Patent Literature

[0007]

Patent Literature 1: JP 2015-111264 A

Summary

Technical Problem

[0008]

However, when a pigment or the like as a coloring agent is contained in order to give the light blocking capability to the photosensitive resin composition, as the content of the pigment is increased, ultraviolet ray or the like at the time of pattern exposure is blocked, so that sensitivity upon exposure decreases. Accordingly, none of the conventionally known photosensitive resin compositions containing pigments have required characteristics to serve as a material for forming a pixel dividing layer of an organic EL display device. Specifically, these photosensitive resin compositions lacked in sensitivity, heat resistance, or light blocking capability.

[0009]

In addition, when a pigment is contained in the photosensitive resin composition in order to improve the light blocking capability, the pigment is peeled off from a cured portion during alkali development, so that development residues caused by the pigment remain in an

opening. Further, as the content of the pigment is increased, the development residues caused by the pigment also increase, and therefore, there has been a problem that it is difficult to achieve the light blocking capability and at the same time suppress the development residues.

[0010]

Furthermore, the development residues caused by the pigment have also been a problem that they cause defects of an organic EL light emitting element, such as generation of dark spots in a light emitting region when the organic EL light emitting element is formed.

[0011]

Thus, an object of the present disclosure is to obtain a negative-type photosensitive resin composition having high sensitivity, capable of obtaining a cured film excellent in heat resistance and light blocking capability, and capable of suppressing generation of development residues caused by a pigment.

Solution to Problem

[0012]

A negative-type photosensitive resin composition according to the present disclosure is a negative-type photosensitive resin composition containing an alkali-soluble resin (A), a radical-polymerizable compound (B), a

photopolymerization initiator (C1), and a pigment (D1).

In this resin composition, the radical-polymerizable compound (B) contains a flexible chain-containing radical-polymerizable compound (B1),

the flexible chain-containing radical-polymerizable compound (B1) contains a compound having (I) a structure derived from a compound having at least three hydroxyl groups in the molecule, (II) at least three ethylenically unsaturated double bond groups, and (III) at least one aliphatic chain,

the aliphatic chain has an average molecular weight of 40 to 500, and

the content of the pigment (D1) is 5 to 70 mass% of the total solid content.

[0012a]

In an aspect, there is provided a negative-type photosensitive resin composition comprising: an alkali-soluble resin (A); a radical-polymerizable compound (B); a photopolymerization initiator (C1); and a pigment (D1),

wherein the radical-polymerizable compound (B) includes a flexible chain-containing radical-polymerizable compound (B1),

the flexible chain-containing radical-polymerizable compound (B1) includes a compound having (I) a structure derived from a compound having at least three hydroxyl

groups in the molecule, (II) at least three ethylenically unsaturated double bond groups, and (III) at least one aliphatic chain,

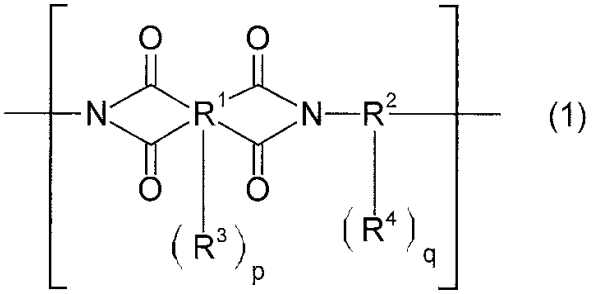
the aliphatic chain has an average molecular weight of 40 to 500,

the content of the pigment (D1) is 5 to 70 mass% of the total solid content,

the alkali-soluble resin (A) includes a first resin (A1),

the first resin (A1) includes at least one selected from the group consisting of a polyimide (A1-1), a polyimide precursor (A1-2), polybenzoxazole (A1-3), and a polybenzoxazole precursor (A1-4), and

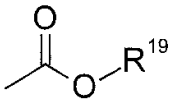
the polyimide (A1-1) contains a structural unit as represented by the following general formula (1):

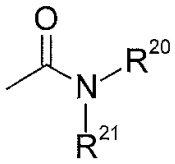


(1)

wherein, in general formula (1), R^1 is a tetravalent to decavalent organic group, and R^2 is a divalent to decavalent organic group, R^3 and R^4 are independently a phenolic hydroxyl group, a sulfonic acid group, a mercapto group, or a substituent group as represented by general

formula (5) or general formula (6), p is an integer of 0 to 6 and q is an integer of 0 to 8,


(5)


(6)

wherein, in general formula (5), R^{19} is an alkyl group containing 1 to 10 carbon atoms, an acyl group containing 2 to 6 carbon atoms, or an aryl group containing 6 to 15 carbon atoms and in general formula (6), R^{20} and R^{21} each independently denote a hydrogen atom, an alkyl group containing 1 to 10 carbon atoms, an acyl group containing 2 to 6 carbon atoms, or an aryl group containing 6 to 15 carbon atoms.

[0012b]

In another aspect, there is provided a negative-type photosensitive resin composition comprising: an alkali-soluble resin (A); a radical-polymerizable compound (B); a photopolymerization initiator (C1); and a pigment (D1),

wherein the radical-polymerizable compound (B) includes a flexible chain-containing radical-polymerizable compound (B1),

the flexible chain-containing radical-polymerizable compound (B1) includes a compound having (I) a structure derived from a compound having at least three hydroxyl

groups in the molecule, (II) at least three ethylenically unsaturated double bond groups, and (III) at least one aliphatic chain,

the aliphatic chain has an average molecular weight of 40 to 500,

the content of the pigment (D1) is 5 to 70 mass% of the total solid content,

the pigment (D1) includes a black organic pigment (D1a-1),

the black organic pigment (D1a-1) includes one or more selected from the group consisting of a benzofuranone based black pigment (D1a-1a), a perylene based black pigment (D1a-1b), and an azo based black pigment (D1a-1c),

the alkali-soluble resin (A) includes a first resin (A1), and

the first resin (A1) includes at least one selected from the group consisting of a polyimide (A1-1), a polyimide precursor (A1-2), polybenzoxazole (A1-3), and a polybenzoxazole precursor (A1-4).

[0012c]

In another aspect, there is provided a negative-type photosensitive resin composition comprising: an alkali-soluble resin (A); a radical-polymerizable compound (B); a photopolymerization initiator (C1); and a pigment (D1),

wherein the content of the pigment (D1) is 5 to 70

mass% of the total solid content,

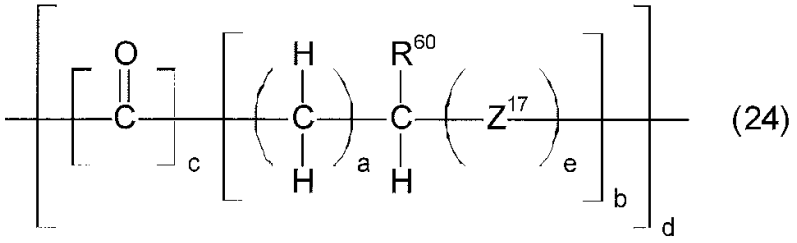
the pigment (D1) includes, as a black organic pigment (D1a-1), one or more selected from the group consisting of a benzofuranone based black pigment (D1a-1a), a perylene based black pigment (D1a-1b), and an azo based black pigment (D1a-1c),

the radical-polymerizable compound (B) includes a flexible chain-containing radical-polymerizable compound (B1),

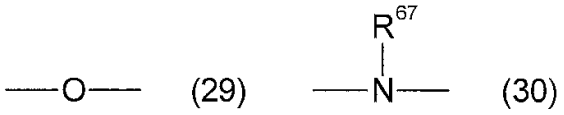
the flexible chain-containing radical-polymerizable compound (B1) includes a compound having (I) a structure derived from a compound having at least three hydroxyl groups in the molecule, (II) at least three ethylenically unsaturated double bond groups, and (III) at least one aliphatic chain,

the aliphatic chain has an average molecular weight of 40 to 500, and

the flexible chain-containing radical-polymerizable compound (B1) includes a compound having a group represented by general formula (24):



(24)



(29) (30)

wherein, in general formula (24), R^{60} is a hydrogen atom or an alkyl group containing 1 to 10 carbon atoms, Z^{17} represents a group represented by general formula (29) or a group represented by general formula (30), a is an integer of 1 to 10, b is an integer of 1 to 4, c is 0 or 1, d is an integer of 1 to 4, and e is 0 or 1, when c is 0, d is 1, in general formula (30), R^{67} is a hydrogen atom or an alkyl group containing 1 to 10 carbon atoms.

[0012d]

In another aspect, there is provided a cured film formed by curing a negative-type photosensitive resin composition as defined above.

[0012e]

In another aspect, there is provided an organic EL display device comprising the cured film as defined above.

[0012f]

In another aspect, there is provided a production method for the organic EL display device, comprising:

(1) a step for forming a coating film of the negative-type photosensitive resin composition as defined above on a substrate;

(2) a step for applying active actinic ray to the coating film of the negative-type photosensitive resin composition through a photomask;

(3) a step for developing it with an alkaline solution to form a pattern of the negative-type photosensitive resin composition; and

(4) a step for heating the pattern to produce a cured pattern of the negative-type photosensitive resin composition

Advantageous Effects

[0013]

According to the negative-type photosensitive resin composition according to the present disclosure, it is possible to obtain a cured film suppressing generation of development residues caused by a pigment and having high sensitivity and excellent heat resistance and light blocking capability.

Brief Description of Drawings

CLAIMS

1. A negative-type photosensitive resin composition comprising: an alkali-soluble resin (A); a radical-polymerizable compound (B); a photopolymerization initiator (C1); and a pigment (D1),

wherein the radical-polymerizable compound (B) includes a flexible chain-containing radical-polymerizable compound (B1),

the flexible chain-containing radical-polymerizable compound (B1) includes a compound having (I) a structure derived from a compound having at least three hydroxyl groups in the molecule, (II) at least three ethylenically unsaturated double bond groups, and (III) at least one aliphatic chain,

the aliphatic chain has an average molecular weight of 40 to 500,

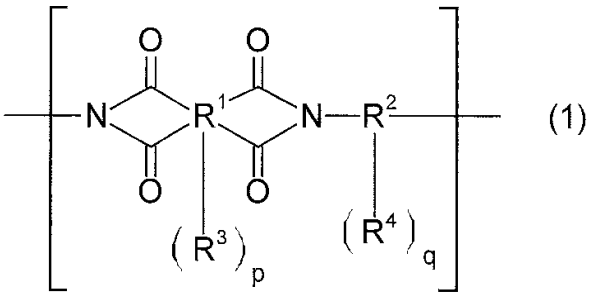
the content of the pigment (D1) is 5 to 70 mass% of the total solid content,

the alkali-soluble resin (A) includes a first resin (A1),

the first resin (A1) includes at least one selected from the group consisting of a polyimide (A1-1), a polyimide precursor (A1-2), polybenzoxazole (A1-3), and a polybenzoxazole precursor (A1-4), and

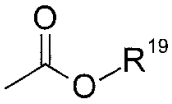
the polyimide (A1-1) contains a structural unit as

represented by the following general formula (1):

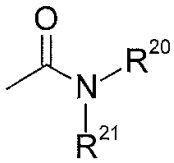


(1)

wherein, in general formula (1), R^1 is a tetravalent to decavalent organic group, and R^2 is a divalent to decavalent organic group, R^3 and R^4 are independently a phenolic hydroxyl group, a sulfonic acid group, a mercapto group, or a substituent group as represented by general formula (5) or general formula (6), p is an integer of 0 to 6 and q is an integer of 0 to 8,



(5)



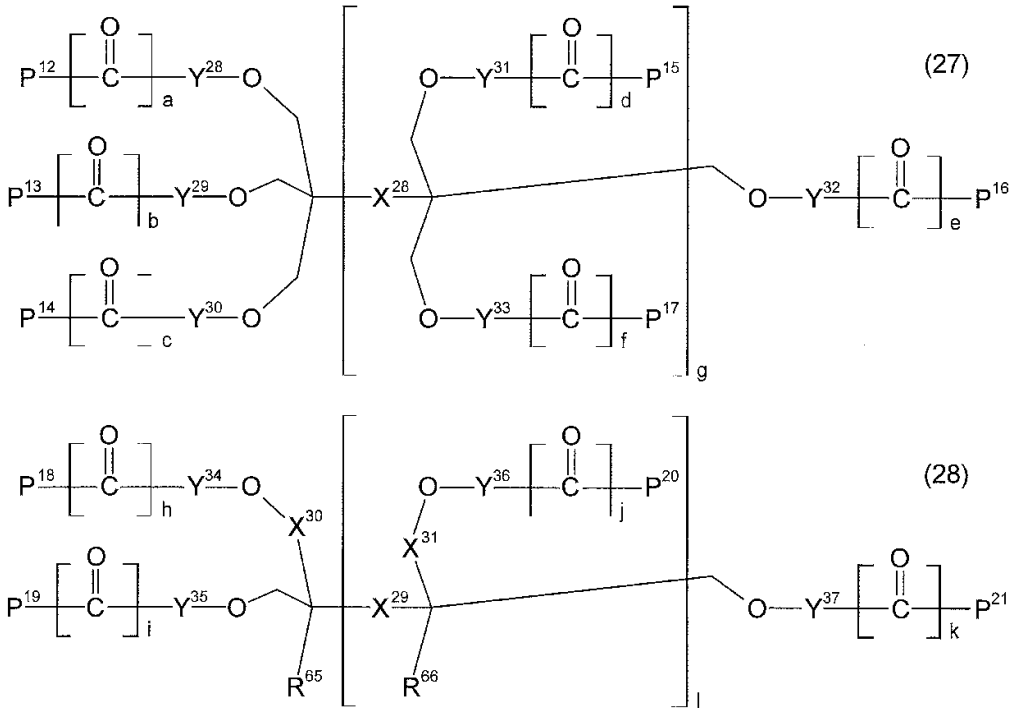
(6)

wherein, in general formula (5), R^{19} is an alkyl group containing 1 to 10 carbon atoms, an acyl group containing 2 to 6 carbon atoms, or an aryl group containing 6 to 15 carbon atoms and in general formula (6), R^{20} and R^{21} each independently denote a hydrogen atom, an alkyl group containing 1 to 10 carbon atoms, an acyl group containing 2 to 6 carbon atoms, or an aryl group containing 6 to 15 carbon atoms.

2. A negative-type photosensitive resin composition as set forth in claim 1,

wherein, as the first resin (A1), one or more selected from the group consisting of the polyimide (A1-1), the polyimide precursor (A1-2), the polybenzoxazole (A1-3), and the polybenzoxazole precursor (A1-4) contains a structural unit having a fluorine atom.

3. A negative-type photosensitive resin composition as set forth in claim 1 or 2, wherein the flexible chain-containing radical-polymerizable compound (B1) includes a compound represented by general formula (27) and/or a compound represented by general formula (28):

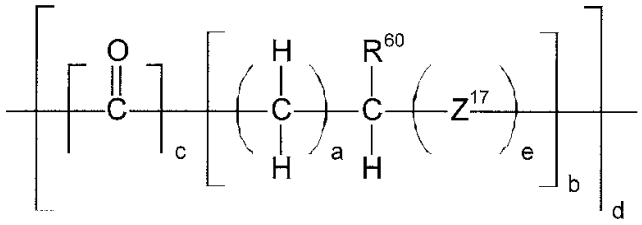
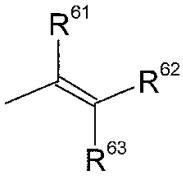


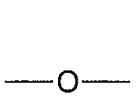
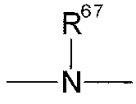
(27)

(28)

wherein, in general formula (27), X^{28} is a divalent

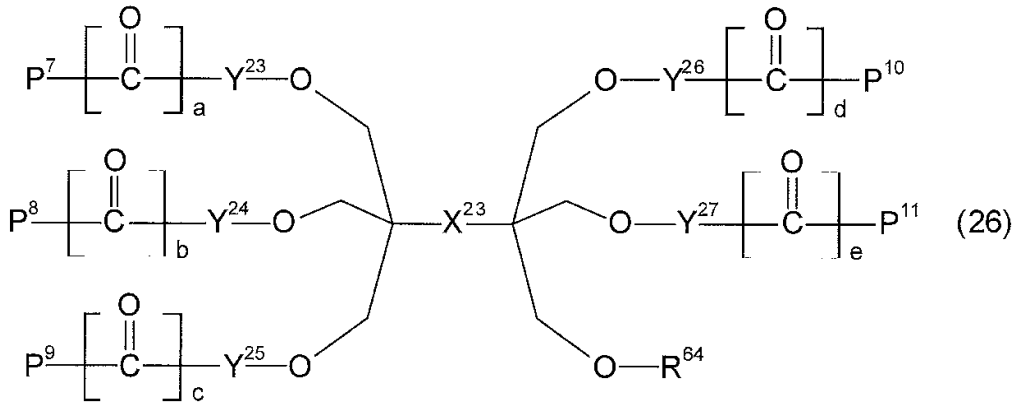
organic group; Y^{28} to Y^{33} are each independently a direct bond or a group represented by general formula (24), and at least one of Y^{28} to Y^{33} is a group represented by general formula (24); P^{12} to P^{17} are each independently a hydrogen atom or a group represented by general formula (25), and at least three of P^{12} to P^{17} are groups represented by general formula (25); a, b, c, d, e, and f are each independently 0 or 1, and g is an integer of 0 to 10; wherein, in general formula (28), X^{29} is a divalent organic group; X^{30} and X^{31} are each independently a direct bond or an alkylene chain containing 1 to 10 carbon atoms; Y^{34} to Y^{37} are each independently a direct bond or a group represented by general formula (24), and at least one of Y^{34} to Y^{37} is a group represented by general formula (24); R^{65} and R^{66} are each independently a hydrogen atom or an alkyl group containing 1 to 10 carbon atoms; P^{18} to P^{21} are each independently a hydrogen atom or a group represented by general formula (25), and at least three of P^{18} to P^{21} are groups represented by general formula (25); and h, i, j, and k are each independently 0 or 1, and l is an integer of 0 to 10:


(24)

(25)


(29)

(30)

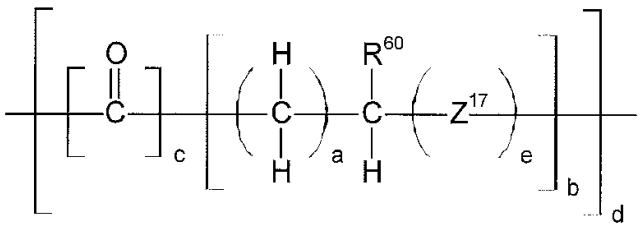
wherein, in general formula (24), R^{60} is a hydrogen atom or an alkyl group containing 1 to 10 carbon atoms; Z^{17} represents a group represented by general formula (29) or a group represented by general formula (30); a is an integer of 1 to 10, b is an integer of 1 to 4, c is 0 or 1, d is an integer of 1 to 4, and e is 0 or 1; when c is 0, d is 1; wherein, in general formula (25), R^{61} to R^{63} are each independently a hydrogen atom, an alkyl group containing 1 to 10 carbon atoms, or an aryl group containing 6 to 15 carbon atoms; and wherein, in general formula (30), R^{67} is a hydrogen atom or an alkyl group containing 1 to 10 carbon atoms.

4. A negative-type photosensitive resin composition as set forth in any one of claims 1 to 3, wherein the flexible chain-containing radical-polymerizable compound (B1) includes a compound represented by general formula (26):

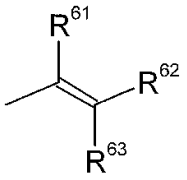


(26)

wherein, in general formula (26), X^{23} is a divalent organic group, Y^{23} to Y^{27} are each independently a direct bond or a group represented by general formula (24), and at least one of Y^{23} to Y^{27} is a group represented by general formula (24) given above, P^{7} to P^{11} are each independently a hydrogen atom or a group represented by general formula (25), and at least three of P^{7} to P^{11} are groups represented by general formula (25) given above, R^{64} is a hydrogen atom, an alkyl group containing 1 to 10 carbon atoms, or an aryl group containing 6 to 15 carbon atoms, and a, b, c, d, and e are each independently 0 or 1:



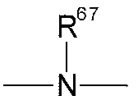
(24)



(25)



(29)



(30)

wherein, in general formula (24), R^{60} is a hydrogen atom or an alkyl group containing 1 to 10 carbon atoms; Z^{17} represents a group represented by general formula (29) or a group represented by general formula (30); a is an integer of 1 to 10, b is an integer of 1 to 4, c is 0 or 1, d is an integer of 1 to 4, and e is 0 or 1; when c is 0, d is 1; wherein, in general formula (25), R^{61} to R^{63} are each independently a hydrogen atom, an alkyl group containing 1 to 10 carbon atoms, or an aryl group containing 6 to 15 carbon atoms; and wherein, in general formula (30), R^{67} is a hydrogen atom or an alkyl group containing 1 to 10 carbon atoms.

5. A negative-type photosensitive resin composition as set forth in any one of claims 1 to 4, wherein the flexible chain-containing radical-polymerizable compound (B1) has at least one lactone-modified chain and/or at least one lactam-modified chain.

6. A negative-type photosensitive resin composition as set forth in any one of claims 1 to 5,

wherein the radical-polymerizable compound (B) further includes a flexible chain-containing bifunctional radical-polymerizable compound (B2),

the flexible chain-containing bifunctional radical-polymerizable compound (B2) includes a compound having (I) a structure derived from a compound having at least two

hydroxyl groups in the molecule, (II) two ethylenically unsaturated double bond groups, and (III) at least one lactone-modified chain and/or lactam-modified chain, and

the average molecular weights of the lactone-modified chain and the lactam-modified chain are 40 to 500.

7. A negative-type photosensitive resin composition as set forth in any one of claims 1 to 6, wherein the pigment (D1) includes one or more selected from the group consisting of a black organic pigment (D1a-1), a black inorganic pigment (D1a-2), and a mixture of two or more color pigments (D1a-3).

8. A negative-type photosensitive resin composition as set forth in any one of claims 1 to 7, wherein the alkali-soluble resin (A) includes an alkali-soluble resin (A) that has no ethylenically unsaturated double bond group.

9. A negative-type photosensitive resin composition as set forth in any one of claims 1 to 8,

wherein the alkali-soluble resin (A) further comprises a second resin (A2), and

the second resin (A2) includes one or more selected from the group consisting of polysiloxane (A2-1), polycyclic side chain-containing resin (A2-2), acrylic resin (A2-3), and acid-modified epoxy resin (A2-4).

10. A negative-type photosensitive resin composition as set forth in any one of claims 1 to 9, wherein the flexible

chain-containing radical-polymerizable compound (B1) accounts for 10 to 50 parts by mass, relative to the total quantity of the alkali-soluble resin (A) and the radical-polymerizable compound (B) which accounts for 100 parts by mass.

11. A negative-type photosensitive resin composition as set forth in any one of claims 7 to 10, wherein the pigment (D1) includes the black organic pigment (D1a-1), and the black organic pigment (D1a-1) includes one or more selected from the group consisting of a benzofuranone based black pigment (D1a-1a), a perylene based black pigment (D1a-1b), and an azo based black pigment (D1a-1c).

12. A negative-type photosensitive resin composition as set forth in claims 7 to 11,

wherein the black organic pigment (D1a-1) further includes a covering layer (DC), and

the covering layer (DC) includes one or more selected from the group consisting of a silica covering layer (DC-1), a metal oxide covering layer (DC-2), and a metal hydroxide covering layer (DC-3).

13. A negative-type photosensitive resin composition comprising: an alkali-soluble resin (A); a radical-polymerizable compound (B); a photopolymerization initiator (C1); and a pigment (D1),

wherein the radical-polymerizable compound (B)

includes a flexible chain-containing radical-polymerizable compound (B1),

the flexible chain-containing radical-polymerizable compound (B1) includes a compound having (I) a structure derived from a compound having at least three hydroxyl groups in the molecule, (II) at least three ethylenically unsaturated double bond groups, and (III) at least one aliphatic chain,

the aliphatic chain has an average molecular weight of 40 to 500,

the content of the pigment (D1) is 5 to 70 mass% of the total solid content,

the pigment (D1) includes a black organic pigment (D1a-1),

the black organic pigment (D1a-1) includes one or more selected from the group consisting of a benzofuranone based black pigment (D1a-1a), a perylene based black pigment (D1a-1b), and an azo based black pigment (D1a-1c),

the alkali-soluble resin (A) includes a first resin (A1), and

the first resin (A1) includes at least one selected from the group consisting of a polyimide (A1-1), a polyimide precursor (A1-2), polybenzoxazole (A1-3), and a polybenzoxazole precursor (A1-4).

14. A negative-type photosensitive resin composition

comprising: an alkali-soluble resin (A); a radical-polymerizable compound (B); a photopolymerization initiator (C1); and a pigment (D1),

wherein the content of the pigment (D1) is 5 to 70 mass% of the total solid content,

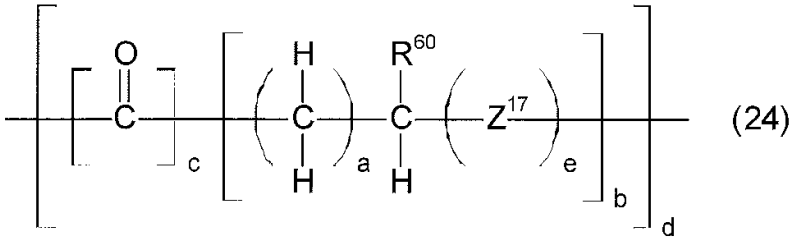
the pigment (D1) includes, as a black organic pigment (D1a-1), one or more selected from the group consisting of a benzofuranone based black pigment (D1a-1a), a perylene based black pigment (D1a-1b), and an azo based black pigment (D1a-1c),

the radical-polymerizable compound (B) includes a flexible chain-containing radical-polymerizable compound (B1),

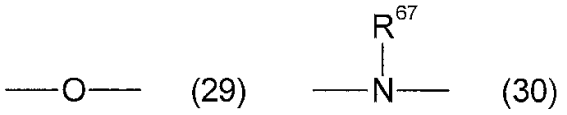
the flexible chain-containing radical-polymerizable compound (B1) includes a compound having (I) a structure derived from a compound having at least three hydroxyl groups in the molecule, (II) at least three ethylenically unsaturated double bond groups, and (III) at least one aliphatic chain,

the aliphatic chain has an average molecular weight of 40 to 500, and

the flexible chain-containing radical-polymerizable compound (B1) includes a compound having a group represented by general formula (24):



(24)



(29) (30)

wherein, in general formula (24), R^{60} is a hydrogen atom or an alkyl group containing 1 to 10 carbon atoms, Z^{17} represents a group represented by general formula (29) or a group represented by general formula (30), a is an integer of 1 to 10, b is an integer of 1 to 4, c is 0 or 1, d is an integer of 1 to 4, and e is 0 or 1, when c is 0, d is 1, in general formula (30), R^{67} is a hydrogen atom or an alkyl group containing 1 to 10 carbon atoms.

15. A negative-type photosensitive resin composition as set forth in claims 13 or 14,

wherein the radical-polymerizable compound (B) further includes a flexible chain-containing bifunctional radical-polymerizable compound (B2),

the flexible chain-containing bifunctional radical-polymerizable compound (B2) includes a compound having (I) a structure derived from a compound having at least two hydroxyl groups in the molecule, (II) two ethylenically unsaturated double bond groups, and (III) at least one

lactone-modified chain and/or lactam-modified chain, and

the average molecular weights of the lactone-modified chain and the lactam-modified chain are 40 to 500.

16. A negative-type photosensitive resin composition as set forth in any one of claims 13 to 15, wherein the black organic pigment (D1a-1) includes a benzofuranone based black pigment (D1a-1a).

17. A cured film formed by curing a negative-type photosensitive resin composition as set forth in any one of claims 1 to 16.

18. An organic EL display device comprising the cured film as set forth in claim 17.

19. A production method for the organic EL display device, comprising:

(1) a step for forming a coating film of the negative-type photosensitive resin composition as set forth in any one of claims 1 to 16 on a substrate;

(2) a step for applying active actinic ray to the coating film of the negative-type photosensitive resin composition through a photomask;

(3) a step for developing it with an alkaline solution to form a pattern of the negative-type photosensitive resin composition; and

(4) a step for heating the pattern to produce a cured pattern of the negative-type photosensitive resin

composition.