

DESCRIPTION

RADIATION SENSITIVE COMPOSITION FOR BLACK RESIST

5 Technical Field

The present invention relates to a radiation sensitive composition for a black resist which is suitable for use in a black matrix and/or spacer for a color filter used in a color liquid crystal display or the like.

10 Background Art

Heretofore, in order to produce a black matrix or spacer for a color filter by use of a black radiation sensitive composition, the radiation sensitive composition in which a black colorant is dispersed is coated on a substrate and
15 then dried, and the resulting coating film is irradiated (hereinafter referred to as "exposed") with radiation via a photomask so as to develop the film, thereby forming a desired pattern.

However, such a black radiation sensitive composition
20 requires use of a substantial amount of the black colorant so as to enhance light shielding properties of the black matrix or spacer to a sufficient degree, and since the exposed radiation is absorbed by the colorant, there naturally occurs a phenomenon that effective intensity of the radiation in
25 the coating film gradually decreases from the surface toward the bottom of the coating film (i.e., toward the vicinity of the surface of the substrate). As a result, a degree of insufficiency of proceeding of a curing reaction in the coating film is liable to gradually increase from the surface
30 toward the bottom, thereby causing such problems that the developed pattern may partially peel off or lost due to low adhesion of the formed pattern to the substrate and that the developed pattern shows poor physical properties of the coating film after heat treated. Further, the conventional

black radiation sensitive composition also has a problem that residues and scums are liable to occur in unexposed portions on the substrate. In addition, the black radiation sensitive composition also has a problem that when an obtained color
5 filter is assembled into a display panel, display defects such as sticking are liable to occur.

Problems to be solved by the Invention

An object of the present invention is to provide a radiation sensitive composition for a black resist which,
10 particularly when assembled into a display panel, does not cause display defects such as sticking, has a high degree of film hardness, provides a very smooth pattern surface, hardly causes residues and scums in unexposed portions on a substrate, and provides a pattern which shows excellent
15 adhesion to the substrate at the time of development.

Means for solving the Problems

Firstly, the present invention comprises a radiation sensitive composition for a black resist (hereinafter also referred to as "first invention") which comprises (A) a
20 colorant containing a black pigment, (B) an alkali soluble resin, (C) a multifunctional monomer and (D) a photopolymerization initiator, wherein the colorant (A) is dispersed by a dispersant containing a compound having an urethane bond.

25 Secondly, the present invention comprises the radiation sensitive composition for a black resist (hereinafter also referred to as "second invention") of the first invention, wherein the compound having an urethane bond which is a dispersant comprises a compound which becomes
30 insoluble in a polar solvent after heat treated at a temperature of not lower than 150°C for at least 30 minutes.

Thirdly, the present invention comprises the radiation sensitive composition for a black resist (hereinafter also referred to as "third invention") of the first or second

invention, wherein the compound having an urethane bond which is a dispersant comprises a compound which has an acid value of 5 to 25 mgKOH/g and an amine value of 0 mgKOH/g.

Fourthly, the present invention comprises the
5 radiation sensitive composition for a black resist (hereinafter also referred to as "fourth invention") of the first or second invention, wherein the compound having an urethane bond which is a dispersant comprises a compound which has an amine value of 5 to 25 mgKOH/g and an acid value of
10 0 mgKOH/g.

Fifthly, the present invention comprises the radiation sensitive composition for a black resist (hereinafter also referred to as "fifth invention") of the first, second, third or fourth invention, wherein the compound having an urethane
15 bond which is a dispersant comprises a compound which has a voltage retention of not lower than 80%.

Sixthly, the present invention comprises the radiation sensitive composition for a black resist (hereinafter also referred to as "sixth invention") of the first, second, third,
20 fourth or fifth invention, wherein the colorant (A) contains C.I. PIGMENT RED 177 and C.I. PIGMENT BLUE 15:4 and/or C.I. PIGMENT BLUE 15:6.

The term "radiation" used herein refers to a visible radiation, an ultraviolet radiation, a far ultraviolet
25 radiation, an electron beam, an X radiation or the like.

Hereinafter, the present invention will be described in detail.

(A) Colorant

A colorant in the present invention comprises a
30 colorant containing a black pigment.

The black pigment can be selected as appropriate according to use of a color filter and may be an inorganic or organic pigment or may be one or a mixture of two or more of these inorganic and organic pigments. The black pigment

in the present invention is preferably a pigment having high color developability and heat resistance, particularly a pigment having high thermal decomposition resistance, particularly preferably carbon black and/or a combination
5 of two or more organic pigments.

Illustrative examples of the carbon black used in the present invention include furnace black such as SAF, SAF-HS, ISAF, ISAF-LS, ISAF-HS, HAF, HAF-LS, HAF-HS, NAF, FEF, FEF-HS, SRF, SRF-LM, SRF-LS, GPF, ECF, N-339 and N-351; thermal black
10 such as FT and MT; and acetylene black.

These carbon blacks can be used solely or in admixture of two or more.

Further, illustrative examples of black inorganic pigments other than the carbon black which are used in the
15 present invention include metal oxides such as a black titanium oxide, a Cu-Fe-Mn oxide and a synthetic black iron oxide.

These inorganic pigments can be used solely or in admixture of two or more.

20 Further, illustrative examples of the organic pigments used in the present invention include compounds classified as pigments according to the Color Index (C.I.: published by The Society of Dyers and Colourists). Specific examples thereof include those provided with color index (C.I.)
25 numbers as set forth below, i.e., C.I. PIGMENT YELLOW 12, C.I. PIGMENT YELLOW 13, C.I. PIGMENT YELLOW 14, C.I. PIGMENT YELLOW 17, C.I. PIGMENT YELLOW 20, C.I. PIGMENT YELLOW 24, C.I. PIGMENT YELLOW 31, C.I. PIGMENT YELLOW 55, C.I. PIGMENT YELLOW 83, C.I. PIGMENT YELLOW 93, C.I. PIGMENT YELLOW 109,
30 C.I. PIGMENT YELLOW 110, C.I. PIGMENT YELLOW 138, C.I. PIGMENT YELLOW 139, C.I. PIGMENT YELLOW 150, C.I. PIGMENT YELLOW 153, C.I. PIGMENT YELLOW 154, C.I. PIGMENT YELLOW 155, C.I. PIGMENT YELLOW 166, and C.I. PIGMENT YELLOW 168;
C.I. PIGMENT ORANGE 36, C.I. PIGMENT ORANGE 43, C.I. PIGMENT

ORANGE 51, C.I. PIGMENT ORANGE 61, and C.I. PIGMENT ORANGE 71;

C.I. PIGMENT RED 9, C.I. PIGMENT RED 97, C.I. PIGMENT RED 122, C.I. PIGMENT RED 123, C.I. PIGMENT RED 149, C.I. PIGMENT
5 RED 168, C.I. PIGMENT RED 176, C.I. PIGMENT RED 177, C.I. PIGMENT RED 180, C.I. PIGMENT RED 209, C.I. PIGMENT RED 215, C.I. PIGMENT RED 224, C.I. PIGMENT RED 242, and C.I. PIGMENT RED 254;

C.I. PIGMENT VIOLET 19, PIGMENT VIOLET 23, and PIGMENT VIOLET
10 29;

C.I. PIGMENT BLUE 15, C.I. PIGMENT BLUE 60, C.I. PIGMENT BLUE 15:3, C.I. PIGMENT BLUE 15:4, and C.I. PIGMENT BLUE 15:6;
C.I. PIGMENT GREEN 7, and C.I. PIGMENT GREEN 36;
C.I. PIGMENT BROWN 23, and C.I. PIGMENT BROWN 25; and
15 C.I. PIGMENT BLACK 1, and C.I. PIGMENT BLACK 7.

These organic pigments can be selected for use as appropriate so as to obtain a desired hue as a black resist.

In the present invention, a particularly preferable organic pigment is a mixture of C.I. PIGMENT RED 177 and C.I.
20 PIGMENT BLUE 15:4 and/or C.I. PIGMENT BLUE 15:6.

Further, an extender may be added to the colorant in the present invention as required. Illustrative examples of such an extender include barium sulfate, barium carbonate, calcium carbonate, silica, basic magnesium carbonate,
25 alumina white, gloss white, satin white, and hydrotalcite.

These extenders may be used solely or in admixture of two or more.

The extender is used in an amount of generally 0 to 100 parts by weight, preferably 5 to 50 parts by weight, more
30 preferably 10 to 40 parts by weight, based on 100 parts by weight of the black pigment.

In the present invention, the black pigment and the extender, in some cases, can be used with their surfaces modified by a polymer.

- Compound having an urethane bond which is a dispersant -

The colorant in the present invention is dispersed by a dispersant (hereinafter referred to as "compound having an urethane bond which is a dispersant") containing a compound
5 having an urethane bond.

The urethane bond is generally represented by a formula $R-NH-COO-R'$ (wherein R and R' each represent an aliphatic, alicyclic or aromatic monovalent or polyvalent organic group, and the polyvalent organic group is bonded to a group having
10 an urethane bond or a group other than the group having an urethane bond), can be present in a lipophilic group and/or a hydrophilic group in the compound having an urethane bond which is a dispersant, and can be present in a main chain and/or a side chain of the compound having an urethane bond
15 which is a dispersant. One or more urethane bonds can be present in the compound having an urethane bond which is a dispersant. When two or more urethane bonds are present in the compound having an urethane bond which is a dispersant, the urethane bonds may be the same or different.

20 Such a compound having an urethane bond which is a dispersant may be, for example, a cationic dispersant, an anionic dispersant, a nonionic dispersant or an ampholytic dispersant. Further, it may also take such a structure as of a silicone-based dispersant or a fluorine-based
25 dispersant.

The compound having an urethane bond which is a dispersant can be characterized by any one or more of the following properties, i.e., whether it can be insolubilized by heat treatment, an acid value, an amine value and voltage
30 retention.

As the compound having an urethane bond which is a dispersant, a dispersant which becomes insoluble in a polar solvent such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone or

γ -butyrolactone after heat treated at a temperature of not lower than 150°C, preferably 150 to 250°C, for at least 30 minutes, preferably for 30 to 90 minutes, is desirable.

Further, as the compound having an urethane bond which
5 is a dispersant, a dispersant having an acid value of 5 to 25 mgKOH/g, preferably 8 to 20 mgKOH/g, and an amine value of 0 mgKOH/g or a dispersant having an amine value of 5 to 25 mgKOH/g, preferably 8 to 20 mgKOH/g, and an acid value of 0 mgKOH/g is desirable.

10 Further, as the compound having an urethane bond which is a dispersant, a dispersant having a voltage retention of not lower than 80%, preferably not lower than 85%, is desirable. In this case, the voltage retention is measured, with a retention time of 16.7 msec, on a liquid crystal cell
15 assembled by use of a substrate obtained by applying a solution to a surface of the substrate, the solution having been prepared by dissolving 1 wt% of the compound having an urethane bond which is a dispersant in a mixture of constituents, excluding a colorant, of the radiation
20 sensitive composition of the present invention, the surface of the substrate having an indium oxide (ITO) film formed thereon; drying the applied solution so as to form a coating film; irradiating the coating film with a radiation; and post-baking the resulting substrate at a temperature of about
25 200 to 250°C.

Illustrative examples of such a compound having an urethane bond which is a dispersant include reaction products of a diisocyanate and/or a triisocyanate and a polyester having a hydroxyl group at one end and/or a polyester having
30 a hydroxyl group at both ends.

Illustrative examples of the diisocyanate include aromatic diisocyanates such as benzene diisocyanates, e.g., benzene-1,3-diisocyanate and benzene-1,4-diisocyanate; toluene diisocyanates, e.g., toluene-2,4-diisocyanate,

toluene-2,5-diisocyanate, toluene-2,6-diisocyanate and toluene-3,5-diisocyanate; and xylene diisocyanates, e.g., 1,2-xylene-3,5-diisocyanate, 1,2-xylene-3,6-diisocyanate, 1,2-xylene-4,6-diisocyanate, 1,3-xylene-2,4-diisocyanate, 1,3-xylene-2,5-diisocyanate, 1,3-xylene-2,6-diisocyanate, 1,3-xylene-4,6-diisocyanate, 1,4-xylene-2,5-diisocyanate, and 1,4-xylene-2,6-diisocyanate. Meanwhile, illustrative examples of the triisocyanate include aromatic triisocyanates such as benzene triisocyanates, e.g., benzene-1,2,4-triisocyanate, benzene-1,2,5-triisocyanate, and benzene-1,3,5-triisocyanate; toluene triisocyanates, e.g., toluene-2,3,5-triisocyanate, toluene-2,3,6-triisocyanate, toluene-2,4,5-triisocyanate, toluene-2,4,6-triisocyanate, toluene-3,4,6-triisocyanate, and toluene-3,5,6-triisocyanate; and xylene triisocyanates, e.g., 1,2-xylene-3,4,6-triisocyanate, 1,2-xylene-3,5,6-triisocyanate, 1,3-xylene-2,4,5-triisocyanate, 1,3-xylene-2,4,6-triisocyanate, 1,3-xylene-3,4,5-triisocyanate, 1,4-xylene-2,3,5-triisocyanate, and 1,4-xylene-2,3,6-triisocyanate.

These diisocyanates and triisocyanates can be used solely or in admixture of two or more.

Further, illustrative examples of the polyester having a hydroxyl group at one end or both ends include polylactones having a hydroxyl group at one end or both ends, such as a polycaprolactone having a hydroxyl group at one end or both ends, a polyvalerolactone having a hydroxyl group at one end or both ends, and a polypropiolactone having a hydroxyl group at one end or both ends; and polycondensation polyesters having a hydroxyl group at one end or both ends, such as a polyethylene terephthalate having a hydroxyl group at one end or both ends and a polybutylene terephthalate having a

hydroxyl group at one end or both ends.

These polyesters having a hydroxyl group at one end or both ends can be respectively used solely or in admixture of two or more.

5 As the compound having an urethane bond which is a dispersant in the present invention, a reaction product of an aromatic diisocyanate and a polylactone having a hydroxyl group at one end and/or a polylactone having a hydroxyl group at both ends is preferred, and a reaction product of a toluene
10 diisocyanate and a polycaprolactone having a hydroxyl group at one end and/or a polycaprolactone having a hydroxyl group at both ends is particularly preferred.

Specific examples of the compound having an urethane bond which is a dispersant having at least one of the foregoing
15 properties include, by trade names, EFKA-46 and EFKA-47 (products of EFKA Chemicals, B.V.), Disperbyk (product of BYK Chemie.), and DISPERON (product of KUSUMOTO CHEMICALS, LTD.).

A weight average molecular weight (hereinafter
20 referred to as "Mw") expressed in terms of polystyrene and measured by gel permeation chromatography (GPC) of the compound having an urethane bond which is a dispersant in the present invention is generally 5,000 to 50,000, preferably 7,000 to 20,000.

25 In the present invention, the compound having an urethane bond which is a dispersants can be used solely or in admixture of two or more.

The compound having an urethane bond which is a dispersant is used in an amount of generally 0.5 to 100 parts
30 by weight, preferably 1 to 70 parts by weight, more preferably 10 to 50 parts by weight, based on 100 parts by weight of the pigment in the colorant. In this case, when the amount of the compound having an urethane bond which is a dispersant is smaller than 0.5, the stability of the pigment dispersant

is liable to deteriorate, while when the amount is larger than 100 parts by weight, properties such as developability as a colored resist may be impaired.

Further, in the present invention, the compound having an urethane bond which is a dispersant can be used in combination with a dispersion assistant.

An example of the above dispersion assistant is a copper phthalocyanine sulfonic acid compound.

Specific examples of the above copper phthalocyanine sulfonic acid compound include copper phthalocyanine sulfonic acid, copper phthalocyanine ammonium sulfonate, copper phthalocyanine tetramethylammonium sulfonate, copper phthalocyanine tetraethylammonium sulfonate, copper phthalocyanine tetra-n-propylammonium sulfonate, copper phthalocyanine tetra-i-propylammonium sulfonate, and copper phthalocyanine tetra-n-butylammonium sulfonate.

These copper phthalocyanine sulfonic acid compounds can be used solely or in admixture of two or more.

The dispersion assistant is generally used in an amount of not larger than 20 parts by weight, preferably not larger than 10 parts by weight, more preferably not larger than 5 parts by weight, based on 100 parts by weight of the pigment in the colorant.

(B) Alkali Soluble Resin

As the alkali soluble resin in the present invention, any resin can be used as appropriate as long as it can serve as a binder for the colorant (A) and is soluble in a developer, particularly preferably an alkali developer, which is used in producing a black matrix and a spacer.

The alkali soluble resin in the present invention is preferably a resin having a carboxyl group, particularly preferably a copolymer (hereinafter simply referred to as "carboxyl-group-containing copolymer") of an ethylenically unsaturated monomer (hereinafter simply referred to as

"carboxyl-group-containing unsaturated monomer") having at least one carboxyl group and other copolymerizable ethylenically unsaturated monomer (hereinafter simply referred to as "other unsaturated monomer").

- 5 Illustrative examples of the carboxyl-group-containing unsaturated monomer include unsaturated monocarboxylic acids such as acrylic acid, methacrylic acid, crotonic acid, α -chloracrylic acid, and cinnamic acid;
- 10 unsaturated dicarboxylic acids (and anhydrides) such as maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, and mesaconic acid;
- unsaturated polycarboxylic acids (and anhydrides) with a
- 15 valence of at least 3;
- mono(2-acryloyloxyethyl)esters of unpolymerizable dicarboxylic acids or mono(2-acryloyloxyethyl)esters such as mono(2-acryloyloxyethyl)succinate, mono(2-methacryloyloxyethyl)succinate,
- 20 mono(2-acryloyloxyethyl)phthalate, and mono(2-methacryloyloxyethyl)phthalate; and
- ω -carboxypolycaprolactonemonoacrylate and ω -carboxypolycaprolactonemonomethacrylate.

These carboxyl-group-containing unsaturated monomers

25 can be used solely or in admixture of two or more.

Further, illustrative examples of the other unsaturated monomer include aromatic vinyl compounds such as styrene, α -methylstyrene, o-vinyltoluene, m-vinyltoluene, p-vinyltoluene, p-chlorostyrene, o-methoxystyrene,

30 m-methoxystyrene, p-methoxystyrene, indene, p-vinylbenzylmethyl ether, and p-vinylbenzylglycidyl ether;

unsaturated carboxylic acid esters such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-propyl acrylate, n-propyl methacrylate, i-propyl acrylate,

i-propyl methacrylate, n-butyl acrylate, n-butyl methacrylate, i-butyl acrylate, i-butyl methacrylate, sec-butyl acrylate, sec-butyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, 3-hydroxypropyl acrylate, 3-hydroxypropyl methacrylate, 2-hydroxybutyl acrylate, 2-hydroxybutyl methacrylate, 3-hydroxybutyl acrylate, 3-hydroxybutyl methacrylate, 4-hydroxybutyl acrylate, 4-hydroxybutyl methacrylate, allyl acrylate, allyl methacrylate, benzyl acrylate, benzyl methacrylate, phenyl acrylate, phenyl methacrylate, 2-methoxyethyl acrylate, 2-methoxyethyl methacrylate, methoxydiethylene glycol acrylate, methoxydiethylene glycol methacrylate, methoxytriethylene glycol acrylate, methoxytriethylene glycol methacrylate, methoxydipropylene glycol acrylate, methoxydipropylene glycol methacrylate, glycerine monoacrylate, and glycerine monomethacrylate; unsaturated carboxylic acid amino alkyl esters such as 2-aminoethylacrylate, 2-aminoethylmethacrylate, 2-dimethylaminoethylacrylate, 2-dimethylaminoethylmethacrylate, 2-aminopropylacrylate, 2-aminopropylmethacrylate, 2-dimethylaminopropylacrylate, 2-dimethylaminopropylmethacrylate, 3-aminopropylacrylate, 3-aminopropylmethacrylate, 3-dimethylaminopropylacrylate, and 3-dimethylaminopropylmethacrylate; unsaturated carboxylic acid glycidyl esters such as glycidyl acrylate and glycidyl methacrylate; carboxylic acid vinyl esters such as vinyl acetate, vinyl propionate, vinyl butyrate, and vinyl benzoate; unsaturated ethers such as vinyl methyl ether, vinyl ethyl ether, allyl glycidyl ether, and methacryl glycidyl ether; vinyl cyanide compounds such as acrylonitrile, methacrylonitrile, α -chloroacrylonitrile, and vinylidene

cyanide;

unsaturated amides such as acrylamide, methacrylamide,
 α -chloroacrylamide, N-(2-hydroxyethyl)acrylamide,
N-(2-hydroxyethyl)methacrylamide, N-methylolacrylamide,
5 and N-methylolmethacrylamide;

N-substituted maleimides such as N-cyclohexylmaleimide,
N-phenylmaleimide, N-o-hydroxyphenylmaleimide,
N-m-hydroxyphenylmaleimide, N-p-hydroxyphenylmaleimide,
N-o-methylphenylmaleimide, N-m-methylphenylmaleimide,
10 N-p-methylphenylmaleimide, N-o-methoxyphenylmaleimide,
N-m-methoxyphenylmaleimide, and
N-p-methoxyphenylmaleimide;

aliphatic conjugated dienes such as 1,3-butadiene, isoprene,
and chloroprene; and

15 macromonomers having a monoacryloyl group or
monomethacryloyl group at ends of a polymer molecular chain,
such as a polystyrene, polymethyl acrylate, polymethyl
methacrylate, poly-n-butyl acrylate, poly-n-butyl
methacrylate, and polysiloxane.

20 These other unsaturated monomers can be used solely or
in admixture of two or more.

As the carboxyl-group-containing copolymer, a
copolymer (hereinafter referred to as

"carboxyl-group-containing copolymer (I)") of a

25 carboxyl-group-containing unsaturated monomer which is
composed essentially of acrylic acid and/or methacrylic acid
and contains mono(2-acryloyloxyethyl)succinate and/or
mono(2-methacryloyloxyethyl)succinate in some cases and at
least one selected from the group consisting of styrene,
30 methyl acrylate, methyl methacrylate, 2-hydroxyethyl
acrylate, 2-hydroxyethyl methacrylate, benzyl acrylate,
benzyl methacrylate, phenyl acrylate, phenyl methacrylate,
glycerine monoacrylate, glycerine monomethacrylate,
N-phenylmaleimide, a polystyrene macromonomer and a

polymethyl methacrylate macromonomer is particularly preferred.

Specific examples of the carboxyl-group-containing copolymer (I) include:

- 5 a copolymer or terpolymer (hereinafter referred to as "carboxyl-group-containing copolymer (Ia)") such as a (meth)acrylic acid/benzyl (meth)acrylate copolymer, a (meth)acrylic acid/styrene/methyl (meth)acrylate copolymer,
- 10 a (meth)acrylic acid/styrene/benzyl (meth)acrylate copolymer, a (meth)acrylic acid/methyl (meth)acrylate/polystyrene macromonomer copolymer, a (meth)acrylic acid/methyl (meth)acrylate/polymethyl
- 15 methacrylate macromonomer copolymer, a (meth)acrylic acid/benzyl (meth)acrylate/polystyrene macromonomer copolymer, a (meth)acrylic acid/benzyl (meth)acrylate/polymethyl methacrylate macromonomer copolymer,
- 20 a (meth)acrylic acid/glycerine mono(meth)acrylate/benzyl (meth)acrylate copolymer, a (meth)acrylic acid/glycerine mono(meth)acrylate/phenyl (meth)acrylate copolymer, or a (meth)acrylic acid/glycerine
- 25 mono(meth)acrylate/N-phenylmaleimide copolymer; a quaternary copolymer (hereinafter referred to as "carboxyl-group-containing copolymer (Ib)") such as a (meth)acrylic acid/2-hydroxyethyl (meth)acrylate/benzyl (meth)acrylate/polystyrene macromonomer copolymer,
- 30 a (meth)acrylic acid/2-hydroxyethyl (meth)acrylate/benzyl (meth)acrylate/polymethyl methacrylate macromonomer copolymer, a (meth)acrylic acid/styrene/benzyl (meth)acrylate/N-phenylmaleimide copolymer,

- a (meth)acrylic acid/styrene/phenyl
(meth)acrylate/N-phenylmaleimide copolymer,
a (meth)acrylic acid/glycerine
mono(meth)acrylate/styrene/benzyl (meth)acrylate
5 copolymer,
a (meth)acrylic acid/glycerine
mono(meth)acrylate/styrene/phenyl (meth)acrylate
copolymer,
a (meth)acrylic acid/glycerine
10 mono(meth)acrylate/styrene/N-phenylmaleimide copolymer,
a (meth)acrylic acid/glycerine mono(meth)acrylate/methyl
(meth)acrylate/benzyl (meth)acrylate copolymer,
a (meth)acrylic acid/glycerine mono(meth)acrylate/methyl
(meth)acrylate/phenyl (meth)acrylate copolymer,
15 a (meth)acrylic acid/glycerine mono(meth)acrylate/methyl
(meth)acrylate/N-phenylmaleimide copolymer,
a (meth)acrylic acid/glycerine
mono(meth)acrylate/2-hydroxyethyl (meth)acrylate/benzyl
(meth)acrylate copolymer,
20 a (meth)acrylic acid/glycerine
mono(meth)acrylate/2-hydroxyethyl (meth)acrylate/phenyl
(meth)acrylate copolymer,
a (meth)acrylic acid/glycerine
mono(meth)acrylate/2-hydroxyethyl
25 (meth)acrylate/N-phenylmaleimide copolymer,
a (meth)acrylic acid/glycerine mono(meth)acrylate/benzyl
(meth)acrylate/phenyl (meth)acrylate copolymer,
a (meth)acrylic
acid/mono[2-(meth)acryloyloxyethyl]succinate/glycerine
30 mono(meth)acrylate/benzyl (meth)acrylate copolymer,
a (meth)acrylic acid/glycerine mono(meth)acrylate/benzyl
(meth)acrylate/N-phenylmaleimide copolymer,
a (meth)acrylic acid/glycerine mono(meth)acrylate/benzyl
(meth)acrylate/polystyrene macromonomer copolymer,

- a (meth)acrylic acid/glycerine mono(meth)acrylate/benzyl
(meth)acrylate/polymethyl methacrylate macromonomer
copolymer,
a (meth)acrylic
5 acid/mono[2-(meth)acryloyloxyethyl]succinate/glycerine
mono(meth)acrylate/phenyl (meth)acrylate copolymer,
a (meth)acrylic acid/glycerine mono(meth)acrylate/phenyl
(meth)acrylate/N-phenylmaleimide copolymer,
a (meth)acrylic acid/glycerine mono(meth)acrylate/phenyl
10 (meth)acrylate/polystyrene macromonomer copolymer,
a (meth)acrylic acid/glycerine mono(meth)acrylate/phenyl
(meth)acrylate/polymethyl methacrylate macromonomer
copolymer,
a (meth)acrylic
15 acid/mono[2-(meth)acryloyloxyethyl]succinate/glycerine
mono(meth)acrylate/N-phenylmaleimide copolymer,
a (meth)acrylic acid/glycerine
mono(meth)acrylate/N-phenylmaleimide/polystyrene
macromonomer copolymer, or
20 a (meth)acrylic acid/glycerine
mono(meth)acrylate/N-phenylmaleimide/polymethyl
methacrylate macromonomer copolymer;
a five-element copolymer (hereinafter referred to as
"carboxyl-group-containing copolymer (Ic)") such as
25 a (meth)acrylic acid/styrene/benzyl
(meth)acrylate/N-phenylmaleimide/polystyrene macromonomer
copolymer,
a (meth)acrylic acid/styrene/benzyl
(meth)acrylate/N-phenylmaleimide/polymethyl methacrylate
30 macromonomer copolymer,
a (meth)acrylic acid/styrene/phenyl
(meth)acrylate/N-phenylmaleimide/polystyrene macromonomer
copolymer,
a (meth)acrylic acid/styrene/phenyl

- (meth)acrylate/N-phenylmaleimide/polymethyl methacrylate
macromonomer copolymer,
a (meth)acrylic acid/glycerine
mono(meth)acrylate/styrene/methyl (meth)acrylate/benzyl
5 (meth)acrylate copolymer,
a (meth)acrylic acid/glycerine
mono(meth)acrylate/styrene/methyl (meth)acrylate/phenyl
(meth)acrylate copolymer,
a (meth)acrylic acid/glycerine
10 mono(meth)acrylate/styrene/methyl
(meth)acrylate/N-phenylmaleimide copolymer,
a (meth)acrylic acid/glycerine
mono(meth)acrylate/styrene/2-hydroxyethyl
(meth)acrylate/benzyl (meth)acrylate copolymer,
15 a (meth)acrylic acid/glycerine
mono(meth)acrylate/styrene/2-hydroxyethyl
(meth)acrylate/phenyl (meth)acrylate copolymer,
a (meth)acrylic acid/glycerine
mono(meth)acrylate/styrene/2-hydroxyethyl
20 (meth)acrylate/N-phenylmaleimide copolymer,
a (meth)acrylic acid/glycerine
mono(meth)acrylate/styrene/benzyl (meth)acrylate/phenyl
(meth)acrylate copolymer,
a (meth)acrylic
25 acid/mono[2-(meth)acryloyloxyethyl]succinate/glycerine
mono(meth)acrylate/styrene/benzyl (meth)acrylate
copolymer,
a (meth)acrylic acid/glycerine
mono(meth)acrylate/styrene/benzyl
30 (meth)acrylate/N-phenylmaleimide copolymer,
a (meth)acrylic acid/glycerine
mono(meth)acrylate/styrene/benzyl
(meth)acrylate/polystyrene macromonomer copolymer,
a (meth)acrylic acid/glycerine

- mono(meth)acrylate/styrene/benzyl
(meth)acrylate/polymethyl methacrylate macromonomer
copolymer,
a (meth)acrylic
5 acid/mono[2-(meth)acryloyloxyethyl]succinate/glycerine
mono(meth)acrylate/styrene/phenyl (meth)acrylate
copolymer,
a (meth)acrylic acid/glycerine
mono(meth)acrylate/styrene/phenyl
10 (meth)acrylate/N-phenylmaleimide copolymer,
a (meth)acrylic acid/glycerine
mono(meth)acrylate/styrene/phenyl
(meth)acrylate/polystyrene macromonomer copolymer,
a (meth)acrylic acid/glycerine
15 mono(meth)acrylate/styrene/phenyl
(meth)acrylate/polymethyl methacrylate macromonomer
copolymer,
a (meth)acrylic
acid/mono[2-(meth)acryloyloxyethyl]succinate/glycerine
20 mono(meth)acrylate/styrene/N-phenylmaleimide copolymer,
a (meth)acrylic acid/glycerine
mono(meth)acrylate/styrene/N-phenylmaleimide/polystyrene
macromonomer copolymer,
a (meth)acrylic acid/glycerine
25 mono(meth)acrylate/styrene/N-phenylmaleimide/polymethyl
methacrylate macromonomer copolymer,
a (meth)acrylic acid/glycerine mono(meth)acrylate/methyl
(meth)acrylate/2-hydroxyethyl (meth)acrylate/benzyl
(meth)acrylate copolymer,
30 a (meth)acrylic acid/glycerine mono(meth)acrylate/methyl
(meth)acrylate/2-hydroxyethyl (meth)acrylate/phenyl
(meth)acrylate copolymer,
a (meth)acrylic acid/glycerine mono(meth)acrylate/methyl
(meth)acrylate/2-hydroxyethyl

- (meth)acrylate/N-phenylmaleimide copolymer,
a (meth)acrylic acid/glycerine mono(meth)acrylate/methyl
(meth)acrylate/benzyl (meth)acrylate/phenyl (meth)acrylate
copolymer,
- 5 a (meth)acrylic
acid/mono[2-(meth)acryloyloxyethyl]succinate/glycerine
mono(meth)acrylate/methyl (meth)acrylate/benzyl
(meth)acrylate copolymer,
a (meth)acrylic acid/glycerine mono(meth)acrylate/methyl
10 (meth)acrylate/benzyl (meth)acrylate/N-phenylmaleimide
copolymer,
a (meth)acrylic acid/glycerine mono(meth)acrylate/methyl
(meth)acrylate/benzyl (meth)acrylate/polystyrene
macromonomer copolymer,
- 15 a (meth)acrylic acid/glycerine mono(meth)acrylate/methyl
(meth)acrylate/benzyl (meth)acrylate/polymethyl
methacrylate macromonomer copolymer,
a (meth)acrylic
acid/mono[2-(meth)acryloyloxyethyl]succinate/glycerine
20 mono(meth)acrylate/methyl (meth)acrylate/phenyl
(meth)acrylate copolymer,
a (meth)acrylic acid/glycerine mono(meth)acrylate/methyl
(meth)acrylate/phenyl (meth)acrylate/N-phenylmaleimide
copolymer,
- 25 a (meth)acrylic acid/glycerine mono(meth)acrylate/methyl
(meth)acrylate/phenyl (meth)acrylate/polystyrene
macromonomer copolymer,
a (meth)acrylic acid/glycerine mono(meth)acrylate/methyl
(meth)acrylate/phenyl (meth)acrylate/polymethyl
30 methacrylate macromonomer copolymer,
a (meth)acrylic
acid/mono[2-(meth)acryloyloxyethyl]succinate/glycerine
mono(meth)acrylate/methyl
(meth)acrylate/N-phenylmaleimide copolymer,

- a (meth)acrylic acid/glycerine mono(meth)acrylate/methyl
(meth)acrylate/N-phenylmaleimide/polystyrene macromonomer
copolymer,
- a (meth)acrylic acid/glycerine mono(meth)acrylate/methyl
5 (meth)acrylate/N-phenylmaleimide/polymethyl methacrylate
macromonomer copolymer,
- a (meth)acrylic acid/glycerine
mono(meth)acrylate/2-hydroxyethyl (meth)acrylate/benzyl
(meth)acrylate/phenyl (meth)acrylate copolymer,
- 10 a (meth)acrylic
acid/mono[2-(meth)acryloyloxyethyl]succinate/glycerine
mono(meth)acrylate/2-hydroxyethyl (meth)acrylate/benzyl
(meth)acrylate copolymer,
- a (meth)acrylic acid/glycerine
15 mono(meth)acrylate/2-hydroxyethyl (meth)acrylate/benzyl
(meth)acrylate/N-phenylmaleimide copolymer,
- a (meth)acrylic acid/glycerine
mono(meth)acrylate/2-hydroxyethyl (meth)acrylate/benzyl
(meth)acrylate/polystyrene macromonomer copolymer,
- 20 a (meth)acrylic acid/glycerine
mono(meth)acrylate/2-hydroxyethyl (meth)acrylate/benzyl
(meth)acrylate/polymethyl methacrylate macromonomer
copolymer,
- a (meth)acrylic
25 acid/mono[2-(meth)acryloyloxyethyl]succinate/glycerine
mono(meth)acrylate/2-hydroxyethyl (meth)acrylate/phenyl
(meth)acrylate copolymer,
- a (meth)acrylic acid/glycerine
mono(meth)acrylate/2-hydroxyethyl (meth)acrylate/phenyl
30 (meth)acrylate/N-phenylmaleimide copolymer,
- a (meth)acrylic acid/glycerine
mono(meth)acrylate/2-hydroxyethyl (meth)acrylate/phenyl
(meth)acrylate/polystyrene macromonomer copolymer,
- a (meth)acrylic acid/glycerine

- mono(meth)acrylate/2-hydroxyethyl (meth)acrylate/phenyl
(meth)acrylate/polymethyl methacrylate macromonomer
copolymer,
a (meth)acrylic
- 5 acid/mono[2-(meth)acryloyloxyethyl]succinate/glycerine
mono(meth)acrylate/2-hydroxyethyl
(meth)acrylate/N-phenylmaleimide copolymer,
a (meth)acrylic acid/glycerine
mono(meth)acrylate/2-hydroxyethyl
- 10 (meth)acrylate/N-phenylmaleimide/polystyrene macromonomer
copolymer,
a (meth)acrylic acid/glycerine
mono(meth)acrylate/2-hydroxyethyl
(meth)acrylate/N-phenylmaleimide/polymethyl methacrylate
- 15 macromonomer copolymer,
a (meth)acrylic
acid/mono[2-(meth)acryloyloxyethyl]succinate/glycerine
mono(meth)acrylate/benzyl (meth)acrylate/phenyl
(meth)acrylate copolymer,
- 20 a (meth)acrylic acid/glycerine mono(meth)acrylate/benzyl
(meth)acrylate/phenyl (meth)acrylate/N-phenylmaleimide
copolymer,
a (meth)acrylic acid/glycerine mono(meth)acrylate/benzyl
(meth)acrylate/phenyl (meth)acrylate/polystyrene
- 25 macromonomer copolymer,
a (meth)acrylic acid/glycerine mono(meth)acrylate/benzyl
(meth)acrylate/phenyl (meth)acrylate/polymethyl
methacrylate macromonomer copolymer,
a (meth)acrylic
- 30 acid/mono[2-(meth)acryloyloxyethyl]succinate/glycerine
mono(meth)acrylate/benzyl
(meth)acrylate/N-phenylmaleimide copolymer,
a (meth)acrylic
acid/mono[2-(meth)acryloyloxyethyl]succinate/glycerine

- mono(meth)acrylate/benzyl (meth)acrylate/polystyrene
macromonomer copolymer,
a (meth)acrylic
acid/mono[2-(meth)acryloyloxyethyl]succinate/glycerine
- 5 mono(meth)acrylate/benzyl (meth)acrylate/polymethyl
methacrylate macromonomer copolymer,
a (meth)acrylic acid/glycerine mono(meth)acrylate/benzyl
(meth)acrylate/N-phenylmaleimide/polystyrene macromonomer
copolymer,
- 10 a (meth)acrylic acid/glycerine mono(meth)acrylate/benzyl
(meth)acrylate/N-phenylmaleimide/polymethyl methacrylate
macromonomer copolymer,
a (meth)acrylic
acid/mono[2-(meth)acryloyloxyethyl]succinate/glycerine
- 15 mono(meth)acrylate/phenyl
(meth)acrylate/N-phenylmaleimide copolymer,
a (meth)acrylic
acid/mono[2-(meth)acryloyloxyethyl]succinate/glycerine
mono(meth)acrylate/phenyl (meth)acrylate/polystyrene
- 20 macromonomer copolymer,
a (meth)acrylic
acid/mono[2-(meth)acryloyloxyethyl]succinate/glycerine
mono(meth)acrylate/phenyl (meth)acrylate/polymethyl
methacrylate macromonomer copolymer,
- 25 a (meth)acrylic acid/glycerine mono(meth)acrylate/phenyl
(meth)acrylate/N-phenylmaleimide/polystyrene macromonomer
copolymer,
a (meth)acrylic acid/glycerine mono(meth)acrylate/phenyl
(meth)acrylate/N-phenylmaleimide/polymethyl methacrylate
- 30 macromonomer copolymer,
a (meth)acrylic
acid/mono[2-(meth)acryloyloxyethyl]succinate/glycerine
mono(meth)acrylate/N-phenylmaleimide/polystyrene
macromonomer copolymer,

- a (meth)acrylic acid/mono[2-(meth)acryloyloxyethyl]succinate/glycerine mono(meth)acrylate/N-phenylmaleimide/polymethyl methacrylate macromonomer copolymer, or
- 5 a (meth)acrylic acid/mono[2-(meth)acryloyloxyethyl]succinate/styrene/benzyl (meth)acrylate/N-phenylmaleimide copolymer; and a six-element copolymer (hereinafter referred to as "carboxyl-group-containing copolymer (Id)") such as
- 10 a (meth)acrylic acid/styrene/2-hydroxyethyl (meth)acrylate/benzyl (meth)acrylate/N-phenylmaleimide/polystyrene macromonomer copolymer,
- a (meth)acrylic acid/styrene/2-hydroxyethyl
- 15 (meth)acrylate/benzyl (meth)acrylate/N-phenylmaleimide/polymethyl methacrylate macromonomer copolymer,
- a (meth)acrylic acid/styrene/2-hydroxyethyl (meth)acrylate/phenyl
- 20 (meth)acrylate/N-phenylmaleimide/polystyrene macromonomer copolymer, or
- a (meth)acrylic acid/styrene/2-hydroxyethyl (meth)acrylate/phenyl (meth)acrylate/N-phenylmaleimide/polymethyl methacrylate
- 25 macromonomer copolymer.

The amount of the carboxyl-group-containing unsaturated monomer in the carboxyl-group-containing copolymer is generally 5 to 50% by weight, preferably 10 to 40% by weight. In this case, when the amount of the

30 carboxyl-group-containing unsaturated monomer is smaller than 5% by weight, solubility of an obtained radiation sensitive composition in an alkali developer is liable to lower. Meanwhile, when the amount is larger than 50% by weight, a formed pattern is liable to fall off from a substrate

or have a rough surface upon development by an alkali developer. In the present invention, the alkali soluble resin preferably has an Mw of 1,000 to 1,000,000, more preferably 5,000 to 100,000.

5 In the present invention, the alkali soluble resins can be used solely or in admixture of two or more.

 In the present invention, the alkali soluble resin is used in an amount of generally 10 to 1,000 parts by weight, preferably 20 to 500 parts by weight, based on 100 parts by
10 weight of the pigment in the colorant (A). In this case, when the amount of the alkali soluble resin is smaller than 10 parts by weight, alkali developability may deteriorate or scums and/or film residues may appear in an area other than an area where the pattern is formed, for example. On the other
15 hand, when the amount is larger than 1,000 parts by weight, the concentration of the colorant lowers accordingly, so that it may become difficult to achieve a desired color concentration as a thin film.

(C) Multifunctional Monomer

20 Illustrative examples of the multifunctional monomer in the present invention include a diacrylate or dimethacrylate of an alkylene glycol such as ethylene glycol or propylene glycol;

 a diacrylate or dimethacrylate of a polyalkylene glycol such
25 as polyethylene glycol or polypropylene glycol;

 a polyacrylate or polymethacrylate of a polyhydric alcohol having at least three hydroxyl groups such as glycerine, trimethylolpropane, pentaerythritol or dipentaerythritol, or the polyacrylate or polymethacrylate modified with a
30 dicarboxylic acid;

 an oligoacrylate or oligomethacrylate of a polyester, epoxy resin, urethane resin, alkyd resin, silicone resin or spirane resin;

 a diacrylate or dimethacrylate of a polymer having hydroxy

group at both ends, such as poly-1,3-butadiene having both ends hydroxylated, hydroxypolyisoprene having both ends hydroxylated or hydroxypolycaprolactone having both ends hydroxylated;

- 5 tris(2-acryloyloxyethyl)phosphate, and
tris(2-methacryloyloxyethyl)phosphate.

Of these multifunctional monomers, a polyacrylate or polymethacrylate of a polyhydric alcohol having at least three hydroxyl groups or the polyacrylate or
10 polymethacrylate modified with a dicarboxylic acid is preferred. More specifically, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, pentaerythritol triacrylate, pentaerythritol trimethacrylate, pentaerythritol triacrylate modified with
15 succinic acid, pentaerythritol trimethacrylate modified with succinic acid, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, dipentaerythritol tetraacrylate, dipentaerythritol tetramethacrylate, dipentaerythritol hexaacrylate and dipentaerythritol
20 hexamethacrylate are preferred, and trimethylolpropane triacrylate, pentaerythritol triacrylate and dipentaerythritol hexaacrylate are particularly preferred in that they provide high pattern strength and a smooth pattern surface and hardly cause scums and/or film residues
25 in an area other than an area where a pattern is formed.

The multifunctional monomers can be used solely or in admixture of two or more.

The multifunctional monomer in the present invention is used in an amount of generally 5 to 500 parts by weight, preferably 20 to 300 parts by weight, based on 100 parts by
30 weight of the alkali soluble resin (B). In this case, when the amount of the multifunctional monomer is smaller than 5 parts by weight, pattern strength and/or smoothness of a surface of a pattern are liable to deteriorate, while when

the amount is larger than 500 parts by weight, alkali developability is liable to lower or scums and/or film residues are liable to appear in an area other than an area where the pattern is formed, for example.

5 Further, in the present invention, some of the above multifunctional monomers can be replaced by monofunctional monomers.

Illustrative examples of such monofunctional monomers include carboxyl-group-containing unsaturated monomers
10 constituting the alkali soluble resin (B), other unsaturated monomers, 2-hydroxy-3-phenoxypropyl acrylate, 2-hydroxy-3-phenoxypropyl methacrylate as well as, as a commercial product, M-5300 (trade name, product of TOA GOSHI KAGAKU KOGYO K.K.).

15 Of these monofunctional monomers, mono(2-acryloyloxyethyl)succinate, mono(2-methacryloyloxyethyl)succinate, ω -carboxypolycaprolactonemonoacrylate (M-5300), ω -carboxypolycaprolactonemonomethacrylate,
20 methoxytriethylene glycol acrylate, methoxytriethylene glycol methacrylate, methoxydipropylene glycol acrylate, methoxydipropylene glycol methacrylate, 2-hydroxy-3-phenoxypropyl acrylate and 2-hydroxy-3-phenoxypropyl methacrylate are preferred.

25 The above monofunctional monomers can be used solely or in admixture of two or more.

The monofunctional monomers can be used in an amount of generally not larger than 90% by weight, preferably not larger than 50% by weight, based on the total amount of the
30 polyfunctional monomers and the monofunctional monomers.

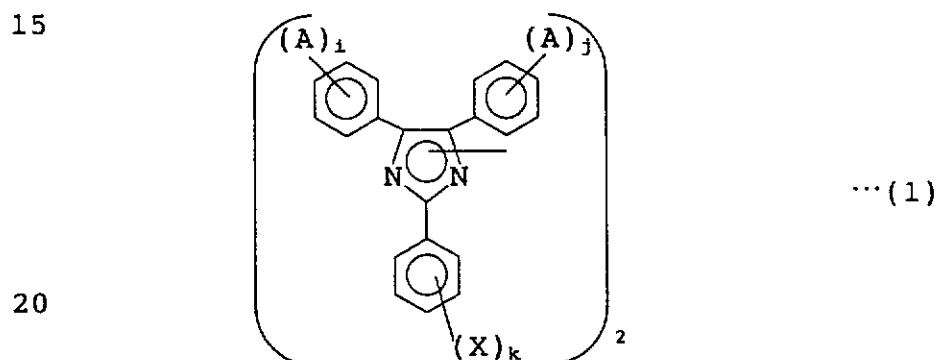
(D) Photopolymerization Initiator

The photopolymerization initiator in the present invention refers to a compound which undergoes decomposition or cleavage of bonds upon exposure so as to produce active

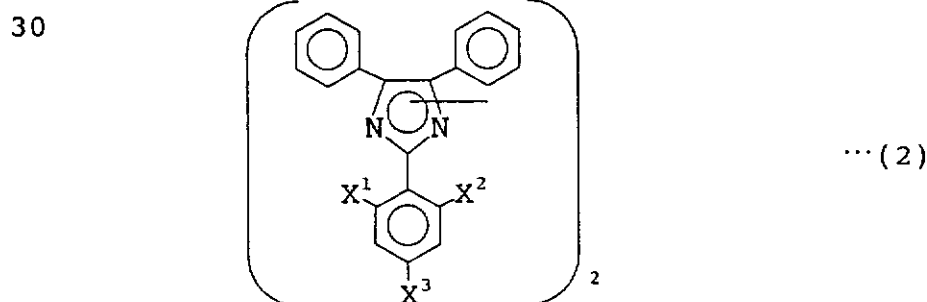
species, such as radicals, anions and cations, which can initiate polymerization of the foregoing multifunctional monomer (C).

Illustrative examples of such a photopolymerization initiator include a compound having an imidazole ring, a compound having a benzoin bond, other photo radical generating agents, and a compound having a trihalomethyl group.

Specific examples of the compound having an imidazole ring include a compound (hereinafter referred to as "biimidazole compound (1)") represented by the following general formula (1) and a compound (hereinafter referred to as "biimidazole compound (2)") represented by the following general formula (2).



(In the general formula (1), X is a hydrogen atom, a halogen atom, a cyano group, an alkyl group having 1 to 4 carbon atoms or an aryl group having 6 to 9 carbon atoms, and a plurality of Xs, if present, may be the same or different; A is -COOO-R (wherein R is an alkyl group having 1 to 4 carbon atoms or an aryl group having 6 to 9 carbon atoms), and a plurality of As, if present, may be the same or different; and i, j and k each are an integer of 1 to 3.)



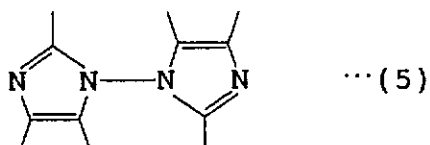
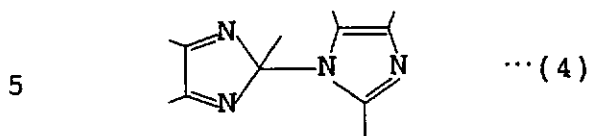
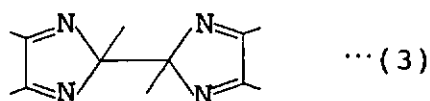
(In the general formula (2), X^1 , X^2 and X^3 each independently represent a hydrogen atom, a halogen atom, a cyano group, an alkyl group having 1 to 4 carbon atoms or an aryl group having 6 to 9 carbon atoms, with the proviso that any two
5 out of or all of X^1 , X^2 and X^3 never represent a hydrogen atom at the same time.)

Illustrative examples of the halogen atoms represented by X , X^1 , X^2 and X^3 in the general formulae (1) and (2) include a chlorine atom, a bromine atom and an iodine atom.

10 Illustrative examples of the alkyl groups having 1 to 4 carbon atoms include a methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, i-butyl group, sec-butyl group, and t-butyl group. Illustrative examples of the aryl group having 6 to 9 carbon atoms include a phenyl group,
15 o-tolyl group, m-tolyl group, and p-tolyl group.

Further, groups represented by R in -COOO-R represented by A in the general formula (1) are the same as the alkyl group having 1 to 4 carbon atoms and aryl group having 6 to 9 carbon atoms exemplified above with respect to X , X^1 , X^2
20 and X^3 .

The general formulae (1) and (2) represent a general structure in which two imidazole units are bonded to each other at position 1 or 2. Hence, the biimidazole compound (1) and the biimidazole compound (2) are a compound whose
25 principal skeleton corresponds to the following formula (3), a compound whose principal skeleton corresponds to the following formula (4), a compound whose principal skeleton corresponds to the following formula (5) or a mixture of any two or all of the compounds (3), (4) and (5).



10 Specific examples of the biimidazole compound (1) and the biimidazole compound (2) will be enumerated below.

 Specific examples of the biimidazole compound (1) include

- 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxy
15 carbonylphenyl)-1,2'-biimidazole,
2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-phenoxy
carbonylphenyl)-1,2'-biimidazole,
2,2'-bis(2,4-dichlorophenyl)-4,4',5,5'-tetrakis(4-ethoxy
carbonylphenyl)-1,2'-biimidazole,
20 2,2'-bis(2,4-dichlorophenyl)-4,4',5,5'-tetrakis
(4-phenoxy carbonylphenyl)-1,2'-biimidazole,
2,2'-bis(2,4,6-trichlorophenyl)-4,4',5,5'-tetrakis
(4-ethoxy carbonylphenyl)-1,2'-biimidazole,
2,2'-bis(2,4,6-trichlorophenyl)-4,4',5,5'-tetrakis(4-
25 phenoxy carbonylphenyl)-1,2'-biimidazole,
2,2'-bis(2-bromophenyl)-4,4',5,5'-tetrakis(4-ethoxy
carbonylphenyl)-1,2'-biimidazole,
2,2'-bis(2-bromophenyl)-4,4',5,5'-tetrakis(4-phenoxy
carbonylphenyl)-1,2'-biimidazole,
30 2,2'-bis(2,4-dibromophenyl)-4,4',5,5'-tetrakis(4-ethoxy
carbonylphenyl)-1,2'-biimidazole,
2,2'-bis(2,4-dibromophenyl)-4,4',5,5'-tetrakis(4-phenoxy
carbonylphenyl)-1,2'-biimidazole,
2,2'-bis(2,4,6-tribromophenyl)-4,4',5,5'-tetrakis

- (4-ethoxy carbonylphenyl)-1,2'-biimidazole,
2,2'-bis(2,4,6-tribromophenyl)-4,4',5,5'-tetrakis(4-
phenoxycarbonylphenyl)-1,2'-biimidazole,
2,2'-bis(2-cyanophenyl)-4,4',5,5'-tetrakis(4-ethoxy
5 carbonylphenyl)-1,2'-biimidazole,
2,2'-bis(2-cyanophenyl)-4,4',5,5'-tetrakis(4-phenoxy
carbonylphenyl)-1,2'-biimidazole,
2,2'-bis(2-methylphenyl)-4,4',5,5'-tetrakis(4-methoxy
carbonylphenyl)-1,2'-biimidazole,
10 2,2'-bis(2-methylphenyl)-4,4',5,5'-tetrakis(4-ethoxy
carbonylphenyl)-1,2'-biimidazole,
2,2'-bis(2-methylphenyl)-4,4',5,5'-tetrakis(4-
phenoxycarbonylphenyl)-1,2'-biimidazole,
2,2'-bis(2-ethylphenyl)-4,4',5,5'-tetrakis(4-methoxy
15 carbonylphenyl)-1,2'-biimidazole,
2,2'-bis(2-ethylphenyl)-4,4',5,5'-tetrakis(4-ethoxy
carbonylphenyl)-1,2'-biimidazole,
2,2'-bis(2-ethylphenyl)-4,4',5,5'-tetrakis(4-phenoxy
carbonylphenyl)-1,2'-biimidazole,
20 2,2'-bis(2-phenylphenyl)-4,4',5,5'-tetrakis(4-methoxy
carbonylphenyl)-1,2'-biimidazole,
2,2'-bis(2-phenylphenyl)-4,4',5,5'-tetrakis(4-ethoxy
carbonylphenyl)-1,2'-biimidazole,
2,2'-bis(2-phenylphenyl)-4,4',5,5'-tetrakis(4-phenoxy
25 carbonylphenyl)-1,2'-biimidazole.

Meanwhile, illustrative examples of the biimidazole compound (2) include

- 2,2'-bis(2,4-dichlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-
biimidazole,
30 2,2'-bis(2,4,6-trichlorophenyl)-4,4',5,5'-tetraphenyl-1,
2'-biimidazole,
2,2'-bis(2,4-dibromophenyl)-4,4',5,5'-tetraphenyl-1,2'-
biimidazole,
2,2'-bis(2,4,6-tribromophenyl)-4,4',5,5'-tetraphenyl-

- 1,2'-biimidazole,
2,2'-bis(2,4-dicyanophenyl)-4,4',5,5'-tetraphenyl-1,2'-
biimidazole,
2,2'-bis(2,4,6-tricyanophenyl)-4,4',5,5'-tetraphenyl-
5 1,2'-biimidazole,
2,2'-bis(2,4-dimethylphenyl)-4,4',5,5'-tetraphenyl-1,2'-
biimidazole,
2,2'-bis(2,4,6-trimethylphenyl)-4,4',5,5'-tetraphenyl-1,
2'-biimidazole,
10 2,2'-bis(2,4-diethylphenyl)-4,4',5,5'-tetraphenyl-1,2'-
biimidazole,
2,2'-bis(2,4,6-triethylphenyl)-4,4',5,5'-tetraphenyl-
1,2'-biimidazole,
2,2'-bis(2,4-diphenylphenyl)-4,4',5,5'-tetraphenyl-1,2'-
15 biimidazole, and
2,2'-bis(2,4,6-triphenylphenyl)-4,4',5,5'-tetraphenyl-1,
2'-biimidazole.

- Of these, as the biimidazole compound (1),
2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxy
20 carbonylphenyl)-1,2'-biimidazole and
2,2'-bis(2-bromophenyl)-4,4',5,5'-tetrakis(4-ethoxy
carbonylphenyl)-1,2'-biimidazole are particularly
preferred, and as the biimidazole compound (2),
2,2'-bis(2,4-dichlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-
25 biimidazole,
2,2'-bis(2,4,6-trichlorophenyl)-4,4',5,5'-tetraphenyl-1,
2'-biimidazole,
2,2'-bis(2,4-dibromophenyl)-4,4',5,5'-tetraphenyl-1,2'-
biimidazole, and
30 2,2'-bis(2,4,6-tribromophenyl)-4,4',5,5'-tetraphenyl-
1,2'-biimidazole are particularly preferred.

The biimidazole compound (1) and the biimidazole
compound (2) have excellent solubility in solvents, cause
no foreign matters such as undissolved materials and deposits.

are so sensitive that they can promote a curing reaction to a sufficient degree upon exposure with a small amount of energy, and have such a high contrast that the curing reaction does not occur in an unexposed portion. Therefore, a coating
5 film after the exposure is distinctly divided into a cured portion which is insoluble in a developer and an uncured portion which has high solubility in the developer, and an excellent black matrix and spacer which are free from a loss and undercut of a pattern can be formed.

10 Further, specific examples of the foregoing compound having a benzoin bond and other photo radical generating agents include 2-hydroxy-2-methyl-1-phenylpropane-1-one, 1-(4-i-propylphenyl)-2-hydroxy-2-methylpropane-1-one, 4-(2-hydroxyethoxy)phenyl-(2-hydroxy-2-propyl)ketone,
15 1-hydroxycyclohexylphenylketone, 2,2-dimethoxy-2-phenylacetophenon, 2-methyl-(4-methylthiophenyl)-2-morpholino-1-propane-1-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butane-1-
20 one, benzophenone, 3,3'-dimethyl-4-methoxybenzophenone, 2,4-diethylthioxanthone, 4-azidebenzaldehyde, 4-azideacetophenone, 4-azidebenzalacetophenone, azidepyrene, 4-diazodiphenylamine, 4-diazo-4'-methoxydiphenylamine,
25 4-diazo-3-methoxydiphenylamine, bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide, dibenzoyl, benzoin isobutyl ether, N-phenylthioacridone, and triphenylpyrylium perchlorate.

Further, specific examples of the foregoing compound
30 having a trihalomethyl group include 1,3,5-tris(trichloromethyl)-s-triazine, 1,3-bis(trichloromethyl)-5-(2-chlorophenyl)-s-triazine, 1,3-bis(trichloromethyl)-5-(4-chlorophenyl)-s-triazine, 1,3-bis(trichloromethyl)-5-(2-methoxyphenyl)-s-triazine,

and

1,3-bis(trichloromethyl)-5-(4-methoxyphenyl)-s-triazine.

Of these compounds having a benzoin bond, compounds having other photo radical generating agents, and compounds

5 having a trihalomethyl group,

2-hydroxy-2-methyl-1-phenylpropane-1-one,

2-methyl-(4-methylthiophenyl)-2-morpholino-1-propane-1-one, and

2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butane-1-one are preferred in that a formed pattern does not peel off
10 from a substrate easily at the time of development and has high pattern strength and sensitivity.

The above photopolymerization initiators can be used solely or in admixture of two or more.

15 In the present invention, as required, the above photopolymerization initiator can also be used in combination with at least one selected from the group consisting of a sensitizer, a hardening accelerator and a photo crosslinking agent or photo sensitizer comprising a
20 polymeric compound (hereinafter referred to as "polymeric photo crosslinking/sensitizing agent").

Specific examples of the sensitizer include

4,4'-bis(dimethylamino)benzophenone,

4,4'-bis(diethylamino)benzophenone,

25 4-diethylaminoacetophenone, 4-dimethylaminopropiophenone, ethyl-4-dimethylaminobenzoate,

2-ethylhexyl-1,4-dimethylaminobenzoate,

2,5-bis(4-diethylaminobenzal)cyclohexanone,

7-diethylamino-3-(4-diethylaminobenzoyl)cumarine, and

30 4-(diethylamino)chalcone.

Further, specific examples of the hardening accelerator include chain transfer agents such as 2-mercaptobenzoimidazole, 2-mercaptobenzothiazole, 2-mercaptobenzooxazole, 2,5-dimercapto-1,3,4-thiadiazole,

2-mercapto-4,6-dimethylaminopyridine,
1-phenyl-5-mercapto-1H-tetrazole, and
3-mercapto-4-methyl-4H-1,2,4-triazole.

Further, the foregoing polymeric photo
5 crosslinking/sensitizing agent is a polymeric compound which
has a functional group capable of serving as a photo
crosslinking agent and/or a photo sensitizer in a main chain
and/or a side chain. Specific examples thereof include a
condensate of 4-azidebenzaldehyde and a polyvinyl alcohol,
10 a condensate of 4-azidebenzaldehyde and a phenol novolac
resin, a homopolymer or copolymer of
4-acryloylphenylcinnamoyl ester, 1,4-polybutadiene, and
1,2-polybutadiene. Of the above sensitizers, hardening
accelerators and polymeric photo crosslinking/sensitizing
15 agents, 4,4'-bis(dimethylamino)benzophenone,
4,4'-bis(diethylamino)benzophenone, and
2-mercaptobenzothiazole are preferred in that a formed
pattern does not peel off from a substrate easily at the time
of development and has high pattern strength and sensitivity.

20 In the present invention, it is particularly preferred
that at least one selected from the group consisting of the
biimidazole compound (1) and the biimidazole compound (2)
and at least one selected from the group consisting of a
benzophenone compound having a benzoin bond, other
25 benzophenone photo radical generating agent, a benzophenone
sensitizer and a thiazole-based hardening accelerator be
used in combination as a photopolymerization initiator.

Specific examples of the above particularly preferred
combination include:

30 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxy
carbonylphenyl)-1,2'-biimidazole/4,4'-bis(diethylamino)
benzophenone,
2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxy
carbonylphenyl)-1,2'-biimidazole/4,4'-bis(diethylamino)

- benzophenone/2-benzyl-2-dimethylamino-1-(4-morpholino
phenyl)butane-1-one,
2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxy
carbonylphenyl)-1,2'-biimidazole/4,4'-bis(diethylamino)
- 5 benzophenone/1-hydroxycyclohexylphenylketone,
2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxy
carbonylphenyl)-1,2'-biimidazole/4,4'-bis(dimethylamino)
benzophenone/1-hydroxycyclohexylphenylketone/2-mercapto
benzothiazole,
- 10 2,2'-bis(2,4-dichlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-
biimidazole/4,4'-bis(diethylamino)benzophenone,
2,2'-bis(2,4-dibromophenyl)-4,4',5,5'-tetraphenyl-1,2'-
biimidazole/4,4'-bis(diethylamino)benzophenone/2-benzyl-
2-dimethylamino-1-(4-morpholinophenyl)butane-1-one,
- 15 2,2'-bis(2,4-dibromophenyl)-4,4',5,5'-tetraphenyl-1,2'-
biimidazole/4,4'-bis(diethylamino)benzophenone/1-hydroxy
cyclohexylphenylketone, and
2,2'-bis(2,4,6-trichlorophenyl)-4,4',5,5'-tetraphenyl-1,
2'-biimidazole/4,4'-bis(dimethylamino)benzophenone/
- 20 1-hydroxy cyclohexylphenylketone/2-mercaptobenzothiazole.

In the present invention, the compound having a benzoin
bond, other photo radical generating agent and the compound
having a trihalomethyl group are used in a total amount of
preferably not larger than 80% by weight of the whole

25 photopolymerization initiator. Further, the sensitizer and
the hardening accelerator are used in a total amount of
preferably not larger than 80% by weight of the whole
photopolymerization initiator. In addition, the polymeric
photo crosslinking/sensitizing agent is used in an amount

30 of generally not larger than 200 parts by weight, preferably
not larger than 180 parts by weight, based on 100 parts by
weight of a total of the biimidazole compound (1) and the
biimidazole compound (2).

The photopolymerization initiator in the present

invention is used in an amount of generally 0.01 to 500 parts by weight, preferably 1 to 300 parts by weight, particularly preferably 10 to 200 parts by weight, based on 100 parts by weight of the multifunctional monomer (C). In this case, when the amount of the photopolymerization initiator is smaller than 0.01 parts by weight, curing by exposure does not proceed sufficiently, whereby a loss and/or undercut of a pattern may occur, while when the amount is larger than 500 parts by weight, a formed pattern is liable to fall off from a substrate at the time of development and scums and/or film residues are liable to appear in an area other than an area where the pattern is formed.

Additives

Further, the radiation sensitive composition for a black resist of the present invention may contain a variety of additives as required.

Illustrative examples of such additives include: polymeric compounds such as a polyvinyl alcohol, polyethylene glycol monoalkyl ether, and poly(fluoroalkylacrylate); surfactants such as a nonionic surfactant, a cationic surfactant, and an anionic surfactant; adhesion accelerators such as vinyl trimethoxysilane, vinyl triethoxysilane, vinyl tris(2-methoxyethoxy)silane, N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropylmethyldimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 3-chloropropylmethyldimethoxysilane, 3-chloropropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, and 3-mercaptopropyltrimethoxysilane;

antioxidants such as 2,2-thiobis(4-methyl-6-t-butylphenol),
and 2,6-di-t-butylphenol;
ultraviolet absorbers such as
2-(3-t-butyl-5-methyl-2-hydroxyphenyl)-5-
5 chlorobenzotriazole, and alkoxybenzophenone; and
agglomeration inhibitors such as sodium polyacrylate.

Further, when the alkali soluble resin (B) is a resin
having a carboxyl group, the radiation sensitive composition
for a black resist of the present invention may also contain
10 an organic acid so as to further improve solubility of a
coating film formed from the composition in an alkali
developer and further suppress occurrence of undissolved
residues after development.

As such an organic acid, an aliphatic carboxylic acid
15 or phenyl-group-containing carboxylic acid having a
molecular weight of not larger than 1,000 is preferred.

Specific examples of the aliphatic carboxylic acid
include monocarboxylic acids such as formic acid, acetic acid,
propionic acid, butyric acid, valeric acid, pivalic acid,
20 caproic acid, diethyl acetate, enanthic acid, and caprylic
acid;
dicarboxylic acids such as oxalic acid, malonic acid,
succinic acid, glutaric acid, adipic acid, pimelic acid,
suberic acid, azelaic acid, sebacic acid, brassylic acid,
25 methylmalonic acid, ethylmalonic acid, dimethylmalonic acid,
methylsuccinic acid, tetramethylsuccinic acid,
cyclohexanedicarboxylic acid, itaconic acid, citraconic
acid, maleic acid, fumaric acid, and mesaconic acid; and
tricarboxylic acids such as tricarballylic acid, aconitic
30 acid, and camphoronic acid.

Meanwhile, illustrative examples of the
phenyl-group-containing carboxylic acid include an aromatic
carboxylic acid having a carboxyl group directly bonded to
a phenyl group, and a carboxylic acid having a carboxyl group

bonded to a phenyl group via a carbon chain. Specific examples thereof include aromatic monocarboxylic acids such as benzoic acid, toluic acid, cumic acid, hemerytic acid, and mesitylenic acid;

- 5 aromatic dicarboxylic acids such as phthalic acid, isophthalic acid, and terephthalic acid;

aromatic polycarboxylic acids having a valence of at least 3 such as trimellitic acid, trimesic acid, melophatic acid, and pyromellitic acid; and

- 10 phenylacetic acid, hydroatropic acid, hydrocinnamic acid, mandelic acid, phenylsuccinic acid, atropic acid, cinnamic acid, cinnamilidenic acid, coumaric acid, and umbellic acid.

Of these organic acids, aliphatic dicarboxylic acids and aromatic dicarboxylic acids such as malonic acid, adipic
15 acid, itaconic acid, citraconic acid, fumaric acid, mesaconic acid and phthalic acid are preferred from the viewpoints of alkali solubility, solubility in solvents to be described later, and prevention of occurrence of scums in an area other than an area where a pattern is formed.

- 20 The organic acids can be used solely or in admixture of two or more.

The organic acid is used in an amount of generally not larger than 10% by weight, preferably not larger than 1% by weight, based on the whole radiation sensitive composition.

- 25 In this case, when the amount of the organic acid exceeds 10% by weight, adhesion of a formed pattern to a substrate is liable to lower.

Solvents

- The radiation sensitive composition for a black resist
30 of the present invention is composed essentially of the foregoing colorant (A), the alkali soluble resin (B), the multifunctional monomer (C), and the photopolymerization initiator (D) and also contains the foregoing additives in some cases. In general, the radiation sensitive composition

is prepared as a liquid composition having the components other than the colorant (A) dissolved in an appropriate solvent.

As such a solvent, any solvent can be selected and used
5 as appropriate as long as it disperses or dissolves the components (A) to (D) and the additive components, does not react with these components and exhibits a moderate degree of volatility.

Specific examples of such a solvent include:

10 (poly)alkylene glycol monoalkyl ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol mono-n-propyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol
15 mono-n-propyl ether, diethylene glycol mono-n-butyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol mono-n-propyl ether, propylene glycol mono-n-butyl ether,
20 dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol mono-n-propyl ether, dipropylene glycol mono-n-butyl ether, tripropylene glycol monomethyl ether, and tripropylene glycol monoethyl ether;
(poly)alkylene glycol monoalkyl ether acetates such as
25 ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether acetate, and propylene glycol monoethyl ether acetate;
30 other ethers such as diethylene glycol dimethyl ether, diethylene glycol methylethyl ether, diethylene glycol diethyl ether, and tetrahydrofuran;
ketones such as methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, 2-heptanone, and 3-heptanone;

alkyl lactates such as methyl 2-hydroxypropionate and ethyl 2-hydroxypropionate;
other esters such as methyl 2-hydroxy-2-methylpropionate, ethyl 2-hydroxy-2-methylpropionate, methyl
5 3-methoxypropionate, ethyl 3-methoxypropionate, methyl 3-ethoxypropionate, ethyl 3-ethoxypropionate, ethyl ethoxyacetate, ethyl hydroxyacetate, methyl 2-hydroxy-3-methylbutyrate, 3-methyl-3-methoxybutyl acetate, 4-methoxybutyl acetate, 3-methyl-3-methoxybutyl
10 propionate, ethyl acetate, n-propyl acetate, i-propyl acetate, n-butyl acetate, i-butyl acetate, n-amyl acetate, i-amyl acetate, n-butyl propionate, ethyl butyrate, n-propyl butyrate, i-propyl butyrate, n-butyl butyrate, methyl pyruvate, ethyl pyruvate, n-propyl pyruvate, methyl
15 acetoacetate, ethyl acetoacetate, and ethyl 2-oxobutyrate; aromatic hydrocarbons such as toluene and xylene; and carboxamides such as N-methylpyrrolidone, N,N-dimethylformamide, and N,N-dimethylacetoamide.

These solvents can be used solely or in admixture of
20 two or more.

Further, in combination with the above solvents, a high boiling solvent such as benzyl ethyl ether, di-n-hexyl ether, acetonylacetone, isophorone, caproic acid, caprylic acid, 1-octanol, 1-nonanol, benzyl alcohol, benzyl acetate, ethyl
25 benzoate, diethyl oxalate, diethyl maleate, γ -butyrolactone, ethylene carbonate, propylene carbonate or ethylene glycol monophenyl ether acetate can be used.

These high boiling solvents can be used solely or in admixture of two or more.

30 Of the foregoing solvents, from the viewpoints of solubility, pigment dispersibility and coatability, propylene glycol monomethyl ether, ethylene glycol monomethyl ether acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate,

diethylene glycol dimethyl ether, cyclohexanone, 2-heptanone, 3-heptanone, ethyl 2-hydroxypropionate, 4-methoxybutyl acetate, 3-methyl-3-methoxybutyl propionate, ethyl 3-methoxypropionate, methyl 3-ethoxypropionate, ethyl 3-ethoxypropionate, n-butyl acetate, i-butyl acetate, n-amyl acetate, i-amyl acetate, n-butyl propionate, ethyl butyrate, i-propyl butyrate, n-butyl butyrate, ethyl pyruvate and the like are preferred, and as the high boiling solvent, γ -butyrolactone is preferred.

10 The solvents are used in an amount of generally 100 to 10,000 parts by weight, preferably 500 to 5,000 parts by weight, based on 100 parts by weight of the alkali soluble resin (B).

Preparation Method of Black Matrix and Spacer

15 Next, a method for preparing a black matrix and a spacer by use of the radiation sensitive composition for a black resist of the present invention will be described.

After the radiation sensitive composition for a black resist of the present invention is applied to a substrate, a solvent is evaporated from the applied composition by pre-baking so as to form a coating film. Then, the coating film is exposed to light in a predetermined pattern via a photomask and then developed by use of an alkali developer. Thereafter, unexposed portions of the coating film are dissolved to be removed, and the resulting substrate is preferably post-baked. Thereby, a black matrix or spacer having a predetermined black pattern thereon can be obtained.

20 a solvent is evaporated from the applied composition by pre-baking so as to form a coating film. Then, the coating film is exposed to light in a predetermined pattern via a photomask and then developed by use of an alkali developer. Thereafter, unexposed portions of the coating film are

25 dissolved to be removed, and the resulting substrate is preferably post-baked. Thereby, a black matrix or spacer having a predetermined black pattern thereon can be obtained.

Illustrative examples of the above substrate include glass, silicon, polycarbonate, polyester, aromatic polyamide, polyamide imide, and polyimide.

30 polyamide, polyamide imide, and polyimide.

Further, as desired, these substrates may be subjected to appropriate pretreatment such as chemical treatment with a silane coupling agent or the like, plasma treatment, ion plating, sputtering, a vapor-phase reaction process or

vacuum deposition.

To apply the radiation sensitive composition for a black resist to the substrate, an appropriate method such as spin coating, cast coating or roller coating can be used.

5 The composition is applied such that the dried coating film has a thickness of generally 0.1 to 10 μm , preferably 0.2 to 7.0 μm , more preferably 0.5 to 6.0 μm .

As the radiation used in preparing the black matrix and spacer, visible radiation, ultraviolet radiation, far
10 ultraviolet radiation, an electron beam or X rays can be used, for example. Radiation having a wavelength of 190 to 450 nm is preferred.

The amount of energy of the irradiated radiation is preferably 10 to 10,000 J/m^2 .

15 Further, as the above alkali developer, an aqueous solution such as sodium carbonate, sodium hydroxide, potassium hydroxide, tetramethylammonium hydroxide, choline, 1,8-diazabicyclo-[5.4.0]-7-undecene or 1,5-diazabicyclo-[4.3.0]-5-nonene is preferred.

20 To the above alkali developer, an appropriate amount of a water-soluble organic solvent or surfactant such as methanol or ethanol can be added. The alkali solution is generally rinsed by water.

As a development method, a shower development method,
25 a spray development method, a dip development method or a paddle development method can be used. The development is preferably carried out at room temperature for 5 to 300 seconds.

The thus prepared black matrix and spacer are extremely
30 useful in, for example, a color liquid crystal display, a color image pickup tube device and a color sensor.

Hereinafter, an embodiment of the present invention will be further described with reference to Examples. However, the present invention is not limited by the following

Examples in any way.

Examples

Example 1

5 100 parts by weight of carbon black and 30 parts by weight of barium sulfate as the colorant (A), 30 parts by weight of compound having an urethane bond which is a dispersant (trade name: Disperbyk-182), 50 parts by weight of methacrylic acid/2-hydroxyethyl methacrylate/benzyl
10 methacrylate/polystyrene macromonomer copolymer (copolymerization weight ratio: 15/15/60/10, $M_w = 25,000$) as the alkali soluble resin (B), 40 parts by weight of dipentaerythritol hexaacrylate as the multifunctional monomer (C), 10 parts by weight of
15 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxy carbonylphenyl)-1,2'-biimidazole, 10 parts by weight of 4,4'-bis(diethylamino)benzophenone and 20 parts by weight of
2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butane-1-
20 one as the photopolymerization initiator (D), and 1,500 parts by weight of ethyl 3-ethoxypropionate as a solvent were mixed together so as to prepare a liquid radiation sensitive composition.

25 The liquid composition was coated on a surface of a soda glass substrate by use of a spin coater. The surface of the substrate had a silica (SiO_2) film for preventing elution of sodium ions formed thereon. The resulting substrate was pre-baked at 90°C for 4 minutes so as to form a coating film having a film thickness of $1.3\ \mu\text{m}$.

30 Then, after the substrate was cooled to room temperature, the coating film was irradiated with an ultraviolet radiation having a wavelength of 365 nm for an energy amount of $2,000\ \text{J/m}^2$ via a photomask by use of a high pressure mercury lamp. Then, the substrate was immersed in

0.04% by weight of potassium hydroxide solution at 23°C for 1 minute so as to develop the coating film, rinsed with ultrapure water, and air-dried. Thereafter, the substrate was post-baked at 250°C for 30 minutes, thereby preparing
5 a black matrix having a black pattern formed on the substrate.

Then, 1% by weight of the dispersant used above was dissolved in a mixture comprising the above components (B) to (D) and solvent. The resulting mixture was spin-coated, to a film thickness of 3 μm , on a glass substrate having an
10 ITO film formed on a surface. The resulting substrate was pre-baked at 80°C for 10 minutes, irradiated with the same ultraviolet radiation as used above for an energy amount of 2,000 J/m^2 , and then post-baked at 220°C for 1 hour. Thereafter, the coated substrate was bonded to another glass
15 substrate having an ITO film formed on a surface, and a liquid crystal was injected between the substrates so as to prepare a liquid crystal cell which was then annealed at 100°C for 1 hour. When voltage retention of the obtained liquid crystal cell was measured at 60°C with a retention time of
20 16.7 milliseconds, it was 86%.

Further, when an acid value and amine value of the dispersant used above were measured by a titration method, the acid value was 0 mgKOH/g and the amine value was 14 mgKOH/g.

25 When the obtained substrate was assembled into a display panel and a display test was conducted, display defects such as sticking were not seen.

Further, neither residues nor scums were seen in unexposed portions on the obtained substrate, and neither
30 peeling nor loss of the pattern was seen. In addition, the pattern had high film hardness and a very smooth surface.
Example 2

140 parts by weight of C.I. PIGMENT RED 177, 60 parts by weight of C.I. PIGMENT BLUE 15:4 and 30 parts by weight

of barium sulfate as the colorant (A), 60 parts by weight of compound having an urethane bond which is a dispersant (trade name: Disperbyk-182), 50 parts by weight of methacrylic acid/2-hydroxyethyl methacrylate/benzyl methacrylate/polystyrene macromonomer copolymer (copolymerization weight ratio: 15/15/60/10, $M_w = 25,000$) as the alkali soluble resin (B), 40 parts by weight of dipentaerythritol hexaacrylate as the multifunctional monomer (C), 10 parts by weight of 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxy carbonylphenyl)-1,2'-biimidazole, 10 parts by weight of 4,4'-bis(diethylamino)benzophenone and 20 parts by weight of 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butane-1-one as the photopolymerization initiator (D), and 1,500 parts by weight of ethyl 3-ethoxypropionate as a solvent were mixed together so as to prepare a liquid radiation sensitive composition.

The liquid composition was coated on a surface of a soda glass substrate by use of a spin coater. The surface of the substrate had a silica (SiO_2) film for preventing elution of sodium ions formed thereon. The resulting substrate was pre-baked at 90°C for 4 minutes so as to form a coating film having a film thickness of 7.0 μm .

Then, a black matrix was formed in the same manner as in Example 1.

When the obtained substrate was assembled into a display panel and a display test was conducted, display defects such as sticking were not seen.

Further, neither residues nor scums were seen in unexposed portions on the obtained substrate, and neither peeling nor loss of the pattern was seen. In addition, the pattern had high film hardness and a very smooth surface.

Example 3

A black matrix was prepared in the same manner as in Example 1 except that as the compound having an urethane bond which is a dispersant, Disperbyk-170 was used in place of Disperbyk-182.

5 A liquid crystal cell was prepared in the same manner as in Example 1 except that a solution obtained by dissolving 1% by weight of the dispersant used above in a mixture comprising the above components (B) to (D) and solvent was used. When voltage retention of the liquid crystal cell was
10 measured in the same manner as in Example 1, it was 87%.

Further, when an acid value and amine value of the dispersant used above were measured by a titration method, the acid value was 11 mgKOH/g and the amine value was 0 mgKOH/g.

15 When the obtained substrate was assembled into a display panel and a display test was conducted, display defects such as sticking were not seen.

Further, neither residues nor scums were seen in unexposed portions on the obtained substrate, and neither
20 peeling nor loss of the pattern was seen. In addition, the pattern had high film hardness and a very smooth surface.
Example 4

A black matrix was prepared in the same manner as in Example 1 except that as the compound having an urethane bond
25 which is a dispersant, Disperbyk-165 was used in place of Disperbyk-182.

A liquid crystal cell was prepared in the same manner as in Example 1 except that a solution obtained by dissolving 1% by weight of the dispersant used above in a mixture
30 comprising the above components (B) to (D) and solvent was used. When voltage retention of the liquid crystal cell was measured in the same manner as in Example 1, it was 87%.

Further, when an acid value and amine value of the dispersant used above were measured by a titration method,

the acid value was 0 mgKOH/g and the amine value was 15 mgKOH/g.

When the obtained substrate was assembled into a display panel and a display test was conducted, display defects such as sticking were not seen.

Further, neither residues nor scums were seen in unexposed portions on the obtained substrate, and neither peeling nor loss of the pattern was seen. In addition, the pattern had high film hardness and a very smooth surface.

10 Example 5

50 parts by weight of carbon black and 15 parts by weight of barium sulfate as the colorant (A), 20 parts by weight of compound having an urethane bond which is a dispersant (trade name: Disperbyk-162), 50 parts by weight of methacrylic acid/2-hydroxyethyl methacrylate/benzyl methacrylate/polystyrene macromonomer copolymer (copolymerization weight ratio: 15/15/60/10, Mw = 25,000) as the alkali soluble resin (B), 40 parts by weight of dipentaerythritol hexaacrylate as the multifunctional monomer (C), 10 parts by weight of 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxy carbonylphenyl)-1,2'-biimidazole, 10 parts by weight of 4,4'-bis(diethylamino)benzophenone and 20 parts by weight of 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butane-1-one as the photopolymerization initiator (D), and 1,500 parts by weight of ethyl 3-ethoxypropionate as a solvent were mixed together so as to prepare a liquid radiation sensitive composition.

30 The liquid composition was coated on a surface of a soda glass substrate by use of a spin coater. The surface of the substrate had a silica (SiO₂) film for preventing elution of sodium ions formed thereon. The resulting substrate was pre-baked at 90°C for 4 minutes so as to form a coating film

having a film thickness of 1.3 μm .

Then, a black matrix was prepared in the same manner as in Example 1.

Then, 1% by weight of the dispersant used above was
5 dissolved in a mixture comprising the above components (B)
to (D) and solvent. The resulting mixture was spin-coated,
to a film thickness of 3 μm , on a glass substrate having an
ITO film formed on a surface. The resulting substrate was
pre-baked at 80°C for 10 minutes, irradiated with the same
10 ultraviolet radiation as used above for an energy amount of
2,000 J/m², and then post-baked at 220°C for 1 hour.
Thereafter, the coated substrate was bonded to another glass
substrate having an ITO film formed on a surface, and a liquid
crystal was injected between the substrates so as to prepare
15 a liquid crystal cell which was then annealed at 100°C for
1 hour. When voltage retention of the obtained liquid
crystal cell was measured at 60°C with a retention time of
16.7 milliseconds, it was 86%.

Further, when an acid value and amine value of the
20 dispersant used above were measured by a titration method,
the acid value was 0 mgKOH/g and the amine value was 14 mgKOH/g.
In addition, the dispersant had an Mw of 16,000.

Furthermore, when an average particle diameter of
barium sulfate used above was measured by means of a
25 transmission electron microscope, it was 0.1 μm .

When the obtained substrate was assembled into a
display panel and a display test was conducted, display
defects such as sticking were not seen.

Further, neither residues nor scums were seen in
30 unexposed portions on the obtained substrate, and neither
peeling nor loss of the pattern was seen. In addition, the
pattern had high film hardness and a very smooth surface.
Example 6

A liquid radiation sensitive composition was prepared

in the same manner as in Example 5.

The liquid composition was coated on a surface of a soda glass substrate by use of a spin coater. The surface of the substrate had a silica (SiO_2) film for preventing elution of sodium ions formed thereon. The resulting substrate was pre-baked at 90°C for 4 minutes so as to form a coating film having a film thickness of $1.3\text{ }\mu\text{m}$.

Then, after the substrate was cooled to room temperature, the coating film was irradiated with an ultraviolet radiation having a wavelength of 365 nm for an energy amount of $2,000\text{ J/m}^2$ via a photomask by use of a high pressure mercury lamp. Then, the substrate was immersed in 0.04% by weight of potassium hydroxide solution at 23°C for 1 minute so as to develop the coating film, rinsed with ultrapure water, and air-dried. Thereafter, the substrate was post-baked at 250°C for 30 minutes, thereby preparing a black spacer having black dot patterns each having a height of $5\text{ }\mu\text{m}$ and a size of $18\text{ }\mu\text{m} \times 18\text{ }\mu\text{m}$ formed on the substrate.

When the obtained substrate was assembled into a display panel and a display test was conducted, display defects such as sticking were not seen.

Further, neither residues nor scums were seen in unexposed portions on the obtained substrate, and neither peeling nor loss of the pattern was seen. In addition, the pattern had high film hardness and a very smooth surface.

Example 7

75 parts by weight of C.I. PIGMENT RED 177, 15 parts by weight of C.I. PIGMENT BLUE 15:4, 10 parts by weight of C.I. PIGMENT YELLOW 150 and 30 parts by weight of barium sulfate as the colorant (A), 60 parts by weight of compound having an urethane bond which is a dispersant (trade name: Disperbyk-162), 70 parts by weight of methacrylic acid/2-hydroxyethyl methacrylate/benzyl methacrylate/polystyrene macromonomer copolymer

(copolymerization weight ratio: 15/15/60/10, $M_w = 25,000$) as the alkali soluble resin (B), 60 parts by weight of dipentaerythritol hexaacrylate as the multifunctional monomer (C), 10 parts by weight of

5 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxy carbonylphenyl)-1,2'-biimidazole, 10 parts by weight of 4,4'-bis(diethylamino)benzophenone and 50 parts by weight of

10 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butane-1-one as the photopolymerization initiator (D), and 1,500 parts by weight of ethyl 3-ethoxypropionate as a solvent were mixed together so as to prepare a liquid radiation sensitive composition.

The liquid composition was coated on a surface of a soda glass substrate by use of a spin coater. The surface of the

15 substrate had a silica (SiO_2) film for preventing elution of sodium ions formed thereon. The resulting substrate was pre-baked at 90°C for 4 minutes so as to form a coating film having a film thickness of $7.0\ \mu\text{m}$.

20 Then, a black matrix was formed in the same manner as in Example 1.

When the obtained substrate was assembled into a display panel and a display test was conducted, display defects such as sticking were not seen.

25 Further, neither residues nor scums were seen in unexposed portions on the obtained substrate, and neither peeling nor loss of the pattern was seen. In addition, the pattern had high film hardness and a very smooth surface.

Example 8

30 A liquid radiation sensitive composition was prepared in the same manner as in Example 7.

The liquid composition was coated on a surface of a soda glass substrate by use of a spin coater. The surface of the substrate had a silica (SiO_2) film for preventing elution of

sodium ions formed thereon. The resulting substrate was pre-baked at 90°C for 4 minutes so as to form a coating film having a film thickness of 7.0 μm.

Then, a black spacer was formed in the same manner as in Example 6.

When the obtained substrate was assembled into a display panel and a display test was conducted, display defects such as sticking were not seen.

Further, neither residues nor scums were seen in unexposed portions on the obtained substrate, and neither peeling nor loss of the pattern was seen. In addition, the pattern had high film hardness and a very smooth surface.

Example 9

75 parts by weight of C.I. PIGMENT RED 177, 15 parts by weight of C.I. PIGMENT BLUE 15:4, 10 parts by weight of C.I. PIGMENT YELLOW 150 and 30 parts by weight of barium sulfate as the colorant (A), 60 parts by weight of compound having an urethane bond which is a dispersant (trade name: Disperbyk-162), 70 parts by weight of methacrylic acid/mono(2-acryloyloxyethyl)succinate/styrene/benzyl methacrylate/N-phenylmaleimide copolymer (copolymerization weight ratio: 25/12/18/15/30, Mw = 20,000) as the alkali soluble resin (B), 60 parts by weight of dipentaerythritol hexaacrylate as the multifunctional monomer (C), 10 parts by weight of 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxy carbonylphenyl)-1,2'-biimidazole, 10 parts by weight of 4,4'-bis(diethylamino)benzophenone and 50 parts by weight of 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butane-1-one as the photopolymerization initiator (D), and 1,500 parts by weight of ethyl 3-ethoxypropionate as a solvent were mixed together so as to prepare a liquid radiation sensitive composition.

The liquid composition was coated on a surface of a soda glass substrate by use of a spin coater. The surface of the substrate had a silica (SiO_2) film for preventing elution of sodium ions formed thereon. The resulting substrate was
5 pre-baked at 90°C for 4 minutes so as to form a coating film having a film thickness of $7.0\text{ }\mu\text{m}$.

Then, a black spacer was formed in the same manner as in Example 6.

When the obtained substrate was assembled into a
10 display panel and a display test was conducted, display defects such as sticking were not seen.

Further, neither residues nor scums were seen in unexposed portions on the obtained substrate, and neither peeling nor loss of the pattern was seen. In addition, the
15 pattern had high film hardness and a very smooth surface.
Example 10

A black spacer was prepared in the same manner as in Example 9 except that as the compound having an urethane bond which is a dispersant, Disperbyk-170 was used in place of
20 Disperbyk-162.

A liquid crystal cell was prepared in the same manner as in Example 1 except that a solution obtained by dissolving 1% by weight of the dispersant used above in a mixture comprising the above components (B) to (D) and solvent was
25 used. When voltage retention of the liquid crystal cell was measured in the same manner as in Example 1, it was 87%.

Further, when an acid value and amine value of the dispersant used above were measured by a titration method, the acid value was 11 mgKOH/g and the amine value was 0
30 mgKOH/g .

When the obtained substrate was assembled into a display panel and a display test was conducted, display defects such as sticking were not seen.

Further, neither residues nor scums were seen in

unexposed portions on the obtained substrate, and neither peeling nor loss of the pattern was seen. In addition, the pattern had high film hardness and a very smooth surface.

Example 11

5 75 parts by weight of C.I. PIGMENT RED 177, 20 parts by weight of C.I. PIGMENT BLUE 15:4, 10 parts by weight of C.I. PIGMENT YELLOW 150 and 30 parts by weight of barium sulfate as the colorant (A), 60 parts by weight of compound having an urethane bond which is a dispersant (trade name: 10 Disperbyk-162), 60 parts by weight of methacrylic acid/2-hydroxyethyl methacrylate/benzyl methacrylate/polystyrene macromonomer copolymer (copolymerization weight ratio: 15/15/60/10, $M_w = 25,000$) and 10 parts by weight of methacrylic 15 acid/mono(2-acryloyloxyethyl)succinate/styrene/benzyl methacrylate/N-phenylmaleimide copolymer (copolymerization weight ratio: 25/12/18/15/30, $M_w = 20,000$) as the alkali soluble resin (B), 60 parts by weight of dipentaerythritol hexaacrylate as the multifunctional monomer (C), 10 parts 20 by weight of 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxy carbonylphenyl)-1,2'-biimidazole, 10 parts by weight of 4,4'-bis(diethylamino)benzophenone and 50 parts by weight of 25 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butane-1-one as the photopolymerization initiator (D), and 1,500 parts by weight of ethyl 3-ethoxypropionate as a solvent were mixed together so as to prepare a liquid radiation sensitive composition.

30 The liquid composition was coated on a surface of a soda glass substrate by use of a spin coater. The surface of the substrate had a silica (SiO_2) film for preventing elution of sodium ions formed thereon. The resulting substrate was pre-baked at 90°C for 4 minutes so as to form a coating film

having a film thickness of 7.0 μm .

Then, a black spacer was formed in the same manner as in Example 6.

When the obtained substrate was assembled into a display panel and a display test was conducted, display defects such as sticking were not seen.

Further, neither residues nor scums were seen in unexposed portions on the obtained substrate, and neither peeling nor loss of the pattern was seen. In addition, the pattern had high film hardness and a very smooth surface. Example 12

75 parts by weight of C.I. PIGMENT RED 177, 15 parts by weight of C.I. PIGMENT BLUE 15:4, 10 parts by weight of C.I. PIGMENT YELLOW 150 and 30 parts by weight of barium sulfate as the colorant (A), 60 parts by weight of compound having an urethane bond which is a dispersant (trade name: Disperbyk-162), 60 parts by weight of methacrylic acid/mono(2-acryloyloxyethyl)succinate/styrene/benzyl methacrylate/N-phenylmaleimide copolymer (copolymerization weight ratio: 25/12/8/15/40, $M_w = 20,000$) and 10 parts by weight of methacrylic acid/mono(2-acryloyloxyethyl)succinate/styrene/benzyl methacrylate/N-phenylmaleimide copolymer (copolymerization weight ratio: 25/12/18/15/30, $M_w = 20,000$) as the alkali soluble resin (B), 60 parts by weight of dipentaerythritol hexaacrylate as the multifunctional monomer (C), 10 parts by weight of 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxy carbonylphenyl)-1,2'-biimidazole, 10 parts by weight of 4,4'-bis(diethylamino)benzophenone and 50 parts by weight of 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butane-1-one as the photopolymerization initiator (D), and 1,500 parts by weight of ethyl 3-ethoxypropionate as a solvent were mixed

together so as to prepare a liquid radiation sensitive composition.

The liquid composition was coated on a surface of a soda glass substrate by use of a spin coater. The surface of the substrate had a silica (SiO_2) film for preventing elution of sodium ions formed thereon. The resulting substrate was pre-baked at 90°C for 4 minutes so as to form a coating film having a film thickness of $7.0\text{ }\mu\text{m}$.

Then, a black spacer was formed in the same manner as in Example 6.

When the obtained substrate was assembled into a display panel and a display test was conducted, display defects such as sticking were not seen.

Further, neither residues nor scums were seen in unexposed portions on the obtained substrate, and neither peeling nor loss of the pattern was seen. In addition, the pattern had high film hardness and a very smooth surface. Example 13

10 parts by weight of carbon black, 50 parts by weight of C.I. PIGMENT RED 177, 15 parts by weight of C.I. PIGMENT BLUE 15:4, 10 parts by weight of C.I. PIGMENT YELLOW 150 and 20 parts by weight of barium sulfate as the colorant (A), 60 parts by weight of compound having an urethane bond which is a dispersant (trade name: Disperbyk-162), 70 parts by weight of methacrylic acid/mono(2-acryloyloxyethyl)succinate/styrene/benzyl methacrylate/N-phenylmaleimide copolymer (copolymerization weight ratio: 25/12/18/15/30, $M_w = 20,000$) as the alkali soluble resin (B), 60 parts by weight of dipentaerythritol hexaacrylate as the multifunctional monomer (C), 10 parts by weight of 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxy carbonylphenyl)-1,2'-biimidazole, 10 parts by weight of 4,4'-bis(diethylamino)benzophenone and 50 parts by weight

of

2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butane-1-one as the photopolymerization initiator (D), and 1,500 parts by weight of ethyl 3-ethoxypropionate as a solvent were mixed
5 together so as to prepare a liquid radiation sensitive composition.

The liquid composition was coated on a surface of a soda glass substrate by use of a spin coater. The surface of the substrate had a silica (SiO_2) film for preventing elution of
10 sodium ions formed thereon. The resulting substrate was pre-baked at 90°C for 4 minutes so as to form a coating film having a film thickness of 7.0 μm .

Then, a black spacer was formed in the same manner as in Example 6.

15 When the obtained substrate was assembled into a display panel and a display test was conducted, display defects such as sticking were not seen.

Further, neither residues nor scums were seen in unexposed portions on the obtained substrate, and neither
20 peeling nor loss of the pattern was seen. In addition, the pattern had high film hardness and a very smooth surface. Comparative Example 1

A black matrix was prepared in the same manner as in Example 1 except that as the dispersant, a
25 polyethyleneimine-polyester-based dispersant (trade name: Solsperse 24000, product of ZENECA LTD.) was used in place of the compound having an urethane bond which is a dispersant (trade name: Disperbyk-182).

A liquid crystal cell was prepared in the same manner
30 as in Example 1 except that a solution obtained by dissolving 1% by weight of the dispersant used above in a mixture comprising the above components (B) to (D) and solvent was used. When voltage retention of the liquid crystal cell was measured in the same manner as in Example 1, it was 71%.

Further, when an acid value and amine value of the dispersant used above were measured by a titration method, the acid value was 24 mgKOH/g and the amine value was 47 mgKOH/g.

- 5 When the obtained substrate was assembled into a display panel and a display test was conducted, sticking occurred.

Effects of the Invention

- 10 The radiation sensitive composition for a black resist of the present invention, particularly when assembled into a display panel, does not cause display defects such as sticking, has a high degree of film hardness, provides a very smooth pattern surface, hardly causes residues and scums in unexposed portions on a substrate, provides a pattern which
- 15 shows excellent adhesion to the substrate at the time of development, and causes neither peeling nor loss of the pattern. Therefore, the radiation sensitive composition for a black resist of the present invention can be very suitably used in a black matrix and/or spacer for a color filter used
- 20 in a color liquid crystal display, a color image pickup tube device, a color sensor, and the like.

CLAIMS

- 5 1. A radiation sensitive composition for a black resist, comprising (A) a colorant containing a black pigment, (B) an alkali soluble resin, (C) a multifunctional monomer, and (D) a photopolymerization initiator, wherein the colorant (A) contains an extender pigment in an amount of
10 5 to 50 parts by weight based on 100 parts by weight of the black pigment and is dispersed by a dispersant containing a compound which has an urethane bond and becomes insoluble in a polar solvent when it is heated at a temperature of not lower than 150°C for at least 30 minutes.
- 15
2. The composition of claim 1, wherein the compound having an urethane bond which is a dispersant
20 comprises a compound having an acid value of 5 to 25 mgKOH/g and an amine value of 0 mgKOH/g.
3. The composition of claim 1, wherein the compound having an urethane bond which is a dispersant
25 comprises a compound having an amine value of 5 to 25 mgKOH/g and an acid value of 0 mgKOH/g.
4. The composition of claim 1, 2 or 3, wherein the compound having an urethane bond which is a dispersant
30 comprises a compound having a voltage retention of not lower than 80%.
5. The composition of claim 1, 2, 3 or 4, wherein the colorant (A) contains C.I. PIGMENT RED 177 and C.I.

PIGMENT BLUE 15:4 and/or C.I. PIGMENT BLUE 15:6.

6. The composition of claim 1, wherein the photopolymerization initiator (D) contains at least one biimidazole compound (1) selected from the group consisting of 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxy carbonylphenyl)-1,2'-biimidazole and 2,2'-bis(2-bromophenyl)-4,4',5,5'-tetrakis(4-ethoxy carbonylphenyl)-1,2'-biimidazole.

10

7. The composition of claim 1, wherein the photopolymerization initiator (D) contains at least one biimidazole compound (2) selected from the group consisting of

15 2,2'-bis(2,4-dichlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole,

2,2'-bis(2,4,6-trichlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole,

2,2'-bis(2,4-dibromophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole, and

20 2,2'-bis(2,4,6-tribromophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole.

8. The composition of claim 6 or 7, wherein the photopolymerization initiator (D) further contains at least one component selected from the group consisting of a benzophenone compound having a benzoin bond, other benzophenone photo radical generating agent, a benzophenone sensitizer and a thiazole-based hardening accelerator.

30

9. The composition of claim 1, wherein the alkali soluble resin (B) comprises at least one selected from the group consisting of a carboxyl-group-containing copolymer (Ia), a carboxyl-group-containing copolymer (Ib), a

carboxyl-group-containing copolymer (Ic), and a
carboxyl-group-containing copolymer (Id).

10. The composition of claim 1, wherein the multifunctional
5 monomer (C) comprises at least one selected from the group
consisting of trimethylolpropane triacrylate,
pentaerythritol triacrylate and dipentaerythritol
hexaacrylate.
- 10 11. The composition of claim 1, wherein the colorant (A)
contains carbon black and/or an organic pigment.
- 15 12. The composition of claim 1, wherein the
compound having an urethane bond which is a dispersant has
at least one property out of the following properties (a)
to (c) (provided that it does not have the properties (a)
and (b) simultaneously):
- 20 (a) having an acid value of 5 to 25 mgKOH/g, preferably 8
to 20 mgKOH/g, and an amine value of 0 mgKOH/g;
(b) having an amine value of 5 to 25 mgKOH/g, preferably 8
to 20 mgKOH/g, and an acid value of 0 mgKOH/g; and
(c) having a voltage retention of not lower than 80%,
25 preferably not lower than 85%.