogen atom, a C_1 - C_{20} alkyl group, a C_2 - C_{20} alkenyl group, a C_3 - C_{30} cycloalkyl group, a C_3 - C_{30} cycloalkenyl group, a C_6 - C_{30} aryl group, a C_1 - C_{20} heteroalkyl group, a C_2 - C_{30} heterocyclic group, and

combinations thereof;

l, m, n and o respectively represent the proportions of corresponding repeating units in the main chain, such that $l+m+n+o = 1$, while $0 < l/(l+m+n+o) < 0.9$, $0.2 < m/(l+m+n+o) < 0.9$, $0 \leq n/(l+m+n+o) < 0.9$, and $0 \leq o/(l+m+n+o) < 0.9$, provided that when R_3 represents a hydrogen atom or a functional group represented by formula (2), n is not 0; and

p represents an integer of 0 or 1.

10 The additive for resist may be a compound in which R_3 represents a hydrogen atom or a functional group having a structure represented by the formula (2); l, m, n and o respectively represent the proportions of corresponding repeating units in the main chain, such that $l+m+n+o = 1$, while $0 < l/(l+m+n+o) < 0.9$, $0.2 < m/(l+m+n+o) < 0.9$, $0 < n/(l+m+n+o) < 0.9$, and $0 \leq o/(l+m+n+o) < 0.9$.

The additive for resist may be a compound in which R_3 represents a functional group having a structure represented by the formula (3); l, m, n and o respectively represent the proportions of corresponding repeating units in the main chain, such that $l+m+n+o = 1$, while $0 < l/(l+m+n+o) < 0.9$, $0.2 < m/(l+m+n+o) < 0.9$, $0 \leq n/(l+m+n+o) < 0.9$, and $0 \leq o/(l+m+n+o) < 0.9$.

25 In the formula (2), R_{21} represents a group that may be selected from the group consisting of a C_1 - C_{10} alkyl group,

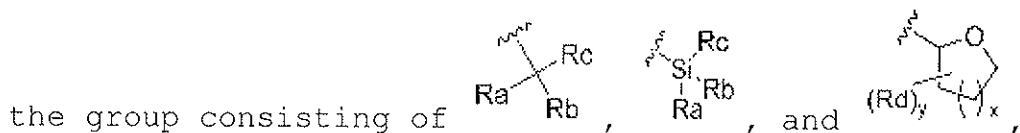
a (C₁-C₁₀ alkoxy)alkyl group, a C₃-C₁₄ monocyclic cycloalkyl group, a C₈-C₁₈ bicyclic cycloalkyl group, a C₁₀-C₃₀ tricyclic cycloalkyl group, a C₁₀-C₃₀ tetracyclic cycloalkyl group, a formyl group, a (C₁-C₁₀ alkyl)carbonyl group, a
5 (C₃-C₁₈ cycloalkyl)carbonyl group, a (C₁-C₁₀ alkyl)carboxyl group, and a (C₃-C₁₈ cycloalkyl)carboxyl group.

In the formula (2), R₂₁ represents a group that may be selected from the group consisting of a formyl group, an acetyl group, a methoxymethyl group, a t-butylcarbonyl
10 group, a t-butyloxycarbonyl group, a cyclohexylcarbonyl group, a cyclopentylcarbonyl group, a cyclooctylcarbonyl group, an adamantylcarbonyl group, and a bicyclo[2,2,1]heptylmethylcarbonyl group.

In the formula (3), R₃₁ represents a group that may be
15 selected from the group consisting of a C₁-C₁₀ fluoroalkyl group, a silyl group, a C₁-C₁₀ alkylsilyl group, a chain-like or branched C₃-C₁₀ alkyl group, a C₃-C₁₄ monocyclic cycloalkyl group, a C₈-C₁₈ bicyclic cycloalkyl group, a C₁₀-C₃₀ tricyclic cycloalkyl group, and a C₁₀-C₃₀ tetracyclic
20 cycloalkyl group.

In the formula (3), R₃₁ represents a group that may be selected from the group consisting of a t-butyl group, a trifluoromethyl group, a trimethylsilyl group, a di(trifluoromethyl)isopropyl group, a pentafluoroethyl
25 group, and a heptafluoropropyl group.

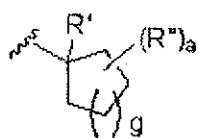
In the formulas (2) and (3), R_{23} and R_{33} each independently represent a group that may be selected from



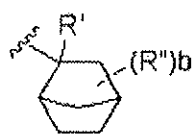
wherein R_a , R_b , R_c and R_d independently represent a group
 5 selected from the group consisting of a C_1 - C_{10} alkyl group, a C_3 - C_{14} monocyclic cycloalkyl group, a C_8 - C_{20} bicyclic cycloalkyl group, a C_{10} - C_{30} tricyclic cycloalkyl group, a C_{10} - C_{30} tetracyclic cycloalkyl group, a $(C_1$ - C_5 alkyl)cycloalkyl group, a hydroxyalkyl group, a C_1 - C_{10}
 10 alkoxy group, a $(C_1$ - C_5 alkoxy)alkyl group, an acetyl group, an acetylalkyl group, a carboxyl group, a $(C_1$ - C_5 alkyl)carboxyl group, and a $(C_3$ - C_{10} cycloalkyl)carboxyl group, or adjacent groups may be bonded to each other to form a saturated or unsaturated C_6 - C_{18} hydrocarbon ring or
 15 a C_5 - C_{18} heterocyclic group; x represents an integer from 0 to 3; and y represents an integer from 0 to 5.

In the formulas (2) and (3), R_{23} and R_{33} each independently represent a group that may be selected from the group consisting of a t-butyl group, a trimethylsilyl group,
 20 group, a hydroxyl-2-ethyl group, a 1-methoxypropyl group, a 1-methoxy-1-methylethyl group, a 1-ethoxypropyl group, a 1-ethoxy-1-methylethyl group, 1-methoxy-1-ethyl group, a 1-ethoxyl-1-ethyl group, a t-butoxy-2-ethyl group, a 1-

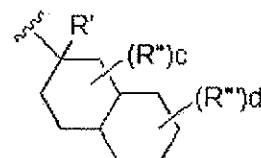
isobutoxy-1-ethyl group, and groups represented by the following formulas (4a) to (4k):



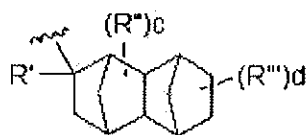
(4a)



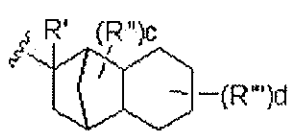
(4b)



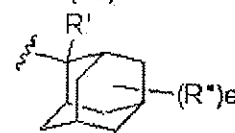
(4c)



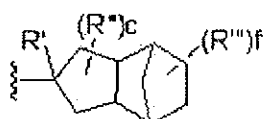
(4d)



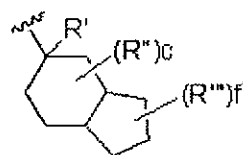
(4e)



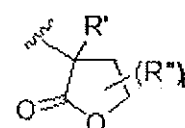
(4f)



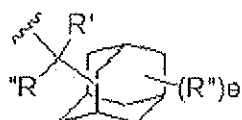
(4g)



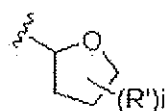
(4h)



(4i)



(4j)



(4k)

In the formulas (4a) to (4k), R', R'' and R''' each
 5 independently represent a hydrogen atom or a C₁-C₁₀ alkyl
 group; a and e each represent an integer from 0 to 15; b
 represents an integer from 0 to 11; c and d each
 independently represent an integer from 0 to 9; f
 represents an integer from 0 to 7; g and i each
 10 independently represent an integer from 0 to 6; h

represents an integer from 0 to 4; $0 \leq c+d \leq 17$; and $0 \leq c+f \leq 15$.

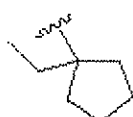
In the formulas (2) and (3), R_{23} and R_{33} each independently represent a group that may be selected from the group consisting of moieties represented by the following formulas (5a) to (5h):



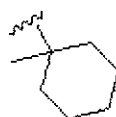
(5a)



(5b)



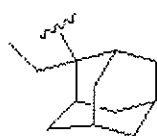
(5c)



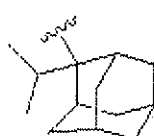
(5d)



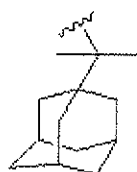
(5e)



(5f)



(5g)



(5h)

In the formula (1), R_4 represents a group that may be selected from the group consisting of a C_1 - C_{10} fluoroalkyl group, a silyl group, a C_1 - C_{10} alkylsilyl group, a chain-like or branched C_3 - C_{10} alkyl group, C_3 - C_{14} monocyclic cycloalkyl group, a C_8 - C_{18} bicyclic cycloalkyl group, a C_{10} - C_{30} tricyclic cycloalkyl group, and a C_{10} - C_{30} tetracyclic cycloalkyl group.

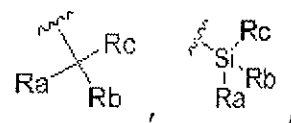
In the formula (1), R_4 represents a group that may be selected from the group consisting of a t-butyl group, a trifluoromethyl group, a trimethylsilyl group, a di(trifluoromethyl)isopropyl group, a pentafluoroethyl

group, and a heptafluoropropyl group.

In the formula (1), R_5 represents a group that may be selected from the group consisting of a hydrogen atom, a C_1 - C_{10} alkyl group, a C_2 - C_{10} alkenyl group, a C_3 - C_{14} monocyclic cycloalkyl group, a C_8 - C_{18} bicyclic cycloalkyl group, C_{10} - C_{30} tricyclic cycloalkyl group, a C_{10} - C_{30} tetracyclic cycloalkyl group, a C_3 - C_{18} cycloalkenyl group, a C_6 - C_{18} aryl group, a C_1 - C_{20} heteroalkyl group, a C_2 - C_{18} heterocyclic group, and combinations thereof.

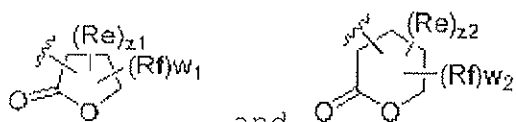
In the formula (1), R_5 may represent an acid-labile

group selected from the group consisting of



and $(Rd)_y$, or a lactone group selected from the group

consisting of

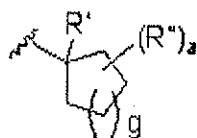


, wherein R_a , R_b , R_c and R_d each independently represent a C_1 - C_{20} alkyl group, a C_3 - C_{30} cycloalkyl group, a $(C_1$ - C_{10} alkyl)cycloalkyl group, a hydroxyalkyl group, a C_1 - C_{20} alkoxy group, a $(C_1$ - C_{10} alkoxy)alkyl group, an acetyl group, an acetylalkyl group, a carboxyl group, a $(C_1$ - C_{10} alkyl)carboxyl group, a $(C_3$ - C_{18} cycloalkyl)carboxyl group, and a C_3 - C_{30} heterocycloalkyl group, or adjacent groups may be bonded to each other to

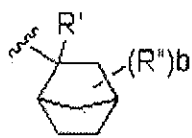
form a saturated or unsaturated C₃-C₃₀ hydrocarbon ring or a C₂-C₃₀ heterocyclic group; R_e and R_f each independently represent a C₁-C₁₀ alkyl group or may be bonded to each other to form a saturated C₃-C₃₀ hydrocarbon ring; x

5 represents an integer from 0 to 3; y represents an integer from 0 to 10; z₁ and w₁ each independently represent an integer from 0 to 3; z₂ and w₂ each independently represent an integer from 0 to 7; $0 \leq z_1 + w_1 \leq 5$; and $0 \leq z_2 + w_2 \leq 5$.

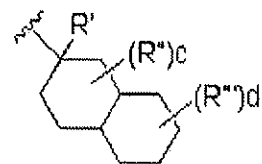
In the formula (1), R₅ represents a group that may be
10 selected from the group consisting of a t-butyl group, a trimethylsilyl group, a hydroxyl-2-ethyl group, a 1-methoxypropyl group, a 1-methoxy-1-methylethyl group, a 1-ethoxypropyl group, a 1-ethoxy-1-methylethyl group, a 1-methoxy-1-ethyl group, a 1-ethoxy-1-ethyl group, a t-
15 butoxy-2-ethyl group, a 1-isobutoxy-1-ethyl group, and groups represented by the following formulas (6a) to (6m):



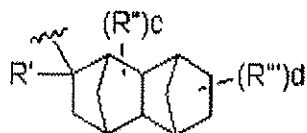
(6a)



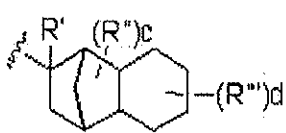
(6b)



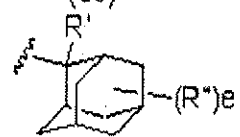
(6c)



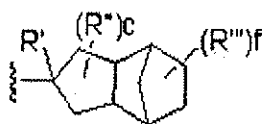
(6d)



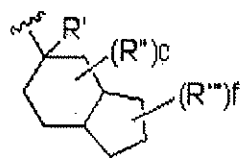
(6e)



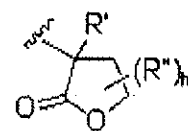
(6f)



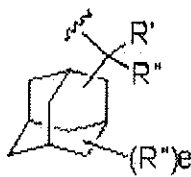
(6g)



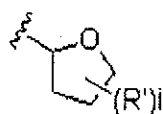
(6h)



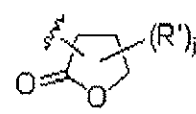
(6i)



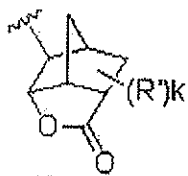
(6j)



(6k)



(6l)



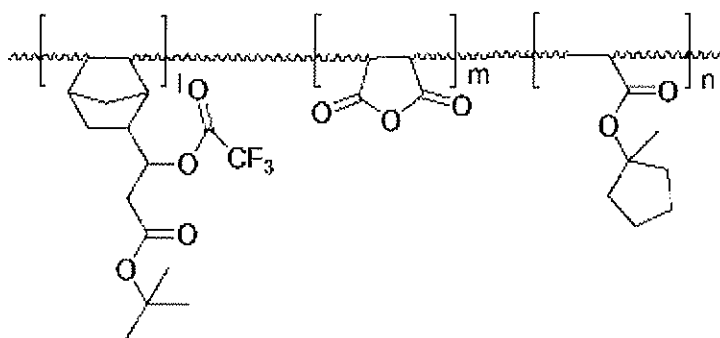
(6m)

wherein in the formulas (6a) to (6m), R', R'' and R''' each independently represent a hydrogen atom or a C₁-C₁₀ alkyl group; a and 3 each represent an integer from 0 to 15; b represents an integer from 0 to 11; c and d each independently represent an integer from 0 to 9; f

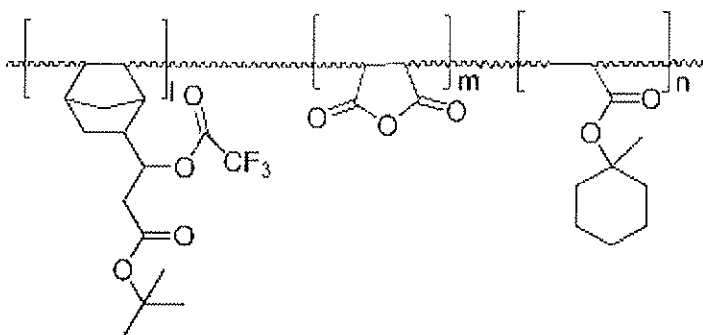
represents an integer from 0 to 7; g, i and k each independently represent an integer from 0 to 6; h and j each independently represent an integer from 0 to 4; $0 \leq c+d \leq 17$; and $0 \leq c+f \leq 15$.

- 5 The additive for resist may be selected from the group consisting of compounds having structures represented by the following formulas (7) to (18):

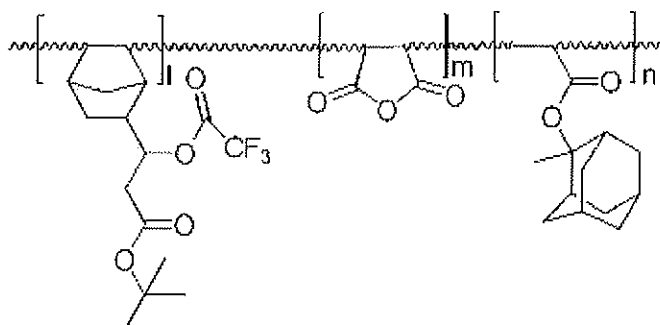
[Chemical Formula 7]



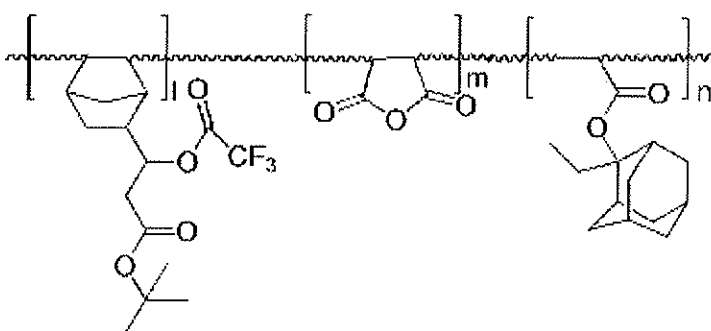
- 10 [Chemical Formula 8]



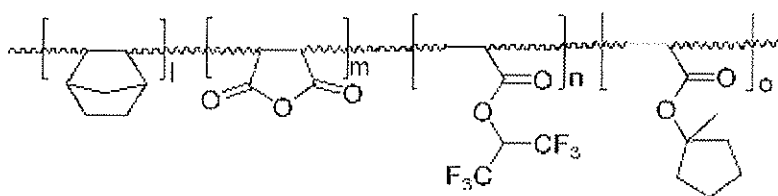
[Chemical Formula 9]



[Chemical Formula 10]

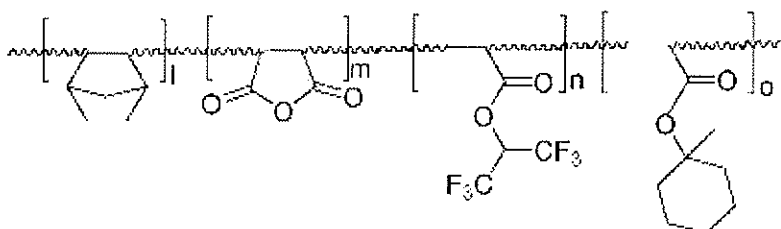


[Chemical Formula 11]

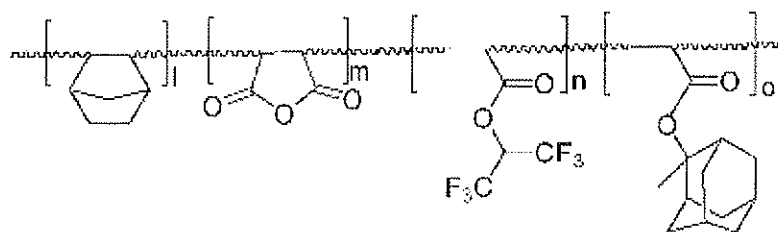


5

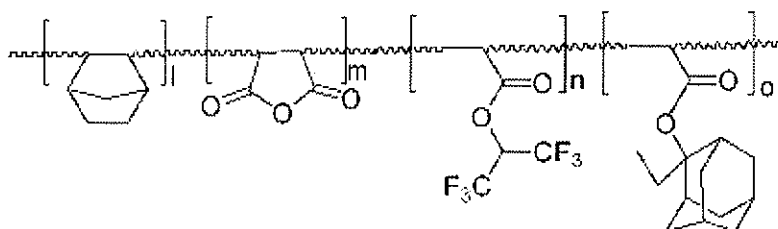
[Chemical Formula 12]



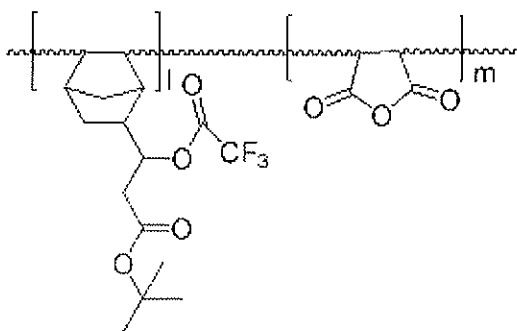
[Chemical Formula 13]



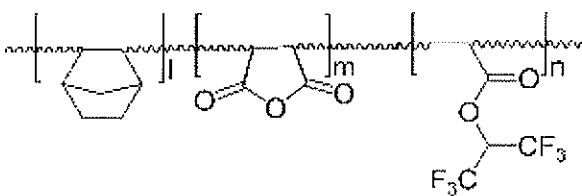
[Chemical Formula 14]



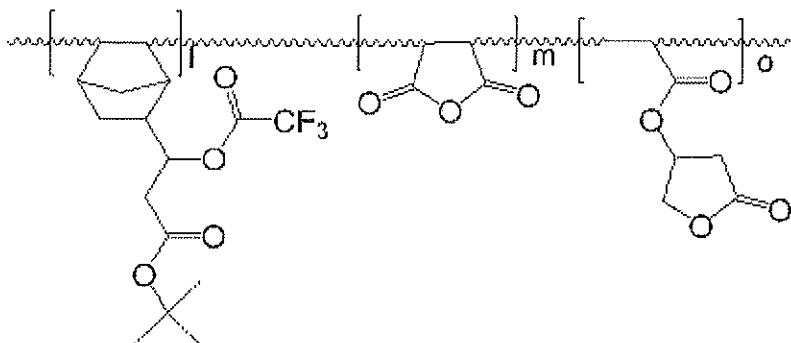
[Chemical Formula 15]



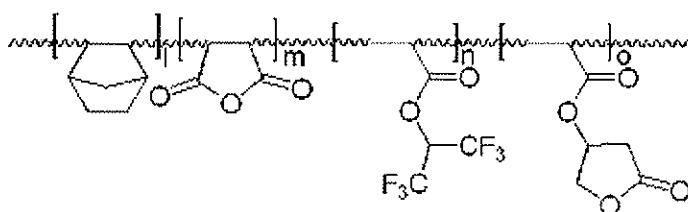
[Chemical Formula 16]



[Chemical Formula 17]



[Chemical Formula 18]



wherein in the formulas (7) to (18), l , m , n and o

5 respectively represent the proportions of corresponding repeating units in the main chain, such that $l+m+n+o = 1$, while $0 < l/(l+m+n+o) < 0.9$, $0.2 < m/(l+m+n+o) < 0.9$, $0 \leq n/(l+m+n+o) < 0.9$, and $0 \leq o/(l+m+n+o) < 0.9$.

In the formula (1), the repeating unit m may be
10 included in the copolymer of the additive for resist in an amount of 30% to 60% by mole.

The additive for resist may have a weight average molecular weight as measured by gel permeation chromatography and calculated relative to polystyrene
15 standards, of 1,000 g/mol to 50,000 g/mol.

The additive for resist may be such that the ratio of the weight average molecular weight and the number average

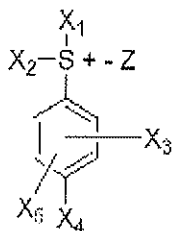
molecular weight is 1 to 5.

A resist composition according to another aspect of the present invention includes the additive for resist according to the present invention, a base polymer for
5 resist, an acid generator, and a solvent.

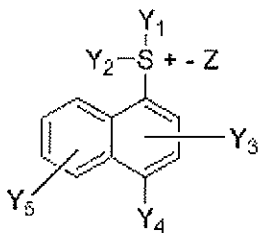
The additive for resist may be included in the resist composition in an amount of 0.05% to 5% by weight relative to the total weight of the resist composition.

The acid generator may be one or more compounds
10 selected from the group consisting of compounds represented by the following formulas (22) and (23):

[Chemical Formula 22]



[Chemical Formula 23]



15 wherein in the formulas (22) and (23),

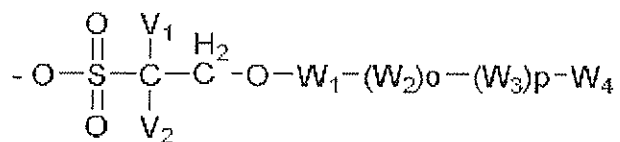
X_1 , X_2 , Y_1 and Y_2 each independently represent any one selected from the group consisting of a C_1 - C_{10} alkyl group, an allyl group, a perfluoroalkyl group, a benzyl group, a

C₆-C₃₀ aryl group, and combinations thereof; X₁ with X₂, and Y₁ with Y₂ may be bonded to each other to form a saturated or unsaturated hydrocarbon ring having 3 to 30 carbon atoms;

5 X₃, X₄, X₅, Y₃, Y₄ and Y₅ each independently represent any one selected from the group consisting of a hydrogen atom, a C₁-C₃₀ alkyl group, a halogen atom, a C₁-C₃₀ alkoxy group, a C₆-C₃₀ aryl group, a thiophenoxy group, a C₁-C₃₀ thioalkoxy group, a C₁-C₂₀ alkoxycarbonylmethoxy group, and
10 combinations thereof; and

Z of the anionic moiety represents OSO₂CF₃, OSO₂C₄F₉, OSO₂C₈F₁₇, N(CF₃)₂, N(C₂F₅)₂, N(C₄F₉)₂, C(CF₃)₃, C(C₂F₅)₃, C(C₄F₉)₃, or a functional group represented by the following formula (24):

15 [Chemical Formula 24]



wherein in the formula (24),

V₁ and V₂ each independently represent a halogen atom;

W₁ represents -(C=O)- or -(SO₂)-;

20 W₂ represents a C₁-C₁₀ alkanediyl group;

W₃ represents any one selected from the group consisting of a C₃-C₃₀ cycloalkyl group, a C₆-C₃₀ aryl group, a C₇-C₃₀ aralkyl group, a C₆-C₃₀ aryloxy group, a C₆-C₃₀

arylthio group, and a C₅-C₃₀ heterocyclic group;

W₄ represents any one selected from group consisting of a hydrogen atom, a halogen atom, a C₁-C₁₀ alkyl group, a C₁-C₁₀ alkoxy group, a C₁-C₁₀ haloalkyl group, a C₁-C₁₀ alkylthio group, a C₆-C₃₀ aryl group, and combinations thereof;

o represents an integer of 0 or 1; and

p represents an integer from 0 to 2.

The acid generator may be included in the resist composition in an amount of 0.3 parts to 10 parts by weight relative to 100 parts of the total solids content in the resist composition.

The resist composition may include an additive selected from the group consisting of an alkali dissolution suppressing agent, an acid diffusion suppressing agent, a surfactant, and mixtures thereof.

A method for forming a resist pattern according to another aspect of the present invention includes a step of applying the resist composition on a substrate to form a resist film; a step of heat treating the resist film and then exposing the resist film in a predetermined pattern; and a step of developing the exposed resist pattern.

The exposure step may be carried out by using a light source selected from the group consisting of a KrF excimer laser, an ArF excimer laser, an extreme ultraviolet laser,

X-rays, and an electron beam.

Specific terms of other embodiments of the present invention will be described in the following detailed description of the invention.

5 The additive for resist according to the present invention can suppress, when applied to a resist composition, leaching caused by water during the exposure of an immersion lithographic process, by increasing the hydrophobicity of the surface of a resist film, and can
10 form a fine resist pattern having excellent sensitivity and resolution.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hereinafter, embodiments of the present invention
15 will be described in detail. However, these embodiments are suggested only for illustrative purposes, and the present invention is not intended to be limited thereto. The present invention is defined only by the scope of the claims that will be described below.

20 Unless particularly stated otherwise, the term "halo-" or "halogen atom" as used herein refers to any one selected from the group consisting of fluorine, chlorine, bromine, and iodine.

Unless particularly stated otherwise, the prefix
25 "hetero-" as used herein means that one to three carbon

atoms are substituted by heteroatoms selected from the group consisting of nitrogen (N), oxygen (O), sulfur (S), and phosphorus (P). For example, a heteroalkyl group means a group in which one to three carbon atoms among the
5 carbon atoms of an alkyl group are substituted by heteroatoms.

Unless particularly stated otherwise, the "alkyl group" as used herein means a linear or branched alkyl group having 1 to 30 carbon atoms, and the alkyl group
10 includes a primary alkyl group, a secondary alkyl group, and a tertiary alkyl group. Specific examples of the alkyl group include, but are not limited to, a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, an isobutyl group, and a t-butyl group.

15 Unless particularly stated otherwise, the "cycloalkyl group" as used herein means a cycloalkyl group having 3 to 30 carbon atoms, and the cycloalkyl group includes a monocyclic group, a bicyclic group, a tricyclic group, and a tetracyclic group. Furthermore, an adamantyl group, a
20 norbornyl group, and a polycyclic cycloalkyl group containing a norbornyl group are also included in the range of the cycloalkyl group.

Unless particularly stated otherwise, the "alkanediyl group" as used herein means a divalent atomic group
25 obtainable by extracting two hydrogen atoms from an alkane,

and may be represented by the formula: $-C_nH_{2n}-$. The "alkenediyl group" as used herein means a divalent atomic group obtainable by extracting two hydrogen atoms from an alkene, and may be represented by the formula: $-C_nH_n-$.

5 Unless particularly stated otherwise, the "aryl group" means a group containing a benzene ring, or a derivative thereof. Examples thereof include a group derived from toluene or xylene, in which an alkyl side chain is bonded to a benzene ring; a group derived from
10 biphenyl, in which two or more benzene rings are linked via single bonds; a group derived from fluorene, xanthenes or anthraquinone, in which two or more benzene rings are linked via a cycloalkyl group or a heterocycloalkyl group; and a group derived from naphthalene or anthracene, in
15 which two or more benzene rings are fused. Unless particularly stated otherwise, the aryl group as used herein means an aryl group having 6 to 30 carbon atoms.

Unless particularly stated otherwise, the "hydrocarbon group" as used herein means a monovalent
20 hydrocarbon group which is composed of carbon and hydrogen only, and contains 3 to 20 carbon atoms. Examples of the hydrocarbon group include aliphatic chain-like and branched hydrocarbon groups, and alicyclic hydrocarbon groups. Specific examples thereof include a hexyl group,
25 a heptyl group, an octyl group, a nonyl group, a decyl

group, an undecyl group, a dodecyl group, a cyclohexyl group, a phenyl group, a tolyl group, a xylyl group, a mesityl group, a benzyl group, a diphenylmethyl group, a triphenylmethyl group, a styryl group, a biphenyl group,
5 and a naphthyl group.

Unless particularly stated otherwise, the "heterocyclic group" as used herein means a cyclic radical having 4 to 20 ring-constituting atoms, in which one or more (for example, 1, 2, 3 or 4) carbon atoms are
10 substituted by heteroatoms (for example, N, O, P or S). The term "heterocyclic" includes a saturated ring, a partially unsaturated ring, and an aromatic ring (that is, a heteroaromatic ring), and also includes cyclic aromatic radicals in which the heteroatoms in the ring are oxidized
15 or quaternized, so that the compound forms, for example, an N-oxide or a quaternary salt. A substituted heterocyclic group contains a heterocyclic ring substituted with, for example, any arbitrary substituent disclosed in the present application, including a carbonyl
20 group.

Examples of the heterocyclic group include, but are not limited to, pyridyl, dihydropyridyl, tetrahydropyridyl (piperidyl), thiazolyl, tetrahydrothiophenyl, tetrahydrothiophenyl sulfate, pyrimidinyl, furanyl,
25 thienyl, pyrrolyl, pyrazolyl, imidazolyl, tetrazolyl,

benzofuranyl, thianaphthalenyl, indolyl, indolenyl,
quinolinyl, isoquinolinyl, benzimidazolyl, piperidinyl, 4-
piperidonyl, pyrrolidinyl, 2-pyrrolidonyl, pyrrolinyl,
tetrahydrofuranyl, tetrahydroquinolinyl,
5 tetrahydroisoquinolinyl, decahydroquinolinyl,
octahydroisoquinolinyl, azocinyl, triazinyl, 6H-1,2,5-
thiadiazinyl, 2H,6H-1,5,2-dithiazinyl, thienyl,
thianthrenyl, pyranyl, isobenzofuranyl, chromenyl,
xanthenyl, phenoxathinyl, 2H-pyrrolyl, isothiazolyl,
10 isoxazolyl, pyrazinyl, pyridazinyl, indolizinyl,
isoindolyl, 3H-indolyl, 1H-indazolyl, purinyl, 4H-
quinolidinyl, phthalazinyl, naphthyridinyl, quinoxalinyl,
quinazolinyl, cinnolinyl, pteridinyl, 4aH-carbazolyl,
carbazolyl, β -carbolinyl, phenanthridinyl, acridinyl,
15 pyrimidinyl, phenanthrolinyl, phenazinyl, phenothiazinyl,
furazanyl, phenoxazinyl, isochromanyl, chromanyl,
imidazolidinyl, imidazolyl, pyrazolidinyl, pyrazolyl,
piperazinyl, indolyl, isoindolyl, quinuclidinyl,
morpholinyl, oxazolidinyl, benzotriazolyl, benzisoxazolyl,
20 oxindolyl, benzoxazolyl, isatinoyl, bistetrahydrofuranyl
(these may be respectively substituted or unsubstituted),
and corresponding N-oxides thereof (for example, pyridyl
N-oxide, and quinolinyl N-oxide), or quaternary salts
thereof.

25 Unless particularly stated otherwise, all the

compounds and substituents as used herein may be substituted or unsubstituted. Here, the term "substituted" means that a hydrogen atom is replaced with any one selected from the group consisting of a halogen atom, a hydroxyl group, a carboxyl group, a cyano group, a
5 nitro group, an amino group, a thio group, a methylthio group, an alkoxy group, a nitrile group, an aldehyde group, an epoxy group, an ether group, an ester group, a carbonyl group, an acetal group, a ketone group, an alkyl group, a
10 perfluoroalkyl group, a cycloalkyl group, a heterocycloalkyl group, an allyl group, a benzyl group, an aryl group, a heteroaryl group, derivatives thereof, and combinations thereof.

Furthermore, unless particularly stated otherwise,
15 the term "combinations thereof" as used herein means that two or more substituents are linked via a single bond or a linking group, or two or more substituents are fused together.

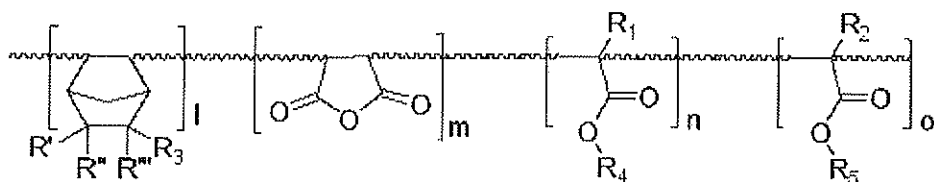
In the case of forming a resist pattern by using a
20 conventional ArF immersion lithographic method, the acid or amine compound contained in the resist film is dissolved in the water enclosed between a projection lens and a wafer substrate, and thereby, there occurred problems such as contamination of the projection lens,
25 pattern destruction caused by shape change or swelling of

a resist pattern, and various defective phenomena such as bubble defects or watermark defects.

In this regard, the inventors of the present invention found that fine patterns can be formed, without
5 the occurrence of any defective phenomena, by introducing a cyclic structure composed of maleic anhydride and a norbornene derivative into the main chain of a copolymer as an additive for the photoresist composition to enhance etching resistance; introducing a hydrophobic group into a
10 side chain of a repeating unit to increase hydrophobicity of the surface of the resist film at the time of exposure, and to suppress leaching caused by water at the time of an immersion lithographic process, while the hydrophobic group is converted to a hydrophilic group at the time of
15 development, and exhibits solubility in a developing liquid; and introducing an acid-labile group into a side chain of a repeating unit to increase solubility in an alkali developing liquid at the time of development. Thus, the inventors of the present invention completed the
20 present invention.

That is, the additive for resist according to an embodiment of the present invention is a multi-component copolymer represented by the following formula (1):

[Chemical Formula 1]



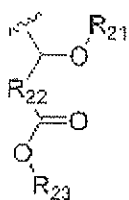
wherein in the formula (1),

R', R'' and R''' each independently represent a group selected from the group consisting of a hydrogen atom, a C₁-C₄ alkyl group, a halogen atom, and a C₁-C₄ haloalkyl group in which one of the hydrogen atoms of an alkyl group is substituted by a halogen atom;

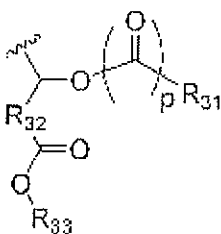
R₁ and R₂ each independently represent a hydrogen atom or a C₁-C₈ alkyl group;

R₃ represents a group selected from the group consisting of a hydrogen atom and functional groups represented by the following formulas (2) and (3):

[Chemical Formula 2]



[Chemical Formula 3]



wherein in the formulas (2) and (3), R₂₁ represents a

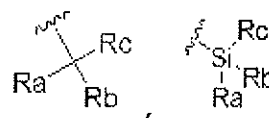
hydrogen atom, or a hydroxyl-protecting group selected from the group consisting of a C₁-C₂₀ alkyl group, a (C₁-C₂₀ alkoxy)alkyl group, a C₃-C₃₀ cycloalkyl group, a formyl group, a (C₁-C₂₀ alkyl)carbonyl group, a (C₃-C₃₀ cycloalkyl)carbonyl group, a (C₁-C₂₀ alkyl)carboxyl group, and a (C₃-C₃₀ cycloalkyl)carboxyl group;

R₃₁ represents a hydrophobic group selected from the group consisting of a C₁-C₂₀ haloalkyl group, an organosilicon group and a C₃-C₂₀ hydrocarbon group, such that if R₃₁ represents an organosilicon group, p represents 0, while if R₃₁ represents a C₁-C₂₀ haloalkyl group or a C₃-C₂₀ hydrocarbon group, p represents 1;

R₂₂ and R₃₂ each independently represent a group selected from the group consisting of a C₁-C₂₀ alkanediyl group, a C₂-C₂₀ alkenediyl group, a C₁-C₂₀ heteroalkanediyl group, a C₂-C₂₀ heteroalkenediyl group, a C₃-C₃₀ cycloalkanediyl group, a C₃-C₃₀ cycloalkenediyl group, a C₂-C₃₀ heterocycloalkanediyl group, and a C₃-C₃₀ heterocycloalkenediyl group;

R₂₃ and R₃₃ each independently represent an acid-labile

group selected from the group consisting of



and , wherein R_a, R_b, R_c and R_d each independently

represent a group selected from the group consisting of a C₁-C₂₀ alkyl group, a C₃-C₃₀ cycloalkyl group, a (C₁-C₁₀ alkyl)cycloalkyl group, a hydroxyalkyl group, a C₁-C₂₀ alkoxy group, a (C₁-C₁₀ alkoxy)alkyl group, an acetyl group,
5 an acetylalkyl group, a carboxyl group, a (C₁-C₁₀ alkyl)carboxyl group, a (C₃-C₁₈ cycloalkyl)carboxyl group, and a C₃-C₃₀ heterocycloalkyl group, or adjacent groups may be bonded to each other to form a C₃-C₃₀ saturated or unsaturated hydrocarbon ring or a C₂-C₃₀ heterocyclic
10 group;

x represents an integer from 0 to 3; y represents an integer from 0 to 10;

R₄ represents a hydrophobic group selected from the group consisting of a C₁-C₂₀ haloalkyl group, an
15 organosilicon group, and a C₃-C₂₀ hydrocarbon group;

R₅ represents a group selected from the group consisting of a hydrogen atom, a C₁-C₂₀ alkyl group, a C₂-C₂₀ alkenyl group, a C₃-C₃₀ cycloalkyl group, a C₃-C₃₀ cycloalkenyl group, a C₆-C₃₀ aryl group, a C₁-C₂₀
20 heteroalkyl group, a C₂-C₃₀ heterocyclic group, and combinations thereof;

l, m, n and o respectively represent the proportions of corresponding repeating units in the main chain, such that $l+m+n+o = 1$, while $0 < l/(l+m+n+o) < 0.9$, $0.2 < m/(l+m+n+o) < 0.9$, $0 \leq n/(l+m+n+o) < 0.9$, and $0 \leq$
25 $o/(l+m+n+o) < 0.9$, and $0 \leq$

$o/(1+m+n+o) < 0.9$, provided that when R_3 represents a hydrogen atom or a functional group represented by formula (2), n is not 0; and

p represents an integer of 0 or 1.

5 Specifically, in the formula (1), it is preferable that R' , R'' and R''' be each independently selected from the group consisting of a hydrogen atom, a methyl group, a fluoro group, and a trifluoromethyl group, and R' , R'' and R''' are more preferably hydrogen atoms.

10 In the formula (1), it is preferable that R_1 and R_2 each independently represent a hydrogen atom or a C_1 - C_4 alkyl group, and more preferably a hydrogen atom or a methyl group.

In the formula (1), R_3 represents a hydrogen atom or a
15 functional group having a structure represented by the above formula (2), and l , m , n and o respectively represent the proportions of corresponding repeating units in the main chain, such that $l+m+n+o = 1$, while $0 < l/(1+m+n+o) < 0.9$, $0.2 < m/(1+m+n+o) < 0.9$, $0 < n/(1+m+n+o) < 0.9$, and $0 \leq o/(1+m+n+o) < 0.9$.
20

Furthermore, in the formula (1), R_3 represents a hydrogen atom or a functional group having a structure represented by the above formula (3), and l , m , n and o respectively represent the proportions of corresponding
25 repeating units in the main chain, such that $l+m+n+o = 1$,

while $0 < 1/(1+m+n+o) < 0.9$, $0.2 < m/(1+m+n+o) < 0.9$, $0 \leq n/(1+m+n+o) < 0.9$, and $0 \leq o/(1+m+n+o) < 0.9$.

In the formula (1), when R_3 represents a functional group having a structure represented by the formula (2) or
5 (3), R_{21} is preferably selected from the group consisting of a C_1 - C_{10} alkyl group, a (C_1 - C_{10} alkoxy)alkyl group, a C_3 - C_{14} monocyclic cycloalkyl group, a C_8 - C_{18} bicyclic cycloalkyl group, a C_{10} - C_{30} tricyclic cycloalkyl group, a C_{10} - C_{30} tetracyclic cycloalkyl group, a formyl group, a (C_1 -
10 C_{10} alkyl)carbonyl group, a (C_3 - C_{18} cycloalkyl)carbonyl group, a (C_1 - C_{10} alkyl)carboxyl group, and (C_3 - C_{18} cycloalkyl)carboxyl group, and more preferably selected from the group consisting of a formyl group, an acetyl group, a methoxymethyl group, a t-butylcarbonyl group, a
15 t-butyloxycarbonyl group, a cyclohexylcarbonyl group, a cyclopentylcarbonyl group, a cyclooctylcarbonyl group, an adamantylcarbonyl group, and a bicyclo[2,2,1]heptylmethylcarbonyl group.

Furthermore, R_{31} is preferably selected from the group
20 consisting of a C_1 - C_{10} fluoroalkyl group, a silyl group, a C_1 - C_{10} alkylsilyl group, a C_3 - C_{10} chain-like or branched alkyl group, a C_3 - C_{14} monocyclic cycloalkyl group, a C_8 - C_{18} bicyclic cycloalkyl group, a C_{10} - C_{30} tricyclic cycloalkyl group, and a C_{10} - C_{30} tetracyclic cycloalkyl group, and more
25 preferably selected from the group consisting of a t-butyl

group, a trifluoromethyl group, a trimethylsilyl group, a di(trifluoromethyl)isopropyl group, a pentafluoroethyl group, and a heptafluoropropyl group.

Furthermore, R_{22} and R_{32} are each independently

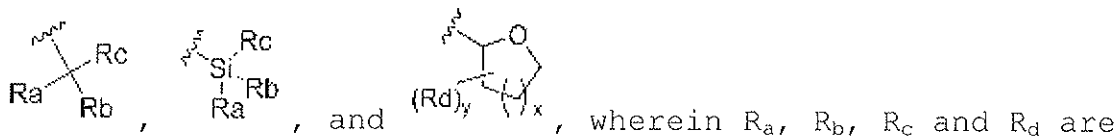
5 preferably selected from the group consisting of a C_1 - C_{10} alkanediyl group, a C_2 - C_{10} alkenediyl group, a C_1 - C_{10} heteroalkanediyl group, a C_2 - C_{10} heteroalkenediyl group, a C_3 - C_{18} cycloalkanediyl group, a C_3 - C_{18} cycloalkenediyl group, a C_2 - C_{18} heterocycloalkanediyl group, and a C_3 - C_{18}

10 heterocycloalkenediyl group, and more preferably selected from the group consisting of methylene, ethylidene, propylidene, trimethylene, tetramethylene, pentamethylene, hexamethylene, heptamethylene, 2,2-dimethylpentamethylene, -OCH₂-, -OCH(Cl)-, -CO-, -COCH₂-, -COCH₂CH₂-, -CH₂-O-CH₂-, -

15 CH₂-O-CH₂CH₂-, -CH₂CH₂-O-CH₂-, -CH₂-O-CH₂CH₂CH₂-, -CH₂CH₂-O-CH₂CH₂-, -CH₂CH₂CH₂-O-CH₂-, -C(CH₃)₂CH₂-, -CH(CH₃)CH₂-, -CH(CH₂CH₃)-, -CH(OCH₃)-, -C(CF₃)(OCH₃)-, -CH₂-S-CH₂-, -CH₂-S-CH₂CH₂-, -CH₂CH₂-S-CH₂-, -CH₂-S-CH₂CH₂CH₂-, -CH₂CH₂-S-CH₂CH₂-, -CH₂CH₂CH₂-S-CH₂-, -CH(CH₂)CH-, -C(CH₂CH₂)-, -CH₂CO-, -

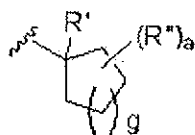
20 CH₂CH₂CO-, -CH(CH₃)CH₂CO-, -CH(OH)-, -C(OH)(CH₃)-, -CH(F)-, -CH(Br)-, -CH(Br)CH(Br)-, -CH=CH-, -CH₂CH=CH-, -CH=CHCH₂-, -CH=CHCO-, -C₇H₉- and -C₁₀H₁₄-.

Furthermore, R_{23} and R_{33} are each independently an acid-labile group selected from the group consisting of

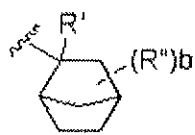


wherein R_a , R_b , R_c and R_d are each independently selected from the group consisting of a C_1 - C_{10} alkyl group, a C_3 - C_{14} monocyclic cycloalkyl group, a C_8 - C_{20} bicyclic cycloalkyl group, a C_{10} - C_{30} tricyclic
 5 cycloalkyl group, a C_{10} - C_{30} tetracyclic cycloalkyl group, a $(C_1$ - C_5 alkyl)cycloalkyl group, a hydroxyalkyl group, a C_1 - C_{10} alkoxy group, a $(C_1$ - C_5 alkoxy)alkyl group, an acetyl group, an acetylalkyl group, a carboxyl group, a $(C_1$ - C_5 alkyl)carboxyl group, and a $(C_3$ - C_{10} cycloalkyl)carboxyl
 10 group, or adjacent groups may be bonded to each other to form a saturated or unsaturated C_6 - C_{18} hydrocarbon ring or a C_5 - C_{18} heterocyclic group. x represents an integer from 0 to 3, and y represents a integer from 0 to 5.

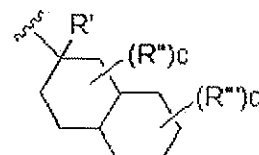
More preferably, R_{23} and R_{33} are each independently an
 15 acid-labile group selected from the group consisting of a t -butyl group, a trimethylsilyl group, a hydroxyl-2-ethyl group, a 1-methoxypropyl group, a 1-methoxy-1-methylethyl group, a 1-ethoxypropyl group, a 1-ethoxy-1-methylethyl group, a 1-methoxy-1-ethyl group, a 1-ethoxy-1-ethyl group,
 20 a t -butoxy-2-ethyl group, a 1-isobutoxy-1-ethyl group, and groups represented by the following formulas (4a) to (4k):



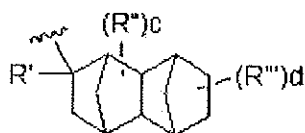
(4a)



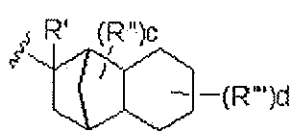
(4b)



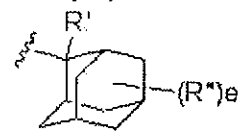
(4c)



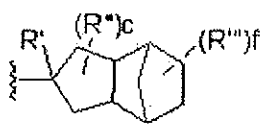
(4d)



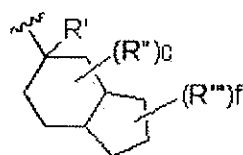
(4e)



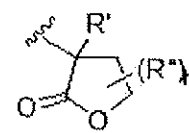
(4f)



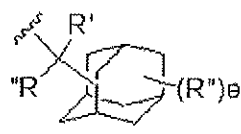
(4g)



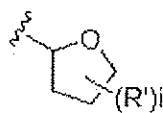
(4h)



(4i)



(4j)

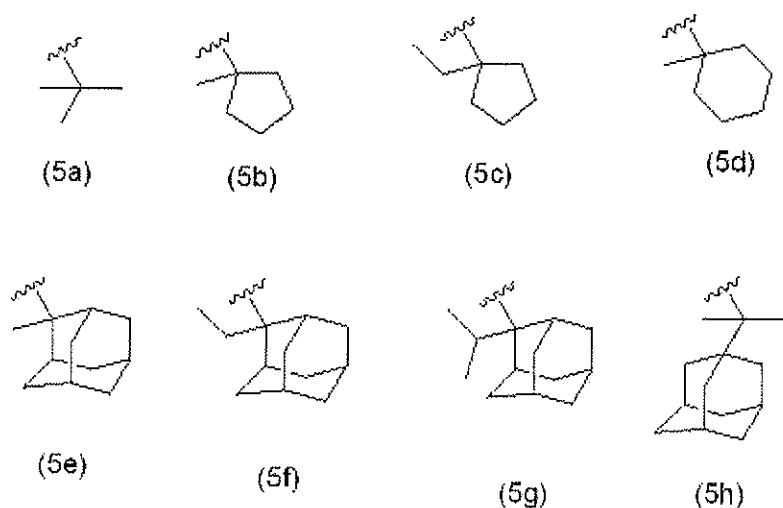


(4k)

wherein in the formulas (4a) to (4k), R', R'' and R''' are each independently selected from the group consisting of a hydrogen atom, a C₁-C₁₀ alkyl group, a C₃-C₁₀ cycloalkyl group, a C₁-C₁₀ alkylsilyl group, and a C₃-C₁₈ cycloalkylsilyl group; a and e each independently represent an integer from 0 to 15; b represents an integer from 0 to 11; c and d each independently represent an integer from 0 to 9; f represents an integer from 0 to 7; g and i each independently represent an integer from 0 to

6; h represents an integer from 0 to 4; $0 \leq c+d \leq 17$; and $0 \leq c+f \leq 15$.

Even more preferably, R_{23} and R_{33} may be each independently selected from the group consisting of
 5 moieties represented by the following formulas (5a) to (5h):

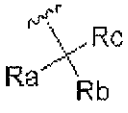
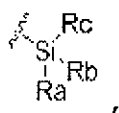


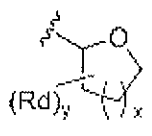
In the formula (1), R_4 is preferably selected from the group consisting of a C_1 - C_{10} fluoroalkyl group, a silyl
 10 group, a C_1 - C_{10} alkylsilyl group, a C_3 - C_{10} chain-like or branched alkyl group, a C_3 - C_{14} monocyclic cycloalkyl group, a C_8 - C_{18} bicyclic cycloalkyl group, a C_{10} - C_{30} tricyclic cycloalkyl group, and a C_{10} - C_{30} tetracyclic cycloalkyl group, and more preferably selected from the group consisting of
 15 a t-butyl group, a trifluoromethyl group, a trimethylsilyl group, a di(trifluoromethyl)isopropyl group, a pentafluoroethyl group, and a heptafluoropropyl group.

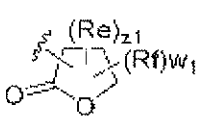
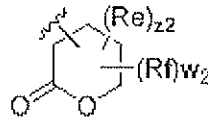
In the formula (1), R_5 is preferably selected from the

group consisting of a hydrogen atom, a C₁-C₁₀ alkyl group, a C₂-C₁₀ alkenyl group, a C₃-C₁₄ monocyclic cycloalkyl group, a C₈-C₁₈ bicyclic cycloalkyl group, a C₁₀-C₃₀ tricyclic cycloalkyl group, C₁₀-C₃₀ tetracyclic cycloalkyl group, a
 5 C₃-C₁₈ cycloalkenyl group, a C₆-C₁₈ aryl group, a C₁-C₂₀ heteroalkyl group, a C₂-C₁₈ heterocyclic group, and combinations thereof.

More preferably, R₅ may be an acid-labile group

selected from the group consisting of , , and

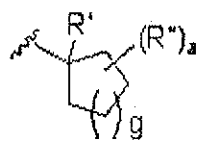
10 , or a lactone group selected from the group

consisting of  and , wherein R_a, R_b,

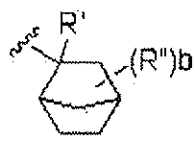
R_c and R_d are each independently selected from the group consisting of a C₁-C₂₀ alkyl group, a C₃-C₃₀ cycloalkyl group, a (C₁-C₁₀ alkyl)cycloalkyl group, a hydroxyalkyl group, a C₁-C₂₀ alkoxy group, a (C₁-C₁₀ alkoxy)alkyl group,
 15 an acetyl group, an acetylalkyl group, a carboxyl group, a (C₁-C₁₀ alkyl)carboxyl group, a (C₃-C₁₈ cycloalkyl)carboxyl group, and a C₃-C₃₀ heterocycloalkyl group, or adjacent groups may be bonded to each other to form a saturated or
 20 unsaturated C₃-C₃₀ hydrocarbon ring or a C₂-C₃₀ heterocyclic

group; R_e and R_f each independently represent a C_1 - C_{10} alkyl group or may be bonded to each other to form a saturated C_3 - C_{30} hydrocarbon ring; x represents an integer from 0 to 3; y represents an integer from 0 to 10; z_1 and w_1 each
5 independently represent an integer from 0 to 3; z_2 and w_2 each independently represent an integer from 0 to 7; $0 \leq z_1 + w_1 \leq 5$; and $0 \leq z_2 + w_2 \leq 5$.

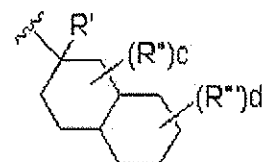
Even more preferably, R_5 may be selected from the group consisting of a t-butyl group, a trimethylsilyl
10 group, a hydroxyl-2-ethyl group, a 1-methoxypropyl group, a 1-methoxy-1-methylethyl group, a 1-ethoxypropyl group, a 1-ethoxy-1-methylethyl group, a 1-methoxy-1-ethyl group, a 1-ethoxy-1-ethyl group, a t-butoxy-2-ethyl group, a 1-isobutoxy-1-ethyl group, and groups represented by the
15 following formulas (6a) to (6m):



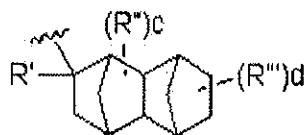
(6a)



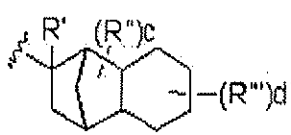
(6b)



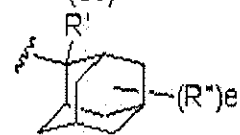
(6c)



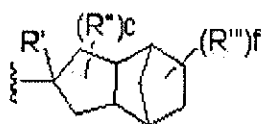
(6d)



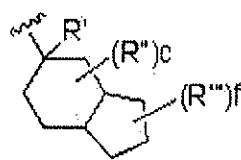
(6e)



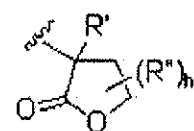
(6f)



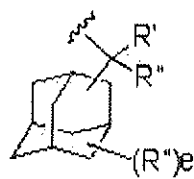
(6g)



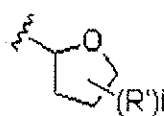
(6h)



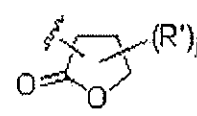
(6i)



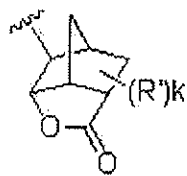
(6j)



(6k)



(6l)



(6m)

wherein in the formulas (6a) to (6m), R', R'' and R''' each independently represent a hydrogen atom, or a C₁-C₁₀ alkyl group; a and e each independently represent an integer from 0 to 15; b represents an integer from 0 to 11; c and d each independently represent an integer from 0 to 9; f

represents an integer from 0 to 7; g, i and k each independently represent an integer from 0 to 6; h and j each independently represent an integer from 0 to 4; $0 \leq c+d \leq 17$; and $0 \leq c+f \leq 15$.

5 When a resist film is formed by applying the additive for resist according to the present invention having a structure such as described above to a resist composition, the additive for resist is located at the surface of the resist film due to the difference in specific gravity, and
10 increases hydrophobicity of the resist film surface. As a result, the additive for resist functions as if the additive forms a separate protective film on the surface of the resist film, and thereby prevents elution of the constituent components of the resist film into water
15 during an immersion lithographic process. Furthermore, a resist film containing the additive for resist is dissolved in a developing solution, at both exposed areas and unexposed areas, in the developing process.

More specifically, the additive for resist according
20 to the present invention contains a hydrophobic group in at least one of the norbornene derivative-derived repeating unit 1 and the acrylic derivative-derived repeating unit n, and thereby increases hydrophobicity of the surface of a resist film at the time of exposure,
25 while suppressing leaching caused by water during a

lithographic process. Furthermore, at the time of development, when the additive for resist is degassed by a developing solution, for example, trimethylammonium hydroxide (TMAH), a hydroxyl group is subsequently
5 produced, and the additive is converted from hydrophobic to hydrophilic, so that defect generation at the surface of the resist film can be suppressed.

Furthermore, the additive for resist according to the present invention contains an acid-labile functional group
10 in each of the norbornene derivative-derived repeating unit l and the acrylic derivative-derived repeating unit o, and thereby is converted from hydrophobic to hydrophilic by a deprotection reaction caused by an acid at an exposed area, and as a result, the additive can exhibit increased
15 solubility in an alkali developing solution at the time of development.

Furthermore, the maleic anhydride-derived repeating unit m in the additive for resist according to the present invention is ring-opened by a developing solution at an
20 unexposed area and forms a carboxyl group, and the repeating unit m thereby further enhances hydrophilic characteristics at the surface. As a result, a lithographic process with fewer defects is enabled.

The repeating units l, m and n that constitute the
25 copolymer of the additive for resist according to the

present invention represent the contents of the respective corresponding repeating units in the main chain, and also mean the substitution ratio by which the copolymer is dissolved in a developing solution. The additive for

5 resist according to the present invention contains the repeating units l, m and n under the conditions that the following relationships are satisfied: $l+m+n = 1$, $0 <$

$l/(l+m+n+o) < 0.9$, $0.2 < m/(l+m+n+o) < 0.9$, $0 \leq$

$n/(l+m+n+o) < 0.9$, and $0 \leq o/(l+m+n+o) < 0.9$. When the

10 additive for resist contains the repeating units at the proportions described above, the additive can exhibit hydrophobicity with less affinity with water at the time of immersion exposure, and particularly, when the additive for resist contains the maleic anhydride-derived repeating

15 unit m at a content of greater than 20% by mole, hydrophobicity is sufficiently increased as a result of ring-opening caused by the alkali solution used as a developing solution, so that the additive for resist can be easily dissolved in the developing solution. More

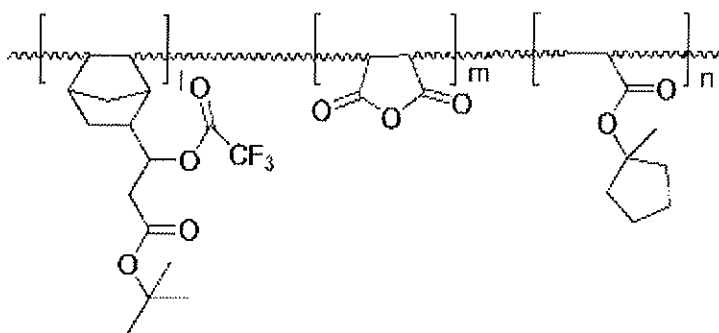
20 preferably, the copolymer contains the maleic anhydride-derived repeating unit m at a content of 30% to 60% by mole.

The additive for resist according to the present invention having a structure such as described above may
25 be a block copolymer, a random copolymer, or a graft

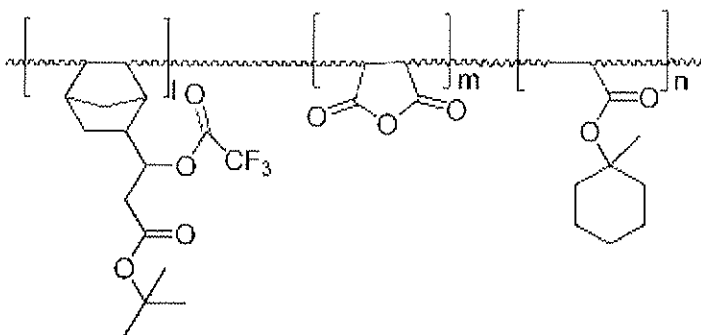
copolymer.

Specific examples of the additive for resist according to the present invention include compounds having structures represented by the following formulas
5 (7) to (18), and the order of the respective repeating units in the structural formulas may vary:

[Chemical Formula 7]

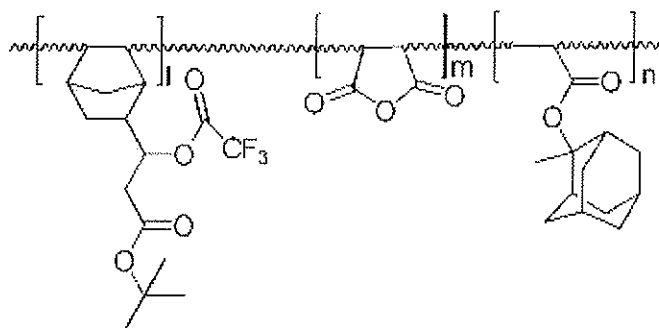


[Chemical Formula 8]

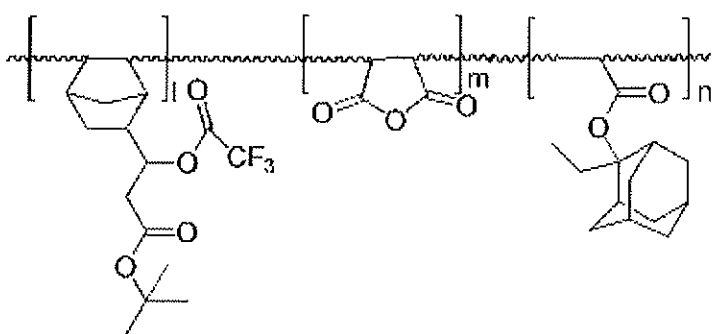


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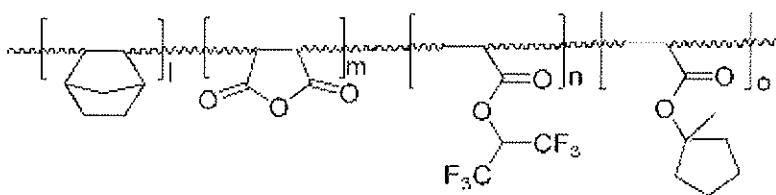
[Chemical Formula 9]



[Chemical Formula 10]

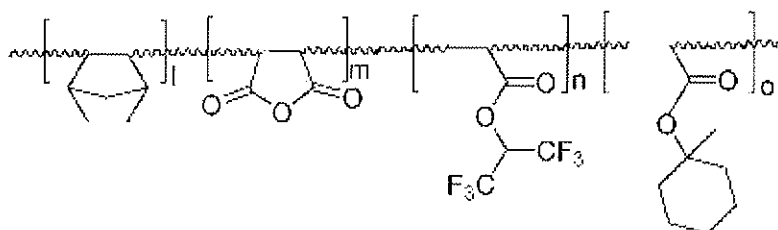


[Chemical Formula 11]

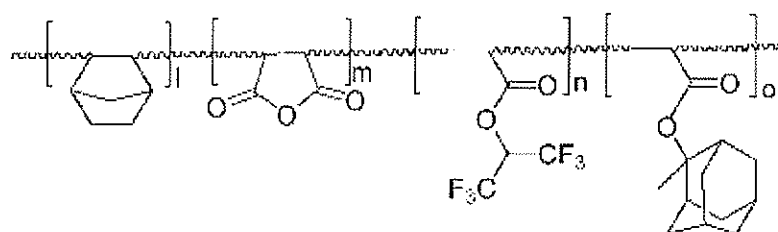


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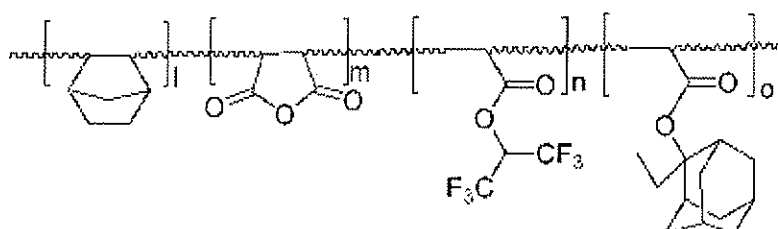
[Chemical Formula 12]



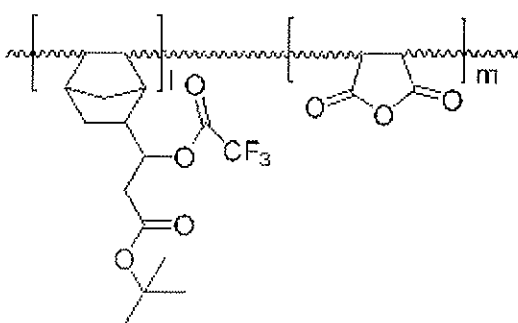
[Chemical Formula 13]



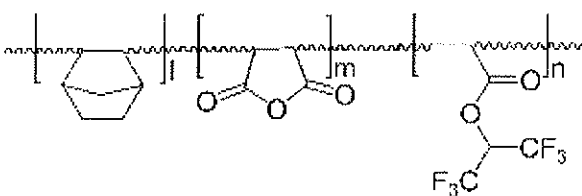
[Chemical Formula 14]



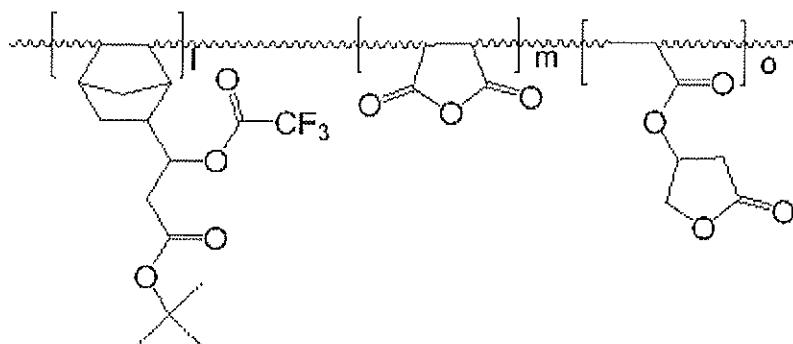
[Chemical Formula 15]



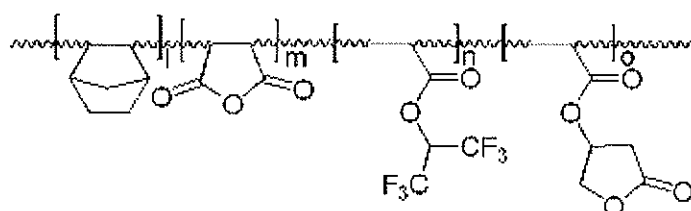
[Chemical Formula 16]



[Chemical Formula 17]



[Chemical Formula 18]



wherein in the formulas (7) to (18), l , m , n and o
 5 respectively represent the proportions of corresponding
 repeating units in the main chain, such that $l+m+n+o = 1$,
 while $0 < l/(l+m+n+o) < 0.9$, $0.2 < m/(l+m+n+o) < 0.9$, $0 \leq$
 $n/(l+m+n+o) < 0.9$, and $0 \leq o/(l+m+n+o) < 0.9$.

The additive for resist according to the present
 10 invention may have a weight average molecular weight
 (hereinafter, referred to as "Mw") as measured by gel
 permeation chromatography (GPC) and calculated relative to
 polystyrene standards, of 1,000 g/mol to 50,000 g/mol. If
 the weight average molecular weight of the additive for
 15 resist is too small, intermixing may occur, or in the case
 of immersion exposure, elution into pure water may occur.
 If the weight average molecular weight is too large,

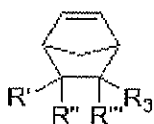
appropriate film forming may not be achieved, or alkali
dissolubility may be decreased. Preferably, it is
preferable that the weight average molecular weight be in
the range of 2,000 g/mol to 20,000 g/mol, from the
5 viewpoint that the additive for resist can exhibit
excellent solubility in developing solutions without a
risk of elution into pure water.

Furthermore, the molecular weight distribution of the
additive for resist, which is the ratio of the weight
10 average molecular weight and the number average molecular
weight (M_w/M_n), is preferably 1 to 5, and more preferably
1 to 3. If the molecular weight distribution of the
polymer is greater than 5, the line edge roughness may be
poor. Therefore, when a copolymer which satisfies the
15 ranges of the weight average molecular weight and the
molecular weight distribution is used as an additive for a
photoresist composition, the photoresist composition may
exhibit appropriate properties in terms of developability,
coatability, and heat resistance.

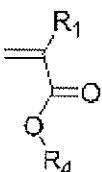
20 The additive for resist according to the present
invention having a structure such as described above can
be produced by polymerizing a norbornene derivative having
a structure represented by formula (19), a maleic
anhydride monomer, and optionally at least one acrylic
25 monomer selected from acrylic monomers having structures

represented by formula (20) and (21), by using a conventional polymerization method, for example, bulk polymerization, solution polymerization, suspension polymerization, bulk suspension polymerization, or
 5 emulsion polymerization.

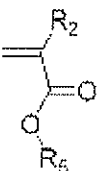
[Chemical Formula 19]



[Chemical Formula 20]



10 [Chemical Formula 21]



wherein in the formulas (19) to (21), R', R'', R''', R_a, R_b, R_c, and R₁ to R₅ respectively have the same meanings as defined above.

15 Preferably, the additive for resist according to the present invention can be polymerization by radical polymerization, and in this case, there are no particular limitations on the radical polymerization initiator as long as a general radical polymerization initiator such as
 20 azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO),

lauryl peroxide, azobisisocapronitrile,
azobisisovaleronitrile or t-butyl hydroperoxide, is used.

Furthermore, as the polymerization solvent, one or
more kinds are selected from benzene, toluene, xylene,
5 benzene halide, diethyl ether, tetrahydrofuran, esters,
ethers, lactones, ketones, amides, and alcohols, and used.

The polymerization temperature used during the
polymerization reaction is appropriately selected in
accordance with the type of the catalyst. Furthermore,
10 the molecular weight distribution of the polymer thus
produced can be appropriately adjusted by varying the
amount of use of the polymerization initiator and the
reaction time. After polymerization is completed, it is
preferable to remove any unreacted monomers and side
15 reaction products remaining in the reaction mixture by
using a solvent-induced precipitation method.

The additive for resist according to the present
invention obtained according to the production methods
described above and by adjusting the type and content of
20 the monomers, has appropriate hydrophobic characteristics,
so that when the additive is used in a resist composition,
the resist composition is transparent to the exposure
light, is not compatible with the liquid for exposure at
the time of immersion exposure, and can reduce the
25 formation of various defects that may be generated during

the exposure process.

Therefore, according to another embodiment of the present invention, a resist composition containing the additive for resist described above is provided.

5 More specifically, the resist composition contains a base polymer for resist, an acid generator, and a solvent, in addition to the additive for resist.

The additive for resist is the same as described previously, and may be incorporated in an amount of 0.05%
10 to 5% by weight relative to the total weight of the resist composition. If the content of the additive for resist is less than 0.05% by weight, the effect obtainable by using the additive is negligible, and if the content is greater than 5% by weight, the resolution of the resist and the
15 roughness are decreased, which is not preferable.

There are no particular limitations on the base polymer for resist, and any base resin that is used at the time of forming a resist film can be used. Specifically, for example, any one or more selected from the group
20 consisting of a (meth)acrylic acid ester polymer, an (α -trifluoromethyl)acrylic acid ester-maleic anhydride copolymer, a cycloolefin-maleic anhydride copolymer, polynorbornene, a polymer compound obtainable by a ring-opening metathesis reaction of a cycloolefin, a polymer
25 compound obtainable by hydrogenating a polymer obtainable

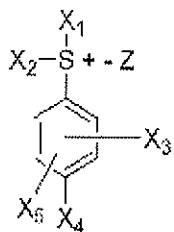
by a ring-opening metathesis reaction of a cycloolefin, a derivative of hydroxystyrene and a (meth)acrylic acid ester, a polymer obtained by copolymerizing one or more of styrene, vinylnaphthalene, vinylanthracene, vinylpyrene, hydroxyvinylnaphthalene, hydroxyvinylanthracene, indene, hydroxyindene, acenaphthylene and norbornadiene, a novolac resin, and mixtures thereof, can be used.

The base polymer may be incorporated at a content of 3% to 20% by weight relative to the total weight of the resist composition. If the content of the polymer is less than 3% by weight, the viscosity of the composition becomes too low so that a film having a desired thickness cannot be formed, and there is a problem that a severe pattern loss occurs due to a relatively larger amount of the photoacid generator. If the content is greater than 20% by weight, the film thickness becomes too large, the film has poor transmission of radiations, and there is a problem that a perpendicular pattern may not be easily obtained.

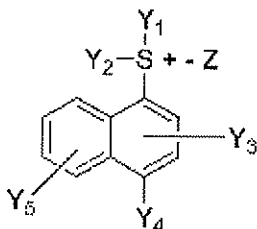
As the acid generator, onium-based photoacid generators (hereinafter, referred to as "PAG") including iodonium salts, sulfonium salts, phosphonium salts, diazonium salts, pyridinium salts, and imides can be used, and preferably, one or more of sulfonium salts having structures represented by the following formulas (22) and

(23) can be used. More preferably, triphenylsulfonium nonaflate can be used.

[Chemical Formula 22]



5 [Chemical Formula 23]



wherein in the formulas (22) and (23),

X_1 , X_2 , Y_1 and Y_2 each independently represent any one selected from the group consisting of a hydrogen atom, a
 10 C_1 - C_{10} alkyl group, an allyl group, a C_1 - C_{10} perfluoroalkyl group, a benzyl group, a C_6 - C_{30} aryl group, and combinations thereof, and X_1 with X_2 , and Y_1 with Y_2 may be bonded to each other and form a saturated or unsaturated C_3 - C_{30} hydrocarbon ring;

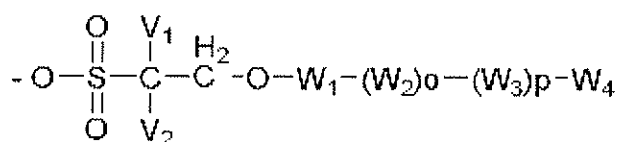
15 X_3 , X_4 , X_5 , Y_3 , Y_4 and Y_5 each independently represent any one selected from the group consisting of a hydrogen atom, a C_1 - C_{30} alkyl group, a halogen atom, a C_1 - C_{30} alkoxy group, a C_6 - C_{30} aryl group, a thiophenoxy group, a C_1 - C_{30} thioalkoxy group, a C_1 - C_{20} alkoxycarbonylmethoxy group, and

combinations thereof;

Z in the anionic moiety represents OSO_2CF_3 , $\text{OSO}_2\text{C}_4\text{F}_9$, $\text{OSO}_2\text{C}_8\text{F}_{17}$, $\text{N}(\text{CF}_3)_2$, $\text{N}(\text{C}_2\text{F}_5)_2$, $\text{N}(\text{C}_4\text{F}_9)_2$, $\text{C}(\text{CF}_3)_3$, $\text{C}(\text{C}_2\text{F}_5)_3$, $\text{C}(\text{C}_4\text{F}_9)_3$, or a functional group represented by the following formula

5 (24):

[Chemical Formula 24]



wherein in the formula (24),

V_1 and V_2 each independently represent a halogen atom;

10 W_1 represents $-(\text{C}=\text{O})-$ or $-(\text{SO}_2)-$;

W_2 represents a C_1 - C_{10} alkanediyl group;

W_3 represents any one selected from the group consisting of a C_3 - C_{30} cycloalkyl group, a C_6 - C_{30} aryl group, a C_7 - C_{30} aralkyl group, a C_6 - C_{30} aryloxy group, a C_6 - C_{30} arylthio group, and a C_5 - C_{30} heterocyclic group;

15 W_4 represents any one selected from the group consisting of a hydrogen atom, a halogen atom, a C_1 - C_{10} alkyl group, a C_1 - C_{10} alkoxy group, a C_1 - C_{10} haloalkyl group, a C_1 - C_{10} alkylthio group, a C_6 - C_{30} aryl group, and
20 combinations thereof;

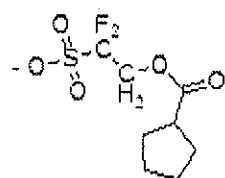
o represents an integer of 0 or 1; and

p represents an integer from 0 to 2.

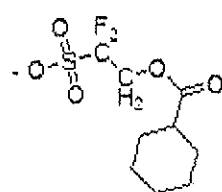
When a cyclic alkyl group is incorporated into the

anion for the acid generator, the acid diffusion length in the resist film is maintained to be appropriately short, high light transmissivity can be exhibited, and as a result, a resist of high resolution can be obtained.

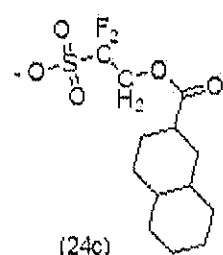
- 5 Preferably, in the formula (24), A in the anionic moiety can be selected from the group consisting of functional groups represented by the following formulas (24a) to (24l) and (25a) to (25x):



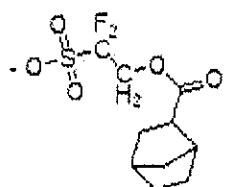
(24a)



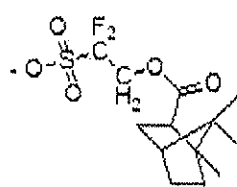
(24b)



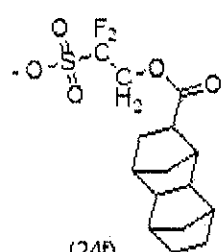
(24c)



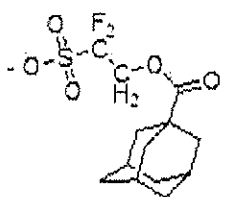
(24d)



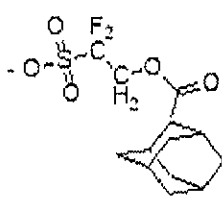
(24e)



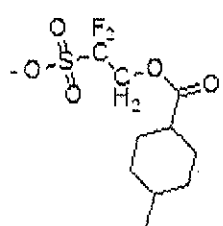
(24f)



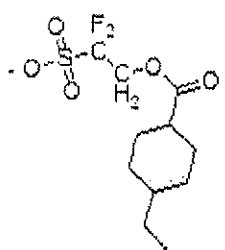
(24g)



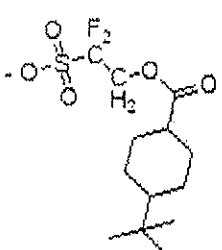
(24h)



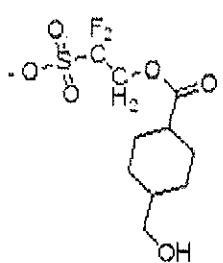
(24i)



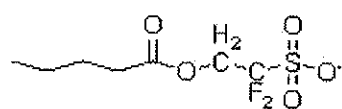
(24j)



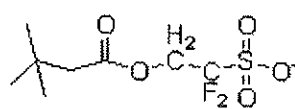
(24k)



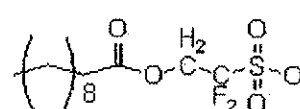
(24l)



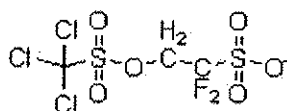
(25a)



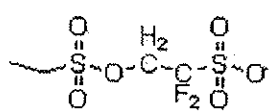
(25b)



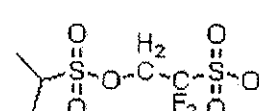
(25c)



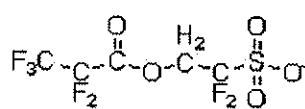
(25d)



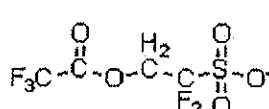
(25e)



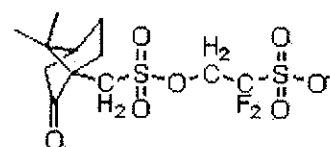
(25f)



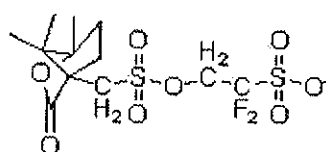
(25g)



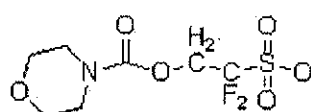
(25h)



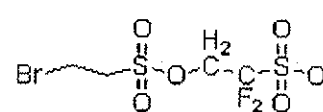
(25i)



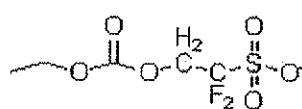
(25j)



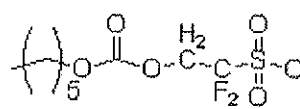
(25k)



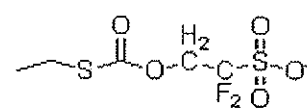
(25l)



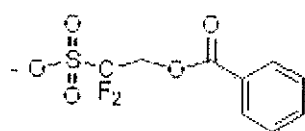
(25m)



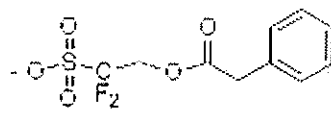
(25n)



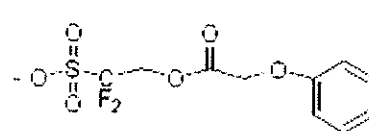
(25o)



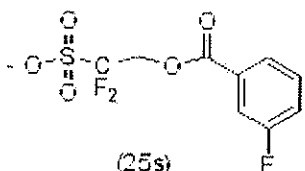
(25p)



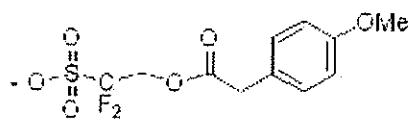
(25q)



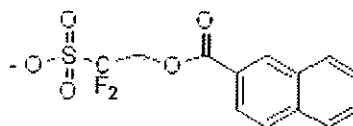
(25r)



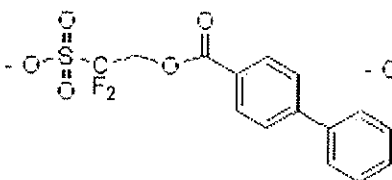
(25s)



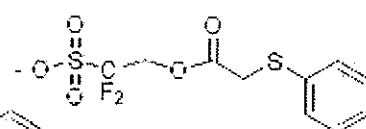
(25t)



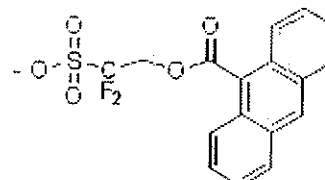
(25u)



(25v)



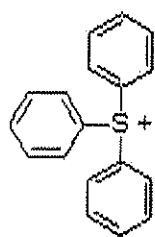
(25w)



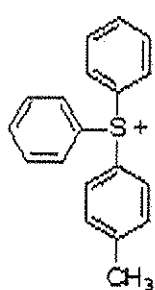
(25x)

Furthermore, in the formulas (22) and (23), the cationic moiety is preferably selected from the group consisting of structures represented by the following

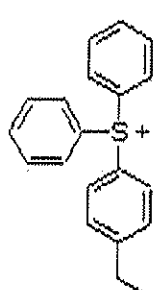
5 formulas (26a) to (26p):



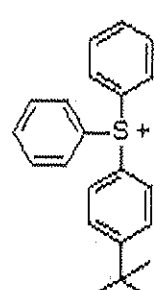
(28a)



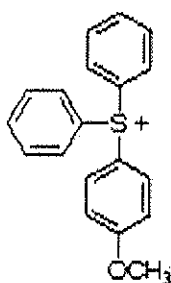
(28b)



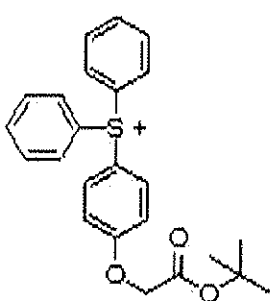
(28c)



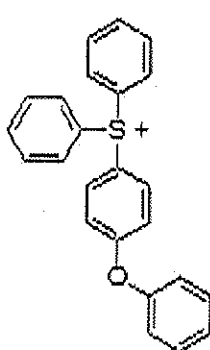
(28d)



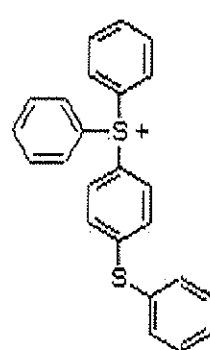
(28e)



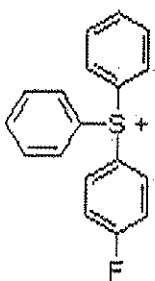
(28f)



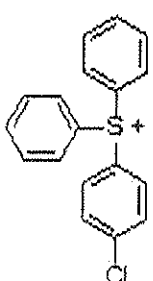
(28g)



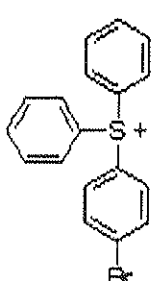
(28h)



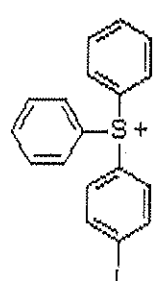
(28i)



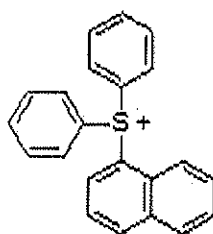
(28j)



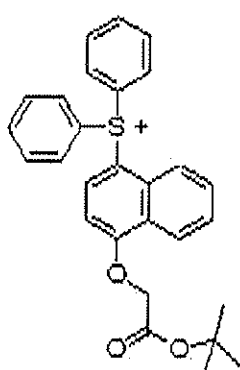
(28k)



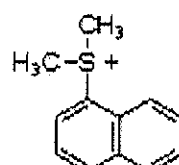
(28l)



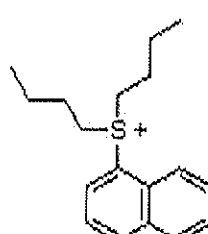
(28m)



(28n)



(28o)



(28p)

The acid generator such as described above can be used singly, or as mixtures of two or more kinds.

Furthermore, the acid generator may be incorporated in an amount of 0.3 parts to 15 parts by weight, preferably 0.5
5 parts to 10 parts by weight, and more preferably 2 parts to 10 parts by weight, relative to 100 parts by weight of the total solids content of the polymer. If the content of the acid generator is greater than 15 parts by weight, perpendicularity of the pattern is markedly deteriorated,
10 and if the content is less than 0.3 parts by weight, there is a risk that bendability of the pattern may decrease.

In order to obtain a uniform and flat resist coating film, it is preferable to use a solution obtained by dissolving the polymer and the acid generator in a solvent
15 having an appropriate evaporation rate and appropriate viscosity. Examples of the solvent that can be used in the present invention include ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether; esters such as methylcellosolve acetate,
20 ethylcellosolve acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, and propylene glycol monopropyl ether acetate; and ketones such as methyl isopropyl ketone, cyclohexanone, methyl 2-hydroxypropionate, ethyl 2-hydroxypropionate, 2-heptanone,
25 ethyl lactate, and γ -butyrolactone. These solvents can be

used singly or as mixtures of two or more kinds.

With regard to the solvent, the amount of use thereof can be appropriately adjusted in accordance with the properties of the solvent, that is, volatility, viscosity
5 and the like, so that a uniform resist film can be formed.

Furthermore, the resist composition according to the present invention can further include other additives according to the purpose such as an increase in coatability.

10 There are no particular limitations on the other additives as long as they are conventionally applied to a resist composition, and specific examples thereof include an alkali dissolution suppressing agent, an acid diffusion suppressing agent, and a surfactant. One kind only, or a
15 mixture of two or more kinds of these may be incorporated into the resist composition.

Any alkali dissolution suppressing agent that is conventionally applied to a resist composition can be used as the alkali dissolution suppressing agent, and specific
20 examples thereof include phenol and carboxylic acid derivatives.

The acid diffusion suppressing agent has a function of controlling the diffusion phenomenon occurring when the acid generated from the acid generator as a result of
25 light irradiation diffuses into the resist film, and

suppressing any chemical reaction in an unexposed area.
When such an acid diffusion suppressing agent is used,
storage stability of a radiation-sensitive resin
composition can be increased, resolution of the resist can
5 be further improved, and the change in the line width in
the resist pattern caused by a fluctuation in the time
taken from exposure to development (PED) can be suppressed.

As such an acid diffusion suppressing agent, a basic
compound can be used, and specific examples thereof
10 include ammonia, amines such as methylamine,
isopropylamine, n-hexylamine, cyclopentylamine,
methylenediamine, ethylenediamine, dimethylamine,
diisopropylamine, diethylenediamine, N,N-
dimethylmethylenediamine, N,N-dimethylethylenediamine,
15 trimethylamine, triethylamine, N,N,N',N'-
tetramethylmethylenediamine, N,N,N',N'-
tetramethylethylenediamine, N,N,N',N'-
tetramethyltetrethylenepentamine, dimethylethylamine,
methylethylpropylamine, benzylamine, phenethylamine,
20 benzyldimethylamine, tetramethylammonium hydroxide, aniline,
N,N-dimethyltoluidine triphenylamine, phenylenediamine,
pyrrole, oxazole, isoxazole, thiazole, isothiazole,
imidazole, pyrazole, pyrroline, pyrrolidine, imidazoline
derivatives, imidazolidine derivatives, pyridine
25 derivatives, pyridazine derivatives, pyrimidine

derivatives, pyrazine derivatives, pyrazoline derivatives, pyrazolidine derivatives, piperidine derivatives, piperazine derivatives, and morpholine; nitrogen-containing compounds such as aminobenzoic acid,

5 indolecarboxylic acid, amino acid derivatives (for example, nicotinic acid, alanine, arginine, and aspartic acid), 3-pyridinesulfonic acid, pyridinium p-toluenesulfonate, 2-hydroxypyridine, aminocresol, 2,4-quinolinediol, 2-(2-hydroxyethyl)pyridine, and 1-(2-hydroxyethyl)piperazine;
10 amide derivatives such as formamide, N-methylformamide, N,N-dimethylformamide, acetamide, N-methylacetamide, N,N-dimethylacetamide, propionamide, and benzamide; and imide derivatives such as phthalimide, succinimide, and maleimide.

15 The acid diffusion suppressing agent may be incorporated in an amount of 0.01 parts to 5 parts by weight, and preferably 0.1 parts to 1 part by weight, relative to 100 parts by weight of the solids content of the polymer. If the content of the acid diffusion
20 suppressing agent is less than 0.01 parts by weight, the influence of the acid diffusion suppressing agent increases with the retention time after exposure, and there is a risk that the shape of the pattern may be affected. If the content is greater than 5 parts by
25 weight, there is a risk that resolution and sensitivity

may be decreased.

The surfactant is intended to improve coatability, developability and the like, and specific examples thereof include, but are not limited to, polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, polyoxyethylene, and polyethylene glycol dilaurate.

The resist composition according to the present invention having a composition such as described above can be dissolved in a developing solution at exposed areas and unexposed areas during the development process after irradiation with an ArF light source, exhibits an improved line width roughness, and exhibits excellent resolution in both C/H patterns and L/S patterns. Furthermore, the resist composition exhibits an excellent process window so that excellent pattern profiles can be obtained regardless of the type of the substrate, and exhibits improved contrast. Accordingly, the resist composition is useful as a positive type chemically amplified photoresist composition which responds to radiation such as far-ultraviolet radiation such as KrF excimer laser light, ArF excimer laser light, or F₂ excimer laser light; X-radiation such as synchrotron radiation; and charged particle radiation such as extreme ultraviolet (EUV).

According to another embodiment of the present invention, a pattern forming method by using the resist

composition is provided.

Specifically, the pattern forming method includes a step of applying the resist composition on a substrate and thereby forming a resist film; a step of heat treating the
5 resist film and then exposing the resist film into a predetermined pattern; and a step of developing the exposed resist pattern.

As the substrate, a wafer substrate can be used, and as the method for coating a substrate, methods such as
10 flow casting or roll coating can be used.

Specifically, the resist composition is applied on a substrate such as a silicon wafer to a film thickness of 0.3 μm to 2.0 μm , and this film is prebaked for 1 minute to 10 minutes at 60°C to 150°C, and preferably for 5
15 minutes at 80°C to 130°C.

Subsequently, the resist film is partially irradiated with radiation in order to form a fine pattern. The radiation that can be used at this time is not particularly limited, but ultraviolet radiation such as I-
20 line; far-ultraviolet radiation such as KrF excimer laser light, ArF excimer laser light, or F₂ excimer laser light; X-radiation; and charged particle radiation such as an electron beam can be used. The radiation can be appropriately selected for use in accordance with the type
25 of the acid generator.

Specifically, radiation is irradiated at a dose of about 1 mJ/cm² to 200 mJ/cm², and preferably about 10 mJ/cm² to 100 mJ/cm², and then the resist film is subjected to post-exposure baking (PEB) for 1 to 5 minutes at 60°C to 150°C, and preferably for 1 to 3 minutes at 80°C to 130°C.

After the exposure process, the exposed resist pattern is developed by using a developing solution for 0.1 to 3 minutes, and preferably for 0.5 to 2 minutes, by a conventional method such as a dipping method, a paddle method or a spray method, and thereby a desired pattern is formed on the substrate. Regarding the developing solution that can be used in this case, an aqueous solution containing sodium hydroxide, potassium hydroxide, sodium carbonate, sodium silicate, sodium methanesilicate, ammonia, ethylamine, n-propylamine, triethylamine, tetramethylammonium hydroxide, tetraethylammonium hydroxide, or the like can be used, and preferably, tetramethylammonium hydroxide may be used.

Furthermore, the developing solution may optionally include other additives such as a surfactant or a water-soluble alcohol.

As discussed above, a fine resist pattern having excellent sensitivity and resolution can be formed by the pattern forming method using the resist composition according to the present invention.

Hereinafter, Examples of the present invention will be described in detail so that a person having ordinary skill in the art to which the present invention is pertained, can easily carry out the present invention.

5 However, the present invention can be realized in various different forms, and is not intended to be limited to the Examples described herein.

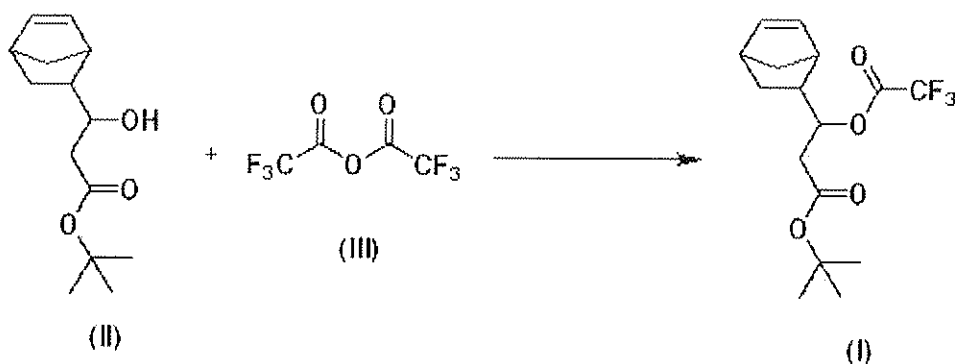
EXAMPLES

10 [Production Example: Synthesis of monomer and polymer]

(Synthesis Example for monomer 1)

Synthesis of 3-bicyclo[2.2.1]hept-5-en-2-yl-3-(2,2,2-trifluoroacetoxy)propionic acid tert-butyl ester

15 (hereinafter, referred to BHP-5) monomer



To a solution prepared by dissolving 100 g of 3-(bicyclo[2.2.1]hept-5-en-2-yl)-(3-hydroxy)propionic acid tert-butyl ester (BHP), 105.75 g of trifluoroacetic anhydride, and 4.67 g of dimethylpyridin-4-ylamine in 1 L

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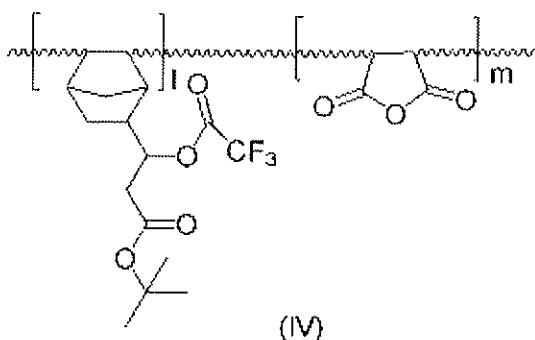
of methylene chloride, 46.71 g of triethylamine was slowly added dropwise at 0°C, and the mixture was stirred for 3 hours at normal temperature. A reaction product thus obtained was dissolved in 500 ml of methylene chloride, and then was washed with acid and distilled water. Only the organic layer was separated. The solvent in the separated organic layer was removed, and thereby 130 g of BHP-5 as an intermediate product (compound (I)) was obtained.

¹H-NMR: δ(ppm) 0.6(d, 1H), 0.82(d, 1H), 1.25(m, 1H), 1.42(m, 1H), 1.58(s, 1H), 1.7(m, 1H), 1.9(m, 1H), 2.08(m, 12H), 2.15~2.6(m, 3H) 2.88(m, 2H), 4.7(m, 1H), 5.15(m, 1H), 5.25(m, 1H), 5.9(s, 1H), 6.22(s, 1H)

(Synthesis Example for polymer 1)

30 g of the monomer for polymerization, BHP-5, produced in Synthesis Example for monomer 1, and 1.65 g of dimethyl azobisisobutyrate as a polymerization initiator were introduced together with 58.2 g of 1,4-dioxane into a flask, and then the compounds were mixed. The interior of the flask was purged with nitrogen by using nitrogen gas, and then the temperature inside the flask was increased to 75°C. When the temperature inside the flask increased to 75°C, a solution prepared by dissolving 8.8 g of maleic anhydride in 58.2 g of 1,4-dioxane was slowly added dropwise into the flask over 2 hours by using a syringe

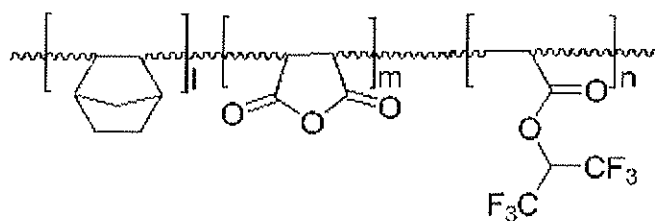
pump. A reaction was carried out for 5 hours at the same
 temperature to complete polymerization, and the
 temperature of the reaction solution thus obtained was
 cooled to room temperature. The reaction solution thus
 5 cooled to room temperature was precipitated by using an
 excess amount of methanol, and then the precipitate was
 filtered. At the time of filtration, the precipitate was
 washed with the same solvent, and then was dried under
 reduced pressure. Thus, 20 g of a polymer (IV) having the
 10 following structural formula was obtained. The weight
 average molecular weight (M_w) of this polymer as
 calculated relative to polystyrene standards was 3,260
 g/mol, and the ratio of the weight average molecular
 weight and the number average molecular weight, M_w/M_n , was
 15 1.38.



(Synthesis Example for polymer 2)

30 g of norbornene as a monomer for polymerization,
 and 6.45 g of dimethyl azobisisobutyrate as a
 20 polymerization initiator were introduced together with

58.2 g of 1,4-dioxane into a flask, and then the compounds were mixed. The interior of the flask was purged with nitrogen by using nitrogen gas, and then the temperature inside the flask was increased to 75°C. When the
5 temperature inside the flask increased to 75°C, a solution prepared by dissolving 18.75 g of maleic anhydride and 42.46 g of 1,1,1,3,3,3-hexafluoroisopropyl acrylate in 138.88 g of 1,4-dioxane was slowly added dropwise into the flask over 2 hours by using a syringe pump. A reaction
10 was carried out for 5 hours at the same temperature to complete polymerization, and the temperature of the reaction solution thus obtained was cooled to room temperature. The reaction solution thus cooled to room temperature was precipitated by using an excess amount of
15 methanol, and then the precipitate was filtered. At the time of filtration, the precipitate was washed with the same solvent, and then was dried under reduced pressure. Thus, 20 g of a polymer (V) having the following structural formula was obtained. The weight average
20 molecular weight (Mw) of this polymer as calculated relative to polystyrene standards was 3,260 g/mol, and the ratio of the weight average molecular weight and the number average molecular weight, Mw/Mn, was 1.38.

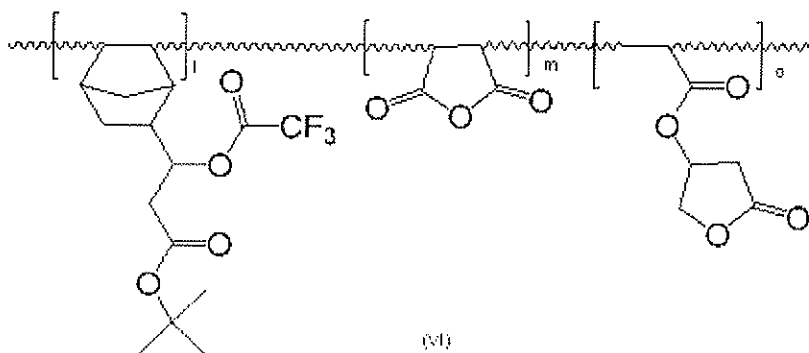


(V)

(Synthesis Example for polymer 3)

30 g of the monomer for polymerization, BHP-5,
 produced in Synthesis Example for monomer 1 as described
 5 above and 2.48 g of dimethyl azobisisobutyrate as a
 polymerization initiator were introduced together with 80
 g of 1,4-dioxane into a flask, and then the compounds were
 mixed. The interior of the flask was purged with nitrogen
 by using nitrogen gas, and then the temperature inside the
 10 flask was increased to 75°C. When the temperature inside
 the flask increased to 75°C, a solution prepared by
 dissolving 8.8 g of maleic anhydride and 14.01 g of γ -
 butyrolactyl methacrylate in 80 g of 1,4-dioxane was
 slowly added dropwise into the flask over 2 hours by using
 15 a syringe pump. A reaction was carried out for 5 hours at
 the same temperature to complete polymerization, and the
 temperature of the reaction solution thus obtained was
 cooled to room temperature. The reaction solution thus
 cooled to room temperature was precipitated by using an
 20 excess amount of methanol, and then the precipitate was
 filtered. At the time of filtration, the precipitate was

washed with the same solvent, and then was dried under reduced pressure. Thus, 42 g of a polymer (VI) having the following structural formula was obtained. The weight average molecular weight (M_w) of this polymer as
 5 calculated relative to polystyrene standards was 4,300 g/mol, and the ratio of the weight average molecular weight and the number average molecular weight, M_w/M_n , was 1.45.



10 **(Synthesis Example for polymer 4)**

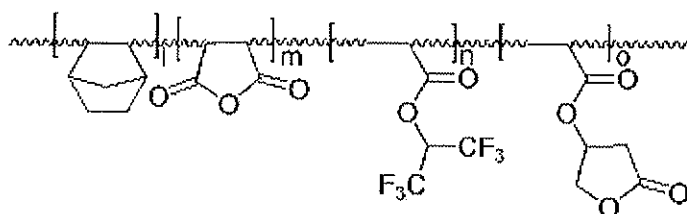
8.45 g of norbornene as a monomer for polymerization and 3.30 g of dimethyl azobisisobutyrate as a polymerization initiator were introduced together with 76.89 g of 1,4-dioxane into a flask, and then the
 15 compounds were mixed. The interior of the flask was purged with nitrogen by using nitrogen gas, and then the temperature inside the flask was increased to 75°C. When the temperature inside the flask increased to 75°C, a solution prepared by dissolving 8.8 g of maleic anhydride,
 20 20 g of 1,1,1,3,3,3-hexafluoroisopropyl acrylate, and

14.01 g of γ -butyrolactyl methacrylate in 76.89 g of 1,4-dioxane was slowly added dropwise into the flask over 2 hours by using a syringe pump. A reaction was carried out for 5 hours at the same temperature to complete

polymerization, and the temperature of the reaction solution thus obtained was cooled to room temperature.

The reaction solution thus cooled to room temperature was precipitated by using an excess amount of methanol, and then the precipitate was filtered. At the time of

filtration, the precipitate was washed with the same solvent, and then was dried under reduced pressure. Thus, 37 g of a polymer (VII) having the following structural formula was obtained. The weight average molecular weight (Mw) of this polymer as calculated relative to polystyrene standards was 4,200 g/mol, and the ratio of the weight average molecular weight and the number average molecular weight, Mw/Mn, was 1.54.

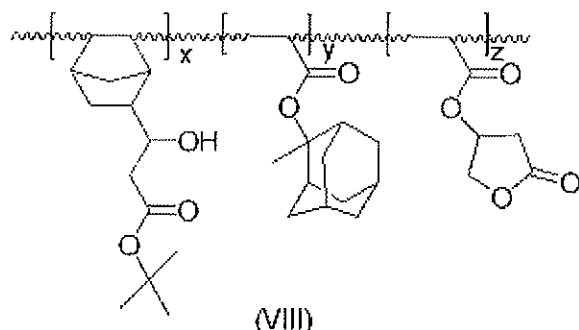


(VII)

(Synthesis Example for polymer 5)

20 g of 3-bicyclo[2,2,1]hept-5-en-2-yl-3-hydroxypropionic acid t-butyl ester (BHP) and 1.93 g of

dimethyl azobisisobutyrate as a polymerization initiator were introduced together with 35.79 g of 1,4-dioxane into a flask, and then the compounds were mixed. The interior of the flask was purged with nitrogen by using nitrogen
5 gas, and then the temperature inside the flask was increased to 75°C. When the temperature inside the flask increased to 75°C, a solution prepared by dissolving 9.24 g of methyladamantane methacrylate and 6.55 g of γ -butyrolactyl methacrylate in 35.79 g of 1,4-dioxane was
10 slowly added dropwise into the flask over 2 hours by using a syringe pump. A reaction was carried out for 5 hours at the same temperature to complete polymerization, and the temperature of the reaction solution thus obtained was cooled to room temperature. The reaction solution thus
15 cooled to room temperature was precipitated by using an excess amount of methanol, and then the precipitate was filtered. At the time of filtration, the precipitate was washed with the same solvent, and then was dried under reduced pressure. Thus, 19 g of a polymer (VIII) having
20 the following structural formula was obtained. The weight average molecular weight (M_w) of this polymer as calculated relative to polystyrene standards was 6,231 g/mol, and the ratio of the weight average molecular weight and the number average molecular weight, M_w/M_n , was
25 1.92.

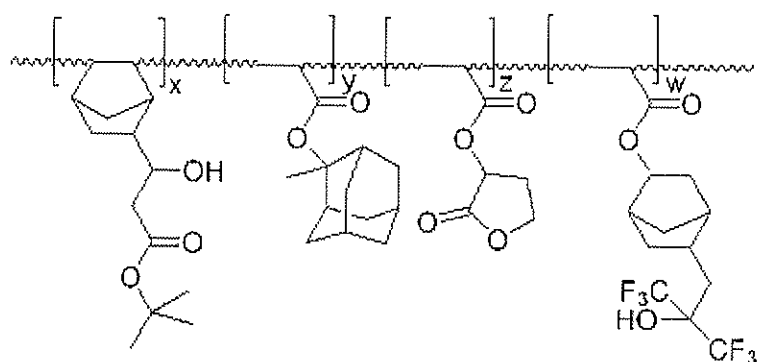


**[Experiment Example: Formation of resist film and
analysis of characteristic of resist film produced]**

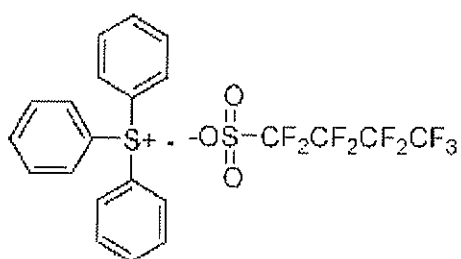
(Example and Comparative Example)

5 As the additive for a resist composition, 1.0 g of
each of the polymers synthesized in Synthesis Examples for
polymer 1 to 5 was dissolved together with 5 g of a base
polymer for resist represented by the following formula
(27) (M_w : 8,500 g/mol, M_w/M_n : 1.75, molar ratio of the
10 respective repeating units ($x:y:z:w$) was 1:1:1:1) and 0.31
g of a photoacid generator represented by the following
formula (28) in 80 g of propylene glycol monoethyl ether
acetate (PGMEA), and then the solution was filtered
through a polypropylene filter having a pore size of 0.2
15 μm . Thus, resist compositions (Examples 1 to 4, and
Comparative Example 1) were prepared.

[Chemical Formula 27]



[Chemical Formula 28]



On a silicon substrate, an anti-reflection film
 5 (BARC) having a thickness of 90 nm was formed, and the
 resist composition prepared as described above was applied
 on the substrate where the anti-reflection film had been
 formed. Subsequently, the substrate was baked for 60
 seconds at 100°C, and thus a resist film having a thickness
 10 of 120 nm was formed.

The sliding angles and the receding contact angles of
 the resist films thus formed were respectively measured.

More specifically, the substrate having the resist
 film formed thereon was maintained horizontally, and 50 μ l
 15 of pure water was added dropwise thereon to form water
 droplets. Subsequently, the silicon substrate was slowly

inclined, and the angle of the silicon substrate at which the water droplets started to slide (sliding angle) and the receding contact angle were measured. The results are presented in the following Table 1.

5 Subsequently, in order to reproduce immersion exposure, the resist film after exposure was rinsed with pure water for 5 minutes. That is, exposure was carried out with an ArF scanner 306C (NA = 0.78, 6% halftone mask) manufactured by Nikon Corp., and rinsing was carried out
10 for 5 minutes while adding pure water. After an exposure for 60 seconds at 110°C, PEB was carried out, and development was carried out with a 2.38 wt% TMAH developing solution for 60 seconds.

The silicon substrate thus produced was cut, and the
15 sensitivity was evaluated. At this time, the amount of exposure by which resolution of 65-nm L/S at 1:1 can be achieved was designated as sensitivity.

[Table 1]

Resist composition	Additive for resist	Sliding angle (°)	Receding contact angle (°)	Sensitivity (mJ/cm ²)
Example 1	Polymer 1 (IV)	89	78	34
Example 2	Polymer 2 (V)	87	76	34
Example 3	Polymer 3 (VI)	82	73	33
Example 4	Polymer 4 (VII)	82	72	33
Comparative Example 1	Polymer 5 (VIII)	75	65	No pattern formed

According to the results described in Table 1, the
20 resist films formed by using the resist compositions of

Examples 1 to 4 that contained the copolymer as the additive for resist according to the present invention, exhibited larger sliding angles and larger receding contact angles as compared with the resist film formed by using the resist composition of Comparative Example 1 that contained the polymer 5 (VIII) as the additive for resist.

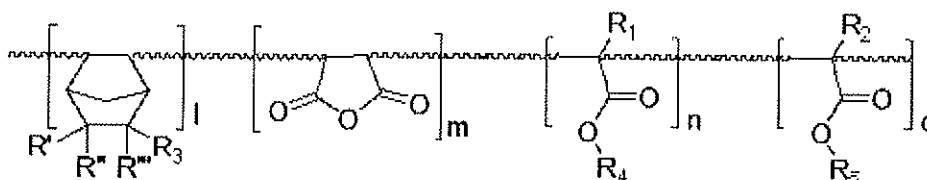
From these results, it can be seen that the resist films produced with the resist compositions of Examples 1 to 4 have sufficient hydrophobicity, and the formation of a protective film against the resist film at the time of immersion exposure is unnecessary. Furthermore, the resist films formed by using the resist compositions of Examples 1 to 4 exhibited improved excellent sensitivity characteristics at the time of immersion exposure, while in the case of the resist composition of Comparative Example 1, pattern formation was not achieved, so that sensitivity measurement could not be performed.

Thus, preferred embodiments of the present invention have been described in detail, but the scope of the present invention is not intended to be limited thereto, and various modifications and improvements made by those having ordinary skill in the art by using the fundamental concept of the present invention are also included in the scope of the present invention.

WHAT IS CLAIMED IS:

1. An additive for resist represented by the following formula (1):

5 [Chemical Formula 1]



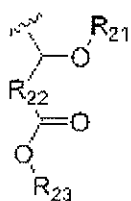
wherein in the formula (1),

R', R'' and R''' each independently represent a group selected from the group consisting of a hydrogen atom, a C₁-C₄ alkyl group, a halogen atom, and a C₁-C₄ haloalkyl group in which one of the hydrogen atoms of an alkyl group is substituted by a halogen atom;

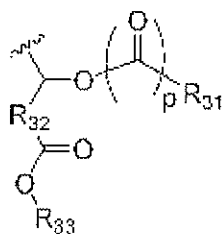
R₁ and R₂ each independently represent a hydrogen atom or a C₁-C₈ alkyl group;

15 R₃ represents a group selected from the group consisting of a hydrogen atom and functional groups represented by the following formulas (2) and (3):

[Chemical Formula 2]



20 [Chemical Formula 3]

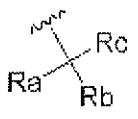
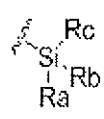


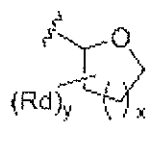
wherein in the formulas (2) and (3), R_{21} represents a hydrogen atom, or a hydroxyl-protecting group selected from the group consisting of a C_1 - C_{20} alkyl group, a (C_1 - C_{20} alkoxy)alkyl group, a C_3 - C_{30} cycloalkyl group, a formyl group, a (C_1 - C_{20} alkyl)carbonyl group, a (C_3 - C_{30} cycloalkyl)carbonyl group, a (C_1 - C_{20} alkyl)carboxyl group, and a (C_3 - C_{30} cycloalkyl)carboxyl group;

R_{31} represents a hydrophobic group selected from the group consisting of a C_1 - C_{20} haloalkyl group, an organosilicon group and a C_3 - C_{20} hydrocarbon group, such that if R_{31} represents an organosilicon group, p represents 0, while if R_{31} represents a C_1 - C_{20} haloalkyl group or a C_3 - C_{20} hydrocarbon group, p represents 1;

R_{22} and R_{32} each independently represent a group selected from the group consisting of a C_1 - C_{20} alkanediyl group, a C_2 - C_{20} alkenediyl group, a C_1 - C_{20} heteroalkanediyl group, a C_2 - C_{20} heteroalkenediyl group, a C_3 - C_{30} cycloalkanediyl group, a C_3 - C_{30} cycloalkenediyl group, a C_2 - C_{30} heterocycloalkanediyl group, and a C_3 - C_{30} heterocycloalkenediyl group;

R_{23} and R_{33} each independently represent an acid-labile

group selected from the group consisting of  , 

and , wherein R_a , R_b , R_c and R_d each independently represent a group selected from the group consisting of a C_1 - C_{20} alkyl group, a C_3 - C_{30} cycloalkyl group, a $(C_1$ - C_{10} alkyl)cycloalkyl group, a hydroxyalkyl group, a C_1 - C_{20} alkoxy group, a $(C_1$ - C_{10} alkoxy)alkyl group, an acetyl group, an acetylalkyl group, a carboxyl group, a $(C_1$ - C_{10} alkyl)carboxyl group, a $(C_3$ - C_{18} cycloalkyl)carboxyl group, and a C_3 - C_{30} heterocycloalkyl group, or adjacent groups may be bonded to each other to form a C_3 - C_{30} saturated or unsaturated hydrocarbon ring or a C_2 - C_{30} heterocyclic group;

x represents an integer from 0 to 3; y represents an integer from 0 to 10;

R_4 represents a hydrophobic group selected from the group consisting of a C_1 - C_{20} haloalkyl group, an organosilicon group, and a C_3 - C_{20} hydrocarbon group;

R_5 represents a group selected from the group consisting of a hydrogen atom, a C_1 - C_{20} alkyl group, a C_2 - C_{20} alkenyl group, a C_3 - C_{30} cycloalkyl group, a C_3 - C_{30} cycloalkenyl group, a C_6 - C_{30} aryl group, a C_1 - C_{20} heteroalkyl group, a C_2 - C_{30} heterocyclic group, and

combinations thereof;

1, m, n and o respectively represent the proportions of corresponding repeating units in the main chain, such that $l+m+n+o = 1$, while $0 < l/(l+m+n+o) < 0.9$, $0.2 <$
5 $m/(l+m+n+o) < 0.9$, $0 \leq n/(l+m+n+o) < 0.9$, and $0 \leq$
 $o/(l+m+n+o) < 0.9$, provided that when R_3 represents a hydrogen atom or a functional group represented by formula (2), n is not 0; and

p represents an integer of 0 or 1.

10

2. The additive for resist according to Claim 1, wherein R_3 represents a hydrogen atom or a functional group having a structure represented by the formula (2); and

1, m, n and o respectively represent the proportions
15 of corresponding repeating units in the main chain, such that $l+m+n+o = 1$, while $0 < l/(l+m+n+o) < 0.9$, $0.2 <$
 $m/(l+m+n+o) < 0.9$, $0 < n/(l+m+n+o) < 0.9$, and $0 \leq$
 $o/(l+m+n+o) < 0.9$.

20

3. The additive for resist according to Claim 1, wherein R_3 represents a hydrogen atom or a functional group having a structure represented by the formula (3); and

1, m, n and o respectively represent the proportions of corresponding repeating units in the main chain, such
25 that $l+m+n+o = 1$, while $0 < l/(l+m+n+o) < 0.9$, $0.2 <$

$m/(1+m+n+o) < 0.9$, $0 \leq n/(1+m+n+o) < 0.9$, and $0 \leq o/(1+m+n+o) < 0.9$.

4. The additive for resist according to Claim 1,
5 wherein in the formula (2), R_{21} represents a group that is selected from the group consisting of a C_1 - C_{10} alkyl group, a (C_1 - C_{10} alkoxy)alkyl group, a C_3 - C_{14} monocyclic cycloalkyl group, a C_8 - C_{18} bicyclic cycloalkyl group, a C_{10} - C_{30} tricyclic cycloalkyl group, a C_{10} - C_{30} tetracyclic cycloalkyl
10 group, a formyl group, a (C_1 - C_{10} alkyl)carbonyl group, a (C_3 - C_{18} cycloalkyl)carbonyl group, a (C_1 - C_{10} alkyl)carboxyl group, and a (C_3 - C_{18} cycloalkyl)carboxyl group.

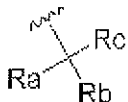
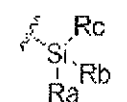
5. The additive for resist according to Claim 1,
15 wherein in the formula (2), R_{21} represents a group that is selected from the group consisting of a formyl group, an acetyl group, a methoxymethyl group, a t-butylcarbonyl group, a t-butyloxycarbonyl group, a cyclohexylcarbonyl group, a cyclopentylcarbonyl group, a cyclooctylcarbonyl
20 group, an adamantylcarbonyl group, and a bicyclo[2,2,1]heptylmethylcarbonyl group.

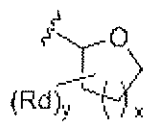
6. The additive for resist according to Claim 1,
wherein in the formula (3), R_{31} represents a group that is
25 selected from the group consisting of a C_1 - C_{10} fluoroalkyl

group, a silyl group, a C₁-C₁₀ alkylsilyl group, a chain-
 like or branched C₃-C₁₀ alkyl group, a C₃-C₁₄ monocyclic
 cycloalkyl group, a C₈-C₁₈ bicyclic cycloalkyl group, a C₁₀-
 C₃₀ tricyclic cycloalkyl group, and a C₁₀-C₃₀ tetracyclic
 5 cycloalkyl group.

7. The additive for resist according to Claim 1,
 wherein in the formula (3), R₃₁ represents a group that may
 be selected from the group consisting of a t-butyl group,
 10 a trifluoromethyl group, a trimethylsilyl group, a
 di(trifluoromethyl)isopropyl group, a pentafluoroethyl
 group, and a heptafluoropropyl group.

8. The additive for resist according to Claim 1,
 15 wherein in the formulas (2) and (3), R₂₃ and R₃₃ each
 independently represent an acid-labile group that may be

selected from the group consisting of , , and

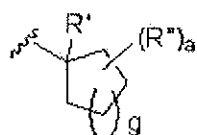


, wherein R_a, R_b, R_c and R_d independently represent

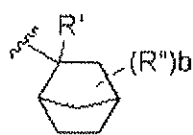
a group selected from the group consisting of a C₁-C₁₀
 20 alkyl group, a C₃-C₁₄ monocyclic cycloalkyl group, a C₈-C₂₀
 bicyclic cycloalkyl group, a C₁₀-C₃₀ tricyclic cycloalkyl
 group, a C₁₀-C₃₀ tetracyclic cycloalkyl group, a (C₁-C₅

alkyl)cycloalkyl group, a hydroxyalkyl group, a C₁-C₁₀ alkoxy group, a (C₁-C₅ alkoxy)alkyl group, an acetyl group, an acetylalkyl group, a carboxyl group, a (C₁-C₅ alkyl)carboxyl group, and a (C₃-C₁₀ cycloalkyl)carboxyl group, or adjacent groups may be bonded to each other to form a saturated or unsaturated C₆-C₁₈ hydrocarbon ring or a C₅-C₁₈ heterocyclic group; x represents an integer from 0 to 3; and y represents an integer from 0 to 5.

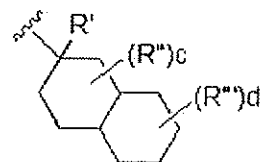
10 9. The additive for resist according to Claim 1, wherein in the formulas (2) and (3), R₂₃ and R₃₃ each independently represent a group that may be selected from the group consisting of a t-butyl group, a trimethylsilyl group, a hydroxyl-2-ethyl group, a 1-methoxypropyl group, 15 a 1-methoxy-1-methylethyl group, a 1-ethoxypropyl group, a 1-ethoxy-1-methylethyl group, 1-methoxy-1-ethyl group, a 1-ethoxy-1-ethyl group, a t-butoxy-2-ethyl group, a 1-isobutoxy-1-ethyl group, and groups represented by the following formulas (4a) to (4k):



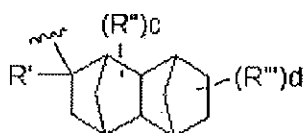
(4a)



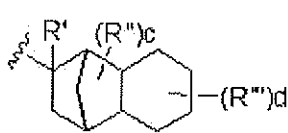
(4b)



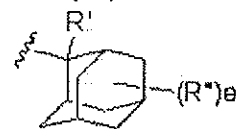
(4c)



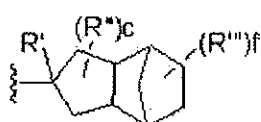
(4d)



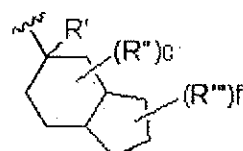
(4e)



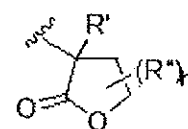
(4f)



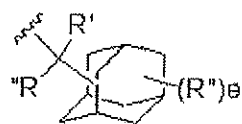
(4g)



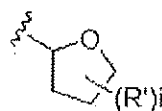
(4h)



(4i)



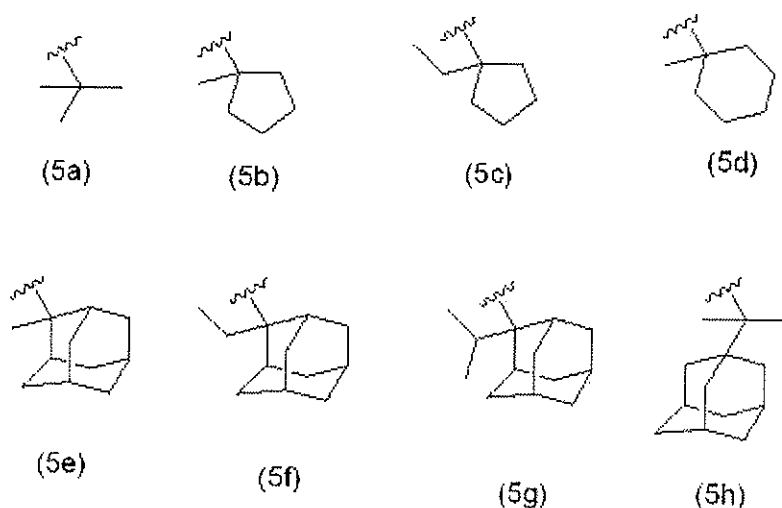
(4j)



(4k)

wherein in the formulas (4a) to (4k), R', R'' and R''' each independently represent a hydrogen atom or a C₁-C₁₀ alkyl group; a and e each represent an integer from 0 to 15; b represents an integer from 0 to 11; c and d each independently represent an integer from 0 to 9; f represents an integer from 0 to 7; g and i each independently represent an integer from 0 to 6; h represents an integer from 0 to 4; $0 \leq c+d \leq 17$; and $0 \leq c+f \leq 15$.

10. The additive for resist according to Claim 1,
 wherein in the formulas (2) and (3), R_{23} and R_{33} each
 independently represent a group selected from the group
 5 consisting of moieties represented by the following
 formulas (5) to (5h):



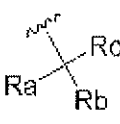
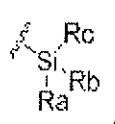
11. The additive for resist according to Claim 1,
 10 wherein in the formula (1), R_4 represents a group that is
 selected from the group consisting of a C_1 - C_{10} fluoroalkyl
 group, a silyl group, a C_1 - C_{10} alkylsilyl group, a chain-
 like or branched C_3 - C_{10} alkyl group, C_3 - C_{14} monocyclic
 cycloalkyl group, a C_8 - C_{18} bicyclic cycloalkyl group, a C_{10} -
 15 C_{30} tricyclic cycloalkyl group, and a C_{10} - C_{30} tetracyclic
 cycloalkyl group.

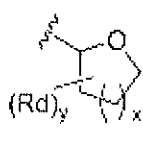
12. The additive for resist according to Claim 1,

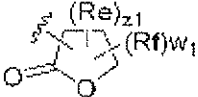
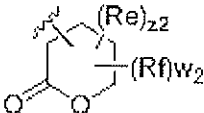
wherein in the formula (1), R_4 represents a group that is selected from the group consisting of a t-butyl group, a trifluoromethyl group, a trimethylsilyl group, a di(trifluoromethyl)isopropyl group, a pentafluoroethyl group, and a heptafluoropropyl group.

13. The additive for resist according to Claim 1, wherein in the formula (1), R_5 represents a group that is selected from the group consisting of a hydrogen atom, a C_1 - C_{10} alkyl group, a C_2 - C_{10} alkenyl group, a C_3 - C_{14} monocyclic cycloalkyl group, a C_8 - C_{18} bicyclic cycloalkyl group, C_{10} - C_{30} tricyclic cycloalkyl group, a C_{10} - C_{30} tetracyclic cycloalkyl group, a C_3 - C_{18} cycloalkenyl group, a C_6 - C_{18} aryl group, a C_1 - C_{20} heteroalkyl group, a C_2 - C_{18} heterocyclic group, and combinations thereof.

14. The additive for resist according to Claim 1, wherein in the formula (1), R_5 represents an acid-labile

group selected from the group consisting of , ,

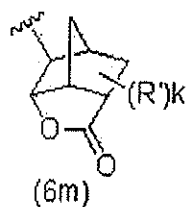
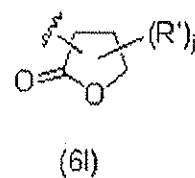
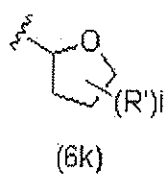
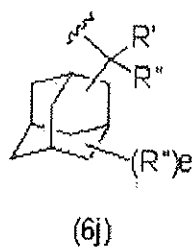
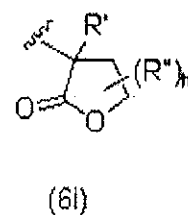
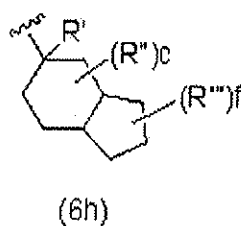
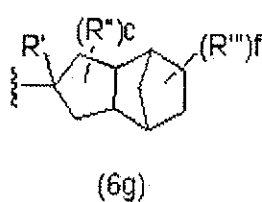
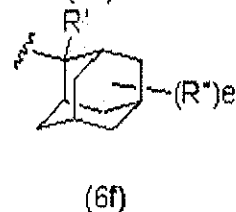
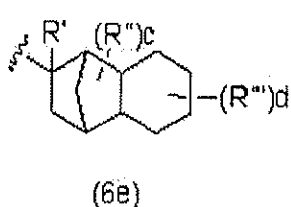
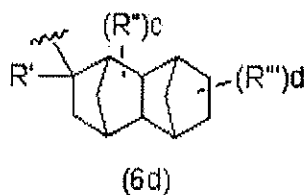
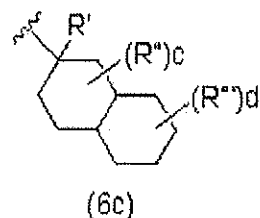
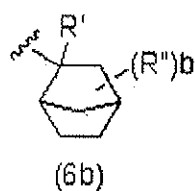
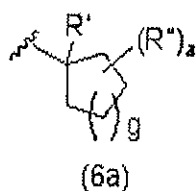
and , or a lactone group selected from the group

consisting of  and , wherein R_a, R_b,

R_c and R_d each independently represent a C₁-C₂₀ alkyl group, a C₃-C₃₀ cycloalkyl group, a (C₁-C₁₀ alkyl)cycloalkyl group, a hydroxyalkyl group, a C₁-C₂₀ alkoxy group, a (C₁-C₁₀ alkoxy)alkyl group, an acetyl group, an acetylalkyl group, a carboxyl group, a (C₁-C₁₀ alkyl)carboxyl group, a (C₃-C₁₈ cycloalkyl)carboxyl group, and a C₃-C₃₀ heterocycloalkyl group, or adjacent groups may be bonded to each other to form a saturated or unsaturated C₃-C₃₀ hydrocarbon ring or a C₂-C₃₀ heterocyclic group; R_e and R_f each independently represent a C₁-C₁₀ alkyl group or may be bonded to each other to form a saturated C₃-C₃₀ hydrocarbon ring; x represents an integer from 0 to 3; y represents an integer from 0 to 10; z₁ and w₁ each independently represent an integer from 0 to 3; z₂ and w₂ each independently represent an integer from 0 to 7; 0 ≤ z₁+w₁ ≤ 5; and 0 ≤ z₂+w₂ ≤ 5.

15. The additive for resist according to Claim 1, wherein in the formula (1), R₅ represents a group that may be selected from the group consisting of a t-butyl group, a trimethylsilyl group, a hydroxyl-2-ethyl group, a 1-methoxypropyl group, a 1-methoxy-1-methylethyl group, a 1-ethoxypropyl group, a 1-ethoxy-1-methylethyl group, a 1-

methoxy-1-ethyl group, a 1-ethoxy-1-ethyl group, a t-butoxy-2-ethyl group, a 1-isobutoxy-1-ethyl group, and groups represented by the following formulas (6a) to (6m):

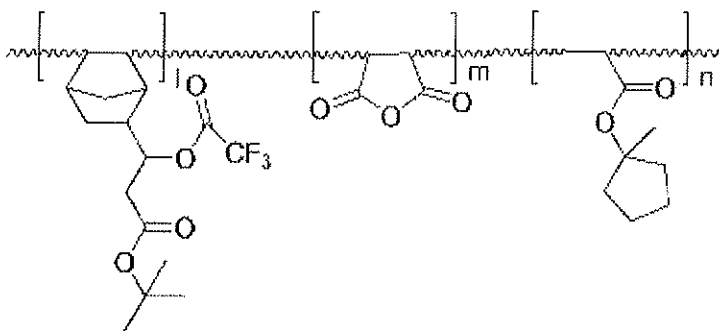


5 wherein in the formulas (6a) to (6m), R', R'' and R''' each independently represent a hydrogen atom or a C₁-C₁₀ alkyl

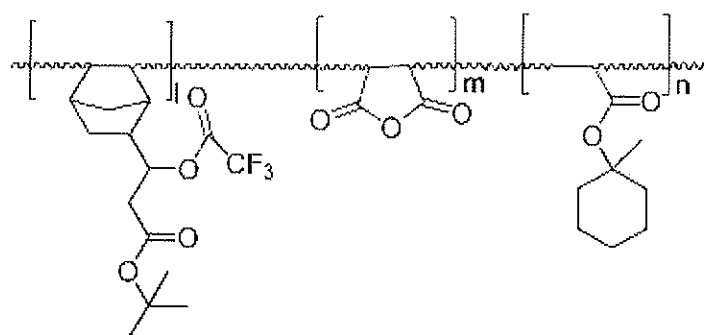
group; a and 3 each represent an integer from 0 to 15; b represents an integer from 0 to 11; c and d each independently represent an integer from 0 to 9; f represents an integer from 0 to 7; g, i and k each independently represent an integer from 0 to 6; h and j each independently represent an integer from 0 to 4; $0 \leq c+d \leq 17$; and $0 \leq c+f \leq 15$.

16. The additive for resist according to Claim 1, wherein the additive for resist is selected from the group consisting of compounds having structures represented by the following formulas (7) to (18):

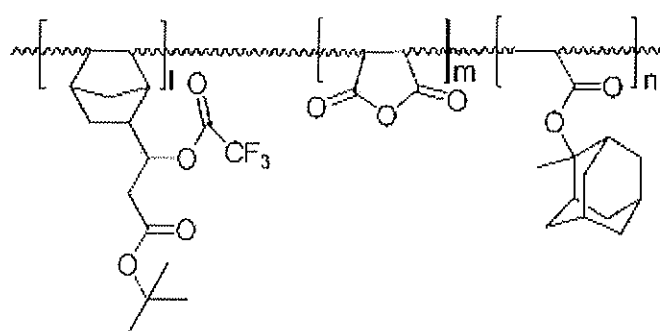
[Chemical Formula 7]



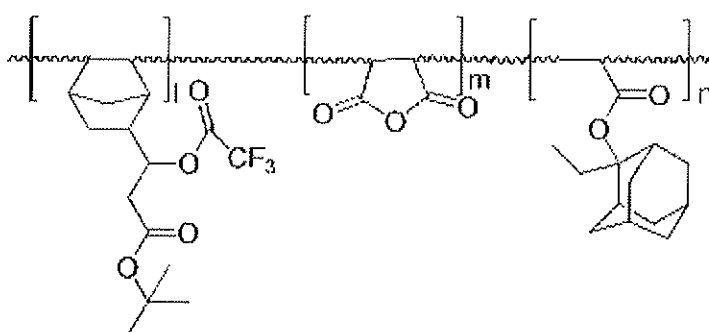
15 [Chemical Formula 8]



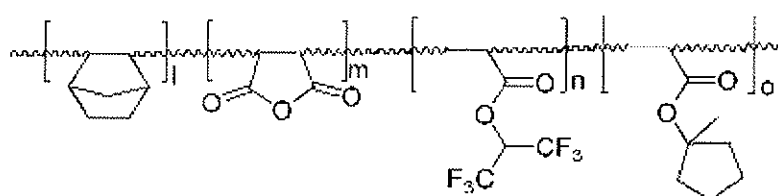
[Chemical Formula 9]



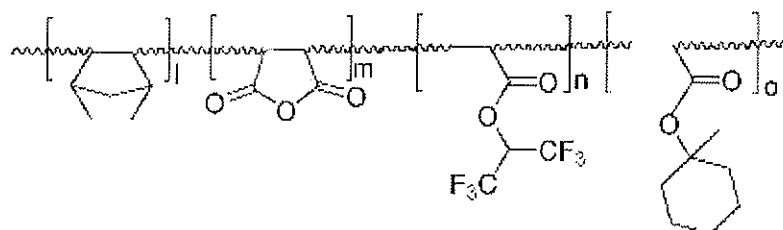
[Chemical Formula 10]



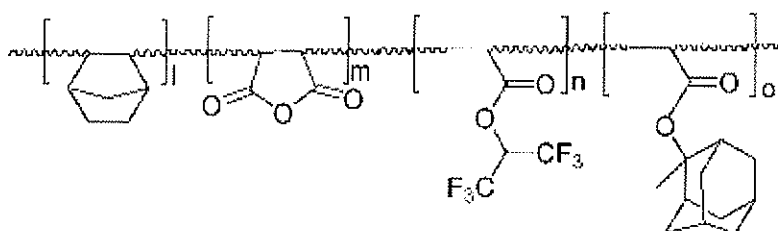
[Chemical Formula 11]



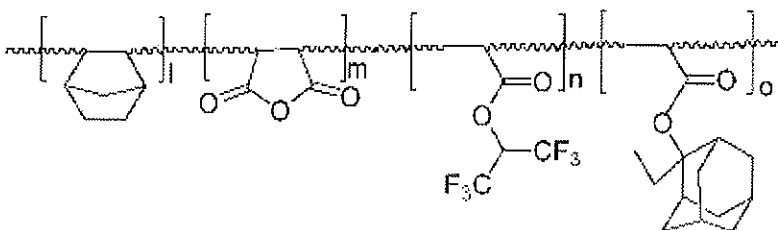
[Chemical Formula 12]



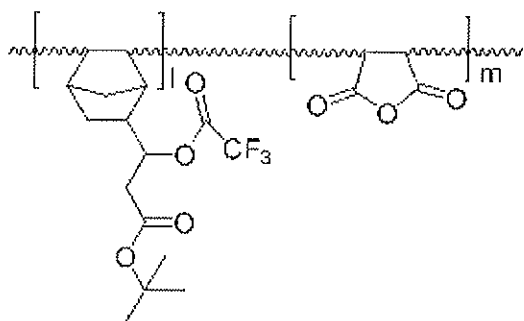
[Chemical Formula 13]



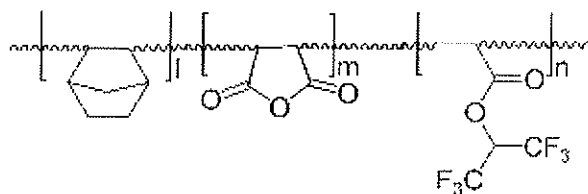
5 [Chemical Formula 14]



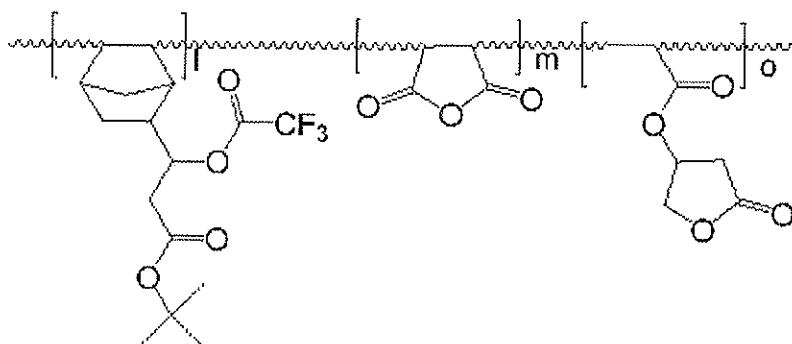
[Chemical Formula 15]



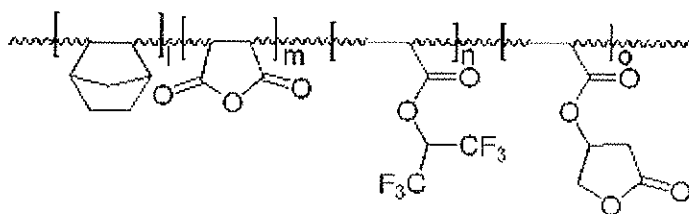
[Chemical Formula 16]



[Chemical Formula 17]



[Chemical Formula 18]



5

wherein in the formulas (7) to (18), l , m , n and o respectively represent the proportions of corresponding repeating units in the main chain, such that $l+m+n+o = 1$, while $0 < l/(l+m+n+o) < 0.9$, $0.2 < m/(l+m+n+o) < 0.9$, $0 \leq n/(l+m+n+o) < 0.9$, and $0 \leq o/(l+m+n+o) < 0.9$.

10

17. The additive for resist according to Claim 1, wherein in the formula (1), the repeating unit m is included in the copolymer of the additive for resist in an

amount of 30% to 60% by mole.

18. The additive for resist according to Claim 1,
having a weight average molecular weight as measured by
5 gel permeation chromatography and calculated relative to
polystyrene standards, of 1,000 g/mol to 50,000 g/mol.

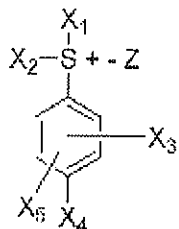
19. The additive for resist according to Claim 1,
wherein the ratio of the weight average molecular weight
10 and the number average molecular weight of the additive
for resist is 1 to 5.

20. A resist composition comprising the additive for
resist according to any one of Claims 1 to 19, a base
15 polymer for resist, an acid generator, and a solvent.

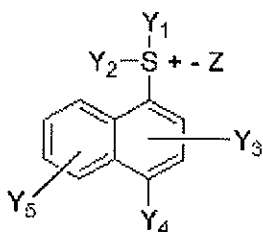
21. The resist composition according to Claim 20,
wherein the additive for resist is incorporated in an
amount of 0.05% to 5% by weight relative to the total
20 weight of the resist composition.

22. The resist composition according to Claim 20,
wherein the acid generator is one or more compounds
selected from the group consisting of compounds
25 represented by the following formulas (22) and (23):

[Chemical Formula 22]



[Chemical Formula 23]



5 wherein in the formulas (22) and (23),

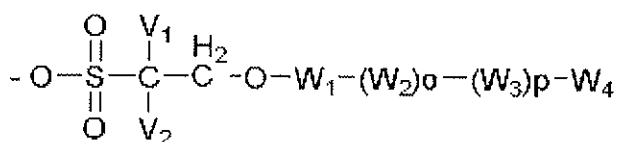
X₁, X₂, Y₁ and Y₂ each independently represent any one selected from the group consisting of a C₁-C₁₀ alkyl group, an allyl group, a perfluoroalkyl group, a benzyl group, a C₆-C₃₀ aryl group, and combinations thereof; X₁ with X₂, and
 10 Y₁ with Y₂ may be bonded to each other to form a saturated or unsaturated hydrocarbon ring having 3 to 30 carbon atoms;

X₃, X₄, X₅, Y₃, Y₄ and Y₅ each independently represent any one selected from the group consisting of a hydrogen
 15 atom, a C₁-C₃₀ alkyl group, a halogen atom, a C₁-C₃₀ alkoxy group, a C₆-C₃₀ aryl group, a thiophenoxy group, a C₁-C₃₀ thioalkoxy group, a C₁-C₂₀ alkoxycarbonylmethoxy group, and combinations thereof; and

Z of the anionic moiety represents OSO₂CF₃, OSO₂C₄F₉,

OSO₂C₈F₁₇, N(CF₃)₂, N(C₂F₅)₂, N(C₄F₉)₂, C(CF₃)₃, C(C₂F₅)₃, C(C₄F₉)₃,
 or a functional group represented by the following formula
 (24):

[Chemical Formula 24]



5

wherein in the formula (24),

V₁ and V₂ each independently represent a halogen atom;

W₁ represents -(C=O)- or -(SO₂)-;

W₂ represents a C₁-C₁₀ alkanediyl group;

10

W₃ represents any one selected from the group
 consisting of a C₃-C₃₀ cycloalkyl group, a C₆-C₃₀ aryl group,
 a C₇-C₃₀ aralkyl group, a C₆-C₃₀ aryloxy group, a C₆-C₃₀
 arylthio group, and a C₅-C₃₀ heterocyclic group;

15

W₄ represents any one selected from group consisting
 of a hydrogen atom, a halogen atom, a C₁-C₁₀ alkyl group, a
 C₁-C₁₀ alkoxy group, a C₁-C₁₀ haloalkyl group, a C₁-C₁₀
 alkylthio group, a C₆-C₃₀ aryl group, and combinations
 thereof;

o represents an integer of 0 or 1; and

20

p represents an integer from 0 to 2.

23. The resist composition according to Claim 20,
 wherein the acid generator is incorporated into the resist

composition in an amount of 0.3 parts to 10 parts by weight relative to 100 parts of the total solids content in the resist composition.

5 24. The resist composition according to Claim 20, further comprising an additive selected from the group consisting of an alkali dissolution suppressing agent, an acid diffusion suppressing agent, a surfactant, and mixtures thereof.

10

 25. A method for forming a resist pattern, the method comprising:

 applying the resist composition according to Claim 20 on a substrate and thereby forming a resist film;

15 heat treating the resist film, and then exposing the resist film in a predetermined pattern; and
 developing the exposed resist pattern.

 26. The method for forming a resist pattern
20 according to Claim 25, wherein the exposure is carried out by using a light source selected from the group consisting of a KrF excimer laser, an ArF excimer laser, an extreme ultraviolet radiation, X-radiation, and an electron beam.