



159159

1

DESCRIPTION



G00002

RADIATION SENSITIVE RESIN COMPOSITION AND COLOR FILTER

5 TECHNICAL FIELD

The present invention relates to a radiation sensitive resin composition useful for the manufacture of a color filter for use in transmission and reflection type color liquid crystal devices and color image pick-up devices, a method of preparing the same, a color filter formed from the radiation sensitive resin composition and a color liquid crystal display device comprising the color filter.

BACKGROUND ART

As means of forming a color filter by using a colored radiation sensitive resin composition, there is known a method in which a coating film of a colored radiation sensitive resin composition is formed on a substrate or a substrate comprising a light screening layer having a desired pattern, exposed to radiation through a photomask having a desired pattern shape (to be referred to as "exposure" hereinafter), developed with an alkali developer to dissolve and remove an unexposed portion and post-baked in a clean oven or on a hot plate so as to obtain color pixels (refer to JP-A 2000-329929 and JP 3639859).

Since substrates used to form a color filter are becoming larger in size, means of applying a radiation sensitive resin composition is shifting from spin coating for dropping the composition on the center of a substrate to slit nozzle coating using a small-diameter liquid ejection portion for applying the radiation sensitive resin composition. In the latter slit nozzle coating, as the diameter of the liquid ejection portion is small and narrow, the radiation sensitive resin composition often remains

around the end of the nozzle after coating. When the resin composition becomes dry, it is dropped on a color filter as dry foreign matter at the time of next coating and greatly reduces the quality of the color filter. Therefore, a jet
5 of a cleaning solvent is applied to the end of the nozzle before coating to clean it. However, the reduction of the quality of the color filter by the dry foreign matter still cannot be prevented effectively, thereby causing a great reduction in product yield.

10 To cope with this problem, a radiation sensitive resin composition for color filters which has cleanability with a cleaning solvent, that is, high solubility in a cleaning solvent even after it is dried is now in demand.

Long service life is desired for a liquid crystal
15 display device comprising a color filter, and the requirement for the burning preventing capability of the color filter is becoming stronger.

The term "burning" is a kind of display failure of a liquid crystal display device and a phenomenon that an image
20 which should not be displayed is displayed on the screen, or a black or white "fog" is displayed over an image which should be displayed. The cause of this phenomenon is considered as follows. That is, charged impurities contained in liquid crystals spread into the liquid crystals
25 and a potential difference applied to align liquid crystal molecules is not maintained for a certain period of time. It has recently been found that the impurities not only are produced at the time of manufacturing liquid crystal molecules but also soak from the inside of the formed color
30 filter.

As disclosed by JP-A 2000-329929, it is known that this phenomenon can be effectively prevented by increasing the purity of a pigment. However, as the impurities may be derived from components other than the pigment contained in

the radiation sensitive resin composition, it cannot be said that increasing the purity of the pigment can always prevent the above phenomenon completely.

Then, the development of a radiation sensitive resin composition for color filters which meets the requirement for high product yield and is free from "burning" at the time of manufacturing a color filter is strongly desired.

DISCLOSURE OF THE INVENTION

10 It is an object of the present invention to provide a radiation sensitive resin composition which can provide a color filter free from "burning" at a high product yield.

It is another object of the present invention to provide a method of preparing the above radiation sensitive resin composition.

15 It is still another object of the present invention to provide a color filter free from "burning" formed from the above radiation sensitive resin composition and a color liquid crystal display device comprising the filter.

20 Firstly, the above objects and advantages of the present invention are attained by a radiation sensitive resin composition comprising (A) a colorant, (B) an alkali-soluble resin, (C) a polyfunctional monomer and (D) a radiation sensitive radical generator, wherein

25 the alkali-soluble resin (B) is manufactured through the living radical polymerization of a polymerizable unsaturated compound and has a weight average molecular weight in terms of polystyrene (Mw) measured by gel permeation chromatography (GPC) of 1,000 to 45,000.

30 Secondly, the above objects and advantages of the present invention are attained by a radiation sensitive resin composition comprising (A) a colorant, (B) an alkali-soluble resin, (C) a polyfunctional monomer and (D) a radiation sensitive radical generator, wherein

the alkali-soluble resin (B) has a group represented by the formula (i) which will be described hereinafter or a group represented by the formula (ii) which will be described hereinafter at at least one of the terminals of a polymer chain constituting the alkali-soluble resin and has a weight average molecular weight in terms of polystyrene (Mw) measured by gel permeation chromatography of 1,000 to 45,000.

Thirdly, the above objects and advantages of the present invention are attained by a method of preparing the above radiation sensitive resin composition by mixing the alkali-soluble resin (B), the polyfunctional monomer (C) and the radiation sensitive radical generator (D) with a pigment dispersion obtained by mixing and dispersing a pigment as the colorant (A) in a solvent in the presence of a dispersant while it is ground.

In the fourth place, the above objects and advantages of the present invention are attained by the above radiation sensitive resin composition which is used for color filters (to be referred to as "radiation sensitive resin composition for color filters" hereinafter).

In the fifth place, the above objects and advantages of the present invention are attained by a color filter formed from the radiation sensitive resin composition for color filters.

In the sixth place, the above objects and advantages of the present invention are attained by a color liquid crystal display device comprising the above color filter.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will be described in detail hereinafter.

Radiation sensitive resin composition

- (A) colorant -

The colorant in the present invention is not particularly limited and may be a pigment, dye or natural coloring matter. Since the development of a high-purity and high-transmission color and heat resistance are required for a color filter, a pigment is preferred, and an organic pigment or carbon black is particularly preferred.

Examples of the above organic pigment are compounds classified into a group of pigments according to color index, specifically compounds having the following color index (C.I.) numbers:

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, 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, C.I. Pigment Yellow 168 and C.I. Pigment Yellow 211;

C.I. Pigment Orange 5, C.I. Pigment Orange 13, C.I. Pigment Orange 14, C.I. Pigment Orange 24, C.I. Pigment Orange 34, C.I. Pigment Orange 36, C.I. Pigment Orange 38, C.I. Pigment Orange 40, C.I. Pigment Orange 43, C.I. Pigment Orange 46, C.I. Pigment Orange 49, C.I. Pigment Orange 61, C.I. Pigment Orange 64, C.I. Pigment Orange 68, C.I. Pigment Orange 70, C.I. Pigment Orange 71, C.I. Pigment Orange 72, C.I. Pigment Orange 73 and C.I. Pigment Orange 74;

C.I. Pigment Red 1, C.I. Pigment Red 2, C.I. Pigment Red 5, C.I. Pigment Red 17, C.I. Pigment Red 31, C.I. Pigment Red 32, C.I. Pigment Red 41, C.I. Pigment Red 122, C.I. Pigment Red 123, C.I. Pigment Red 144, C.I. Pigment Red 149, C.I. Pigment Red 166, C.I. Pigment Red 168, C.I. Pigment Red 170, C.I. Pigment Red 171, C.I. Pigment Red 175, C.I. Pigment Red 176, C.I. Pigment Red 177, C.I. Pigment Red 178, C.I. Pigment

Red 179, C.I. Pigment Red 180, C.I. Pigment Red 185, C.I. Pigment Red 187, C.I. Pigment Red 202, C.I. Pigment Red 206, C.I. Pigment Red 207, C.I. Pigment Red 209, C.I. Pigment Red 214, C.I. Pigment Red 220, C.I. Pigment Red 221, C.I. Pigment Red 224, C.I. Pigment Red 242, C.I. Pigment Red 243, C.I. Pigment Red 254, C.I. Pigment Red 255, C.I. Pigment Red 262, C.I. Pigment Red 264 and C.I. Pigment Red 272; C.I. Pigment Violet 1, C.I. Pigment Violet 19, C.I. Pigment Violet 23, C.I. Pigment Violet 29, C.I. Pigment Violet 32, C.I. Pigment Violet 36 and C.I. Pigment Violet 38; C.I. Pigment Blue 15, C.I. Pigment Blue 15:3, C.I. Pigment Blue 15:4, C.I. Pigment Blue 15:6, C.I. Pigment Blue 60 and C.I. Pigment Blue 80; C.I. Pigment Green 7 and C.I. Pigment Green 36; C.I. Pigment Brown 23 and C.I. Pigment Brown 25; and C.I. Pigment Black 1 and C.I. Pigment Black 7.

Out of these organic pigments, C.I. Pigment Yellow 83, C.I. Pigment Yellow 139, C.I. Pigment Yellow 138, C.I. Pigment Yellow 150, C.I. Pigment Yellow 180, C.I. Pigment Red 177, C.I. Pigment Red 254, C.I. Pigment Blue 15:3 1, C.I. Pigment Blue 15:4, C.I. Pigment Blue 15:6, C.I. Pigment Green 7, C.I. Pigment Green 36, C.I. Pigment Violet 23, C.I. Pigment Blue 60 or C.I. Pigment Blue 80 is preferred.

The above organic pigments may be used alone or in combination of two or more, and a mixture of an organic pigment and carbon black may also be used.

In the present invention, the radiation sensitive resin composition can be prepared by a suitable method. When a pigment is used as the colorant, it is preferably mixed and dispersed in a solvent in the presence of a dispersant while it is ground by a bead mill or a roll mill to prepare a pigment dispersion which is then mixed with the components (B), (C) and (D) and optionally with an additional solvent and other additives which will be described hereinafter to

prepare the radiation sensitive resin composition.

Although the above dispersant used to prepare the above pigment dispersion may be a cationic, anionic, nonionic or ampholytic dispersant, a dispersant which comprises a compound having an urethane bond (to be referred to as "urethane-based dispersant" hereinafter) is preferred.

The above urethane-based dispersant is represented by the formula $R-NH-COO-R'$ (R and R' are each an aliphatic, alicyclic or aromatic monovalent or polyvalent organic group, and the polyvalent organic group is bonded to a group having another urethane bond or another group). That is, the urethane bond may exist in a lipophilic group and/or hydrophilic group contained in the urethane-based dispersant or the main chain and/or side chain of the urethane-based dispersant, and further one or more urethane bonds can exist in the urethane-based dispersant. When two or more urethane bonds are existent in the urethane-based dispersant, the groups bonded to the urethane bonds may be the same or different.

The urethane-based dispersant is, for example, a reaction product of a diisocyanate and/or a triisocyanate and a polyester having a hydroxyl group at one terminal and/or a polyester having a hydroxyl group at both terminals.

Examples of the diisocyanate include benzene diisocyanates such as benzene-1,3-diisocyanate and benzene-1,4-diisocyanate; toluene diisocyanates such as toluene-2,4-diisocyanate, toluene-2,5-diisocyanate, toluene-2,6-diisocyanate and toluene-3,5-diisocyanate; and other aromatic diisocyanates such as xylene diisocyanates including 1,2-xylene-3,5-diisocyanate, 1,2-xylene-3,6-diisocyanate, 1,3-xylene-2,4-diisocyanate, 1,3-xylene-2,5-diisocyanate, 1,3-xylene-4,6-diisocyanate, 1,4-xylene-2,5-diisocyanate and 1,4-xylene-2,6-diisocyanate.

Examples of the above triisocyanate include benzene triisocyanates such as benzene-1,2,4-triisocyanate, benzene-1,2,5-triisocyanate and benzene-1,3,5-triisocyanate; toluene triisocyanates such as toluene-2,3,5-triisocyanate, toluene-2,3,6-triisocyanate, toluene-2,4,5-triisocyanate and toluene-2,4,6-triisocyanate; and other aromatic triisocyanates such as xylene triisocyanates including 1,2-xylene-3,4,5-triisocyanate, 1,2-xylene-3,4,6-triisocyanate, 1,3-xylene-2,4,5-triisocyanate, 1,3-xylene-2,4,6-triisocyanate, 1,3-xylene-4,5,6-triisocyanate, 1,4-xylene-2,3,5-triisocyanate and 1,4-xylene-2,3,6-triisocyanate.

These diisocyanates and triisocyanates may be used alone or in combination of two or more.

Examples of the polyester having a hydroxyl group at one terminal and the polyester having a hydroxyl group at both terminals include polylactones having a hydroxyl group at one terminal or both terminals such as polycaprolactone having a hydroxyl group at one terminal or both terminals, polyvalerolactone having a hydroxyl group at one terminal or both terminals and polypropiolactone having a hydroxyl group at one terminal or both terminals; and polycondensation polyesters having a hydroxyl group at one terminal or both terminals such as polyethylene terephthalate having a hydroxyl group at one terminal or both terminals and polybutylene terephthalate having a hydroxyl group at one terminal or both terminals.

These polyesters having a hydroxyl group at one terminal and these polyester having a hydroxyl group at both terminals may be used alone or in combination of two or more.

The urethane-based dispersant in the present invention

is preferably a reaction product of an aromatic diisocyanate and a polylactone having a hydroxyl group at one terminal and/or a polylactone having a hydroxyl group at both terminals, particularly preferably a reaction product of
5 toluene diisocyanate and polycaprolactone having a hydroxyl group at one terminal and/or polycaprolactone having a hydroxyl group at both terminals.

Examples of the urethane-based dispersant as trade names include Disperbyk161 and Disperbyk170 (of BYK-Chemie
10 Japan KK), EFKA (of EFKA CHEMICALS B.V.) and Disparon (of Kusumoto Kasei Co., Ltd.).

The weight average molecular weight in terms of polystyrene (Mw) measured by GPC of the urethane-based dispersant in the present invention is preferably 5,000 to
15 50,000, more preferably 7,000 to 20,000.

The above urethane-based dispersants may be used alone or in combination of two or more.

A (meth)acrylic dispersant composed of a (co)polymer of a (meth)acrylic monomer is also preferred as the
20 dispersant.

Examples of the (meth)acrylic dispersant as trade names include Disperbyk2000 and Disperbyk2001 (of BYK-Chemie Japan KK).

The above (meth)acrylic dispersants may be used alone
25 or in combination of two or more.

The amount of the dispersant used to prepare the pigment dispersion is preferably 100 parts or less by weight, more preferably 0.5 to 100 parts by weight, much more preferably 1 to 70 parts by weight, particularly preferably 10 to 50
30 parts by weight based on 100 parts by weight of the pigment. When the amount of the dispersant is larger than 100 parts by weight, developability may be impaired.

The solvent used to prepare the pigment dispersion may be identical to the solvent used to prepare a liquid radiation

sensitive resin composition which will be described hereinafter.

The amount of the solvent used to prepare the pigment dispersion is preferably 500 to 1,000 parts by weight, more preferably 700 to 900 parts by weight based on 100 parts by weight of the pigment.

To prepare the pigment dispersion by using a bead mill, glass beads or titania beads having a diameter of about 0.5 to 10 mm are used to mix and disperse a pigment mixed solution comprising a pigment, a solvent and a dispersant preferably while it is cooled with cooling water or the like.

In this case, the filling rate of the beads is preferably 50 to 80 % of the capacity of the mill, and the amount of the pigment mixed solution injected is preferably about 20 to 50 % of the capacity of the mill. The treating time is preferably 2 to 50 hours, more preferably 2 to 25 hours.

To prepare the pigment dispersion by using a roll mill, a three-roll mill or a two-roll mill is used to mix and disperse the pigment mixed solution preferably while it is cooled with cooling water or the like.

The interval between rolls is preferably 10 μ m or less, and the shearing force is preferably about 10^8 dyn/sec. The treating time is preferably 2 to 50 hours, more preferably 2 to 25 hours.

- (B) alkali-soluble resin -

The alkali-soluble resin in the present invention is a resin (to be referred to as "resin (B)" hereinafter) which is manufactured through the living radical polymerization of a polymerizable unsaturated compound and has a weight average molecular weight in terms of polystyrene (Mw) measured by gel permeation chromatography (GPC) of 1,000 to 45,000.

Preferably, the resin (B) serves as a binder for the pigment (A) and has solubility in a developer, preferably an alkali developer which is used in a developing step for manufacturing a color filter. The resin (B) is, for example,
5 a resin having at least one acid functional group such as a carboxyl group, carboxylic anhydride group or phenolic hydroxyl group, and/or an alcoholic hydroxyl group (these acid functional groups and alcoholic hydroxyl group are generally referred to as "alkali-soluble functional group"
10 hereinafter), preferably a copolymer (to be referred to as "alkali-soluble copolymer" hereinafter) of a polymerizable unsaturated compound having an acid functional group and another copolymerizable unsaturated compound.

The alkali-soluble copolymer is preferably a copolymer
15 (to be referred to as "alkali-soluble copolymer (I)" hereinafter) of a monomer mixture of (b1) an unsaturated carboxylic acid and/or an unsaturated carboxylic anhydride (to be referred to as "unsaturated compound (b1)" hereinafter) and (b2) another copolymerizable unsaturated
20 compound (to be referred to as "unsaturated compound (b2)" hereinafter).

Examples of the unsaturated compound (b1) include unsaturated monocarboxylic acids such as (meth)acrylic acid, crotonic acid, α -chloroacrylic acid and cinnamic acid;
25 unsaturated dicarboxylic acids and anhydrides thereof such as maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride and mesaconic acid; unsaturated polycarboxylic acids having three or more carboxyl groups and anhydrides thereof;
30 mono[(meth)acryloyloxyalkyl]esters of a polycarboxylic acid having two or more carboxyl groups such as mono[2-(meth)acryloyloxyethyl]succinate and mono[2-(meth)acryloyloxyethyl]phthalate; and mono(meth)acrylates of a polymer having a carboxyl group and

a hydroxyl group at both terminals such as ω -carboxypolycaprolactone mono(meth)acrylate.

Out of these unsaturated compounds (b1), (meth)acrylic acid, mono[2-(meth)acryloyloxyethyl]succinate and
 5 ω -carboxypolycaprolactone mono(meth)acrylate are particularly preferred.

The above unsaturated compounds (b1) may be used alone or in combination of two or more.

Examples of the unsaturated compound (b2) include
 10 aromatic vinyl compounds such as styrene, α -methylstyrene, o-hydroxystyrene, m-hydroxystyrene, p-hydroxystyrene, o-hydroxy- α -methylstyrene, m-hydroxy- α -methylstyrene, p-hydroxy- α -methylstyrene, p-styrenesulfonic acid, o-vinyltoluene, m-vinyltoluene, p-vinyltoluene,
 15 p-chlorostyrene, o-methoxystyrene, m-methoxystyrene, p-methoxystyrene, o-vinylbenzylmethyl ether, m-vinylbenzylmethyl ether, p-vinylbenzylmethyl ether, o-vinylbenzylglycidyl ether, m-vinylbenzylglycidyl ether and p-vinylbenzylglycidyl ether; indenenes such as indene and
 20 1-methylindene; N-(substituted)aryl maleimides such as N-phenylmaleimide, N-o-hydroxyphenylmaleimide, N-m-hydroxyphenylmaleimide, N-p-hydroxyphenylmaleimide, N-o-methylphenylmaleimide, N-m-methylphenylmaleimide, N-p-methylphenylmaleimide, N-o-methoxyphenylmaleimide,
 25 N-m-methoxyphenylmaleimide and N-p-methoxyphenylmaleimide, and N-substituted maleimides such as N-cyclohexylmaleimide; macromonomers having a (meth)acryloyl group at a terminal of a polymer molecular chain (to be simply referred to as "macromonomer" hereinafter) such as polystyrene, polymethyl
 30 (meth)acrylate, poly-n-butyl (meth)acrylate and polysiloxane; unsaturated carboxylates such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, i-propyl (meth)acrylate, n-butyl (meth)acrylate, i-butyl (meth)acrylate, sec-butyl

- (meth)acrylate, t-butyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, allyl (meth)acrylate, benzyl (meth)acrylate, cyclohexyl (meth)acrylate, phenyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 2-phenoxyethyl (meth)acrylate, methoxydiethylene glycol (meth)acrylate, methoxytriethylene glycol (meth)acrylate, methoxypropylene glycol (meth)acrylate, methoxydipropylene glycol (meth)acrylate, isobornyl (meth)acrylate, tricyclo[5.2.1.0^{2,6}]decan-8-yl (meth)acrylate, 2-hydroxy-3-phenoxypropyl (meth)acrylate and glycerol (meth)acrylate; unsaturated aminoalkyl carboxylates such as 2-aminoethyl (meth)acrylate, 2-dimethylaminoethyl (meth)acrylate, 2-aminopropyl (meth)acrylate, 2-dimethylaminopropyl (meth)acrylate, 3-aminopropyl (meth)acrylate and 3-dimethylaminopropyl (meth)acrylate; unsaturated glycidyl carboxylates such as glycidyl (meth)acrylate; vinyl carboxylates such as vinyl acetate, vinyl propionate, vinyl butyrate and vinyl benzoate; unsaturated ethers such as vinyl methyl ether, vinyl ethyl ether and allyl glycidyl ether; vinyl cyanide compounds such as (meth)acrylonitrile, α -chloroacrylonitrile and vinylidene cyanide; unsaturated amides such as (meth)acrylamide, α -chloroacrylamide and N-2-hydroxyethyl (meth)acrylamide; and aliphatic conjugated dienes such as 1,3-butadiene, isoprene, chloroprene and isoprenesulfonic acid.
- Out of these unsaturated compounds (b2), styrene, macromonomers, N-substituted maleimides, methyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, allyl (meth)acrylate, benzyl (meth)acrylate, phenyl (meth)acrylate and glycerol mono(meth)acrylate are

particularly preferred. Out of the macromonomers, polystyrene macromonomer and polymethyl (meth)acrylate macromonomer are particularly preferred, and out of the N-substituted maleimides, N-phenylmaleimide and
5 N-cyclohexylmaleimide are particularly preferred.

The above unsaturated compounds (b2) may be used alone or in combination of two or more.

The alkali-soluble copolymer (I) is preferably a copolymer (to be referred to as "carboxyl group-containing
10 copolymer (I-1)" hereinafter) of a monomer mixture containing (b1) at least one unsaturated compound selected from the group consisting of (meth)acrylic acid, mono[2-(meth)acryloyloxyethyl]succinate and ω-carboxypolycaprolactone mono(meth)acrylate and (b2) at
15 least one unsaturated compound selected from the group consisting of polystyrene macromonomer, polymethyl (meth)acrylate macromonomer, N-phenylmaleimide, N-cyclohexylmaleimide, 2-hydroxyethyl (meth)acrylate, benzyl (meth)acrylate and glycerol mono(meth)acrylate and
20 optionally (b2) at least one unsaturated compound selected from the group consisting of styrene, methyl (meth)acrylate, allyl (meth)acrylate and phenyl (meth)acrylate.

The alkali-soluble copolymer (I-1) is preferably a copolymer (to be referred to as "carboxyl group-containing
25 copolymer (I-2)" hereinafter) of a monomer mixture of (b1) an unsaturated compound which contains (meth)acrylic acid as an essential component and optionally mono[2-(meth)acryloyloxyethyl]succinate and (b2) at least one unsaturated compound selected from the group consisting
30 of polystyrene macromonomer, polymethyl (meth)acrylate macromonomer, N-phenylmaleimide, N-cyclohexylmaleimide, 2-hydroxyethyl (meth)acrylate, benzyl (meth)acrylate and glycerol mono(meth)acrylate and optionally (b2) at least one unsaturated compound selected from the group consisting of

styrene, methyl (meth)acrylate, allyl (meth)acrylate and phenyl (meth)acrylate.

Specific examples of the carboxyl group-containing copolymer (I-2) include a copolymer of (meth)acrylic acid
 5 and 2-hydroxyethyl (meth)acrylate, copolymer of (meth)acrylic acid, polystyrene macromonomer and benzyl (meth)acrylate, copolymer of (meth)acrylic acid, polymethyl (meth)acrylate macromonomer and benzyl (meth)acrylate, copolymer of (meth)acrylic acid, benzyl (meth)acrylate and
 10 glycerol mono(meth)acrylate, copolymer of (meth)acrylic acid, 2-hydroxyethyl (meth)acrylate and phenyl (meth)acrylate, copolymer of (meth)acrylic acid, 2-hydroxyethyl (meth)acrylate and styrene, copolymer of (meth)acrylic acid, benzyl (meth)acrylate and glycerol
 15 mono(meth)acrylate, copolymer of (meth)acrylic acid, 2-hydroxyethyl (meth)acrylate and benzyl (meth)acrylate, copolymer of (meth)acrylic acid, polystyrene macromonomer, 2-hydroxyethyl (meth)acrylate and benzyl (meth)acrylate, copolymer of (meth)acrylic acid, polymethyl (meth)acrylate
 20 macromonomer, 2-hydroxyethyl (meth)acrylate and benzyl (meth)acrylate, copolymer of (meth)acrylic acid, N-phenylmaleimide, allyl (meth)acrylate and styrene, copolymer of (meth)acrylic acid, N-phenylmaleimide, benzyl (meth)acrylate and styrene, copolymer of (meth)acrylic acid,
 25 N-cyclohexylmaleimide, allyl (meth)acrylate and styrene, copolymer of (meth)acrylic acid, N-cyclohexylmaleimide, benzyl (meth)acrylate and styrene, copolymer of (meth)acrylic acid, N-phenylmaleimide, benzyl (meth)acrylate, glycerol mono(meth)acrylate and styrene,
 30 copolymer of (meth)acrylic acid, mono[2-(meth)acryloyloxyethyl]succinate, benzyl (meth)acrylate and glycerol mono(meth)acrylate, copolymer of (meth)acrylic acid, mono[2-(meth)acryloyloxyethyl]succinate,

- N-phenylmaleimide, allyl (meth)acrylate and styrene,
 copolymer of (meth)acrylic acid,
 mono[2-(meth)acryloyloxyethyl]succinate,
 N-phenylmaleimide, benzyl (meth)acrylate and styrene,
 5 copolymer of (meth)acrylic acid,
 mono[2-(meth)acryloyloxyethyl]succinate,
 N-cyclohexylmaleimide, allyl (meth)acrylate and styrene,
 copolymer of (meth)acrylic acid,
 mono[2-(meth)acryloyloxyethyl]succinate,
 10 N-cyclohexylmaleimide, benzyl (meth)acrylate and styrene,
 copolymer of (meth)acrylic acid,
 mono[2-(meth)acryloyloxyethyl]succinate,
 N-phenylmaleimide, benzyl (meth)acrylate, glycerol
 mono(meth)acrylate and styrene.
- 15 Specific examples of the carboxyl group-containing
 copolymer (I-1) include a copolymer of (meth)acrylic acid,
 ω -carboxypolycaprolactone mono(meth)acrylate,
 N-phenylmaleimide, benzyl (meth)acrylate, glycerol
 mono(meth)acrylate and styrene, copolymer of (meth)acrylic
 20 acid, ω -carboxypolycaprolactone mono(meth)acrylate and
 2-hydroxyethyl (meth)acrylate, copolymer of (meth)acrylic
 acid, ω -carboxypolycaprolactone mono(meth)acrylate,
 polystyrene macromonomer and benzyl (meth)acrylate,
 copolymer of (meth)acrylic acid, ω -carboxypolycaprolactone
 25 mono(meth)acrylate, polymethyl (meth)acrylate macromonomer
 and benzyl (meth)acrylate, copolymer of (meth)acrylic acid,
 ω -carboxypolycaprolactone mono(meth)acrylate, benzyl
 (meth)acrylate and glycerol mono(meth)acrylate, copolymer
 of (meth)acrylic acid, ω -carboxypolycaprolactone
 30 mono(meth)acrylate, 2-hydroxyethyl (meth)acrylate and
 phenyl (meth)acrylate, copolymer of (meth)acrylic acid,
 ω -carboxypolycaprolactone mono(meth)acrylate,
 2-hydroxyethyl (meth)acrylate and styrene, copolymer of
 (meth)acrylic acid, ω -carboxypolycaprolactone

mono(meth)acrylate, benzyl (meth)acrylate and glycerol
 mono(meth)acrylate, copolymer of (meth)acrylic acid,
 ω-carboxypolycaprolactone mono(meth)acrylate,
 2-hydroxyethyl (meth)acrylate and benzyl (meth)acrylate,
 5 copolymer of (meth)acrylic acid, ω-carboxypolycaprolactone
 mono(meth)acrylate, polystyrene macromonomer,
 2-hydroxyethyl (meth)acrylate and benzyl (meth)acrylate,
 copolymer of (meth)acrylic acid, ω-carboxypolycaprolactone
 mono(meth)acrylate, polymethyl (meth)acrylate macromonomer,
 10 2-hydroxyethyl (meth)acrylate and benzyl (meth)acrylate,
 copolymer of (meth)acrylic acid, ω-carboxypolycaprolactone
 mono(meth)acrylate, N-phenylmaleimide, allyl
 (meth)acrylate and styrene, copolymer of (meth)acrylic acid,
 ω-carboxypolycaprolactone mono(meth)acrylate,
 15 N-phenylmaleimide, benzyl (meth)acrylate and styrene,
 copolymer of (meth)acrylic acid, ω-carboxypolycaprolactone
 mono(meth)acrylate, N-cyclohexylmaleimide, allyl
 (meth)acrylate and styrene, copolymer of (meth)acrylic acid,
 ω-carboxypolycaprolactone mono(meth)acrylate,
 20 N-cyclohexylmaleimide, benzyl (meth)acrylate and styrene,
 copolymer of (meth)acrylic acid, ω-carboxypolycaprolactone
 mono(meth)acrylate, N-phenylmaleimide, benzyl
 (meth)acrylate, glycerol mono(meth)acrylate and styrene,
 copolymer of (meth)acrylic acid, ω-carboxypolycaprolactone
 25 mono(meth)acrylate,
 mono[2-(meth)acryloyloxyethyl]succinate, benzyl
 (meth)acrylate and glycerol mono(meth)acrylate, copolymer
 of (meth)acrylic acid, ω-carboxypolycaprolactone
 mono(meth)acrylate,
 30 mono[2-(meth)acryloyloxyethyl]succinate,
 N-phenylmaleimide, allyl (meth)acrylate and styrene,
 copolymer of (meth)acrylic acid, ω-carboxypolycaprolactone
 mono(meth)acrylate,
 mono[2-(meth)acryloyloxyethyl]succinate,

N-phenylmaleimide, benzyl (meth)acrylate and styrene,
 copolymer of (meth)acrylic acid, ω -carboxypolycaprolactone
 mono(meth)acrylate,
 mono[2-(meth)acryloyloxyethyl]succinate,
 5 N-cyclohexylmaleimide, allyl (meth)acrylate and styrene,
 copolymer of (meth)acrylic acid, ω -carboxypolycaprolactone
 mono(meth)acrylate,
 mono[2-(meth)acryloyloxyethyl]succinate,
 N-cyclohexylmaleimide, benzyl (meth)acrylate and styrene,
 10 and copolymer of (meth)acrylic acid,
 ω -carboxypolycaprolactone mono(meth)acrylate,
 mono[2-(meth)acryloyloxyethyl]succinate,
 N-phenylmaleimide, benzyl (meth)acrylate, glycerol
 mono(meth)acrylate and styrene.

15 The polymerization ratio of the unsaturated compound
 having an alkali-soluble functional group in the resin (B)
 is preferably 1 to 100 wt%, more preferably 5 to 30 wt%,
 particularly preferably 10 to 30 wt% based on the total of
 all the unsaturated compounds. When the polymerization
 20 ratio of the unsaturated compound having an acid functional
 group is lower than 1 wt%, the solubility in an alkali
 developer of the obtained resin may lower.

 The copolymerization ratio of the unsaturated compound
 having an alkali-soluble functional group in the
 25 alkali-soluble copolymer is preferably 1 to 40 wt%, more
 preferably 5 to 30 wt%, particularly preferably 10 to 30 wt%
 based on the total of all the unsaturated compounds. When
 the copolymerization ratio of the unsaturated compound
 having an acid functional group is lower than 1 wt%, the
 30 solubility in an alkali developer of the obtained
 alkali-soluble copolymer may lower and when the
 copolymerization ratio is higher than 40 wt%, the solubility
 in an alkali developer of the obtained alkali-soluble
 copolymer becomes too high, whereby the pattern shape may

be impaired.

A description is subsequently given of living radical polymerization for the manufacture of the resin (B).

5 The resin (B) may be manufactured by carrying out the living radical polymerization of a polymerizable unsaturated compound having an acid functional group preferably together with another copolymerizable unsaturated compound in a solvent in the presence of a radical polymerization initiator which forms a living radical.

10 When a compound having a functional group which may deactivate an active radical such as a carboxyl group is to be used as the polymerizable unsaturated compound for living radical polymerization, the resin (B) can be obtained by deprotecting the functional group after polymerization is
15 carried out by optionally protecting the functional group contained in the polymerizable unsaturated compound by esterification so as to prevent the deactivation of a growth terminal.

Examples of the radical polymerization initiator for
20 the living radical polymerization of the polymerizable unsaturated compound include TEMPO proposed by Georges et al (M.K. Georges, R.P.N. Veregin, P.M. Kazmaier, G.K. Hamer, *Macromolecules*, 1993, vol. 26, p. 2987), a combination of copper bromide and a bromide-containing ester compound
25 proposed by Matyjaszewski et al (Matyjaszewski, K. Coca, S. Gaynor, G. wei, M. Woodworth, B.E. *Macromolecules*, 1997, vol. 30, p. 7348), a combination of carbon tetrachloride and a ruthenium (II) complex proposed by Hamasaki et al (Hamasaki, S. Kamigaito, M. Sawamoto, M. *Macromolecules*, 2002, vol. 35,
30 p. 2934), and a combination of a thiocarbonyl compound having a chain transfer constant larger than 0.1 and a radical initiator disclosed by Japanese Patent No.3639859
Description, JP-A 2002-500251 and JP-A 2004-518773.

A radical polymerization initiator whose active

radical as a growth terminal is not deactivated is suitably selected according to the type of the polymerizable unsaturated compound in use as the preferred radical polymerization initiator used for living radical
 5 polymerization. In consideration of polymerization efficiency and a metal-free radical polymerization initiator, a combination of a thiocarbonylthio compound which is a molecular weight control agent and a radical initiator is preferred.

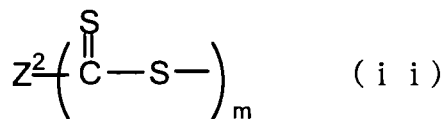
10 The combination of a thiocarbonylthio compound and a radical initiator is described in detail in the following patent documents besides Japanese Patent No.3639859 Description, JP-A 2002-500251 and JP-A 2004-518773.

As described by Japanese Patent No.3639859 Description,
 15 JP-A 2002-500251, JP-A 2004-518773 and JP-A 2002-508409, a random copolymer or block copolymer having a narrow molecular weight distribution can be obtained by carrying out the living radical polymerization of the polymerizable unsaturated compound in the presence of the thiocarbonylthio
 20 compound and the radical initiator. Since a functional group can be introduced into the obtained random copolymer and block copolymer, it has been found that the copolymer may also be used for aqueous gels (refer to JP-A 2002-512653), photoresists (refer to JP-A 2003-527458) and surfactants
 25 (Japanese Patent No.3634843 Description).

In the present invention, the resin (B) is preferably a resin (to be referred to as "resin (B1)" hereinafter) having a group represented by the following formula (i) (to be referred to as "terminal group (i)" hereinafter) or a group
 30 represented by the following formula (ii) (to be referred to as "terminal group (ii)" hereinafter) at at least one of the terminals of a polymer chain constituting the resin.



[In the formula (i), Z^1 is a hydrogen atom, chlorine atom, carboxyl group, cyano group, alkyl group having 1 to 20 carbon atoms, monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, monovalent heterocyclic group having 3 to 20 carbon atoms and hetero atoms or monovalent group having -OR, -SR, -N(R)₂, -OC(=O)R, -C(=O)OR, -C(=O)N(R)₂, -P(=O)(OR)₂, -P(=O)(R)₂ or a polymer chain (R's are each independently an alkyl group having 1 to 18 carbon atoms, alkenyl group having 2 to 18 carbon atoms, monovalent aromatic hydrocarbon group having 6 to 18 carbon atoms or monovalent heterocyclic group having 3 to 18 carbon atoms and hetero atoms), with the proviso that the above alkyl group having 1 to 20 carbon atoms, the monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, the monovalent heterocyclic group having 3 to 20 carbon atoms and R may be substituted.]



[In the formula (ii), Z^2 is a group having a valence of m derived from an alkane having 1 to 20 carbon atoms, group having a valence of m derived from an aromatic hydrocarbon having 6 to 20 carbon atoms, group having a valence of m derived from a heterocyclic compound having 3 to 20 carbon atoms and hetero atoms or group having a valence of m and a polymer chain, with the proviso that the group having a valence of m derived from an alkane having 1 to 20 carbon atoms, the group having a valence of m derived from an aromatic hydrocarbon having 6 to 20 carbon atoms and the group having a valence of m derived from a heterocyclic compound having 3 to 20 carbon atoms may be substituted, and m is an integer of 2 or more.]

When the number of polymer chains constituting the resin (B1) is only one, the terminal group (i) is bonded to

any one of the terminals of the polymer chain. The terminal group (i), the terminal group (ii) or a chain stopping group may be bonded to the other terminal. This "chain stopping group" is a group which is determined by reaction conditions at the time of living radical polymerization. When the above terminal group (ii) is bonded to the polymer chain, a (m-1) number of bonds (-S) which are not connected to the polymer chain in the terminal group (ii) are bonded to the chain stopping group. The chain stopping group may be R^1 in the formula (1) or R^2 in the formula (2) which will be described hereinafter.

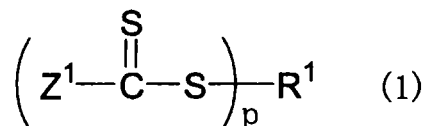
When the number of the polymer chains constituting the resin is 2 or more, the polymer chains are bonded to the terminal group (ii) at one terminal, whereby the resin has a branched structure. The terminal group (i), terminal group (ii) or the chain stopping group may be bonded to the other terminals of the polymer chains. When the above terminal group (ii) is bonded to the other terminals of the polymer chains, the (m-1) number of bonds (S-) which are not bonded to the polymer chains in the terminal group (ii) can be bonded to the terminal group (i), the terminal group (ii) or the chain stopping group. The chain stopping group may be R^1 in the formula (1) or R^2 in the formula (2) which will be described hereinafter.

In the formula (i), the alkyl group having 1 to 20 carbon atoms which may be substituted, the monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms which may be substituted, the monovalent heterocyclic group having 3 to 20 carbon atoms and hetero atoms which may be substituted and R which may be substituted and the monovalent group having a polymer chain of Z^1 are the same as the respective groups of Z^1 in the formula (1) which will be described hereinafter, including preferred groups.

In the formula (ii), the group having a valence of m

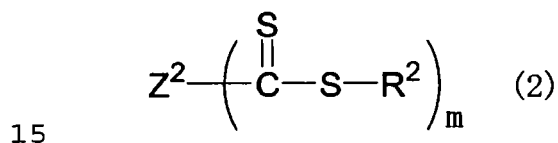
derived from an alkane having 1 to 20 carbon atoms which may be substituted, the group having a valence of m derived from an aromatic hydrocarbon having 6 to 20 carbon atoms which may be substituted, the group having a valence of m derived from a heterocyclic compound having 3 to 20 carbon atoms and hetero atoms which may be substituted and the group having a valence of m and a polymer chain of Z^2 are the same as the respective groups of Z^2 in the formula (2) which will be described hereinafter, including preferred groups.

The resin (B1) may be manufactured through the living radical polymerization of the polymerizable unsaturated compound using a thiocarbonylthio compound represented by the following formula (1) or (2) as a molecular weight control agent. A radical initiator is preferably used for the living radical polymerization.



[In the formula (1), Z^1 is as defined in the above formula (i), p is an integer of 1 or more, and R^1 is an alkyl group having 1 to 20 carbon atoms, monovalent alicyclic hydrocarbon group having 3 to 20 carbon atoms, monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, monovalent heterocyclic group having 3 to 20 carbon atoms and hetero atoms or monovalent group having -OR, -SR, -N(R)₂ or a polymer chain (R's are each independently an alkyl group having 1 to 18 carbon atoms, alkenyl group having 2 to 18 carbon atoms, monovalent aromatic hydrocarbon group having 6 to 18 carbon atoms or monovalent heterocyclic group having 3 to 18 carbon atoms and hetero atoms) when p = 1, or a group having a valence of p derived from an alkane having 1 to 20 carbon atoms, group having a valence of p derived from an aromatic hydrocarbon

having 6 to 20 carbon atoms, group having a valence of p derived from a heterocyclic compound having 3 to 20 carbon atoms and hetero atoms or group having a valence of p and a polymer chain when $p \geq 2$, with the proviso that the alkyl group having 1 to 20 carbon atoms, the monovalent alicyclic hydrocarbon group having 3 to 20 carbon atoms, the monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, the monovalent heterocyclic group having 3 to 20 atoms, the group having a valence of p derived from an alkane having 1 to 20 carbon atoms, the group having a valence of p derived from an aromatic hydrocarbon having 6 to 20 carbon atoms and the group having a valence of p derived from a heterocyclic compound having 3 to 20 atoms may be substituted.]



[In the formula (2), Z^2 and m are as defined in the above formula (ii), and R^2 is an alkyl group having 1 to 20 carbon atoms, monovalent alicyclic hydrocarbon group having 3 to 20 carbon atoms, monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, monovalent heterocyclic group having 3 to 20 carbon atoms and hetero atoms, or monovalent group having -OR, -SR, -N(R)₂ or a polymer chain (R's are each independently an alkyl group having 1 to 18 carbon atoms, alkenyl group having 2 to 18 carbon atoms, monovalent aromatic hydrocarbon group having 6 to 18 carbon atoms or monovalent heterocyclic group having 3 to 18 carbon atoms and hetero atoms), with the proviso that the alkyl group having 1 to 20 carbon atoms, the monovalent alicyclic hydrocarbon group having 3 to 20 carbon atoms, the monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, the monovalent heterocyclic group having 3 to 20 atoms and R may

be substituted.]

In the formula (1), examples of the alkyl group having 1 to 20 carbon atoms of Z^1 include methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, i-butyl group, 5 sec-butyl group, t-butyl group, n-pentyl group, 1,1-dimethylpropyl group, neopentyl group, n-hexyl group, n-heptyl group, n-octyl group, 1,1-dimethyl-3,3-dimethylbutyl group, n-nonyl group, n-decyl group, n-dodecyl group, n-tetradecyl group, 10 n-hexadecyl group, n-octadecyl group and n-eicosyl group.

Examples of the monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms of Z^1 include phenyl group, 1-naphthyl group, 2-naphthyl group, 1-anthracenyl group, 9-anthracenyl group, benzyl group, α -methylbenzyl group, 15 α,α -dimethylbenzyl group and phenethyl group.

Examples of the monovalent heterocyclic group having 3 to 20 carbon atoms and hetero atoms of Z^1 include epoxy group, aziridinyl group, 2-furanyl group, 3-furanyl group, 2-tetrahydrofuranyl group, 3-tetrahydrofuranyl group, 20 1-pyrrole group, 2-pyrrole group, 3-pyrrole group, 1-pyrrolidinyl group, 2-pyrrolidinyl group, 3-pyrrolidinyl group, 1-pyrazole group, 2-pyrazole group, 3-pyrazole group, 2-tetrahydropyranyl group, 3-tetrahydropyranyl group, 4-tetrahydropyranyl group, 2-thianyl group, 3-thianyl group, 25 4-thianyl group, 2-pyridinyl group, 3-pyridinyl group, 4-pyridinyl group, 2-piperidinyl group, 3-piperidinyl group, 4-piperidinyl group, 2-morpholinyl group and 3-morpholinyl group.

Examples of the alkyl group having 1 to 18 carbon atoms, 30 the monovalent aromatic hydrocarbon group having 6 to 18 carbon atoms and the monovalent heterocyclic group having 3 to 18 carbon atoms and hetero atoms of R in -OR, -SR, -N(R)₂, -OC(=O)R, -C(=O)OR, -C(=O)N(R)₂, -P(=O)(OR)₂, -P(=O)(R)₂ of Z^1 include groups having 18 or less carbon atoms or total

number of atoms out of the alkyl groups having 1 to 20 carbon atoms, the monovalent aromatic hydrocarbon groups having 6 to 20 carbon atoms and the monovalent heterocyclic groups having 3 to 20 carbon atoms and hetero atoms enumerated for
 5 Z^1 .

Examples of the alkenyl group having 2 to 18 carbon atoms of R include vinyl group, 1-propenyl group, 2-propenyl group, 1-butenyl group, 2-butenyl group, 3-butenyl group, 1-pentenyl group, 2-pentenyl group, 3-pentenyl group,
 10 4-pentenyl group, 1-hexenyl group, 2-hexenyl group, 3-hexenyl group, 4-hexenyl group and 5-hexenyl group.

The substituents for the alkyl group having 1 to 20 carbon atoms, the monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, the monovalent heterocyclic
 15 group having 3 to 20 carbon atoms and hetero atoms and R may be suitably selected from hydroxyl group, carboxyl group, carboxylate group, sulfonic acid group, sulfonate group, isocyanato group, cyano group, vinyl group, epoxy group, silyl group and halogen atom, -OR, -SR, -N(R)₂, -OC(=O)R,
 20 -C(=O)OR, -C(=O)N(R)₂, -P(=O)(OR)₂ and -P(=O)(R)₂ enumerated for Z^1 , and alkyl group having 1 to 18 carbon atoms, alkenyl group having 2 to 18 carbon atoms, monovalent aromatic hydrocarbon group having 6 to 18 carbon atoms, monovalent heterocyclic group having 3 to 18 carbon atoms and hetero
 25 atoms enumerated for R. One or more of the substituents of the same kind or different kinds may be existent in a substituted derivative. It is preferred that the total number of carbon atoms or the total number of atoms of the substituent(s) in the substituted derivative should not be
 30 larger than 20.

Example of the monovalent group having a polymer chain of Z^1 include α -olefins such as ethylene and propylene; aromatic vinyl compounds such as styrene and α -methylstyrene; vinyl halides such as vinyl fluoride, vinyl

chloride and vinylidene chloride; unsaturated alcohols such as vinyl alcohol and allyl alcohol; esters of an unsaturated alcohol such as vinyl acetate and allyl acetate; unsaturated carboxylic acids such as (meth)acrylic acid and

5 p-vinylbenzoic acid; (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, i-propyl (meth)acrylate, n-butyl (meth)acrylate, t-butyl (meth)acrylate, n-hexyl (meth)acrylate and cyclohexyl (meth)acrylate;

10 (meth)acrylamides such as (meth)acrylamide and N,N-dimethyl (meth)acrylamide;

Unsaturated nitriles such as (meth)acrylonitrile and vinylidene cyanide; monovalent groups having an addition polymerization polymer chain formed from at least one

15 unsaturated compound such as a conjugated diene, such as butadiene and isoprene; polyethers such as polyoxyethylene which may be etherified at a terminal and polyoxypropylene which may be etherified at a terminal; and monovalent groups having a polycondensation polymer chain or polyaddition

20 polymer chain, such as polyesters, polyamides and polyimides. In these monovalent groups having a polymer chain, the polymer chain may be bonded to the carbon atom of a thiocarbonyl group in the formula (1) directly or through a bond such as $-\text{CH}_2-\text{COO}-$ or $-\text{C}(\text{CH}_3)(\text{CN})\text{CH}_2\text{CH}_2-\text{COO}-$. In this

25 case, it should be understood that the group is a monovalent group having a polymer chain including the bond.

In the formula (1), a plurality of Z^1 's may be the same or different.

In the formula (1), when $p = 1$, R^1 is an alkyl group

30 having 1 to 20 carbon atoms, monovalent alicyclic hydrocarbon group having 3 to 20 carbon atoms, monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, monovalent heterocyclic group having 3 to 20 carbon atoms and hetero atoms, or monovalent group having $-\text{OR}$, $-\text{SR}$, $-\text{N}(\text{R})_2$ or a

polymer chain, with the proviso that the alkyl group having 1 to 20 carbon atoms, the monovalent alicyclic hydrocarbon group having 3 to 20 carbon atoms, the monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, the monovalent heterocyclic group having 3 to 20 carbon atoms and hetero atoms and R may be substituted.

Examples of the alkyl group having 1 to 20 carbon atoms, the monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, the monovalent heterocyclic group having 3 to 20 atoms, and the monovalent group having -OR, -SR, -N(R)₂, substituted derivative thereof or a polymer chain are those enumerated for the respective groups of Z¹. In the monovalent group having a polymer chain of R¹ (p = 1), the polymer chain may be bonded to the sulfur atoms in the formula (1) directly or through a bond such as -CH₂-COO- or -C(CH₃)(CN)CH₂CH₂-COO-. It is understood that this is the same as Z¹.

Examples of the monovalent alicyclic hydrocarbon group having 3 to 20 carbon atoms include cyclopentyl group, cyclohexyl group, cyclopentenyl group and cyclohexenyl group.

The substituent for the monovalent alicyclic hydrocarbon group having 3 to 20 carbon atoms may be suitably selected from groups enumerated for the substituents for the alkyl group having 1 to 20 carbon atoms, the monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, the monovalent heterocyclic group having 3 to 20 carbon atoms and hetero atoms and R of Z¹. One or more of the substituents of the same kind or different kinds may be existent in the substituted derivative. It is preferred that the total number of carbon atoms or the total number of atoms of the substituent(s) in the substituted derivative should not be larger than 20.

When $p \geq 2$, R¹ is a group having a valence of p derived

from an alkane having 1 to 20 carbon atoms, group having a valence of p derived from an aromatic hydrocarbon having 6 to 20 carbon atoms, group having a valence of p derived from a heterocyclic compound having 3 to 20 carbon atoms and hetero
 5 atoms or group having a valence of p and a polymer chain, with the proviso that the group having a valence of p derived from an alkane, the group having a valence of p derived from an aromatic hydrocarbon and the group having a valence of p derived from a heterocyclic compound having 3 to 20 atoms
 10 may be substituted.

Examples of the alkane having 1 to 20 carbon atoms include methane, ethane, propane, n-butane, i-butane, n-pentane, i-pentane, neopentane, n-hexane, n-heptane, n-octane, n-nonane, n-decane, n-dodecane, n-tetradecane,
 15 n-hexadecane, n-octadecane and n-eicosan.

Examples of the aromatic hydrocarbon group having 6 to 20 carbon atom include benzene, 1,4-dimethylbenzene (in this case, for example, the carbon atoms of methyl groups at the 1- and 4-positions are bonded to the sulfur atoms in
 20 the formula (1)), 1,2,4,5-tetramethylbenzene (in this case, the carbon atoms of methyl groups at the 1-, 2-, 4- and 5-positions are bonded to the sulfur atoms in the formula (1)), 1,2,3,4,5,6-hexamethylbenzene (in this case, the carbon atoms of methyl groups at the 1-, 2-, 3-, 4-, 5- and
 25 6-positions are bonded to the sulfur atoms in the formula (1)), 1,4-di-i-propylbenzene (in this case, carbon atoms at the 2-positions of i-propyl groups at the 1- and 4-positions are bonded to the sulfur atoms in the formula (1)), naphthalene and anthracene.

30 Examples of the heterocyclic compound having 3 to 20 atoms include oxirane, aziridine, furan, tetrahydrofuran, pyrrole, pyrrolidine, pyrazole, tetrahydropyran, thiane, pyridine, piperidine and morpholine.

The substituents for the group having a valence of p

derived from an alkane having 1 to 20 carbon atoms, the group having a valence of p derived from an aromatic hydrocarbon having 6 to 20 carbon atoms and the group having a valence of p derived from a heterocyclic compound having 3 to 20 atoms
 5 may be suitably selected from groups enumerated for the substituents for the alkyl group having 1 to 20 carbon atoms, the monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, the monovalent heterocyclic group having 3 to 20 carbon atoms and hetero atoms and R of Z^1 . One or more
 10 of the substituents of the same kind or different kinds may be existent in a substituted derivative. It is preferred that the total number of carbon atoms or the total number of atoms of the substituent(s) in the substituted derivative should not be larger than 20.

15 Examples of the polymer chain which provides a group having a valence of p of R^1 are the same as an addition polymerization polymer chain, polyaddition polymer chain and polycondensation polymer chain enumerated for the monovalent group having a polymer chain of Z^1 . In the group having a
 20 valence of p and a polymer chain of R^1 , the polymer chain may be bonded to the sulfur atoms in the formula (1) directly or through a bond such $-\text{CH}_2-\text{COO}-$ or $-\text{C}(\text{CH}_3)(\text{CN})\text{CH}_2\text{CH}_2-\text{COO}-$. It can be understood that this is the same as Z^1 .

In the formula (2), examples of the alkane having 1
 25 to 20 carbon atoms which provides the group having a valence of m of Z^2 are the same as compounds enumerated for the alkane having 1 to 20 carbon atoms which provides the group having a valence of p of R^1 .

30 Examples of the aromatic hydrocarbon having 6 to 20 carbon atoms which provides the group having a valence of m of Z^2 are the same as compounds enumerated for the aromatic hydrocarbon having 6 to 20 carbon atoms which provides the group having a valence of p of R^1 .

Examples of the heterocyclic compound having 3 to 20

carbon atoms and hetero atoms which provides the group having a valence of m of Z^2 are the same as compounds enumerated for the heterocyclic compound having 3 to 20 carbon atoms and hetero atoms which provides the group having a valence of p of R^1 .

The substituents for the group having a valence of m derived from an alkane having 1 to 20 carbon atoms, the group having a valence of m derived from an aromatic hydrocarbon having 6 to 20 carbon atoms and the group having a valence of m derived from a heterocyclic compound having 3 to 20 atoms of Z^2 may be suitably selected from groups enumerated for the substituents for the alkyl group having 1 to 20 carbon atoms, the monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, the monovalent heterocyclic group having 3 to 20 carbon atoms and hetero atoms and R of Z^1 . One or more of the substituents of the same kind or different kinds may be existent in the substituted derivative. It is preferred that the total number of carbon atoms or the total number of atoms of the substituent(s) in the substituted derivative should not be larger than 20.

Examples of the polymer chain which provides the group having a valence of m of Z^2 are the same as the addition polymerization polymer chain, polyaddition polymer chain and polycondensation polymer chain enumerated for the above monovalent group having a polymer chain of Z^1 . In the group having a valence of m and a polymer chain of Z^2 , the polymer chain may be bonded to the carbon atom of the thiocarbonyl group in the formula (2) directly or through a bond such as $-\text{CH}_2-\text{COO}-$ or $-\text{C}(\text{CH}_3)(\text{CN})\text{CH}_2\text{CH}_2-\text{COO}-$. It can be understood that this is the same as Z^1 .

In the formula (2), the alkyl group having 1 to 20 carbon atoms, the monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, the monovalent heterocyclic group having 3 to 20 carbon atoms and hetero atoms and the monovalent group

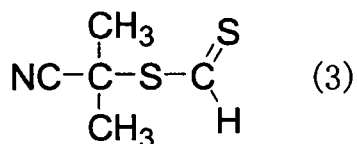
having -OR, -SR, -N(R)₂ or a polymer chain of R² and their substituted derivatives are the same as groups enumerated for the respective groups of Z¹. In the monovalent group having a polymer chain of R², the polymer chain may be bonded
 5 to the sulfur atoms in the formula (2) directly or through a bond such as -CH₂-COO- or -C(CH₃)(CN)CH₂CH₂-COO-. It can be understood that this is the same as Z¹.

Examples of the monovalent alicyclic hydrocarbon group having 3 to 20 carbon atoms of R² and its substituted
 10 derivative are the same as groups enumerated for the monovalent alicyclic hydrocarbon group having 3 to 20 carbon atoms of R¹ (p = 1) and its substituted derivatives.

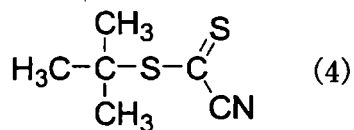
In the formula (2), a plurality of R²'s may be the same or different.

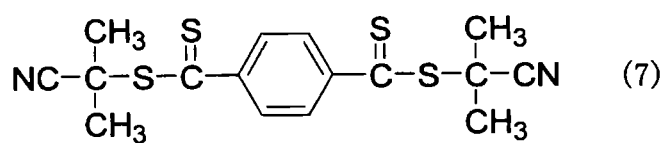
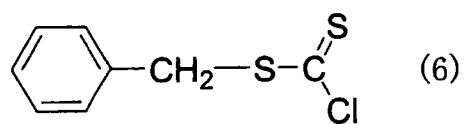
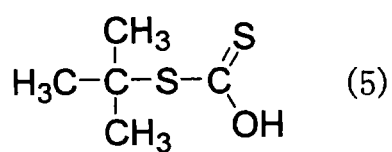
15 When the connection portion between Z² and -C(=S)-S-R² is an aliphatic carbon atom in the formula (2), the aliphatic carbon atom in Z² is bonded to -C(=S)-S-R², when the connection portion is an aromatic carbon atom, the aromatic carbon atom in Z² is bonded to -C(=S)-S-R², and when the connection portion
 20 is a sulfur atom, the sulfur atom in -SR representing Z² is bonded to -C(=S)-S-R².

Particularly preferred examples of the thiocarbonylthio compound in the present invention include compounds represented by the following formulas (3) to (22).

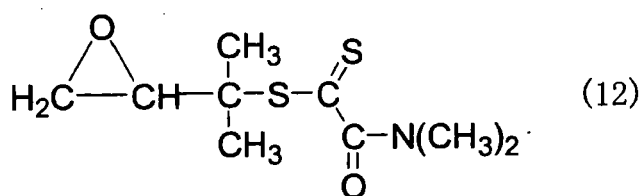
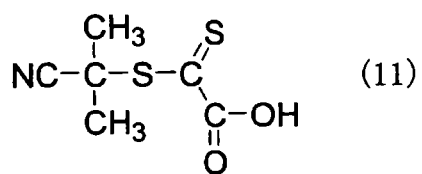
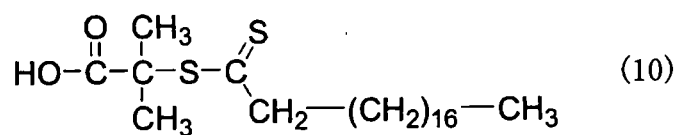
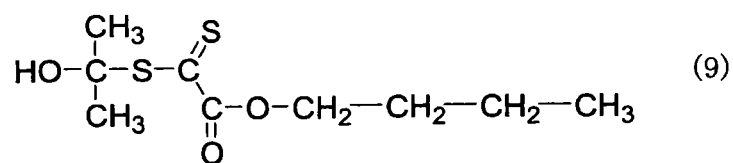
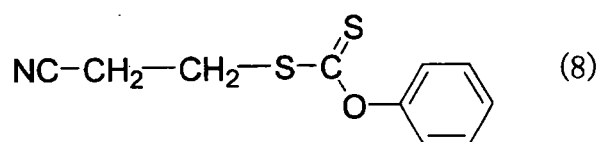


25

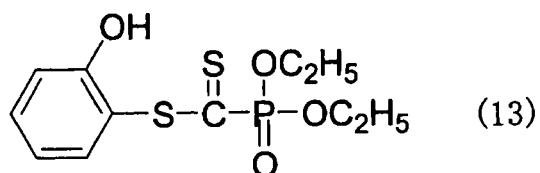


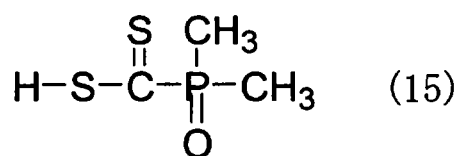
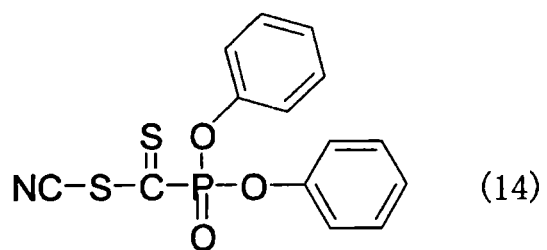


5

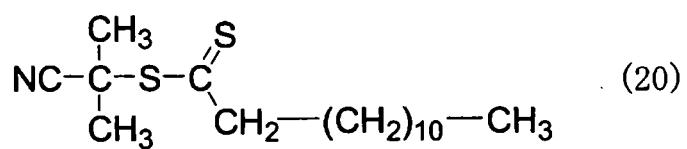
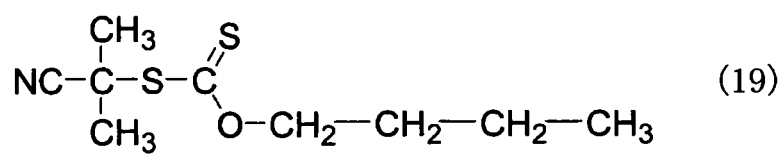
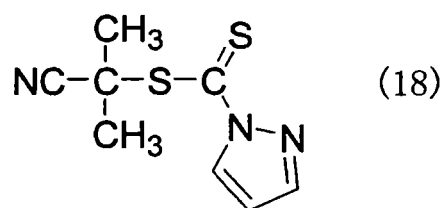
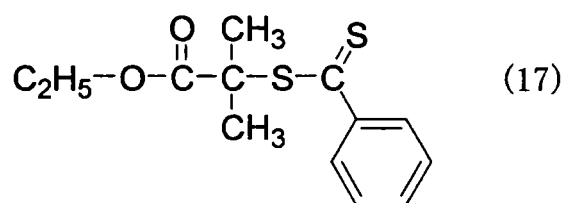
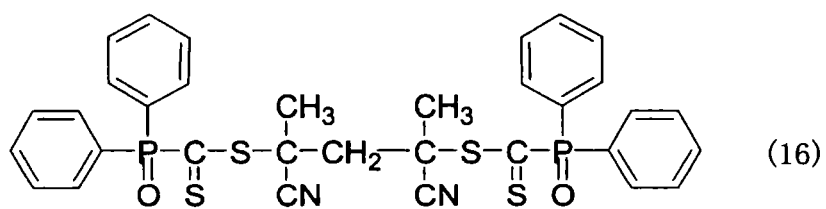


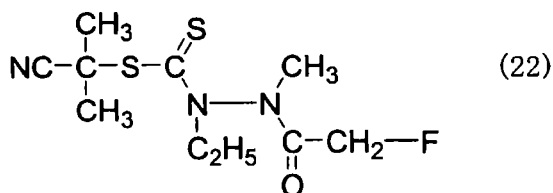
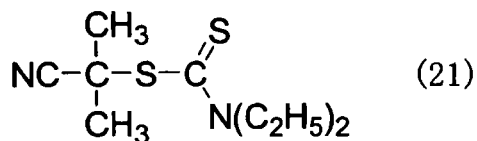
10





5





5 These thiocarbonylthio compounds may be used alone or in combination of two or more.

 In the present invention, another molecular weight control agent, for example, one or more of α -methylstyrene dimer and t-dodecylmercaptan may be used together with the
10 thiocarbonylthio compound for living radical polymerization.

 The radical initiator used for living radical polymerization is not particularly limited and radical initiators which are generally known as radical
15 polymerization initiators may be used. Examples of the radical initiator include azo compounds such as 2,2'-azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile) and 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile); organic
20 peroxides such as benzoyl peroxide, lauroyl peroxide, 1,1'-bis(t-butylperoxy)cyclohexane and t-butylperoxyvalate; hydrogen peroxide; and redox initiators composed of these peroxides and reducing agents.

 These radical initiators may be used alone or in
25 combination of two or more.

 The solvent used for living radical polymerization is not particularly limited as far as an active radical is not deactivated. Examples of the solvent include propylene

glycol monoalkyl ethers such as propylene glycol monomethyl ether and propylene glycol monoethyl ether; (poly)alkylene glycol alkyl ether acetates such as ethylene glycol methyl ether acetate, ethylene glycol ethyl ether acetate, 5 diethylene glycol methyl ether acetate, diethylene glycol ethyl ether acetate, propylene glycol methyl ether acetate, propylene glycol ethyl ether acetate, dipropylene glycol methyl ether acetate and dipropylene glycol ethyl ether acetate; (poly)alkylene glycol dialkyl ethers such as 10 diethylene glycol dimethyl ether, diethylene glycol methyl ethyl ether, diethylene glycol diethyl ether, dipropylene glycol dimethyl ether, dipropylene glycol methyl ethyl ether and dipropylene glycol diethyl ether; other ethers such as tetrahydrofuran; ketones such as methyl ethyl ketone, 15 cyclohexanone, 2-heptanone and 3-heptanone; ketoalcohols such as diacetone alcohol (that is, 4-hydroxy-4-methylpentan-2-one) and 4-hydroxy-4-methylhexan-2-one; alkyl lactates such as methyl lactate and ethyl lactate; other esters such as ethyl 20 2-hydroxy-2-methylpropionate, ethyl hydroxyacetate, methyl 2-hydroxy-3-methylbutanoate, methyl 3-methoxypropionate, ethyl 3-methoxypropionate, methyl 3-ethoxypropionate, ethyl 3-ethoxypropionate, ethyl ethoxyacetate, 3-methyl-3-methoxybutylacetate, 25 3-methyl-3-methoxybutylpropionate, ethyl acetate, n-propyl acetate, i-propyl acetate, n-butyl acetate, i-butyl acetate, n-pentyl formate, i-pentyl acetate, n-butyl propionate, ethyl butyrate, n-propyl butyrate, i-propyl butyrate, n-butyl butyrate, methyl pyruvate, ethyl pyruvate, n-propyl 30 pyruvate, methyl acetoacetate, ethyl acetoacetate and ethyl 2-oxobutanoate; aromatic hydrocarbons such as toluene and xylene; and amides such as N-methylpyrrolidone, N,N-dimethylformamide and N,N-dimethylacetamide.

Out of these solvents, propylene glycol monomethyl

ether, ethylene glycol monomethyl ether acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, dipropylene glycol methyl ether acetate, diethylene glycol dimethyl ether, diethylene glycol methyl ethyl ether, dipropylene glycol dimethyl ether, cyclohexanone, 2-heptanone, 3-heptanone, ethyl 3-methoxypropionate, methyl 3-ethoxypropionate, ethyl 3-ethoxypropionate, 3-methyl-3-methoxybutylpropionate, n-butyl acetate, i-butyl acetate, n-pentyl formate, i-pentyl acetate, n-butyl propionate, ethyl butyrate, i-propyl butyrate, n-butyl butyrate and ethyl pyruvate are preferred from the viewpoints of the solubility for each component, pigment dispersibility and coatability of the radiation sensitive resin composition.

The above solvents may be used alone or in combination of two or more.

The amount of the thiocarbonylthio compound used for living radical polymerization is preferably 0.1 to 50 parts by weight, more preferably 0.2 to 16 parts by weight based on 100 parts by weight of the total of all the polymerizable unsaturated compounds. The amount of the radical polymerization initiator is preferably 0.1 to 50 parts by weight, more preferably 0.1 to 20 parts by weight based on 100 parts by weight of the total of all the polymerizable unsaturated compounds.

The polymerization temperature is preferably 0 to 150°C, more preferably 50 to 120°C. The polymerization time is preferably 10 minutes to 20 hours, more preferably 30 minutes to 6 hours.

M_w (weight average molecular weight in terms of polystyrene measured by gel permeation chromatography (GPC)) of the resin (B) is 1,000 to 45,000, preferably 3,000 to 20,000, particularly preferably 4,000 to 10,000.

M_w/M_n (M_n is a number average molecular weight in terms

of polystyrene measured by GPC) of the resin (B) is preferably 1 to 2.0, more preferably 1 to 1.7, particularly preferably 1 to 1.4.

5 A radiation sensitive resin composition having excellent developability is obtained by using an alkali-soluble resin having the above specific Mw, preferably the above specific Mn and/or Mw/Mn, whereby pixels having a sharp pattern edge can be formed, the residue, stain or film residue is hardly produced on the substrate or light
10 screening layer of an unexposed portion at the time of development, a high product yield can be realized without producing dry foreign matter at the time of manufacturing a color filter due to high cleanability with an organic solvent, and the "burning" of a color filter can be
15 effectively prevented.

In the present invention, the resins (B) may be used alone or in combination of two or more.

The amount of the resin (B) in the present invention is preferably 10 to 1,000 parts by weight, more preferably
20 20 to 500 parts by weight based on 100 parts by weight of the pigment (A). When the amount of the resin (B) is smaller than 10 parts by weight, alkali developability may lower, or a stain or the film residue may be produced on the substrate or light screening layer of an unexposed portion and when
25 the amount is larger than 1,000 parts by weight, the concentration of the pigment becomes relatively low, thereby making it difficult to achieve the target color density of a thin film.

30 - (C) polyfunctional monomer -

The polyfunctional monomer in the present invention is a monomer having two or more polymerizable unsaturated bonds.

Examples of the polyfunctional monomer include

di(meth)acrylates of an alkylene glycol such as ethylene glycol and propylene glycol; di(meth)acrylates of a polyalkylene glycol such as polyethylene glycol having a polymerization degree of 1 or more and polypropylene glycol having a polymerization degree of 1 or more;
 5 poly(meth)acrylates of a polyhydric alcohol having 3 or more hydroxyl groups and dicarboxylic acid modified products thereof such as glycerin, trimethylolpropane, pentaerythritol and dipentaerythritol;
 10 oligo(meth)acrylates such as polyester, epoxy resin, urethane resin, alkyd resin, silicone resin and spiran resin; di(meth)acrylates of a polymer having a hydroxyl group at both terminals such as poly-1,3-butadiene having a hydroxyl group at both terminals, polyisoprene having a hydroxyl group
 15 at both terminals and polycaprolactone having a hydroxyl group at both terminals; and tris[2-(meth)acryloyloxyethyl]phosphate:

Out of these polyfunctional monomers, poly(meth)acrylates of a polyhydric alcohol having 3 or more
 20 hydroxyl groups and dicarboxylic acid modified products thereof are preferred, as exemplified by trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol penta(meth)acrylate and dipentaerythritol
 25 hexa(meth)acrylate. Out of these, trimethylolpropane triacrylate, pentaerythritol triacrylate and dipentaerythritol hexaacrylate are particularly preferred because they provide pixels having excellent strength and surface smoothness and rarely produce a stain or the film
 30 residue on the substrate or light screening layer of an unexposed portion.

The above polyfunctional monomers may be used alone or in combination of two or more.

The amount of the polyfunctional monomer in the present

invention is preferably 5 to 500 parts by weight, more preferably 20 to 300 parts by weight based on 100 parts by weight of the resin (B). When the amount of the polyfunctional monomer is smaller than 5 parts by weight, the strength and surface smoothness of the pixels may degrade and when the amount is larger than 500 parts by weight, alkali developability may lower, or a stain or the film residue may be produced on the substrate or light screening layer of an unexposed portion.

10 In the present invention, the polyfunctional monomer may be used in combination with a monofunctional monomer having one polymerizable unsaturated bond.

 Examples of the above monofunctional monomer include unsaturated monomers (b1) and unsaturated monomers (b2) enumerated for the above alkali-soluble copolymer (I), N-vinyl containing nitrogen heterocyclic compounds such as N-vinylsuccinimide, N-vinylpyrrolidone, N-vinylphthalimide, N-vinyl-2-piperidone, N-vinyl- ϵ -caprolactam, N-vinylpyrrole, N-vinylpyrrolidine, N-vinylimidazole, N-vinylimidazolidine, N-vinylindole, N-vinylindoline, N-vinylbenzimidazole, N-vinylcarbazole, N-vinylpiperidine, N-vinylpiperazine, N-vinylmorpholine and N-vinylphenoxazine; and N-(meth)acryloylmorpholine and commercially available M-5300, M-5400 and M-5600 (of Toagosei Chemical Industry Co., Ltd.).

 These monofunctional monomers may be used alone or in combination of two or more.

 The amount of the monofunctional monomer is preferably 90 wt% or less, more preferably 50 wt% or less based on the total of the polyfunctional monomer and the monofunctional monomer. When the amount of the monofunctional monomer is larger than 90 wt%, the strength and surface smoothness of the pixels may degrade.

- (D) radiation sensitive radical generator -

The radiation sensitive radical generator (to be simply referred to as "radical generator" hereinafter) in the present invention is a compound which forms a radical capable of initiating the polymerization of the above polyfunctional monomer (C) and the optionally used monofunctional monomer upon exposure to radiation such as visible radiation, ultraviolet radiation, far ultraviolet radiation, electron radiation or X-radiation.

The radical generator is, for example, an acetophenone compound, biimidazole compound, triazine compound, benzoin compound, benzophenone compound, α -diketone compound, polynuclear quinone compound, xanthone compound and diazo compound.

Although the radical generators may be used alone or in combination of two or more in the present invention, at least one selected from the group consisting of an acetophenone compound, biimidazole compound and triazine compound is preferred as the radical generator in the present invention.

In the present invention, the amount of the radical generator is preferably 0.01 to 80 parts by weight, more preferably 1 to 60 parts by weight based on 100 parts by weight of the polyfunctional monomer (C) or the total of the polyfunctional monomer and the monofunctional monomer. When the amount of the radical generator is smaller than 0.01 part by weight, it may be difficult to obtain a color filter having a predetermined pixel pattern due to incomplete curing by exposure and when the amount is larger than 80 parts by weight, the formed pixels may fall off from the substrate during development.

Examples of the acetophenone compound out of the preferred radical generators in the present invention include 2-hydroxy-2-methyl-1-phenylpropan-1-one,

2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one,

2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butanone-1, 1-hydroxycyclohexyl·phenyl ketone,

5 2,2-dimethoxy-1,2-diphenylethan-1-one, 1,2-octanedione and 1-[4-(phenylthio)phenyl]-2-(O-benzoyloxime).

Out of these acetophenone compounds,

2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1,

10 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butanone-1, 1,2-octanedione and

1-[4-(phenylthio)phenyl]-2-(O-benzoyloxime) are particularly preferred.

The above acetophenone compounds may be used alone or
15 in combination of two or more.

When the acetophenone compound is used as the radical generator in the present invention, the amount of the acetophenone compound is preferably 0.01 to 80 parts by weight, more preferably 1 to 60 parts by weight, particularly
20 preferably 1 to 30 parts by weight based on 100 parts by weight of the polyfunctional monomer (C) or the total of the polyfunctional monomer and the monofunctional monomer.

When the amount of the acetophenone compound is smaller than 0.01 part by weight, it may be difficult to obtain a color
25 filter having a predetermined pixel pattern due to incomplete curing by exposure. When the amount is larger than 80 parts by weight, the formed pixels may fall off from the substrate during development.

Examples of the above biimidazole compound include
30 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxycarbonylphenyl)-1,2'-biimidazole,
2,2'-bis(2-bromophenyl)-4,4',5,5'-tetrakis(4-ethoxycarbonylphenyl)-1,2'-biimidazole,
2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetraphenyl-

1,2'-biimidazole,
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-
5 1,2'-biimidazole,
2,2'-bis(2-bromophenyl)-4,4',5,5'-tetraphenyl-1,2'-
biimidazole,
2,2'-bis(2,4-dibromophenyl)-4,4',5,5'-tetraphenyl-
1,2'-biimidazole and
10 2,2'-bis(2,4,6-tribromophenyl)-4,4',5,5'-tetraphenyl-
1,2'-biimidazole.

Out of these biimidazole compounds,
2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-
biimidazole,
15 2,2'-bis(2,4-dichlorophenyl)-4,4',5,5'-tetraphenyl-
1,2'-biimidazole and
2,2'-bis(2,4,6-trichlorophenyl)-4,4',5,5'-tetraphenyl-
1,2'-biimidazole are preferred, and
2,2'-bis(2,4-dichlorophenyl)-4,4',5,5'-tetraphenyl-
20 1,2'-biimidazole is particularly preferred.

These biimidazole compounds have excellent solubility
in a solvent, do not form foreign matter such as an undissolved
product and a precipitate, have high sensitivity, fully
promote a curing reaction by exposure with a small amount
25 of energy and do not cause a curing reaction in an unexposed
portion. Therefore, the coating film obtained after
exposure is clearly divided into a cured portion insoluble
in a developer and an uncured portion having high solubility
in a developer, thereby making it possible to form a
30 high-definition color filter having a predetermined pixel
pattern which is not undercut.

The above biimidazole compounds may be used alone or
in combination of two or more.

When the biimidazole compound is used as the radical

generator in the present invention, the amount of the biimidazole compound is preferably 0.01 to 40 parts by weight, more preferably 1 to 30 parts by weight, particularly preferably 1 to 20 parts by weight based on 100 parts by weight of the polyfunctional monomer (C) or the total of the polyfunctional monomer and the monofunctional monomer. When the amount of the biimidazole compound is smaller than 0.01 part by weight, it may be difficult to obtain a color filter having a predetermined pixel pattern due to incomplete curing by exposure. When the amount is larger than 40 parts by weight, the formed pixels may fall off from the substrate and the film surface of the pixels may be roughened during development.

When the biimidazole compound is used as the radical generator in the present invention, it is preferably used in combination with the following hydrogen donor to further improve sensitivity.

The term "hydrogen donor" as used herein means a compound which can provide a hydrogen atom to a radical formed from the biimidazole compound upon exposure.

The hydrogen donor in the present invention is preferably a mercaptan compound or an amine compound defined hereinbelow.

The above mercaptan compound is a compound having a benzene ring or a hetero ring as a mother nucleus and 1 or more, preferably 1 to 3, more preferably 1 or 2 mercapto groups directly bonded to the mother nucleus (to be referred to as "mercaptan hydrogen donor" hereinafter).

The above amine compound is a compound having a benzene ring or a hetero ring as a mother nucleus and 1 or more, preferably 1 to 3, more preferably 1 or 2 amino groups directly bonded to the mother nucleus (to be referred to as "amine hydrogen donor" hereinafter).

These hydrogen donors may have a mercapto group and

an amino group at the same time.

A detailed description is subsequently given of these hydrogen donors.

The mercaptan hydrogen donor may have at least one
5 benzene ring or hetero ring, or both of them. When it has two or more of the rings, a fused ring may or may not be formed.

When the mercaptan hydrogen donor has two or more mercapto groups, as far as at least one free mercapto group remains, at least one of the other mercapto groups may be
10 substituted by an alkyl, aralkyl or aryl group. Further, as far as at least one free mercapto group remains, the mercaptan hydrogen donor may have a structural unit in which two sulfur atoms are bonded together by a divalent organic group such as an alkylene group or a structural unit in which
15 two sulfur atoms are bonded together in the form of a disulfide.

Further, the mercaptan hydrogen donor may be substituted by a carboxyl group, alkoxycarbonyl group, substituted alkoxycarbonyl group, phenoxycarbonyl group,
20 substituted phenoxycarbonyl group or nitrile group at a position other than the mercapto group(s).

Examples of this mercaptan hydrogen donor include 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, 2-mercaptobenzimidazole,
25 2,5-dimercapto-1,3,4-thiadiazole and 2-mercapto-2,5-dimethylaminopyridine.

Out of these mercaptan hydrogen donors, 2-mercaptobenzothiazole and 2-mercaptobenzoxazole are preferred, and 2-mercaptobenzothiazole is particularly
30 preferred.

The amine hydrogen donor may have at least one benzene ring or hetero ring, or both of them. When it has two or more of the rings, a fused ring may or may not be formed.

At least one amino group of the amine hydrogen donor

may be substituted by an alkyl group or substituted alkyl group. The amine hydrogen donor may be substituted by a carboxyl group, alkoxycarbonyl group, substituted alkoxycarbonyl group, phenoxycarbonyl group, substituted phenoxycarbonyl group or nitrile group at a position other than the amino group(s).

Examples of the above amine hydrogen donor include 4,4'-bis(dimethylamino)benzophenone, 4,4'-bis(diethylamino)benzophenone, 10 4-diethylaminoacetophenone, 4-dimethylaminopropiophenone, ethyl-4-dimethylaminobenzoate, 4-dimethylaminobenzoic acid and 4-dimethylaminobenzonitrile.

Out of these amine hydrogen donors, 4,4'-bis(dimethylamino)benzophenone and 15 4,4'-bis(diethylamino)benzophenone are preferred, and 4,4'-bis(diethylamino)benzophenone is particularly preferred.

The amine hydrogen donor serves as a sensitizer even when a radical generator other than a biimidazole compound 20 is used.

In the present invention, the above hydrogen donors may be used alone or in combination of two or more. A combination of at least one mercaptan hydrogen donor and at least one amine hydrogen donor is preferably used because 25 the formed pixels hardly fall off from the substrate during development and have high strength and sensitivity.

Preferred examples of the combination of the mercaptan hydrogen donor and the amine hydrogen donor include a combination of 2-mercaptobenzothiazole and 30 4,4'-bis(dimethylamino)benzophenone, combination of 2-mercaptobenzothiazole and 4,4'-bis(diethylamino)benzophenone, combination of 2-mercaptobenzoxazole and 4,4'-bis(dimethylamino)benzophenone, and combination of

2-mercaptobenzoxazole and
 4,4'-bis(diethylamino)benzophenone. Out of these
 combinations, a combination of 2-mercaptobenzothiazole and
 4,4'-bis(diethylamino)benzophenone and a combination of
 5 2-mercaptobenzoxazole and
 4,4'-bis(diethylamino)benzophenone are more preferred, and
 a combination of 2-mercaptobenzothiazole and
 4,4'-bis(diethylamino)benzophenone is particularly
 preferred.

10 The weight ratio of the mercaptan hydrogen donor to
 the amine hydrogen donor in the combination of the mercaptan
 hydrogen donor and the amine hydrogen donor is preferably
 1:1 to 1:4, more preferably 1:1 to 1:3.

 When the hydrogen donor is used in conjunction with
 15 the biimidazole compound in the present invention, the amount
 of the hydrogen donor is preferably 0.01 to 40 parts by weight,
 more preferably 1 to 30 parts by weight, particularly
 preferably 1 to 20 parts by weight based on 100 parts by weight
 of the polyfunctional monomer (C) or the total of the
 20 polyfunctional monomer and the monofunctional monomer.
 When the amount of the hydrogen donor is smaller than 0.01
 part by weight, its effect of improving sensitivity may lower.
 When the amount is larger than 40 parts by weight, the formed
 pixels may fall off from the substrate during development.

25 Examples of the above triazine compound include
 triazine compounds having a halomethyl group such as
 2,4,6-tris(trichloromethyl)-s-triazine,
 2-methyl-4,6-bis(trichloromethyl)-s-triazine,
 2-[2-(5-methylfuran-2-yl)ethenyl]-4,6-
 30 bis(trichloromethyl)-s-triazine,
 2-[2-(furan-2-yl)ethenyl]-4,6-bis(trichloromethyl)-s-
 triazine, 2-[2-(4-diethylamino-2-methylphenyl)ethenyl]-
 4,6-bis(trichloromethyl)-s-triazine,
 2-[2-(3,4-dimethoxyphenyl)ethenyl]-

4,6-bis(trichloromethyl)-s-triazine,
2-(4-methoxyphenyl)-4,6-bis(trichloromethyl)-s-triazine,
2-(4-ethoxystyryl)-4,6-bis(trichloromethyl)-s-triazine
and 2-(4-n-butoxyphenyl)-4,6-bis(trichloromethyl)-s-
5 triazine.

Out of these triazine compounds,
2-[2-(3,4-dimethoxyphenyl)ethenyl]-4,6-
bis(trichloromethyl)-s-triazine is particularly preferred.

The above triazine compounds may be used alone or in
10 combination of two or more.

When the triazine compound is used as the radical
generator in the present invention, the amount of the
triazine compound is preferably 0.01 to 40 parts by weight,
more preferably 1 to 30 parts by weight, particularly
15 preferably 1 to 20 parts by weight based on 100 parts by weight
of the polyfunctional monomer (C) or the total of the
polyfunctional monomer and the monofunctional monomer.
When the amount of the triazine compound is smaller than 0.01
part by weight, it may be difficult to obtain a color filter
20 having a predetermined pixel pattern due to incomplete curing
by exposure. When the amount is larger than 40 parts by
weight, the formed pixels may fall off from the substrate
during development.

25 - Other additives -

The radiation sensitive resin composition of the
present invention comprises the above components (A) to (D)
as essential components and may further contain other
additives as required.

30 The above other additives include a filler such as glass
or alumina; polymer compound such as polyvinyl alcohol or
poly(fluoroalkylacrylate); surfactant such as a nonionic,
cationic or anionic surfactant; adhesion accelerator such
as vinyl trimethoxysilane, vinyl triethoxysilane, vinyl

- tris(2-methoxyethoxy)silane,
 N-(2-aminoethyl)-3-aminopropyl·methyl·dimethoxysilane,
 N-(2-aminoethyl)-3-aminopropyltrimethoxysilane,
 3-aminopropyltriethoxysilane,
 5 3-glycidoxypropyltrimethoxysilane,
 3-glycidoxypropyl·methyl·dimethoxysilane,
 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane,
 3-chloropropyl·methyl·dimethoxysilane,
 3-chloropropyltrimethoxysilane,
 10 3-methacryloyloxypropyltrimethoxysilane or
 3-mercaptopropyltrimethoxysilane; antioxidant such as
 2,2-thiobis(4-methyl-6-t-butylphenol) or
 2,6-di-t-butylphenol; ultraviolet light absorber such as
 2-(3-t-butyl-5-methyl-2-hydroxyphenyl)-5-
 15 chlorobenzotriazole or alkoxybenzophenone; and cohesion
 inhibitor such as sodium polyacrylate.

Preparation of liquid composition

The radiation sensitive resin composition of the
 20 present invention is generally mixed with a solvent to be
 prepared as a liquid composition.

A suitable solvent may be selected and used as long
 as it disperses or dissolves the components (A) to (D) and
 other additives constituting the radiation sensitive
 25 composition, does not react with these components and has
 suitable volatility.

Examples of the solvent include propylene glycol
 monoalkyl ethers such as propylene glycol monomethyl ether
 and propylene glycol monoethyl ether; (poly)alkylene glycol
 30 alkyl ether acetates such as ethylene glycol methyl ether
 acetate, ethylene glycol ethyl ether acetate, diethylene
 glycol methyl ether acetate, diethylene glycol ethyl ether
 acetate, propylene glycol methyl ether acetate, propylene
 glycol ethyl ether acetate, dipropylene glycol methyl ether.

acetate and dipropylene glycol ethyl ether acetate;
 (poly)alkylene glycol dialkyl ethers such as diethylene
 glycol dimethyl ether, diethylene glycol methyl ethyl ether,
 diethylene glycol diethyl ether, dipropylene glycol dimethyl
 5 ether, dipropylene glycol methyl ethyl ether and dipropylene
 glycol diethyl ether; other ethers such as tetrahydrofuran;
 ketones such as methyl ethyl ketone, cyclohexanone,
 2-heptanone and 3-heptanone; ketoalcohols such as diacetone
 alcohol (that is, 4-hydroxy-4-methylpentan-2-one) and
 10 4-hydroxy-4-methylhexan-2-one; alkyl lactates such as
 methyl lactate and ethyl lactate; other esters such as ethyl
 2-hydroxy-2-methylpropionate, ethyl hydroxyacetate, methyl
 2-hydroxy-3-methylbutanoate, methyl 3-methoxypropionate,
 ethyl 3-methoxypropionate, methyl 3-ethoxypropionate,
 15 ethyl 3-ethoxypropionate, ethyl ethoxyacetate,
 3-methyl-3-methoxybutylacetate,
 3-methyl-3-methoxybutylpropionate, ethyl acetate, n-propyl
 acetate, i-propyl acetate, n-butyl acetate, i-butyl acetate,
 n-pentyl formate, i-pentyl acetate, n-butyl propionate,
 20 ethyl butyrate, n-propyl butyrate, i-propyl butyrate,
 n-butyl butyrate, methyl pyruvate, ethyl pyruvate, n-propyl
 pyruvate, methyl acetoacetate, ethyl acetoacetate and ethyl
 2-oxobutanoate; aromatic hydrocarbons such as toluene and
 xylene; and amides such as N-methylpyrrolidone,
 25 N,N-dimethylformamide and N,N-dimethylacetamide.

Out of these solvents, propylene glycol monomethyl
 ether, ethylene glycol monomethyl ether acetate, propylene
 glycol monomethyl ether acetate, propylene glycol monoethyl
 ether acetate, dipropylene glycol methyl ether acetate,
 30 diethylene glycol dimethyl ether, diethylene glycol methyl
 ethyl ether, dipropylene glycol dimethyl ether,
 cyclohexanone, 2-heptanone, 3-heptanone, ethyl
 3-methoxypropionate, methyl 3-ethoxypropionate, ethyl
 3-ethoxypropionate, 3-methyl-3-methoxybutylpropionate,

n-butyl acetate, i-butyl acetate, n-pentyl formate, i-pentyl acetate, n-butyl propionate, ethyl butyrate, i-propyl butyrate, n-butyl butyrate and ethyl pyruvate are particularly preferred from the viewpoints of solubility, pigment dispersibility and coatability.

The above solvents may be used alone or in combination of two or more.

Further, 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 benzoate, diethyl oxalate, diethyl maleate, γ -butyrolactone, ethylene carbonate, propylene carbonate or ethylene glycol monophenyl ether acetate may be used in conjunction with the above solvent.

These high-boiling solvents may be used alone or in combination of two or more.

The amount of the solvent is not particularly limited but desirably a value which ensures that the total amount of all the components excluding the solvent of the composition becomes preferably 5 to 50 wt%, particularly preferably 10 to 40 wt% from the viewpoints of the coatability and stability of the obtained liquid composition.

Color filter forming method

A description is subsequently given of the method of forming the color filter of the present invention from the radiation sensitive resin composition of the present invention.

The method of forming the color filter comprises at least the following steps (1) to (4):

- (1) forming a coating film of the radiation sensitive resin composition for color filters of the present invention on a substrate;
- (2) exposing at least part of the coating film to radiation;

- (3) developing the coating film after exposure; and
- (4) heating the coating film after development (to be referred to as "post-baking" hereinafter).

Each of the above steps will be described hereinbelow.

5

- step (1) -

A light screening layer is optionally formed on the surface of the substrate to define a portion for the formation of pixels, and then a liquid radiation sensitive resin
10 composition for color filters containing, for example, a red pigment is applied to the substrate and prebaked to evaporate the solvent so as to form a coating film.

The substrate used in this step is made of glass, silicon, polycarbonate, polyester, aromatic polyamide,
15 polyamide-imide, polyimide, polyether sulfone, ring open polymer of a cyclic olefin or hydrogenated product thereof.

The substrate may be optionally subjected to a pre-treatment such as chemical treatment with a silane coupling agent, plasma treatment, ion plating, sputtering,
20 gas-phase reaction or vacuum deposition.

As means of applying the liquid composition to the substrate, a suitable coating technique such as rotational coating, i.e., spin coating, cast coating, roll coating or slit-nozzle coating may be employed. Slit-nozzle coating
25 is preferred because the radiation sensitive resin composition of the present invention has high solubility in a cleaning solvent even after it is dried.

As for prebaking conditions, the coating film is preferably prebaked at 70 to 110°C for 2 to 4 minutes.

30 The thickness of the formed coating film after the removal of the solvent is preferably 0.1 to 10 μm , more preferably 0.2 to 8.0 μm , particularly preferably 0.2 to 6.0 μm .

- step (2) -

Thereafter, at least part of the formed coating film is exposed to radiation through a photomask having a suitable pattern.

5 The radiation used in this step is selected from visible radiation, ultraviolet radiation, far ultraviolet radiation, electron radiation and X-radiation. Radiation having a wavelength of 190 to 450 nm is preferred.

10 The dose of the radiation is preferably about 10 to 10,000 J/m².

- step (3) -

Thereafter, the exposed coating film is developed with preferably an alkali developer to dissolve and remove an
15 unexposed portion of the coating film so as to form a pattern.

 The above alkali developer is preferably an aqueous solution of sodium carbonate, sodium hydroxide, potassium hydroxide, tetramethylammonium hydroxide, choline,
18-diazabicyclo-[5.4.0]-7-undecene or
20 1,5-diazabicyclo-[4.3.0]-5-nonene.

A suitable amount of a water-soluble organic solvent such as methanol or ethanol, or a surfactant may be added to the above alkali developer. The coating film is preferably rinsed with water after alkali development.

25 Shower development, spray development, dip (immersion) development or puddle development may be employed.

 As for development conditions, the coating film is preferably developed at normal temperature for about 5 to
30 300 sec.

- step (4) -

By post-baking the developed coating film, a substrate having a predetermined pixel pattern composed of a cured

product of the radiation sensitive resin composition can be obtained.

As for post-baking conditions, the coating film is preferably heated at 180 to 230°C for about 20 to 40 minutes.

5 The thickness of the pixel film formed as described above is preferably 0.5 to 5.0 μm , more preferably 1.5 to 3.0 μm .

By repeating the above steps (1) to (4) using liquid radiation sensitive resin compositions for color filters
10 containing green and blue pigments, green and blue pixel patterns are formed on the same substrate, thereby making it possible to form a colored layer having predetermined red, green and blue pixel patterns on the substrate. In the present invention, the order of forming these color pixel
15 patterns is not limited to the above order.

Color filter

The color filter of the present invention is formed from the radiation sensitive resin composition for color
20 filters of the present invention.

The color filter of the present invention is extremely useful for transmission and reflection type color liquid crystal display devices, color image pick-up devices, color sensors, etc.

25

Color liquid crystal display device

The color liquid crystal display device of the present invention comprises the color filter of the present invention.

30 The color liquid crystal display device of the present invention may have a suitable structure. For example, it may have a structure that the color filter is formed on a substrate separate from a drive substrate having a thin film transistor (TFT) and the drive substrate and the substrate

having the color filter are opposed to each other with a liquid crystal layer between them. Alternatively, it may have a structure that a substrate manufactured by forming the color filter on the surface of a drive substrate having a thin film transistor (TFT) and a substrate having ITO (tin doped indium oxide) electrodes are opposed to each other with a liquid crystal layer between them. The latter structure can significantly improve the numerical aperture, thereby making it possible to obtain a bright high-definition liquid crystal display device.

Radiation sensitive resin composition (II)

A radiation sensitive resin composition (to be referred to as "radiation sensitive resin composition (II)" hereinafter) which comprises (A) a pigment, (B) an alkali-soluble resin, (C) a polyfunctional monomer and (D) a radiation sensitive radical generator, the alkali-soluble resin (B) having a content of a component having an Mw of less than 1,000 of 0 to 30 wt%, a content of a component having an Mw of 1,000 to 10,000 of 50 to 100 wt%, preferably 70 to 100 wt%, more preferably 90 to 100 wt%, a content of a component having an Mw of more than 10,000 and 45,000 or less of 0 to 45 wt%, and a content of a component having an Mw of more than 45,000 of 0 to 5 wt%, and having an Mw of 1,000 to 10,000, preferably 2,000 to 8,000 as the entire resin (to be referred to as "resin (ii)" hereinafter), may also be used to form a color filter.

The above components (A), (C) and (D) used in the radiation sensitive resin composition of the present invention may be used as the components (A), (C) and (D) in the radiation sensitive resin composition (II), and the radiation sensitive resin composition (II) may be mixed with the above other additives enumerated for the radiation sensitive resin composition of the present invention.

Further, the radiation sensitive resin composition (II) is mixed with any one of the above solvents enumerated for the liquid radiation sensitive resin composition of the present invention to be prepared as a liquid composition.

5 The resin (ii) can be obtained by carrying out the radical polymerization of a monomer mixture of the above unsaturated monomer (b1) and the above unsaturated monomer (b2) and purifying the obtained copolymer by a re-precipitation method using two or more organic solvents
10 which differ from each other in polarity (to be referred to as "purification method" hereinafter).

 The purification method will be described hereinbelow.

 Radical polymerization for manufacturing the resin (ii) is not particularly limited and may be carried out in
15 accordance with a commonly used method.

 When the solvent used for polymerization is a good solvent in the following re-precipitation method, the copolymer after polymerization may be purified as a polymer solution directly or after its concentration is adjusted,
20 or the copolymer may be separated from the polymer solution obtained by polymerization in accordance with a commonly used method and purified as a solid.

 After radical polymerization, the obtained copolymer is purified by the re-precipitation method using two or more
25 organic solvents which differ from each other in polarity. That is, after insoluble impurities are removed from the solution of the copolymer in the good solvent by filtration or centrifugation as required, the obtained solution is injected into a large amount, for example, 5 to 10 times the
30 volume of the copolymer solution of a precipitating medium (poor solvent) to re-precipitate the copolymer for purification. At this point, out of the impurities contained in the copolymer solution, impurities soluble in the precipitating medium remain in a liquid phase to be separated

from the copolymer.

Examples of a combination of the good solvent and the precipitating medium used in this re-precipitation method include a combination of diethylene glycol monomethyl ether acetate and n-hexane, a combination of methyl ethyl ketone and n-hexane, a combination of diethylene glycol monomethyl ether acetate and n-heptane, and a combination of methyl ethyl ketone and n-heptane.

For the re-precipitation of the copolymer, it is desired that the copolymer solution should be added little by little while the precipitating medium is stirred violently, thereby making it possible to minimize the amount of impurities to be included in the precipitate. The purity of the copolymer can be increased by repeating re-precipitation a plurality of times, and a precipitate which is very fine and not suitable for filtration can be separated by centrifugation.

When more strict purification is required, fractional precipitation is preferred as one of re-precipitation techniques. That is, the copolymer is dissolved in a good solvent and the solvent conditions, for example, the type, composition and temperature of the solvent are finely changed to precipitate the copolymer as a solute, whereby the copolymer is divided into a plurality of fractions which slightly differ from one another in solubility to be recovered. In this method, the precipitating medium is generally added to the copolymer solution. The ratio of the good solvent and the precipitating medium, that is, the mixing ratio of the good solvent may be changed at a fixed temperature, or the temperature may be changed by fixing the mixing ratio of the good solvent. By using this method, the copolymer having a narrow molecular weight range can be recovered at a high yield. Each fraction of the copolymer recovered by fractional precipitation can be acquired as a

solid by concentrating and drying one or more fractions according to the value of M_w .

The copolymer obtained by re-precipitation can be further purified by adsorption/affinity chromatography or
5 dialysis as required.

M_n of the resin (ii) is preferably 600 to 10,000, more preferably 1,200 to 8,000.

M_w/M_n of the resin (ii) is preferably 1 to 2.0, more preferably 1 to 1.7, particularly preferably 1 to 1.4.

10 By using the resin (ii) having the above specific M_w , preferably the above specific M_n and/or M_w/M_n , the radiation sensitive resin composition (II) having high developability is obtained, whereby pixels having a sharp pattern edge can be formed, the residue, stain or film residue is hardly
15 produced on the substrate or light screening layer of an unexposed portion during development, high product yield can be realized without producing dry foreign matter at the time of manufacturing a color filter due to high cleanability with an organic solvent, and the "burning" of the color filter
20 can be effectively prevented.

In the radiation sensitive resin composition (II), the resins (ii) may be used alone or in combination of two or more.

25 The radiation sensitive resin composition of the present invention can provide a color filter free from "burning" at a high product yield and is suitable for slit-nozzle coating.

The radiation sensitive resin composition of the present invention is advantageously used for the manufacture
30 of a color filter for CCD.

Examples

The following examples are provided for the purpose of further illustrating the present invention but are in no

way to be taken as limiting.

Mw and Mn of the resin obtained in each of the following Synthesis Examples were measured by gel permeation chromatography (GPC) based on the following specifications.

5 Device: GPC-101 (of Showa Denko K.K.)

Column: GPC-KF-801, GPC-KF-802, GPC-KF-803 and GPC-KF-804 were combined.

Transfer phase: tetrahydrofuran containing 0.5 wt% of phosphoric acid

10

Comparative Synthesis Example 1

10 parts by weight of 2,2'-azobisisobutyronitrile and 400 parts by weight of diethylene glycol monomethyl ether acetate were fed to a flask equipped with a cooling tube and a stirrer, 30 parts by weight of methacrylic acid, 31.2 parts by weight of N-phenylmaleimide, 20 parts by weight of benzyl methacrylate, 18.8 parts by weight of styrene and 10 parts by weight of α -methylstyrene dimer as a molecular weight control agent were then fed to the flask, the inside of the flask was substituted by nitrogen, the resulting mixture was stirred gently, and the obtained reaction solution was heated at 80°C to be polymerized by maintaining that temperature for 3 hours. The reaction solution was then heated at 100°C, 2 parts by weight of 2,2'-azobisisobutyronitrile was added, and polymerization was further continued for 1 hour to obtain a resin solution (solid content of 20.1 wt%). This resin had an Mw of 5,000 and an Mw/Mn of 3.6. This resin was designated as resin (b-1).

30 Synthesis Examples 1 to 20

2 parts by weight of 2,2'-azobisisobutyronitrile, amounts shown in Table 1 of the compounds represented by the above formulas (3) to (22) as molecular weight control agents and 200 parts by weight of diethylene glycol monomethyl ether

acetate were fed to a flask equipped with a cooling tube and a stirrer, 30 parts by weight of methacrylic acid, 31.2 parts by weight of N-phenylmaleimide, 20 parts by weight of benzyl methacrylate and 18.8 parts by weight of styrene were then
5 fed to the flask, the inside of the flask was substituted by nitrogen, the resulting mixtures were stirred gently, and the obtained reaction solutions were heated at 80°C to be polymerized by maintaining that temperature for 3 hours. The reaction solutions were then heated at 100°C, 1 part by weight
10 of 2,2'-azobisisobutyronitrile was added, and polymerization was further continued for 1 hour to obtain solutions of resins (B-1) to (B-20) shown in Table 1. When the solid contents, Mw and Mw/Mn of the obtained resins were measured, the measurement results shown in Table 1 were
15 obtained.

Table 1

	Thiocarbonylthio compound		resin (B)			resin name
	Formula No.	Amount (parts by weight)	Mw	Mw/Mn	0 solid content (% by weight)	
S.Ex. 1	(3)	2.7	5,000	1.4	34.2	(B-1)
S.Ex. 2	(4)	3.0	5,000	1.4	34.2	(B-2)
S.Ex. 3	(5)	2.8	5,000	1.4	34.2	(B-3)
S.Ex. 4	(6)	3.8	5,000	1.4	34.2	(B-4)
S.Ex. 5	(7)	3.5	5,000	1.4	34.2	(B-5)
S.Ex. 6	(8)	4.2	5,000	1.4	34.2	(B-6)
S.Ex. 7	(9)	4.5	5,000	1.4	34.2	(B-7)
S.Ex. 8	(10)	7.9	5,000	1.4	34.2	(B-8)
S.Ex. 9	(11)	3.6	5,000	1.4	34.2	(B-9)
S.Ex. 10	(12)	4.4	5,000	1.4	34.2	(B-10)
S.Ex. 11	(13)	5.8	5,000	1.4	34.2	(B-11)
S.Ex. 12	(14)	6.4	5,000	1.4	34.2	(B-12)
S.Ex. 13	(15)	2.9	5,000	1.4	34.2	(B-13)
S.Ex. 14	(16)	6.4	5,000	1.4	34.2	(B-14)
S.Ex. 15	(17)	5.1	5,000	1.4	34.2	(B-15)
S.Ex. 16	(18)	4.0	5,000	1.4	34.2	(B-16)
S.Ex. 17	(19)	4.1	5,000	1.4	34.2	(B-17)
S.Ex. 18	(20)	6.0	5,000	1.4	34.2	(B-18)
S.Ex. 19	(21)	4.1	5,000	1.4	34.2	(B-19)
S.Ex. 20	(22)	5.3	5,000	1.4	34.2	(B-20)

S.Ex.: Synthesis Examples

Evaluation of voltage retention

Comparative Example 1

40 parts by weight of a mixture of C.I. Pigment Red
5 254 and C.I. Pigment Yellow 139 in a weight ratio of 50/50
as the pigment (A), 10 parts by weight of Disperbyk2001 as
a dispersant and 100 parts by weight of ethyl
3-ethoxypropionate as a solvent were mixed and dispersed
together by the Diamond Fine Mill bead mill (bead diameter
10 of 1.0 mm) (trade name, manufactured by Mitsubishi Materials
Corporation) for 12 hours to prepare a pigment dispersion.

100 parts by weight of this pigment dispersion, 70 parts
by weight of the resin (b-1) as the alkali-soluble resin,
80 parts by weight of dipentaerythritol hexaacrylate as the
15 polyfunctional monomer (C), 50 parts by weight of
2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butanone-
1 as the radical generator (D) and 1,000 parts by weight of
propylene glycol monomethyl ether acetate as a solvent were
mixed together to prepare a liquid composition (r-1).

20 Thereafter, the liquid composition (r-1) was applied
to a soda glass substrate having an SiO_2 film for preventing
the elution of sodium ions and ITO (indium-tin oxide alloy)
electrodes deposited in a predetermined shape on the surface
with a spin coater and prebaked in a clean oven at 90°C for
25 10 minutes to form a $2.0\text{ }\mu\text{m}$ -thick coating film.

Thereafter, the coating film was exposed to $5,000\text{ J/m}^2$
of radiation having wavelengths of 365 nm, 405 nm and 436
nm with a high-pressure mercury lamp without using a
photomask. This substrate was immersed in a developer
30 composed of a 0.04 wt% aqueous solution of potassium
hydroxide at 23°C for 1 minute to be developed, rinsed with
super fine water, dried with air and further post-baked at
 250°C for 30 minutes to be cured so as to form red pixels
on the substrate. The film thickness of the pixels was 1.60

μm.

Then, the substrate having these pixels and a substrate having ITO electrodes deposited in a predetermined shape were bonded together with a sealing agent containing 0.8 mm glass
5 beads, and the MLC6608 liquid crystals (trade name) manufactured by Merk Co., Ltd. were injected into the space between these substrates to manufacture a liquid crystal cell.

The liquid crystal cell was then placed in a
10 thermostatic chamber at 60°C to measure its voltage retention by using the VHR-1A (trade name) liquid crystal voltage retention measuring system of Toyo Technica Co., Ltd. The application voltage was 5.5 V rectangular waves and the measurement frequency was 60 Hz. The voltage retention is
15 a value obtained by dividing the potential difference of the liquid crystal cells after 16.7 ms by voltage applied for 0 ms. The results are shown in Table 2.

When the voltage retention of the liquid crystal cell is 90 % or less, the liquid crystal cell cannot maintain
20 application voltage at a predetermined level for 16.7 ms and cannot align the liquid crystals fully. Therefore, a liquid crystal display device comprising a color filter formed from the liquid composition has a high probability of causing "burning". The above results are shown in Table 2.

25

Examples 1 to 20

Liquid compositions (R-1) to (R-20) were prepared in the same manner as in Comparative Example 1 except that 70 parts by weight of the resins (B-1) to (B-20) were used in
30 place of the resin (b-1) to manufacture liquid crystal cells and measure the voltage retentions of the liquid crystal cells in the same manner as in Comparative Example 1. The voltage retentions of the liquid crystal cells were all 92 %. Therefore, color liquid crystal display devices comprising

color filters formed from the liquid compositions (R-1) to (R-20) have a low probability of causing "burning". The above results are shown in Table 2.

5

Table 2

	Liquid composition	voltage retention (%)	prevention of burning
C.Ex.1	r-1	42	×
Ex.1	R-1	92	○
Ex.2	R-2	92	○
Ex.3	R-3	92	○
Ex.4	R-4	92	○
Ex.5	R-5	92	○
Ex.6	R-6	92	○
Ex.7	R-7	92	○
Ex.8	R-8	92	○
Ex.9	R-9	92	○
Ex.10	R-10	92	○
Ex.11	R-11	92	○
Ex.12	R-12	92	○
Ex.13	R-13	92	○
Ex.14	R-14	92	○
Ex.15	R-15	92	○
Ex.16	R-16	92	○
Ex.17	R-17	92	○
Ex.18	R-18	92	○
Ex.19	R-19	92	○
Ex.20	R-20	92	○

C.Ex.: Comparative Example Ex.:Example

Radiation sensitive resin compositions comprising a red pigment were evaluated herein. The same results were obtained from radiation sensitive resin compositions

comprising blue, green, yellow and black pigments.

Comparative Synthesis Example 2

2.5 parts by weight of 2,2'-azobisisobutyronitrile and
5 200 parts by weight of diethylene glycol monomethyl ether
acetate were fed to a flask equipped with a cooling tube and
a stirrer, 30 parts by weight of methacrylic acid, 31.2 parts
by weight of N-phenylmaleimide, 20 parts by weight of benzyl
methacrylate, 18.8 parts by weight of styrene and 3 parts
10 by weight of α -methylstyrene dimer (chain transfer agent)
were then fed to the flask, the inside of the flask was
substituted by nitrogen, the resulting mixture was stirred
gently, and the obtained reaction solution was heated at 80°C
to be polymerized by maintaining that temperature for 3 hours.
15 The reaction solution was then heated at 100°C, 0.5 part by
weight of 2,2'-azobisisobutyronitrile was added, and
polymerization was further continued for 1 hour to obtain
a resin solution (solid content of 33.2 wt%). This resin
had an Mw of 14,000 and an Mw/Mn of 2.1. This resin was
20 designated as resin (b-2).

Immersion test

Comparative Example 2

The liquid composition (r-1) was applied to a 4
25 inch-diameter soda glass substrate having an SiO₂ film for
preventing the elution of sodium ions on the surface with
a spin coater and left in a clean room at 23°C for 12 hours
to be dried so as to form a coating film.

When this substrate was immersed in 100 cc of propylene
30 glycol monomethyl ether acetate for 2 minutes, the coating
film was completely dissolved.

Examples 21 to 40

Coating films were formed on a soda glass substrate

in the same manner as in Comparative Example 2 except that the liquid compositions (R-1) to (R-20) were used in place of the liquid composition (r-1).

When the substrates were immersed in 100 cc of propylene glycol monomethyl ether acetate for 2 minutes, the coating films were completely dissolved.

Comparative Example 3

A liquid composition (r-2) was prepared in the same manner as in Comparative Example 1 except that 70 parts by weight of the resin (b-2) was used in place of the resin (b-1). Thereafter, a coating film was formed on a soda glass substrate in the same manner as in Comparative Example 2 except that the liquid composition (r-2) was used in place of the liquid composition (r-1).

When the substrate was immersed in 100 cc of propylene glycol monomethyl ether acetate for 2 minutes, the coating film was not dissolved completely and a large amount of foreign matter was seen in the liquid.

Coating test

Comparative Example 4

The liquid composition (r-1) was applied to a soda glass substrate having an SiO_2 film for preventing the elution of sodium ions on the surface by using the TR63210S-CL (trade name) slit nozzle type coating device for color filters of Tokyo Ohka Kogyo Co., Ltd. and left at normal temperature for 1 hour to be dried so as to form a coating film.

When the liquid composition (r-1) was applied to a new soda glass substrate with TR63210S-CL after the slit nozzle was blow cleaned with propylene glycol monomethyl ether acetate, it could be applied without producing foreign matter on the formed coating film.

Examples 41 to 60

When a coating test was made in the same manner as in Comparative Example 4 except that the liquid compositions (R-1) to (R-20) were used in place of the liquid composition (r-1), they could be applied without producing foreign matter on the formed coating films.

Comparative Example 5

When a coating test was made in the same manner as in Comparative Example 4 except that the liquid composition (r-2) was used in place of the liquid composition (r-1), foreign matter was produced on the formed coating film and therefore, a satisfactory coating film could not be formed.

CLAIMS

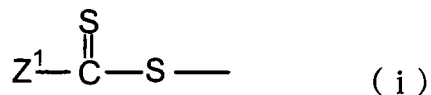
1. A radiation sensitive resin composition comprising (A) a colorant, (B) an alkali-soluble resin, (C) a polyfunctional monomer and (D) a radiation sensitive radical generator, wherein

the alkali-soluble resin (B) is manufactured through the living radical polymerization of a polymerizable unsaturated compound and has a weight average molecular weight in terms of polystyrene (Mw) measured by gel permeation chromatography of 1,000 to 45,000.

2. The radiation sensitive resin composition according to claim 1, wherein when the number average molecular weight in terms of polystyrene measured by gel permeation chromatography of the alkali-soluble resin (B) is represented by Mn, the Mw/Mn ratio of the alkali-soluble resin (B) is 1 to 2.0.

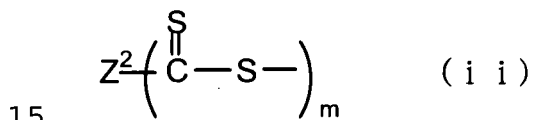
3. The radiation sensitive resin composition according to claim 1 or 2, wherein the alkali-soluble resin (B) is a copolymer of a monomer mixture of (b1) an unsaturated carboxylic acid and/or an unsaturated carboxylic anhydride and (b2) another unsaturated compound.

4. The radiation sensitive resin composition according to any one of claims 1 to 3, wherein the alkali-soluble resin (B) has a group represented by the following formula (i) or a group represented by the following formula (ii) at at least one of the terminals of a polymer chain constituting the alkali-soluble resin:



wherein Z¹ is a hydrogen atom, chlorine atom, carboxyl group,

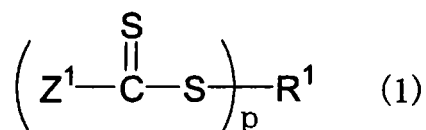
cyano group, alkyl group having 1 to 20 carbon atoms, monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, monovalent heterocyclic group having 3 to 20 carbon atoms and hetero atoms or a monovalent group having -OR, -SR, -N(R)₂, -OC(=O)R, -C(=O)OR, -C(=O)N(R)₂, -P(=O)(OR)₂, -P(=O)(R)₂ or a polymer chain (R's are each independently an alkyl group having 1 to 18 carbon atoms, alkenyl group having 2 to 18 carbon atoms, monovalent aromatic hydrocarbon group having 6 to 18 carbon atoms or monovalent heterocyclic group having 3 to 18 carbon atoms and hetero atoms), with the proviso that the alkyl group having 1 to 20 carbon atoms, the monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, the monovalent heterocyclic group having 3 to 20 atoms and R may be substituted,



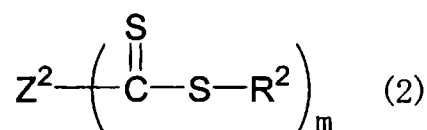
wherein Z² is a group having a valence of m derived from an alkane having 1 to 20 carbon atoms, group having a valence of m derived from an aromatic hydrocarbon having 6 to 20 carbon atoms, group having a valence of m derived from a heterocyclic compound having 3 to 20 carbon atoms and hetero atoms or group having a valence of m and a polymer chain, with the proviso that the group having a valence of m derived from an alkane having 1 to 20 carbon atoms, the group having a valence of m derived from an aromatic hydrocarbon having 6 to 20 carbon atoms and the group having a valence of m derived from a heterocyclic compound having 3 to 20 atoms may be substituted, and m is an integer of 2 or more.

5. The radiation sensitive resin composition according to claim 4, wherein the alkali-soluble resin (B) is a resin manufactured through the living radical polymerization of a polymerizable unsaturated compound using a

thiocarbonylthio compound represented by the following formula (1) or (2) as a molecular weight control agent:



wherein Z^1 is as defined in the above formula (i), p is an integer of 1 or more, and R^1 is an alkyl group having 1 to 20 carbon atoms, monovalent alicyclic hydrocarbon group having 3 to 20 carbon atoms, monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, monovalent heterocyclic group having 3 to 20 carbon atoms and hetero atoms or monovalent group having $-\text{OR}$, $-\text{SR}$, $-\text{N}(\text{R})_2$ or a polymer chain (R' 's are each independently an alkyl group having 1 to 18 carbon atoms, alkenyl group having 2 to 18 carbon atoms, monovalent aromatic hydrocarbon group having 6 to 18 carbon atoms or monovalent heterocyclic group having 3 to 18 carbon atoms and hetero atoms) when $p = 1$, or a group having a valence of p derived from an alkane having 1 to 20 carbon atoms, group having a valence of p derived from an aromatic hydrocarbon having 6 to 20 carbon atoms, group having a valence of p derived from a heterocyclic compound having 3 to 20 carbon atoms and hetero atoms or group having a valence of p and a polymer chain when $p \geq 2$, with the proviso that the alkyl group having 1 to 20 carbon atoms, the monovalent alicyclic hydrocarbon group having 3 to 20 carbon atoms, the monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, the monovalent heterocyclic group having 3 to 20 atoms, R , the group having a valence of p derived from an alkane having 1 to 20 carbon atoms, the group having a valence of p derived from an aromatic hydrocarbon having 6 to 20 carbon atoms and the group having a valence of p derived from a heterocyclic compound having 3 to 20 atoms may be substituted,



wherein Z^2 and m are as defined in the above formula (ii), and R^2 is an alkyl group having 1 to 20 carbon atoms, monovalent alicyclic hydrocarbon group having 3 to 20 carbon
 5 atoms, monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, monovalent heterocyclic group having 3 to 20 carbon atoms and hetero atoms, or monovalent group having -OR, -SR, -N(R)₂ or a polymer chain (R's are each independently an alkyl group having 1 to 18 carbon atoms,
 10 alkenyl group having 2 to 18 carbon atoms, monovalent aromatic hydrocarbon group having 6 to 18 carbon atoms or monovalent heterocyclic group having 3 to 18 carbon atoms and hetero atoms), with the proviso that the alkyl group having 1 to 20 carbon atoms, the monovalent alicyclic
 15 hydrocarbon group having 3 to 20 carbon atoms, the monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, the monovalent heterocyclic group having 3 to 20 atoms and R may be substituted.

20 6. A radiation sensitive resin composition comprising (A) a colorant, (B) an alkali-soluble resin, (C) a polyfunctional monomer and (D) a radiation sensitive radical generator, wherein

the alkali-soluble resin (B) has a group represented
 25 by the above formula (i) or a group represented by the above formula (ii) at at least one of the terminals of a polymer chain constituting the alkali-soluble resin and a weight average molecular weight in terms of polystyrene (Mw) measured by gel permeation chromatography of 1,000 to 45,000.

30

7. A method of preparing the radiation sensitive resin composition of any one of claims 1 to 6, comprising the step

of:

mixing the alkali-soluble resin (B), the polyfunctional monomer (C) and the radiation sensitive radical generator (D) with a pigment dispersion obtained by
5 mixing and dispersing a pigment as the colorant (A) in a solvent in the presence of a dispersant while it is ground.

8. The radiation sensitive resin composition according to any one of claims 1 to 6 which is used for color filters.
10

9. A color filter formed from the radiation sensitive resin composition of claim 8.

10. A color liquid crystal display device comprising the
15 color filter of claim 9.