

**RADIATION-SENSITIVE RESIN COMPOSITION FOR FORMING COLORED
LAYER AND COLOR FILTER**

BACKGROUND OF THE INVENTION

Field of the Invention

[0001]

The present invention relates to a radiation-sensitive resin composition used in the formation of a colored layer for a color filter used in a transmissive or reflective color liquid crystal display device, a color imaging tube element and the like, a color filter having a colored layer formed using the radiation-sensitive resin composition, and a liquid crystal display device provided with the color filter.

Description of the Related Art

[0002]

As a method for forming a color filter using a colored radiation-sensitive resin composition, a method including forming a coating of a colored radiation-sensitive resin composition on a substrate or on a substrate on which a light shielding layer of a desired pattern is formed beforehand, irradiating it with radiation through a photomask having a desired pattern shape (hereinafter, referred to as "exposure"), developing it by an alkali developer to dissolve and remove unexposed portions, and then performing post-

baking by a clean oven or a hot plate to obtain pixels of each color (see, for example, JP-A-2000-329929) is known.

Since the size of the substrate used for forming a color filter has been increased in recent years, a coating method of a colored radiation-sensitive resin composition has been changing from a system using a center-dropping spin coater to a system using a slit nozzle having a liquid ejection portion for applying a colored radiation-sensitive resin composition with a smaller diameter. In the latter slit-nozzle system, a colored radiation-sensitive resin composition remains on the periphery of a nozzle tip end after completing the coating due to the small diameter (narrowness) of the liquid ejection portion in many cases, and when this composition is dried, it drops on a color filter as dry foreign substances during the next coating, thereby significantly deteriorating the quality of the color filter. Therefore, a jet cleaning for ejecting a cleaning solvent on a nozzle tip end is usually performed before coating, however, deterioration of the quality of the color filter due to dry foreign substances can not yet be effectively prevented, which becomes a big factor of reduction in product yield.

Accordingly, in order to cope with such a problem, a colored radiation-sensitive resin composition having cleaning performance by a cleaning solvent, that is, high

solubility in a cleaning solvent even after drying has been demanded in recent years.

[0003]

Further, it has been recently required for a color liquid crystal display device provided with a color filter to have a longer operating life, and the demand for burn-in prevention capability of a color filter has been increased more than ever.

Herein, "burn-in" is a kind of display failures of a color liquid crystal display device, and is a phenomenon where an image which should not be inherently displayed is displayed on a screen, or black or white "haze" is overlappingly displayed on an image to be inherently displayed. This phenomenon is considered to be caused by which impurities charged in a liquid crystal is diffused in a liquid crystal and the potential difference applied for orienting liquid crystal molecules is not maintained for a fixed period of time, and it has been recently revealed that the impurities are not only those formed during the production of liquid crystal molecules but those eluted from the formed color filter. In addition, as disclosed in, for example, JP-A-2000-329929, it is known that it is effective to increase pigment purity for prevention of "burn-in", however, there is also a possibility that impurities are derived from components other than pigments in a colored radiation-sensitive

resin composition, and therefore it cannot be said that it is sufficient to only increase the pigment purity.

Therefore, the development of a further improved colored radiation-sensitive resin composition which satisfies recent high product yield requirement during the production of a color filter and does not cause "burn-in" has been strongly demanded.

Meanwhile, International Publication No. WO 07/029871 discloses that a radiation-sensitive resin composition containing an alkali-soluble resin which is polymerized using a disulfide compound such as tetraethylthiuram disulfide or bis(pyrazol-1-yl-thiocarbonyl) disulfide as a molecular weight controlling agent is effective for improving the solubility in a cleaning solvent after drying and preventing "burn-in". However, these disulfide compounds easily cause a change with the elapse of time due to degradation during storage after synthesis and are thus very difficult to be handled.

SUMMARY OF THE INVENTION

[0004]

The present invention provides a colored radiation-sensitive resin composition for forming a colored layer which can form a color filter not causing "burn-in" at a high product yield, and has high solubility in a cleaning solvent even after drying, or the like. The present invention also provides a radiation-sensitive resin

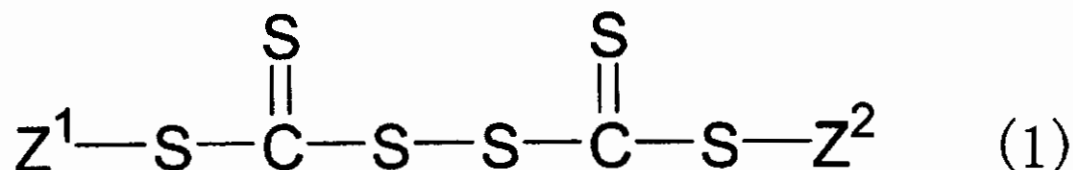
composition for forming a colored layer which contains an alkali-soluble resin more suitable for mass production by using a disulfide compound having good storage stability as a molecular weight controlling agent.

[0005]

Firstly, the present invention provides a radiation-sensitive resin composition for forming a colored layer which contains (A) a colorant, (B) an alkali-soluble resin, (C) a polyfunctional monomer and (D) a photopolymerization initiator, wherein the alkali-soluble resin (B) contains a copolymer produced by polymerizing a polymerizable unsaturated compound containing (b1) one or more selected from the group consisting of polymerizable unsaturated carboxylic acids and polymerizable unsaturated carboxylic acid anhydrides in the presence of a compound represented by the following formula (1).

The term "colored layer" as used in the present invention means a layer containing a pixel and/or a black matrix.

[0006]



[0007]

In the formula (1), Z^1 and Z^2 represent an alkyl group having 4 to 18 carbon atoms or an optionally substituted benzyl group and are independent of each other.

[0008]

Secondly, the present invention provides a color filter provided with a colored layer formed using the radiation-sensitive resin composition for forming the colored layer.

[0009]

Thirdly, the present invention provides a color liquid crystal display device provided with the color filter.

[0010]

The radiation-sensitive resin composition for forming the colored layer of the present invention can provide a color filter not causing "burn-in" at a high product yield, and has high solubility in a cleaning solvent even after drying, and therefore is also suitable, for example, for application by a slit nozzle.

DETAILED DESCRIPTION OF THE INVENTION

[0011]

Hereinafter, the present invention will be described in detail.

Radiation-sensitive Resin Composition for Forming Colored Layer

- (A) Colorant -

The colorant in the present invention is not limited and may be any of a pigment, a dye or a natural coloring matter, however, since color development with high purity and high light transmittance, or high light shielding property and high heat resistance are required for a color filter, a pigment is preferred, and an organic pigment or carbon black is more preferred.

Examples of the organic pigment include compounds classified into a pigment in terms of Color Index, and specifically those having the following Color Index (C.I.) Number like below.

[0012]

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 180, C.I. Pigment Yellow 211;

[0013]

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;

[0014]

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;

[0015]

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, C.I. Pigment Green 36 and C.I. Pigment Green 58;

C.I. Pigment Brown 23 and C.I. Pigment Brown 25; and
C.I. Pigment Black 1 and C.I. Pigment Black 7.

[0016]

Among these organic pigments, it is preferred to select at least one of the group consisting of C.I. Pigment Yellow 83, C.I. Pigment Yellow 138, C.I. Pigment Yellow 139, C.I. Pigment Yellow 150, C.I. Pigment Yellow 180, C.I. Pigment Red 177, C.I. Pigment Red 242, C.I. Pigment Red 254, C.I. Pigment Blue 15:3, 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 Green 58; and C.I. Pigment Violet 23, C.I. Pigment Blue 60 and C.I. Pigment Blue 80.

The organic pigments can be used singly or as a mixture of two or more thereof, and although an organic pigment and carbon black can also be mixed for use, an organic pigment is preferably used when forming a pixel, and two or more organic pigments and/or carbon blacks are preferably used when forming a black matrix.

[0017]

When the colorant is a pigment in the present invention, the composition is preferably prepared by

mixing and dispersing the pigment in a solvent in the presence of a dispersant, while pulverizing, for example, using a beads mill or a roll mill to form a pigment dispersion fluid, adding the later described components (B), (C) and (D), and additional solvents and later described other additives as required to this pigment dispersion fluid, and mixing them.

[0018]

As the dispersant used for preparing the pigment dispersion fluid, a cationic, anionic, nonionic or amphoteric dispersant, for example, can be appropriately used. Nonetheless, a dispersant containing a compound having a urethane bond (hereinafter, referred to as "urethane-based dispersant") is preferred.

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

[0019]

Examples of such a urethane-based dispersant include reaction products of diisocyanates and/or triisocyanates with polyesters having a hydroxyl group at one end and/or polyesters having hydroxyl groups at both ends.

Examples of the diisocyanates include other aromatic diisocyanates such as 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 xylene diisocyanates such as 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.

[0020]

Examples of the triisocyanates include other aromatic triisocyanates such as 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 xylene triisocyanates such as 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 can be each used singly or as a mixture of two or more thereof.

[0021]

Examples of the polyesters having a hydroxyl group at one end and/or the polyesters having hydroxyl groups at both ends include polylactones having a hydroxyl group at one end or hydroxyl groups both ends such as polycaprolactones having a hydroxyl group at one end or hydroxyl groups both ends, polyvalerolactones having a hydroxyl group at one end or hydroxyl groups both ends, and polypropiolactones having a hydroxyl group at one end or hydroxyl groups both ends; and polycondensation polyesters having a hydroxyl group at one end or hydroxyl groups both ends such as polyethylene terephthalate having a hydroxyl group at one end or hydroxyl groups both ends, and polybutylene terephthalate having a hydroxyl group at one end or hydroxyl groups both ends.

These polyesters having a hydroxyl group at one end and/or the polyesters having hydroxyl groups at both ends can be each used singly or as a mixture of two or more thereof.

[0022]

As the urethane-based dispersant in the present invention, reaction products of aromatic diisocyanates and/or triisocyanates with polylactones having a hydroxyl

group at one end and/or polylactones having hydroxyl groups at both ends are preferred, and reaction products of toluene diisocyanates with polycaprolactones having a hydroxyl group at one end and/or polycaprolactones having hydroxyl groups at both ends are more preferred.

Specific examples of such a urethane-based dispersant include, by trade name, the series of Disperbyk 161, Disperbyk 170 (all produced by BYK Chemie (BYK)), EFKA (produced by EFKA Chemicals BV (EFKA)), Disperon (produced by Kusumoto Chemicals, Ltd.), and Solsperse (produced by The Lubrizol Corporation).

The urethane-based dispersant in the present invention has a Mw of usually 5,000 to 50,000, and preferably 7,000 to 20,000.

The urethane-based dispersant can be used singly or as a mixture of two or more thereof.

[0023]

Further, a (meth)acrylic dispersant containing a (co)polymer of (meth)acrylic monomers is also preferred as a dispersant.

Specific examples of such a (meth)acrylic dispersant include, by trade name, Disperbyk 2000 and Disperbyk 2001 (all produced by BYK Chemie (BYK)).

The (meth)acrylic dispersant can be used singly or as a mixture of two or more thereof.

[0024]

The amount of the dispersant used when preparing a pigment dispersion fluid is usually 100 parts by weight or less, preferably 0.5 to 100 parts by weight, more preferably 1 to 70 parts by weight and even more preferably 10 to 50 parts by weight, based on 100 parts by weight of a pigment. When the amount of a dispersant used exceeds 100 parts by weight, developability or the like may be impaired.

In addition, examples of a solvent used when preparing a pigment dispersion fluid include those same as the solvents exemplified by the later described liquid compositions of radiation-sensitive resin compositions.

The amount of the solvent used when preparing a pigment dispersion fluid is usually 200 to 1,200 parts by weight and preferably 300 to 1,000 parts by weight, based on 100 parts by weight of a pigment.

[0025]

When a pigment dispersion fluid is prepared using a bead mill, the preparation can be preferably performed by mixing and dispersing a pigment mixed solution containing a pigment, a solvent and a dispersant while cooling with cooling water or the like, for example, using glass beads or titania beads having a diameter of about 0.5 to 10 mm.

In this case, the filling factor of beads is usually 50 to 80% of a mill capacity, and the amount of the pigment mixed solution injected is usually about 20 to 50% of a mill capacity. In addition, the treatment time

is usually about 2 to 50 hours, and preferably 2 to 25 hours.

Further, when a pigment dispersion fluid is prepared using a roll mill, the preparation can be preferably performed by treating a pigment mixed solution while cooling with cooling water or the like, for example, using a three roll mill or a two roll mill.

In this case, the roll gap is preferably 10 μm or less, and the shearing force is usually about 10^8 dyn/sec. In addition, the treatment time is usually 2 to 50 hours, and preferably 2 to 25 hours.

[0026]

- (B) Alkali-Soluble Resin -

The alkali-soluble resin in the present invention includes a resin (hereinafter, referred to as "resin (B)") containing a copolymer (hereinafter, referred to as "copolymer (BI)") produced by polymerizing a polymerizable unsaturated compound (hereinafter, also referred to as "polymerizable unsaturated compound") containing (b1) at least one selected from the group consisting of polymerizable unsaturated carboxylic acids and polymerizable unsaturated carboxylic acid anhydrides (hereinafter, these compounds are collectively referred to as "unsaturated compound (b1)") in the presence of the compound represented by the formula (1) (hereinafter, referred to as "molecular weight controlling agent (1)").

[0027]

Examples of the unsaturated compound (b1) include:
unsaturated monocarboxylic acids such as
(meth)acrylic acid, crotonic acid, α -chloroacrylic acid
and cinnamic acid;

unsaturated dicarboxylic acids or anhydrides thereof
such as maleic acid, maleic anhydride, fumaric acid,
itaconic acid, itaconic anhydride, citraconic acid,
citraconic anhydride and mesaconic acid;

trivalent or higher unsaturated polycarboxylic acids
or anhydrides thereof;

mono[(meth)acryloyloxyalkyl] esters of divalent or
higher polycarboxylic acids 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 on both ends such as ω -
carboxypolycaprolactone mono(meth)acrylate.

[0028]

Among these unsaturated compounds (b1),
(meth)acrylic acid, mono[2-(meth)acryloyloxyethyl]
succinate, ω -carboxypolycaprolactone mono(meth)acrylate
and the like are preferred.

In the copolymer (B1), the polymerizable unsaturated
carboxylic acid and polymerizable unsaturated carboxylic
acid anhydride can each be used singly or as a mixture of
two or more thereof.

[0029]

Further, in the copolymer (B1), the unsaturated compound (b1) is preferably polymerized with other polymerizable unsaturated compounds polymerizable with the unsaturated compounds (b1) (hereinafter, referred to as "unsaturated compounds (b2)").

Examples of the unsaturated compound (b2) include:

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-styrene sulfonic acid, o-vinyltoluene, m-vinyltoluene, p-vinyltoluene, p-chlorostyrene, o-methoxystyrene, m-methoxystyrene, p-methoxystyrene, o-vinylbenzyl methyl ether, m-vinylbenzyl methyl ether, p-vinylbenzyl methyl ether, o-vinylbenzyl glycidyl ether, m-vinylbenzyl glycidyl ether and p-vinylbenzyl glycidyl ether;

indenes such as indene and 1-methylindene;

[0030]

macromonomers having a (meth)acryloyl group at one end of the polymer molecular chain (hereinafter, simply referred to as "macromonomers") such as polystyrene, polymethyl (meth)acrylate, poly-n-butyl (meth)acrylate and polysiloxane;

aryl maleimides substituted at N-position 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, N-m-methoxyphenylmaleimide and N-p-methoxyphenylmaleimide; maleimides substituted at N-position such as N-cyclohexylmaleimide;

[0031]

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-ethylhexyl (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}]decane-8-yl (meth)acrylate, 2-hydroxy-3-phenoxypropyl (meth)acrylate, glycerol (meth)acrylate and (meth)acrylate of ethylene oxide adduct of p-cumylphenol;

[0032]

unsaturated aminoalkyl carboxylates such as 2-aminoethyl (meth)acrylate, 2-dimethylaminoethyl (meth)acrylate, 2-aminopropyl (meth)acrylate, 2-dimethylaminopropyl 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 isoprene sulfonic acid.

[0033]

Among these unsaturated compounds (b2), styrene, macromonomers, maleimides substituted at N-position, methyl (meth)acrylate, n-butyl(meth)acrylate, 2-ethylhexyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, allyl (meth)acrylate, benzyl (meth)acrylate, phenyl (meth)acrylate, glycerol mono(meth)acrylate, (meth)acrylate of ethylene oxide adduct of p-cumylphenol and the like are preferred, and among the macromonomers,

polystyrene macromonomer and polymethyl (meth)acrylate macromonomer are preferred, and among the maleimides substituted at N-position, N-phenylmaleimide and N-cyclohexylmaleimide are preferred.

The unsaturated compound (b2) can be used singly or as a mixture of two or more thereof.

[0034]

In the present invention, more specifically, preferred examples of the copolymer (BI) include a copolymer of a monomer mixture (hereinafter, referred to as "copolymer (BI-1)") containing: at least one unsaturated compound (b1) selected from the group consisting of (meth)acrylic acid, mono[2-(meth)acryloyloxyethyl] succinate and ω -carboxypolycaprolactone mono(meth)acrylate; at least one unsaturated compound (b2) selected from the group consisting of polystyrene macromonomer and polymethyl (meth)acrylate macromonomer, N-phenylmaleimide, N-cyclohexylmaleimide, 2-hydroxyethyl (meth)acrylate, benzyl (meth)acrylate, glycerol mono(meth)acrylate and (meth)acrylate of ethylene oxide adduct of p-cumylphenol; and further optionally at least one unsaturated compound (b2) selected from the group consisting of styrene, methyl (meth)acrylate, n-butyl(meth)acrylate, 2-ethylhexyl (meth)acrylate, allyl (meth)acrylate and phenyl (meth)acrylate.

[0035]

More specifically, more preferred examples of the copolymer (BI-1) include a copolymer of a monomer mixture (hereinafter, referred to as "copolymer (BI-2)") containing: (meth)acrylic acid as an essential component; further optionally an unsaturated compound (b1) containing mono[2-(meth)acryloyloxyethyl] succinate; at least one unsaturated compound (b2) selected from the group consisting of polystyrene macromonomer and polymethyl (meth)acrylate macromonomer, N-phenylmaleimide, N-cyclohexylmaleimide, 2-hydroxyethyl (meth)acrylate, benzyl (meth)acrylate, glycerol (meth)acrylate and (meth)acrylate of ethylene oxide adduct of p-cumylphenol; and further optionally at least one unsaturated compound (b2) selected from the group consisting of styrene, methyl (meth)acrylate, n-butyl(meth)acrylate, 2-ethylhexyl (meth)acrylate, allyl (meth)acrylate and phenyl (meth)acrylate.

[0036]

Examples of the copolymer (BI-2) include:

(meth)acrylic acid/2-hydroxyethyl (meth)acrylate copolymer,

(meth)acrylic acid/polystyrene macromonomer/benzyl (meth)acrylate copolymer,

(meth)acrylic acid/polymethyl(meth)acrylate macromonomer/benzyl (meth)acrylate copolymer,

(meth)acrylic acid/benzyl(meth)acrylate/glycerol mono(meth)acrylate copolymer,

(meth)acrylic acid/2-hydroxyethyl
(meth)acrylate/phenyl (meth)acrylate copolymer,
(meth)acrylic acid/2-hydroxyethyl
(meth)acrylate/styrene copolymer,
(meth)acrylic acid/benzyl (meth)acrylate/glycerol
mono(meth)acrylate copolymer,
(meth)acrylic acid/2-hydroxyethyl
(meth)acrylate/benzyl (meth)acrylate copolymer,
[0037]
(meth)acrylic acid/polystyrene macromonomer/2-
hydroxyethyl (meth)acrylate/benzyl (meth)acrylate
copolymer,
(meth)acrylic acid/polymethyl (meth)acrylate
macromonomer/2-hydroxyethyl
(meth)acrylate/benzyl (meth)acrylate copolymer,
(meth)acrylic acid/N-phenylmaleimide/allyl
(meth)acrylate/styrene copolymer,
(meth)acrylic acid/N-phenylmaleimide/benzyl
(meth)acrylate/styrene copolymer,
(meth)acrylic acid/N-cyclohexylmaleimide/allyl
(meth)acrylate/styrene copolymer,
(meth)acrylic acid/N-cyclohexylmaleimide/benzyl
(meth)acrylate/styrene copolymer,
(meth)acrylic acid/N-phenylmaleimide/benzyl
(meth)acrylate/glycerol mono(meth)acrylate/styrene
copolymer,

(meth)acrylic acid/N-phenylmaleimide/(meth)acrylate
of ethylene oxide adduct of p-cumylphenol/styrene
copolymer,

[0038]

(meth)acrylic acid/mono[2-(meth)acryloyloxyethyl]
succinate/benzyl (meth)acrylate/glycerol
mono(meth)acrylate copolymer,

(meth)acrylic acid/mono[2-(meth)acryloyloxyethyl]
succinate/N-phenylmaleimide/allyl (meth)acrylate/styrene
copolymer,

(meth)acrylic acid/mono[2-(meth)acryloyloxyethyl]
succinate/N-phenylmaleimide/benzyl (meth)acrylate/styrene
copolymer,

(meth)acrylic acid/mono[2-(meth)acryloyloxyethyl]
succinate/N-cyclohexylmaleimide/allyl
(meth)acrylate/styrene copolymer,

(meth)acrylic acid/mono[2-(meth)acryloyloxyethyl]
succinate/N-cyclohexylmaleimide/benzyl
(meth)acrylate/styrene copolymer, and

(meth)acrylic acid/mono[2-(meth)acryloyloxyethyl]
succinate/N-phenylmaleimide/benzyl
(meth)acrylate/glycerol mono(meth)acrylate/styrene
copolymer.

[0039]

Further, examples of the copolymer (BI-1) include:

(meth)acrylic acid/ ω -carboxypolycaprolactone
mono(meth)acrylate/N-phenylmaleimide/benzyl

(meth)acrylate/glycerol mono(meth)acrylate/styrene
copolymer,

(meth)acrylic acid/ ω -carboxypolycaprolactone
mono(meth)acrylate/2-hydroxyethyl (meth)acrylate
copolymer,

(meth)acrylic acid/ ω -carboxypolycaprolactone
mono(meth)acrylate/polystyrene macromonomer/benzyl
(meth)acrylate copolymer,

(meth)acrylic acid/ ω -carboxypolycaprolactone
mono(meth)acrylate/polymethyl (meth)acrylate
macromonomer/benzyl (meth)acrylate copolymer,

(meth)acrylic acid/ ω -carboxypolycaprolactone
mono(meth)acrylate/benzyl (meth)acrylate/glycerol
mono(meth)acrylate copolymer,

(meth)acrylic acid/ ω -carboxypolycaprolactone
mono(meth)acrylate/2-hydroxyethyl (meth)acrylate/phenyl
(meth)acrylate copolymer,

(meth)acrylic acid/ ω -carboxypolycaprolactone
mono(meth)acrylate/2-hydroxyethyl (meth)acrylate/styrene
copolymer,

(meth)acrylic acid/ ω -carboxypolycaprolactone
mono(meth)acrylate/benzyl (meth)acrylate/glycerol
mono(meth)acrylate copolymer,

(meth)acrylic acid/ ω -carboxypolycaprolactone
mono(meth)acrylate/2-hydroxyethyl
(meth)acrylate/benzyl (meth)acrylate copolymer,

[0040]

(meth)acrylic acid/ ω -carboxypolycaprolactone
mono(meth)acrylate/polystyrene macromonomer/2-
hydroxyethyl (meth)acrylate/benzyl (meth)acrylate
copolymer,

(meth)acrylic acid/ ω -carboxypolycaprolactone
mono(meth)acrylate/polymethyl (meth)acrylate
macromonomer/2-hydroxyethyl
(meth)acrylate/benzyl (meth)acrylate copolymer,

(meth)acrylic acid/ ω -carboxypolycaprolactone
mono(meth)acrylate/N-phenylmaleimide/allyl
(meth)acrylate/styrene copolymer,

(meth)acrylic acid/ ω -carboxypolycaprolactone
mono(meth)acrylate/N-phenylmaleimide/benzyl
(meth)acrylate/styrene copolymer,

(meth)acrylic acid/ ω -carboxypolycaprolactone
mono(meth)acrylate/N-cyclohexylmaleimide/allyl
(meth)acrylate/styrene copolymer,

(meth)acrylic acid/ ω -carboxypolycaprolactone
mono(meth)acrylate/N-cyclohexylmaleimide/benzyl
(meth)acrylate/styrene copolymer,

(meth)acrylic acid/ ω -carboxypolycaprolactone
mono(meth)acrylate/N-phenylmaleimide/benzyl
(meth)acrylate/glycerol mono(meth)acrylate/styrene
copolymer,

[0041]

(meth)acrylic acid/ ω -carboxypolycaprolactone
mono(meth)acrylate/mono[2-(meth)acryloyloxyethyl]

succinate/benzyl (meth)acrylate/glycerol

mono(meth)acrylate copolymer,

(meth)acrylic acid/ ω -carboxypolycaprolactone

mono(meth)acrylate/mono[2-(meth)acryloyloxyethyl]

succinate/N-phenylmaleimide/allyl (meth)acrylate/styrene
copolymer,

(meth)acrylic acid/ ω -carboxypolycaprolactone

mono(meth)acrylate/mono[2-(meth)acryloyloxyethyl]

succinate/N-phenylmaleimide/benzyl (meth)acrylate/styrene
copolymer,

(meth)acrylic acid/ ω -carboxypolycaprolactone

mono(meth)acrylate/mono[2-(meth)acryloyloxyethyl]

succinate/N-cyclohexylmaleimide/allyl

(meth)acrylate/styrene copolymer,

(meth)acrylic acid/ ω -carboxypolycaprolactone

mono(meth)acrylate/mono[2-(meth)acryloyloxyethyl]

succinate/N-cyclohexylmaleimide/benzyl

(meth)acrylate/styrene copolymer, and

(meth)acrylic acid/ ω -carboxypolycaprolactone

mono(meth)acrylate/mono[2-(meth)acryloyloxyethyl]

succinate/N-phenylmaleimide/benzyl

(meth)acrylate/glycerol mono(meth)acrylate/styrene
copolymer.

[0042]

In the copolymer (BI), the copolymerization ratio of the unsaturated compound (b1) is preferably 1 to 40 wt%, more preferably 5 to 30 wt% and even more preferably 10

to 30 wt%, based on the total of unsaturated compounds. When the copolymerization ratio of the unsaturated compound (b1) is less than 1 wt%, there is a tendency that the solubility of the resulting copolymer in an alkali developer is decreased. On the other hand, when the copolymerization ratio is more than 40 wt%, the solubility of the resulting copolymer in an alkali developer is too high, and thereby the pattern shape may be impaired.

[0043]

Next, a polymerization method for producing the copolymer (BI) will be described.

For example, the polymerization can be performed by polymerizing a polymerizable unsaturated compound constituting the copolymer (BI) using a radical polymerization initiator in a solvent in the presence of a molecular weight controlling agent (1), and thereby a polymer (BI) with controlled molecular weight and molecular weight distribution can be obtained.

[0044]

The molecular weight controlling agent (1) used for the present invention has a bis(alkylmercapto-thiocarbonyl)disulfide or bis(benzylmercapto-thiocarbonyl)disulfide structure, and a radiation-sensitive resin composition containing an alkali-soluble resin produced using this molecular weight controlling agent is effective for improving the solubility in a

cleaning solvent after drying and preventing "burn-in". In addition, the molecular weight controlling agent used in the present invention is stable with the elapse of time, and even when it is used after synthesized and stored, the resulting alkali-soluble resin has good quality.

[0045]

In the formula (1) representing the molecular weight controlling agent (1), examples of the alkyl group having 4 to 18 carbon atoms of Z^1 or Z^2 include an n-butyl group, a t-butyl group, an n-heptyl group, an n-hexyl group, an n-pentyl group, an n-octyl group, an n-nonyl group, an n-decyl group, an n-dodecyl group, a t-dodecyl group, an n-tetradecyl group, an n-hexadecyl group and an n-octadecyl group.

Among these alkyl groups, an n-hexyl group, an n-pentyl group, an n-octyl group, an n-decyl group, an n-dodecyl group and the like are preferred, and an n-octyl group, an n-decyl group, an n-dodecyl group and the like are preferred.

Further, examples of the optionally substituted benzyl group of Z^1 or Z^2 in the formula (1) include a benzyl group, an o-chlorobenzyl group, a p-chlorobenzyl group, an o-cyanobenzyl group, a p-cyanobenzyl group, an o-methoxybenzyl group and a p-methoxybenzyl group.

Among these optionally substituted benzyl groups, a benzyl group is preferred.

In the polymerization, the molecular weight controlling agent (1) can be used singly or as a mixture of two or more thereof.

Furthermore, one or more of other molecular weight controlling agents, for example, α -methylstyrene dimmer and t-dodecylmercaptan can also be used together with the molecular weight controlling agent (1) upon the polymerization.

[0046]

Further, the polymerization of a polymerizable unsaturated compound in the presence of the molecular weight controlling agent (1) may take the form of living radical polymerization in which an active radical is formed at the growing end of the polymer chain.

When the polymerization takes the form of living radical polymerization and the polymerizable unsaturated compound contains a compound having a functional group which may deactivate an active radical such as a carboxyl group, the copolymer (BI) can also be obtained by esterification for protection of the functional group followed by deprotection, in order to prevent the growing end from being deactivated, if necessary.

[0047]

The radical polymerization initiator is appropriately selected depending on the type of the polymerizable unsaturated compound used, and examples thereof include:

azo compounds such as 2,2'-azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), 4,4'-azobis(4-cyanovaleric acid), dimethyl-2,2'-azobis(2-methylpropionate) and 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile); organic peroxides such as benzoyl peroxide, lauroyl peroxide, t-butylperoxypivalate and 1,1-bis(t-butylperoxy)cyclohexane; and redox-type initiators containing hydrogen peroxide or the oxides and reducing agents.

Among these radical polymerization initiators, azo compounds such as 2,2'-azobisisobutyronitrile and 2,2'-azobis(2,4-dimethylvaleronitrile) are preferred from the viewpoint that side reaction products are difficult to be formed by oxygen and the like.

The radical polymerization initiator can be used singly or as a mixture of two or more thereof.

[0048]

Examples of the solvent used for the polymerization include, propylene glycol monoalkyl ethers such as propylene glycol monomethyl ether and propylene glycol monoethyl ether;

(poly)alkylene glycol monoalkyl ether acetates such as ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether acetate,

propylene glycol monoethyl ether acetate, dipropylene glycol monomethyl ether acetate, and dipropylene glycol monoethyl ether acetate;

(poly)alkylene glycol diethers such as 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, cyclohexanone, 2-heptanone and 3-heptanone;

ketoalcohols such as diacetone alcohol (i.e. 4-hydroxy-4-methylpentane-2-one) and 4-hydroxy-4-methylhexane-2-one;

[0049]

lactic acid alkyl esters such as methyl lactate and ethyl lactate;

the other esters such as ethyl 2-hydroxy-2-methylpropanoate, ethyl hydroxyacetate, methyl 2-hydroxy-3-methylbutanoate, methyl 3-methoxypropionate, ethyl 3-methoxypropionate, methyl 3-ethoxypropionate, ethyl 3-ethoxypropionate, ethyl ethoxyacetate, 3-methyl-3-methoxybutyl acetate, 3-methyl-3-methoxybutyl propionate, 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 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.

However, the solvent is not limited to described above.

[0050]

Among these solvents, from the viewpoint that an active radical does not deactivated during living radical polymerization, and from the viewpoints of dissolving properties, pigment dispersibility, coating properties and the like of each component of the resulting radiation-sensitive resin composition, preferred are propylene glycol monoethyl ether, ethylene glycol monomethyl ether acetate, diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, dipropylene glycol monomethyl 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-methoxybutyl propionate, n-butyl acetate, i-butyl acetate, n-pentyl formate, i-pentyl acetate, n-butyl propionate,

ethyl butyrate, i-propyl butyrate, n-butyl butyrate, ethyl pyruvate and the like.

The solvents can be used singly or as a mixture of two or more thereof.

[0051]

In the polymerization, the amount of the radical polymerization initiator used is usually 0.1 to 50 parts by weight and preferably 0.1 to 20 parts by weight, based on 100 parts by weight of a polymerizable unsaturated compound.

Further, the amount of the molecular weight controlling agent (1) used is usually 0.1 to 50 parts by weight, preferably 0.2 to 16 parts by weight and more preferably 0.4 to 8 parts by weight, based on 100 parts by weight of a polymerizable unsaturated compound. When the amount of the molecular weight controlling agent (1) used is less than 0.1 parts by weight, the effect of controlling the molecular weight and molecular weight distribution tends to be reduced. On the other hand, when the amount is more than 50 parts by weight, a component with a low molecular weight may be preferentially produced.

In addition, the amount of other molecular weight controlling agents used is usually 200 wt% or less and preferably 40 wt% or less, based on the total of molecular weight controlling agents. When the ratio of other molecular weight controlling agents used is more

than 200 wt%, the desired effect of the present invention may be impaired.

Further, the amount of the solvent used is usually 50 to 1,000 parts by weight and preferably 100 to 500 parts by weight, based on 100 parts by weight of a polymerizable unsaturated compound.

Furthermore, the polymerization temperature is usually 0 to 150°C and preferably 50 to 120°C, and the polymerization time is usually 10 minutes to 20 hours and preferably 30 minutes to 6 hours.

[0052]

The copolymer (BI) has a weight average molecular weight (M_w) in terms of polystyrene as measured by gel permeation chromatography (GPC) of preferably 1,000 to 10,000 and more preferably 4,000 to 10,000, and a ratio of M_w to a number average molecular weight (M_n) in terms of polystyrene as measured by gel permeation chromatography (GPC) (M_w/M_n) of preferably 1.0 to 2.0 and more preferably 1.0 to 1.7.

The copolymer (BI) having such M_w and M_w/M_n can be used to thereby obtain a radiation-sensitive resin composition excellent in developability. Thereby, a colored layer having a sharp pattern edge can be formed, and simultaneously residues, scumming and film residues hardly occur on the unexposed portions of the substrate or on the light shielding layer during developing, and high production yield can also be realized without

generating dry foreign substances during the production of a color filter due to high cleaning performance by an organic solvent, and "burn-in" of a color filter can be more effectively prevented.

In the present invention, the copolymer (BI) can be used singly or as a mixture of two or more thereof.

[0053]

Further, in the present invention, one or more other alkali-soluble resins can be used together with the copolymer (BI).

The other alkali-soluble resins are not limited as long as they acts as a binder for the colorant (A) and they are soluble in a developer used in the developing process when a colored layer is formed, preferably an alkali developer, and examples thereof include addition polymerization-type, polyaddition-type and polycondensation-type resins, for example, resins having an acid functional group (e.g. carboxyl group, carboxylic acid anhydride group and phenolic hydroxyl group) and/or an alcoholic hydroxyl group.

[0054]

In the present invention, the amount of the resin (B) used is usually 10 to 1,000 parts by weight and preferably 20 to 500 parts by weight, based on 100 parts by weight of a colorant (A). When the amount of the resin (B) used is less than 10 parts by weight, there may appear flaws, for example, alkali developability may be

lowered, or scumming and film residues may occur on the unexposed portions of the substrate or on the light shielding layer. On the other hand, when the amount is more than 1,000 parts by weight, it may become difficult to achieve color density to be aimed as a thin film since the colorant concentration relatively decreases.

Further, the ratio of the copolymer (BI) used to the resin (B) is usually 50 to 100 wt%, and preferably 80 to 100 wt%. When the ratio of the copolymer (BI) used is less than 50 wt%, the desired effect of the present invention may be impaired.

[0055]

- (C) Polyfunctional Monomer -

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

Examples of such a polyfunctional monomer include:

di(meth)acrylates of alkylene glycols such as ethylene glycol and propylene glycol;

di(meth)acrylates of polyalkylene glycols such as diethylene glycol or higher polyethylene glycol, and dipropylene glycol or higher polypropylene glycol;

poly(meth)acrylates of polyhydric alcohols having three or more valences such as glycerin, trimethylolpropane, pentaerythritol and dipentaerythritol, and the dicarboxylic acid-modified compounds thereof;

oligo(meth)acrylates of compounds such as polyesters, epoxy resins, urethane resins, alkyd resins, silicone resins and spiran resins;

di(meth)acrylates of polymers having hydroxyl groups at the both ends such as poly-1,3-butadiene having hydroxyl groups at the both ends, polyisoprene having hydroxyl groups at the both ends and polycaprolactone having hydroxyl groups at the both ends; and

tris[2-(meth)acryloyloxyethyl]phosphate.

[0056]

Among these polyfunctional monomers, poly(meth)acrylate of polyhydric alcohols having three or more valences and the dicarboxylic acid-modified compounds thereof are preferred. Specifically, preferred examples thereof include trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol penta(meth)acrylate and dipentaerythritol hexa(meth)acrylate. Trimethylolpropane triacrylate, pentaerythritol triacrylate and dipentaerythritol hexaacrylate are more preferred since the colored layer has high strength and excellent surface smoothness, and scumming, film residues and the like hardly occur on the unexposed portions of the substrate and on the light shielding layer.

The polyfunctional monomers can be used singly or as a mixture of two or more thereof.

[0057]

The amount of the polyfunctional monomer used in the present invention is usually 5 to 500 parts by weight and preferably 20 to 300 parts by weight, based on 100 parts by weight of the resin (B). When the amount of the polyfunctional monomer used is less than 5 parts by weight, the strength or surface smoothness of the colored layer tends to decrease. On the other hand, when the amount is more than 500 parts by weight, there may appear negative results, for example, alkali developability may be lowered, or scumming, film residues and the like tend to occur on the unexposed portions of the substrate and on the light shielding layer.

[0058]

Further, in the present invention, a part of the polyfunctional monomer can be replaced with a monofunctional monomer having one polymerizable unsaturated bond.

Examples of the monofunctional monomer include: N-vinyl nitrogen-containing 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-vinylpiperadine, N-vinylmorpholine and N-vinylphenoxazine; N-(meth)acryloylmorpholine; and M-

5300, M-5400 and M-5600 (products of TOAGOSEI CO., LTD.) as a commercial product, in addition to the unsaturated compounds (b1) and the unsaturated compounds (b2) exemplified in the copolymer (BI).

These monofunctional monomers can be used singly or as a mixture of two or more thereof.

The ratio of the monofunctional monomers used is usually 90 wt% or less and preferably 50 wt% or less, based on the total amount of a polyfunctional monomer and a monofunctional monomer. When the ratio of the monofunctional monomers used is more than 90 wt%, the strength or surface smoothness of the resulting colored layer tends to decrease.

[0059]

- (D) Photopolymerization Initiator -

The photopolymerization initiator (D) in the present invention is a compound which generates radicals which can start polymerization of the polyfunctional monomer(C) and a monofunctional monomer optionally used by exposure of radiation such as visible rays, ultraviolet rays, far-ultraviolet rays, electron beams or X-rays.

Examples of such a photopolymerization initiator include acetophenone compounds, biimidazole compounds, triazine compounds, carbazole compounds, benzoin compounds, benzophenone compounds, α -diketone compounds, multinuclear quinone compounds, xanthone compounds and phosphine compounds.

In the present invention, the photopolymerization initiator can be used singly or as a mixture of two or more thereof, however, the photopolymerization initiator in the present invention is preferably at least one selected from the group consisting of acetophenone compounds, biimidazole compounds, triazine compounds and carbazole compounds.

[0060]

Among the photopolymerization initiator preferred in the present invention, specific examples of the acetophenone compounds include 2-hydroxy-2-methyl-1-phenylpropan-1-one, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butanone-1, 1-hydroxycyclohexyl phenyl ketone and 2,2-dimethoxy-1,2-diphenylethane-1-one, 1,2-octanedione and 1-[4-(phenylthio)phenyl]-2-(O-benzoyloxime).

Among these acetophenone compounds, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butaneone-1, 1,2-octanedione, 1-[4-(phenylthio)phenyl]-2-(O-benzoyloxime) and the like are preferred.

The acetophenone compounds can be used singly or as a mixture of two or more thereof.

[0061]

Further, specific examples of the biimidazole compound include 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-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 2,2'-bis(2,4,6-tribromophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole.

[0062]

Among these biimidazole compounds, 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-1,2'-biimidazole and the like are preferred, and 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole is more preferred.

[0063]

These biimidazole compounds are excellent in solubility in a solvent and thus do not produce foreign substances such as insoluble matter and deposit, and they also have high sensitivity and therefore curing reaction can proceed sufficiently by exposure of small energy, so that curing reaction does not occur in the unexposed portions. Therefore, the coating after exposure is

definitely divided into cured portions which are insoluble in the developer and uncured portions having high solubility in the developer, whereby a high-definition color filter in which the colored layer pattern without undercut is arranged according to the predetermined pattern can be formed.

The biimidazole compounds can be used singly or a mixture of two or more thereof.

[0064]

In the present invention, when a biimidazole compound is used as a photopolymerization initiator, the following hydrogen donors are preferably used together with it since they can further improve the sensitivity.

The term "hydrogen donor" as used herein means a compound which can donate a hydrogen atom to a radical generated from a biimidazole compound by exposure.

As a hydrogen donor in the present invention, mercaptan compounds, amine compounds and the like defined below are preferred.

[0065]

The mercaptan compound contains a compound which has a benzene ring or a heterocyclic ring as a mother nucleus, and one or more, preferably 1 to 3, and more preferably 1 to 2 mercapto groups which are directly bound to the mother nucleus (hereinafter, referred to as "mercaptan hydrogen donor").

The amine compound contains a compound which has a benzene ring or a heterocyclic ring as a mother nucleus and one or more, preferably 1 to 3 and more preferably 1 to 2 amino groups which are directly bound to the mother nucleus (hereinafter, referred to as "amine hydrogen donor").

It is to be noted that these hydrogen donors can also have a mercapto group and an amino group simultaneously.

[0066]

Hereinafter, the hydrogen donor will be more specifically described.

The mercaptan hydrogen donor can have one or more benzene rings or heterocyclic rings, and can have both of a benzene ring and a heterocyclic ring simultaneously, and when the donor has two or more of these rings, a fused ring may be formed or not.

In addition, when the mercaptan hydrogen donor has two or more mercapto groups, as long as one or more free mercapto groups remain, one or more of the remaining mercapto group may be substituted with an alkyl, aralkyl or aryl group, and further as long as one or more free mercapto groups remain, it may have a structural unit in which two sulfur atoms are bound to each other through a divalent organic group such as an alkylene group or a structural unit in which two sulfur atoms are bound to each other as a disulfide form.

Furthermore, the mercaptan hydrogen donor may be substituted at a position other than the mercapto group with a carboxyl group, an alkoxycarbonyl group, a substituted alkoxycarbonyl group, a phenoxycarbonyl group, a substituted phenoxycarbonyl group, a nitrile group or the like.

[0067]

Specific examples of such a mercaptan hydrogen donor include 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, 2-mercaptobenzimidazole, 2,5-dimercapto-1,3,4-thiadiazole and 2-mercapto-2,5-dimethylaminopyridine.

Among these mercaptan hydrogen donors, 2-mercaptobenzothiazole and 2-mercaptobenzoxazole are preferred, and 2-mercaptobenzothiazole is more preferred.

[0068]

Further, the amine hydrogen donor can have one or more benzene rings or heterocyclic rings, and can have both of a benzene ring and a heterocyclic ring simultaneously, and when the donor has two or more of these rings, a fused ring may be formed or not.

Furthermore, the amine hydrogen donor may be substituted on one or more of the amino groups with an alkyl group or a substituted alkyl group, and may be substituted at a position other than the amino group with a carboxyl group, an alkoxycarbonyl group, a substituted alkoxycarbonyl group, a phenoxycarbonyl group, a

substituted phenoxy carbonyl group, a nitrile group or the like.

[0069]

Specific examples of such an amine hydrogen donor include 4,4'-bis(dimethylamino)benzophenone, 4,4'-bis(diethylamino)benzophenone, 4-diethylaminoacetophenone, 4-dimethylaminopropiophenone, ethyl 4-dimethylaminobenzoate, 4-dimethylaminobenzoic acid and 4-dimethylaminobenzonitrile.

Among these amine hydrogen donors, 4,4'-bis(dimethylamino)benzophenone and 4,4'-bis(diethylamino)benzophenone are preferred, and 4,4'-bis(diethylamino)benzophenone is more preferred.

It is to be noted that the amine hydrogen donor has a function as a sensitizer even when a photopolymerization initiator except biimidazole compounds is used.

[0070]

In the present invention, the hydrogen donor can be used singly or as a mixture of two or more thereof, however, it is preferred that one or more mercaptan hydrogen donors and one or more amine hydrogen donors are used in combination since it is difficult for the formed pixel to fall off from the substrate during development and the pixel has also high strength and sensitivity.

Specific examples of the combination of a mercaptan hydrogen donor and an amine hydrogen donor include 2-

mercaptobenzothiazole/4,4'-bis(dimethylamino)benzophenone,
2-mercaptobenzothiazole/4,4'-
bis(diethylamino)benzophenone, 2-
mercaptobenzoxazole/4,4'-bis(dimethylamino)benzophenone
and 2-mercaptobenzoxazole/4,4'-
bis(diethylamino)benzophenone, and more preferred
combinations are 2-mercaptobenzothiazole/4,4'-
bis(diethylamino)benzophenone, and 2-
mercaptobenzoxazole/4,4'-bis(diethylamino)benzophenone,
and the preferred combination is 2-
mercaptobenzothiazole/4,4'-bis(diethylamino)benzophenone.

In the combination of a mercaptan hydrogen donor and
an amine hydrogen donor, the weight ratio of the
mercaptan hydrogen donor to the amine hydrogen donor is
usually 1:1 to 1:4, and preferably 1:1 to 1:3.

[0071]

In the present invention, when the hydrogen donor
and a biimidazole compound are used in a combination, the
amount of the hydrogen donor used is preferably 0.01 to
40 parts by weight, more preferably 1 to 30 parts by
weight and even more preferably 1 to 20 parts by weight,
based on 100 parts by weight of the total of a
polyfunctional monomer (C) and a monofunctional monomer.
When the amount of the hydrogen donor used is less than
0.01 parts by weight, the effect of improving the
sensitivity tends to decrease. On the other hand, when
the amount is more than 40 parts by weight, the formed

colored layer easily tends to fall off from the substrate during development.

[0072]

Further, specific examples of the triazine compounds include a triazine compound 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-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-triazine.

[0073]

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

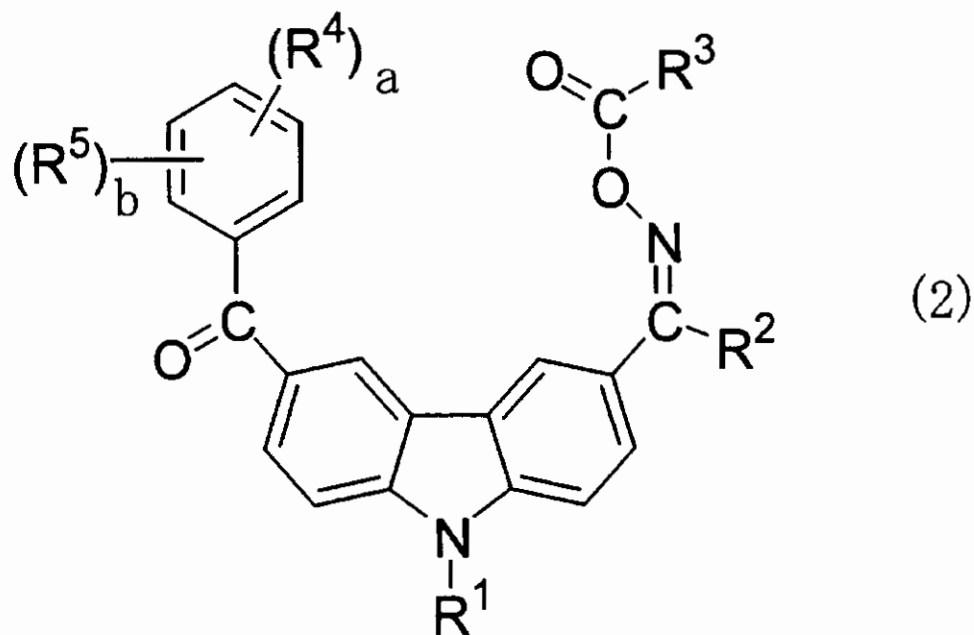
The triazine compounds can be used singly or as a mixture of two or more thereof.

[0074]

Furthermore, examples of the carbazole compound include a compound represented by the following formula (2) (hereinafter, referred to as "carbazole compound (2)") and a compound represented by the following formula

(3) (hereinafter, referred to as "carbazole compound (3)"):

[0075]

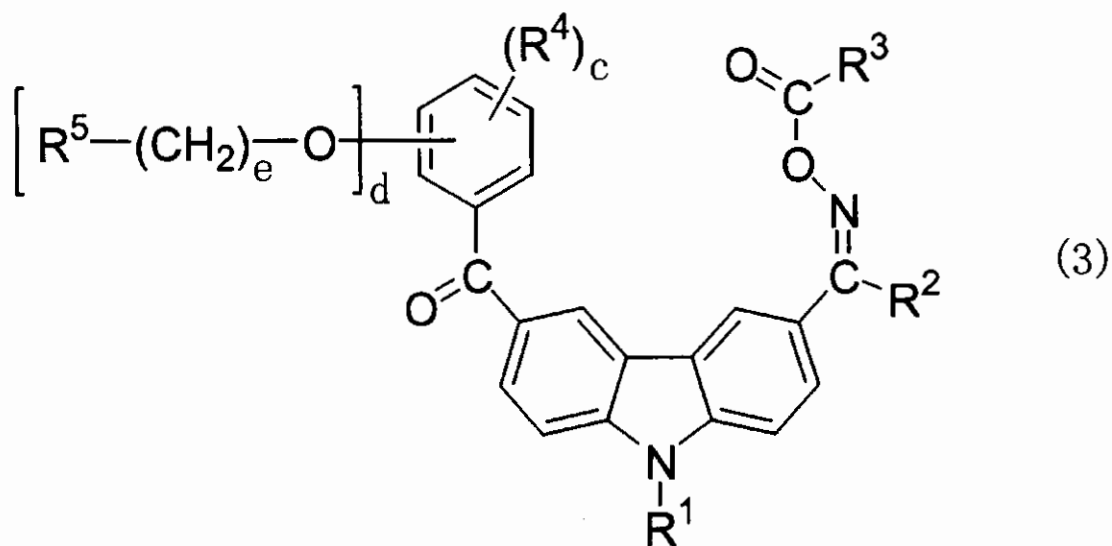


[0076]

wherein R¹ represents an alkyl group having 1 to 20 carbon atoms, a cycloalkyl group having 3 to 8 carbon atoms or a phenyl group; R² and R³ represent, independently of each other, a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, a cycloalkyl group having 3 to 8 carbon atoms, an optionally substituted phenyl group or a monovalent alicyclic group having 7 to 20 carbon atoms (except for the cycloalkyl group); R⁴ represents an alkyl group having 1 to 12 carbon atoms, a cycloalkyl group having 3 to 8 carbon atoms, an alkoxy group having 1 to 12 carbon atoms or a cycloalkyloxy group having 3 to 8 carbon atoms, and a plurality of R⁴

present may be the same or different with each other; R^5 represents a monovalent oxygen-containing heterocyclic group having 4 to 20 carbon atoms, a monovalent nitrogen-containing heterocyclic group having 4 to 20 carbon atoms or a monovalent sulfur-containing heterocyclic group having 4 to 20 carbon atoms, and a plurality of R^5 present may be the same or different with each other; "a" represents an integer of 0 to 5, "b" represents an integer of 0 to 5, and $(a+b) \leq 5$;

[0077]



[0078]

wherein R^1 represents an alkyl group having 1 to 20 carbon atoms, a cycloalkyl group having 3 to 8 carbon atoms or a phenyl group; R^2 and R^3 represent, independently of each other, a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, a cycloalkyl group having 3 to 8 carbon atoms, an optionally substituted

phenyl group or a monovalent alicyclic group having 7 to 20 carbon atoms (except for the cycloalkyl group); R^4 represents an alkyl group having 1 to 12 carbon atoms, a cycloalkyl group having 3 to 8 carbon atoms, an alkoxy group having 1 to 12 carbon atoms or a cycloalkyloxy group having 3 to 8 carbon atoms, and a plurality of R^4 present may be the same or different with each other; R^5 represents a monovalent oxygen-containing heterocyclic group having 4 to 20 carbon atoms, a monovalent nitrogen-containing heterocyclic group having 4 to 20 carbon atoms or a monovalent sulfur-containing heterocyclic group having 4 to 20 carbon atoms, and a plurality of R^5 present may be the same or different with each other; "c" represents an integer of 0 to 5, "d" represents an integer of 1 to 5, and $(c+d) \leq 5$; and "e" represents an integer of 0 to 6.

[0079]

In the formulas (2) and (3), examples of the alkyl group having 1 to 20 carbon atoms of R^1 include a methyl group, an ethyl group, an n-propyl group, an i-propyl group, an n-butyl group, a sec-butyl group, a t-butyl group, an n-pentyl group, an n-hexyl group, an n-heptyl group, an n-octyl group, an n-nonyl group, an n-decyl group, an n-undecyl group and an n-dodecyl group.

Examples of the cycloalkyl group having 3 to 8 carbon atoms of R^1 include a cyclopentyl group and a cyclohexyl group.

[0080]

In the formulas (2) and (3), preferred examples of R^1 include a methyl group and an ethyl group.

[0081]

In the formulas (2) and (3), examples of the alkyl group having 1 to 20 carbon atoms of R^2 and R^3 include a methyl group, an ethyl group, an n-propyl group, an i-propyl group, an n-butyl group, a sec-butyl group, a t-butyl group, an n-pentyl group, an n-hexyl group, an n-heptyl group, an n-octyl group, an n-nonyl group, an n-decyl group, an n-undecyl group and an n-dodecyl group.

In addition, examples of the cycloalkyl group having 3 to 8 carbon atoms of R^2 and R^3 include a cyclopentyl group and a cyclohexyl group.

[0082]

Examples of a substituent for the phenyl group of R^2 and R^3 include: alkyl groups having 1 to 6 carbon atoms such as a methyl group, an ethyl group, an n-propyl group, an i-propyl group, an n-butyl group, a sec-butyl group, a t-butyl group, an n-pentyl group and an n-hexyl group; cycloalkyl groups having 3 to 6 carbon atoms such as a cyclopentyl group and a cyclohexyl group; alkoxy groups having 1 to 6 carbon atoms such as a methoxy group, an ethoxy group, an n-propoxy group, an i-propoxy group, an n-butoxy group and a t-butoxy group; cycloalkyloxy groups having 3 to 6 carbon atoms such as a cyclopentyloxy group

and a cyclohexyloxy group; a phenyl group; and halogen atoms such as a fluorine atom and a chlorine atom.

[0083]

Further, examples of the monovalent alicyclic group having 7 to 20 carbon atoms of R^2 and R^3 (except for the cycloalkyl group) include a group having a 1-alkylcycloalkane skeleton, a group having a bicycloalkane skeleton, a group having a tricycloalkane skeleton, a group having a spiroalkane skeleton, a group having a terpene skeleton, and a group having an adamantane skeleton.

[0084]

In the formulas (2) and (3), preferred examples of R^2 and R^3 include a hydrogen atom, a methyl group and an ethyl group.

[0085]

In the formulas (2) and (3), examples of the alkyl group having 1 to 12 carbon atoms of R^4 include a methyl group, an ethyl group, an n-propyl group, an i-propyl group, an n-butyl group, a sec-butyl group, a t-butyl group, an n-pentyl group, an n-hexyl group, an n-heptyl group, an n-octyl group, an n-nonyl group, an n-decyl group, an n-undecyl group and an n-dodecyl group.

In addition, examples of the cycloalkyl group having 3 to 8 carbon atoms of R^4 include a cyclopentyl group and a cyclohexyl group.

[0086]

Examples of the alkoxyl group having 1 to 12 carbon atoms of R^4 include a methoxy group, an ethoxy group, an n-propoxy group, an i-propoxy group, an n-butoxy group, a t-butoxy group, an n-pentyloxy group, an n-hexyloxy group, an n-heptyloxy group, an n-octyloxy group, an n-nonyloxy group, an n-decyloxy group, an n-undecyloxy group and an n-dodecyloxy group.

In addition, examples of the cycloalkyloxy group having 3 to 8 carbon atoms of R^4 include a cyclopentyloxy group and a cyclohexyloxy group.

[0087]

In the formulas (2) and (3), preferred examples of R^4 include a methyl group, an ethyl group, n-propyl group, an i-propyl group, an n-butyl group, a methoxy group and an ethoxy group.

[0088]

In the formulas (2) and (3), examples of the monovalent oxygen-containing heterocyclic group having 4 to 20 carbon atoms of R^5 , the monovalent nitrogen-containing heterocyclic group having 4 to 20 carbon atoms or the monovalent sulfur-containing heterocyclic group having 4 to 20 carbon atoms include a thioranyl group, an azepinyl group, a dihydroazepinyl group, a dioxolanyl group, a triazinyl group, an oxathianyl group, a thiazolyl group, an oxadiadinyl group, a dioxaindanyl group, a diphianaphthalenyl group, a furanyl group, a thiophenyl group, a pyrrolyl group, an oxazolyl group, an

isooxazolyl group, a thiazolyl group, an isothiazolyl group, a pyrazolyl group, a furazanyl group, a pyranyl group, a pyridinyl group, a pyridazinyl group, a pyrimidyl group, a pyradinyl group, a pyrrolinyl group, a morphonyl group, a piperadinyl group, a quinuclidinyl group, an indolyl group, an isoindolyl group, a benzofuranyl group, a benzothiophenyl group, an indolidinyl group, a chromenyl group, a quinolinyl group, an isoquinolinyl group, a purinyl group, a quinazolinyl group, a cinnolinyl group, a phthaladinyl group, a puteridinyl group, a carbazolyl group, an acrydinyl group, a phenanthridinyl group, a thioxanthenyl group, a phenazinyl group, a phenothiazinyl group, a phenoxathinyl group, a phenoxazinyl group, a thianthrenyl group, a tetrahydrofuranyl group and a tetrahydropyranyl group.

[0089]

In the formulas (2) and (3), preferred examples of R^5 include a tetrahydrofuranyl group and a tetrahydropyranyl group.

[0090]

In the formula (2), "a" is preferably 0, 1 or 2 and more preferably 1; and "b" is preferably 0 or 1 and more preferably 0.

[0091]

In the formula (3), "c" is preferably 0, 1 or 2 and more preferably 1; "d" is preferably 1; and "e" is preferably 0, 1 or 2 and more preferably 1.

[0092]

Specific examples of the carbazole compound (2) include 1-[9-ethyl-6-benzoyl-9.H.-carbazol-3-yl]-1,2-nonane-2-oxime-O-benzoate, 1-[9-ethyl-6-benzoyl-9.H.-carbazol-3-yl]-1,2-nonane-2-oxime-O-acetate, 1-[9-ethyl-6-benzoyl-9.H.-carbazol-3-yl]-1,2-pentane-2-oxime-O-acetate, 1-[9-ethyl-6-benzoyl-9.H.-carbazol-3-yl]-octane-1-onoxime-O-acetate, 1-[9-ethyl-6-(2-methylbenzoyl)-9.H.-carbazol-3-yl]-ethane-1-onoxime-O-benzoate, 1-[9-ethyl-6-(2-methylbenzoyl)-9.H.-carbazol-3-yl]-ethane-1-onoxime-O-acetate, 1-[9-ethyl-6-(1,3,5-trimethylbenzoyl)-9.H.-carbazol-3-yl]-ethane-1-onoxime-O-benzoate, 1-[9-n-butyl-6-(2-ethylbenzoyl)-9.H.-carbazol-3-yl]-ethane-1-onoxime-O-benzoate,

[0093]

ethanone-1-[9-ethyl-6-(2-methyl-4-tetrahydrofuranyl benzoyl)-9.H.-carbazol-3-yl]-1-(O-acetyloxime), ethanone-1-[9-ethyl-6-(2-methyl-4-tetrahydropyranyl benzoyl)-9.H.-carbazol-3-yl]-1-(O-acetyloxime), ethanone-1-[9-ethyl-6-(2-methyl-5-tetrahydrofuranyl benzoyl)-9.H.-carbazol-3-yl]-1-(O-acetyloxime), ethanone-1-[9-ethyl-6-(2-methyl-5-tetrahydropyranyl benzoyl)-9.H.-carbazol-3-yl]-1-(O-acetyloxime), and ethanone-1-[9-ethyl-6-{2-methyl-4-(2,2-dimethyl-1,3-dioxolanyl)benzoyl}-9.H.-carbazol-3-yl]-1-(O-acetyloxime).

[0094]

Further, specific examples of the carbazole compound (3) include ethanone-1-[9-ethyl-6-(2-methyl-4-tetrahydrofuranylmethoxy benzoyl)-9.H.-carbazol-3-yl]-1-(O-acetyloxime), ethanone-1-[9-ethyl-6-(2-methyl-4-tetrahydropyranylmethoxy benzoyl)-9.H.-carbazol-3-yl]-1-(O-acetyloxime), ethanone-1-[9-ethyl-6-(2-methyl-5-tetrahydrofuranylmethoxy benzoyl)-9.H.-carbazol-3-yl]-1-(O-acetyloxime), ethanone-1-[9-ethyl-6-(2-methyl-5-tetrahydropyranylmethoxy benzoyl)-9.H.-carbazol-3-yl]-1-(O-acetyloxime), and ethanone-1-[9-ethyl-6-{2-methyl-4-(2,2-dimethyl-1,3-dioxolanyl)methoxybenzoyl}-9.H.-carbazol-3-yl]-1-(O-acetyloxime).

[0095]

Among these carbazole compounds (2) and carbazole compounds (3), 1-[9-ethyl-6-(2-methylbenzoyl)-9.H.-carbazol-3-yl]-ethane-1-onoxime-O-acetate, ethanone-1-[9-ethyl-6-(2-methyl-4-tetrahydrofuranylmethoxy benzoyl)-9.H.-carbazol-3-yl]-1-(O-acetyloxime), ethanone-1-[9-ethyl-6-{2-methyl-4-(2,2-dimethyl-1,3-dioxolanyl)methoxybenzoyl}-9.H.-carbazol-3-yl]-1-(O-acetyloxime) and the like are preferred, and 1-[9-ethyl-6-(2-methylbenzoyl)-9.H.-carbazol-3-yl]-ethane-1-onoxime-O-acetate, ethanone-1-[9-ethyl-6-{2-methyl-4-(2,2-dimethyl-1,3-dioxolanyl)methoxybenzoyl}-9.H.-carbazol-3-yl]-1-(O-acetyloxime) and the like are more preferred.

[0096]

In the present invention, the amount of the photopolymerization initiator used is usually 0.01 to 200 parts by weight, preferably 1 to 120 parts by weight and more preferably 1 to 100 parts by weight, based on 100 parts by weight of the total of a polyfunctional monomer [C] and an optionally used monofunctional monomer. When the amount of the photopolymerization initiator used is less than 0.01 parts by weight, curing by exposure becomes insufficient, and it may become difficult to obtain a pattern array in which the colored layer pattern is arranged according to a predetermined pattern. On the other hand, when the amount is more than 200 parts by weight, the formed colored layer may easily fall off from the substrate during development, and scumming, film residues and the like tend to easily occur on the unexposed portions of the substrate or on the light shielding layer.

In addition, in the present invention, one or more sensitizer, curing accelerator or polymer photocrosslinking and sensitizing agent can also be used together with the photopolymerization initiator, if necessary.

[0097]

- Other Additives -

The radiation-sensitive resin composition for forming the colored layer of the present invention

contains the components (A) to (D) as basic components, but can also further contain other additives as required.

Examples of the other additives include:

fillers such as glass and alumina;

polymer compounds such as polyvinyl alcohols and poly(fluoroalkyl acrylate);

surfactants such as nonionic surfactants, cationic surfactants and anionic surfactants;

adhesion accelerators such as vinyltrimethoxysilane, vinyltriethoxysilane, vinyltris(2-methoxyethoxy)silane, N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropylmethyldimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 3-chloropropylmethyldimethoxysilane, 3-chloropropyltrimethoxysilane, 3-methacryloyloxypropyltrimethoxysilane and 3-mercaptopropyltrimethoxysilane;

antioxidants such as 2,2-thiobis(4-methyl-6-t-butylphenol) and 2,6-di-t-butylphenol;

UV absorbers such as 2-(3-t-butyl-5-methyl-2-hydroxyphenyl)-5-chlorobenzotriazole and alkoxybenzophenone;

coagulation inhibitors such as sodium polyacrylate.

Preparation of Liquid Composition

The radiation-sensitive resin composition for forming the colored layer of the present invention is usually prepared as a liquid composition by blending with a solvent.

As the solvent, any solvent can be appropriately selected and used as long as it can disperse or dissolve the components (A) to (D) constituting the radiation-sensitive resin composition and other additive components and does not react with these components and has moderate volatility.

[0099]

Examples of such a solvent include:

propylene glycol monoalkyl ethers such as propylene glycol monomethyl ether and propylene glycol monoethyl ether;

(poly)alkylene glycol monoalkyl ether acetate such as ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, dipropylene glycol monomethyl ether acetate and dipropylene glycol monoethyl ether acetate;

(poly)alkylene glycol diethers such as 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, cyclohexanone, 2-heptanone and 3-heptanone;

ketoalcohols such as diacetone alcohol (i.e. 4-hydroxy-4-methylpentane-2-one) and 4-hydroxy-4-methylhexane-2-one;

[0100]

lactic acid alkyl esters such as methyl lactate and ethyl lactate;

other esters such as ethyl 2-hydroxy-2-methylpropanoate, ethyl hydroxyacetate, methyl 2-hydroxy-3-methylbutanoate, methyl 3-methoxypropionate, ethyl 3-methoxypropanoate, methyl 3-ethoxypropionate, ethyl 3-ethoxypropanoate, ethyl ethoxyacetate, 3-methoxybutyl acetate, 3-methyl-3-methoxybutyl acetate, 3-methyl-3-methoxybutyl propionate, 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 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.

[0101]

Among these solvents, propylene glycol monomethyl ether, ethylene glycol monomethyl ether acetate, diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, dipropylene glycol monomethyl ether acetate, diethylene glycol dimethyl ether, diethylene glycol methyl ethyl ether, dipropylene glycol dimethyl ether, cyclohexanone, 2-heptanone, 3-heptanone, ethyl 3-methoxypropanoate, methyl 3-ethoxypropionate, ethyl 3-ethoxypropanoate, 3-methoxydibutyl acetate, 3-methyl-3-methoxybutyl propionate, n-butyl acetate, i-butyl acetate, n-pentyl formate, i-pentyl acetate, n-butyl propionate, ethyl butyrate, i-propyl butyrate, n-butyl butyrate, ethyl pyruvate and the like are preferred from the viewpoints of dissolving properties, pigment dispersibility coating properties and the like.

The solvents can be used singly or as a mixture of two or more thereof.

[0102]

Further, solvents which has high boiling point 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 and ethylene glycol monophenyl ether acetate can be used together with the solvents.

The high boiling point solvents can be used singly or as a mixture of two or more thereof.

[0103]

The amount of the solvent used is not limited, but is desirably such an amount that the total concentration of respective components except the solvent of the composition is preferably 5 to 50 wt% and more preferably 10 to 40 wt%, from the viewpoints of coating properties and stability of the liquid composition to be obtained.

[0104]

Method For Forming Color Filter

Next, a method for forming the color filter of the present invention will be described using the radiation-sensitive resin composition for forming the colored layer of the present invention.

The method for forming the color filter usually includes at least the following steps (1) to (4).

(1) A step of forming a coating of the radiation-sensitive resin composition for forming the colored layer of the present invention on a substrate

(2) A step of exposing at least a part of the coating

(3) A step of developing the coating after exposure

(4) A step of heat-treating (hereinafter, referred to as "post-baking") the coating after development

Hereinafter, these steps will be described sequentially.

[0105]

- Step (1) -

At first, a light shielding layer is formed on the surface of a substrate to section the parts each forming a pixel as required, and a liquid composition of the radiation-sensitive resin composition for forming the colored layer which contains, for example, a red pigment is applied on this substrate, and then the substrate is subjected to pre-baking to evaporate a solvent and thereby forming a coating.

Examples of the substrate used in this step include ring-opened polymers of the cyclic olefin or hydrogenated substances thereof in addition to glass, silicon, polycarbonates, polyesters, aromatic polyamides, polyamide-imides, polyimides and polyethersulfones.

In addition, these substrates can also be subjected to an appropriate pretreatment such as chemical treatment by silane coupling agents or the like, plasma treatment, ion plating, sputtering, a gas phase reaction method and vacuum deposition as desired.

Appropriate coating methods such as rotary coating (spin coating), flow casting coating, roll coating and coating with a slit nozzle can be adopted for applying a

liquid composition to the substrate, however, the radiation-sensitive resin composition in the present invention has high solubility in a cleaning solvent even after drying, and therefore this composition is suitable for coating with a slit nozzle.

Pre-baking is usually performed by the condition of 70 to 110°C for about 2 to 4 minutes.

The coating thickness is usually 0.1 to 10 μm , preferably, 0.2 to 8.0 μm and more preferably 0.2 to 6.0 μm as a film thickness after the solvent is removed.

[0106]

- Step (2) -

Then, at least a part of the formed coating is exposed. When a part of the coating is exposed, it is usually exposed through a photomask having an appropriate pattern.

As radiation used for this step, for example, visible rays, ultraviolet rays, far-ultraviolet rays, electron beams and X-rays, can be employed, however, radiation having a wavelength in the range of 190 to 450 nm is preferred.

The exposure amount of radiation is usually about 10 to 10,000 J/m².

[0107]

- Step (3) -

Then, the exposed coating is preferably developed with an alkali developer and unexposed portions of the coating are dissolved and removed to form a pattern.

As the alkali developer, aqueous solutions of, for example, sodium carbonate, sodium hydroxide, potassium hydroxide, tetramethylammonium hydroxide, choline, 1,8-diazabicyclo-[5.4.0]-7-undecene and 1,5-diazabicyclo-[4.3.0]-5-nonene are preferred.

An appropriate amount of water-soluble organic solvents such as methanol and ethanol or surfactants can also be added to the alkali developer. It is to be noted that the coating is usually rinsed with water after alkali development.

As the developing processing method, a shower developing method, a spray developing method, a dip (immersion) developing method, a puddle developing method and the like can be applied.

The developing condition at ordinary temperature for about 5 to 300 seconds is preferred.

[0108]

- Step (4) -

Consequently, the coating after development is post-baked, and thereby the substrate in which a pixel pattern constituted of the cured radiation-sensitive resin composition is arranged in a predetermined pattern can be obtained.

Post-baking is preferably performed by the condition of 180 to 230°C for about 20 to 40 minutes.

The film thickness of the thus formed pixels is usually 0.5 to 5.0 μm and preferably 1.5 to 3.0 μm .

[0109]

Further, green and blue pixel patterns are formed on the same substrate by repeating the steps (1) to (4) using a liquid composition of the radiation-sensitive resin composition for forming the colored layer which contains a green or blue pigment, and thereby a colored layer in which pixel patterns of the three primary colors of red, green and blue are arranged in a predetermined pattern can be formed on the substrate. However, the order of forming pixel patterns of respective colors in the present invention is not limited to the above order.

In addition, a black matrix can be treated in the same manner as the above pixel pattern formation procedure except that a liquid composition of the radiation-sensitive resin composition for forming the colored layer containing a black pigment is used.

[0110]

Color Filter

The color filter of the present invention is provided with a colored layer formed using the radiation-sensitive resin composition for forming the colored layer of the present invention.

The color filter of the present invention is extremely useful for, for example, transmissive or reflective color liquid crystal display devices, color imaging tube elements, color sensors or the like.

[0111]

Color Liquid Crystal Display Device

The color liquid crystal display device of the present invention is provided with the color filter of the present invention.

The color liquid crystal display device of the present invention can have an appropriate structure. For example, the color liquid crystal display device can have a structure where a color filter is formed on another substrate other than a driving substrate having a thin film transistor (TFT) disposed thereon, and the driving substrate and the substrate having the color filter formed thereon are opposed to each other through a liquid crystal layer, and can also have a structure where a substrate in which a color filter is formed on the surface of the driving substrate having a thin film transistor (TFT) disposed thereon and a substrate having an ITO (indium oxide doped with tin) electrode formed thereon are opposed to each other through a liquid crystal layer. The latter structure has an advantage that the numerical aperture can be improved significantly and therefore a color liquid crystal display device which is bright and has high definition can be obtained.

[Examples]

[0112]

Hereinafter, the embodiments of the present invention will be more specifically described by way of Examples. The present invention is, however, not limited to the following Examples.

The Mw and Mn of a resin obtained in each of the following Synthesis Examples were measured by gel permeation chromatography (GPC) according to the following specification.

Apparatus: GPC-101 (manufactured by SHOWA DENKO K.K.)

Column: Columns GPC-KF-801, GPC-KF-802, GPC-KF-803 and GPC-KF-804 were connected with each other for use.

Mobile phase: Tetrahydrofuran containing 0.5 wt% phosphoric acid

[0113]

[Production of Copolymer for Comparison]

Synthesis Example 1

A flask equipped with a cooling tube and a stirrer was charged with 3 parts by weight of 2,2'-azobisisobutyronitrile, 4 parts by weight of bis(pyrazol-1-yl-thiocarbonyl)disulfide immediately after synthesis and 200 parts by weight of dipropylene glycol dimethyl ether, and subsequently with 20 parts by weight of methacrylic acid, 31.2 parts by weight of N-phenylmaleimide, 30 parts by weight of benzyl

methacrylate and 18.8 parts by weight of styrene. After the flask was purged with nitrogen gas, the reaction solution was heated to 80°C while gently stirring and held at this temperature to perform polymerization for 3 hours. Then, the reaction solution was heated to 100°C and 2 parts by weight of 2,2'-azobisisobutyronitrile was added thereto. Polymerization was continued for another 1 hour, and thereby a copolymer solution (solid content concentration = 33.1 wt%) was obtained. This copolymer had a Mw of 5,200 and a Mw/Mn of 1.4. This copolymer was designated as "copolymer (β -1)".

[0114]

Synthesis Example 2

A flask equipped with a cooling tube and a stirrer was charged with 3 parts by weight of 2,2'-azobisisobutyronitrile, 4 parts by weight of bis(pyrazol-1-yl-thiocarbonyl)disulfide left to stand at room temperature for 2 months after synthesis and 200 parts by weight of dipropylene glycol dimethyl ether, and subsequently with 20 parts by weight of methacrylic acid, 31.2 parts by weight of N-phenylmaleimide, 30 parts by weight of benzyl methacrylate and 18.8 parts by weight of styrene. After the flask was purged with nitrogen gas, the reaction solution was heated to 80°C while gently stirring and held at this temperature to perform polymerization for 3 hours. Then, the reaction solution was heated to 100°C and 2 parts by weight of 2,2'-

azobisisobutyronitrile was added thereto. Polymerization was continued for another 1 hour, and thereby a copolymer solution (solid content concentration = 33.1 wt%) was obtained. This copolymer had a Mw of 10,500 and a Mw/Mn of 1.9. This copolymer was designated as "copolymer (β -2)".

Synthesis Example 2 is an example of producing a copolymer in the same manner as in Synthesis Example 1 except that bis(pyrazol-1-yl-thiocarbonyl)disulfide left to stand at room temperature for 2 months after synthesis was used. The obtained copolymer (β -2) has a higher molecular weight and a higher Mw/Mn as compared with the copolymer (β -1) obtained in Synthesis Example 1. Accordingly, it shows that bis(pyrazol-1-yl-thiocarbonyl)disulfide does not have good storage stability.

[0115]

Synthesis Example 3

A flask equipped with a cooling tube and a stirrer was charged with 10 parts by weight of 2,2'-azobisisobutyronitrile, 400 parts by weight of dipropylene glycol dimethyl ether, and subsequently with 20 parts by weight of methacrylic acid, 31.2 parts by weight of N-phenylmaleimide, 30 parts by weight of benzyl methacrylate, 18.8 parts by weight of styrene and 10 parts by weight of α -methylstyrene dimer (molecular weight controlling agent). After the flask was purged

with nitrogen gas, the reaction solution was heated to 80°C while gently stirring and held at this temperature to perform polymerization for 3 hours. Then, the reaction solution was heated to 100°C and 2 parts by weight of 2,2'-azobisisobutyronitrile was added thereto. Polymerization was continued for another 1 hour, and thereby a copolymer solution (solid content concentration = 20.1 wt%) was obtained. This copolymer had a Mw of 5,000 and a Mw/Mn of 3.6. This copolymer was designated as "copolymer (β -3)".

[0116]

Synthesis Example 4

A flask equipped with a cooling tube and a stirrer was charged with 2.5 parts by weight of 2,2'-azobisisobutyronitrile and 200 parts by weight of dipropylene glycol dimethyl ether, and subsequently with 20 parts by weight of methacrylic acid, 31.2 parts by weight of N-phenylmaleimide, 30 parts by weight of benzyl methacrylate, 18.8 parts by weight of styrene and 3 parts by weight of α -methylstyrene dimer (molecular weight controlling agent). After the flask was purged with nitrogen gas, the reaction solution was heated to 80°C while gently stirring and held at this temperature to perform polymerization for 3 hours. Then, the reaction solution was heated to 100°C and 0.5 parts by weight of 2,2'-azobisisobutyronitrile was added thereto. Polymerization was continued for another 1 hour, and

thereby a copolymer solution (solid content concentration = 33.2 wt%) was obtained. This copolymer had a Mw of 14,000 and a Mw/Mn of 2.1. This copolymer was designated as "copolymer (β -4)".

[0117]

[Production of Copolymer (BI)]

Synthesis Example 5

A flask equipped with a cooling tube and a stirrer was charged with 3 parts by weight of 2,2'-azobisisobutyronitrile, 4 parts by weight of bis(n-octylmercapto-thiocarbonyl)disulfide immediately after synthesis and 200 parts by weight of dipropylene glycol dimethyl ether, and subsequently with 20 parts by weight of methacrylic acid, 31.2 parts by weight of N-phenylmaleimide, 30 parts by weight of benzyl methacrylate and 18.8 parts by weight of styrene. After the flask was purged with nitrogen gas, the reaction solution was heated to 80°C while gently stirring and held at this temperature to perform polymerization for 3 hours. Then, the reaction solution was heated to 100°C and 2 parts by weight of 2,2'-azobisisobutyronitrile was added thereto. Polymerization was continued for another 1 hour, and thereby a copolymer solution (solid content concentration = 33.0 wt%) was obtained. This copolymer had a Mw of 5,000 and a Mw/Mn of 1.5. This copolymer was designated as "copolymer (B-1)".

[0118]

Synthesis Example 6

A flask equipped with a cooling tube and a stirrer was charged with 3 parts by weight of 2,2'-azobisisobutyronitrile, 4 parts by weight of bis(n-dodecylmercapto-thiocarbonyl)disulfide immediately after synthesis and 200 parts by weight of dipropylene glycol dimethyl ether, and subsequently with 20 parts by weight of methacrylic acid, 31.2 parts by weight of N-phenylmaleimide, 30 parts by weight of benzyl methacrylate and 18.8 parts by weight of styrene. After the flask was purged with nitrogen gas, the reaction solution was heated to 80°C while gently stirring and held at this temperature to perform polymerization for 3 hours. Then, the reaction solution was heated to 100°C and 2 parts by weight of 2,2'-azobisisobutyronitrile was added thereto. Polymerization was continued for another 1 hour, and thereby a copolymer solution (solid content concentration = 32.8 wt%) was obtained. This copolymer had a Mw of 5,200 and a Mw/Mn of 1.4. This copolymer was designated as "copolymer (B-2)".

[0119]

Synthesis Example 7

A flask equipped with a cooling tube and a stirrer was charged with 3 parts by weight of 2,2'-azobisisobutyronitrile, 4 parts by weight of bis(benzylmercapto-thiocarbonyl)disulfide immediately after synthesis and 200 parts by weight of dipropylene

glycol dimethyl ether, and subsequently with 20 parts by weight of methacrylic acid, 31.2 parts by weight of N-phenylmaleimide, 30 parts by weight of benzyl methacrylate and 18.8 parts by weight of styrene. After the flask was purged with nitrogen gas, the reaction solution was heated to 80°C while gently stirring and held at this temperature to perform polymerization for 3 hours. Then, the reaction solution was heated to 100°C and 2 parts by weight of 2,2'-azobisisobutyronitrile was added thereto. Polymerization was continued for another 1 hour, and thereby a resin solution (solid content concentration = 33.1 wt%) was obtained. This resin had a Mw of 5,250 and a Mw/Mn of 1.6. This resin was designated as "resin (B-3)".

[0120]

Synthesis Example 8

A flask equipped with a cooling tube and a stirrer was charged with 3 parts by weight of 2,2'-azobisisobutyronitrile, 4 parts by weight of bis(n-octylmercapto-thiocarbonyl)disulfide left to stand at room temperature for 3 months after synthesis and 200 parts by weight of dipropylene glycol dimethyl ether, and subsequently with 20 parts by weight of methacrylic acid, 31.2 parts by weight of N-phenylmaleimide, 30 parts by weight of benzyl methacrylate and 18.8 parts by weight of styrene. After the flask was purged with nitrogen gas, the reaction solution was heated to 80°C while gently

stirring and held at this temperature to perform polymerization for 3 hours. Then, the reaction solution was heated to 100°C and 2 parts by weight of 2,2'-azobisisobutyronitrile was added thereto. Polymerization was continued for another 1 hour, and thereby a copolymer solution (solid content concentration = 32.7 wt%) was obtained. This copolymer had a Mw of 5,400 and a Mw/Mn of 1.5. This copolymer was designated as "copolymer (B-4)".

[0121]

Synthesis Example 9

A flask equipped with a cooling tube and a stirrer was charged with 3 parts by weight of 2,2'-azobisisobutyronitrile, 4 parts by weight of bis(n-dodecylmercapto-thiocarbonyl)disulfide left to stand at room temperature for 3 months after synthesis and 200 parts by weight of dipropylene glycol dimethyl ether, and subsequently with 20 parts by weight of methacrylic acid, 31.2 parts by weight of N-phenylmaleimide, 30 parts by weight of benzyl methacrylate and 18.8 parts by weight of styrene. After the flask was purged with nitrogen gas, the reaction solution was heated to 80°C while gently stirring and held at this temperature to perform polymerization for 3 hours. Then, the reaction solution was heated to 100°C and 2 parts by weight of 2,2'-azobisisobutyronitrile was added thereto. Polymerization was continued for another 1 hour, and thereby a copolymer

solution (solid content concentration = 32.7 wt%) was obtained. This copolymer had a Mw of 5,500 and a Mw/Mn of 1.5. This copolymer was designated as "copolymer (B-5)".

[0122]

Synthesis Example 10

A flask equipped with a cooling tube and a stirrer was charged with 3 parts by weight of 2,2'-azobisisobutyronitrile, 4 parts by weight of bis(benzylmercapto-thiocarbonyl)disulfide left to stand at room temperature for 3 months after synthesis and 200 parts by weight of dipropylene glycol dimethyl ether, and subsequently with 20 parts by weight of methacrylic acid, 31.2 parts by weight of N-phenylmaleimide, 30 parts by weight of benzyl methacrylate and 18.8 parts by weight of styrene. After the flask was purged with nitrogen gas, the reaction solution was heated to 80°C while gently stirring and held at this temperature to perform polymerization for 3 hours. Then, the reaction solution was heated to 100°C and 2 parts by weight of 2,2'-azobisisobutyronitrile was added thereto. Polymerization was continued for another 1 hour, and thereby a copolymer solution (solid content concentration = 32.7 wt%) was obtained. This copolymer had a Mw of 5,400 and a Mw/Mn of 1.5. This copolymer was designated as "copolymer (B-6)".

[0123]

[Immersion Test]

Comparative Example 1

A mixed solution containing 40 parts by weight of a mixture of C.I. Pigment Red 242/C.I. Pigment Red 254/C.I. Pigment Yellow 139 (weight ratio = 45/40/15) as a pigment (A), 10 parts by weight of Disperbyk 2001 (in terms of solid content) as a dispersant and 100 parts by weight of ethyl 3-ethoxypropanoate as a solvent was mixed and dispersed with Diamond Fine Mill (trade name, a bead mill (bead diameter: 1.0 mm) manufactured by Mitsubishi Materials Corporation) for 12 hours to prepare a pigment dispersion fluid.

Subsequently, 100 parts by weight of this pigment dispersion fluid, 70 parts by weight of the copolymer (β -1) (in terms of solid content) as an alkali-soluble resin (B), 80 parts by weight of dipentaerythritol hexaacrylate as a polyfunctional monomer (C), 50 parts by weight of 2-benzyl-2-dimethyl amino-1-(4-morpholinophenyl)butanone-1 as a photopolymerization initiator (D) and 1000 parts by weight of propylene glycol monomethyl ether acetate as solvents were mixed to prepare a liquid composition (r-1).

Next, the liquid composition (r-1) was spin-coated onto a soda glass substrate having a diameter of 4 inches, the surface on which an SiO₂ film for preventing the elution of sodium ions was formed, and then the coated substrate was left to stand in a clean room at 23°C for 12 hours and dried to form a coating.

Then, this substrate was immersed in 100 cc of propylene glycol monomethyl ether acetate for 2 minutes, so that the coating was completely dissolved.

[0124]

Comparative Example 2

A liquid composition (r-2) was prepared to form a coating on a soda glass substrate in the same manner as in Comparative Example 1 except that 70 parts by weight of the copolymer (β -2) (in terms of solid content) was used in place of the copolymer (β -1).

Then, this substrate was immersed in 100 cc of propylene glycol monomethyl ether acetate for 2 minutes, so that the coating was not completely dissolved and a large amount of foreign substances was observed in the solution.

[0125]

Comparative Example 3

A liquid composition (r-3) was prepared to form a coating on a soda glass substrate in the same manner as in Comparative Example 1 except that 70 parts by weight of the copolymer (β -3) (in terms of solid content) was used in place of the copolymer (β -1).

Next, this substrate was immersed in 100 cc of polypropylene glycol monomethyl ether acetate for 2 minutes, so that the coating was completely dissolved.

[0126]

Comparative Example 4

A liquid composition (r-4) was prepared to form a coating on a soda glass substrate in the same manner as in Comparative Example 1 except that 70 parts by weight of the copolymer (β -4) (in terms of solid content) was used in place of the copolymer (β -1).

Next, this substrate was immersed in 100 cc of polyethylene glycol monomethyl ether acetate for 2 minutes, so that the coating was not completely dissolved and a large amount of foreign substances was observed in the developer.

[0127]

Example 1

A liquid composition (R-1) was prepared to form a coating on a soda glass substrate in the same manner as in Comparative Example 1 except that 70 parts by weight of the copolymer (B-1) (in terms of solid content) was used in place of the copolymer (β -1).

Next, this substrate was immersed in 100 cc of polyethylene glycol monomethyl ether acetate for 2 minutes, so that the coating was completely dissolved.

[0128]

Example 2

A liquid composition (R-2) was prepared to form a coating on a soda glass substrate in the same manner as in Comparative Example 1 except that 70 parts by weight of the copolymer (B-2) (in terms of solid content) was used in place of the copolymer (β -1).

Next, this substrate was immersed in 100 cc of polypropylene glycol monomethyl ether acetate for 2 minutes, so that the coating was completely dissolved.

[0129]

Example 3

A liquid composition (R-3) was prepared to form a coating on a soda glass substrate in the same manner as in Comparative Example 1 except that 70 parts by weight of the copolymer (B-3) (in terms of solid content) was used in place of the copolymer (β -1).

Next, this substrate was immersed in 100 cc of polypropylene glycol monomethyl ether acetate for 2 minutes, so that the coating was completely dissolved.

[0130]

Example 4

A liquid composition (R-4) was prepared to form a coating on a soda glass substrate in the same manner as in Comparative Example 1 except that 70 parts by weight of the copolymer (B-4) (in terms of solid content) was used in place of the copolymer (β -1).

Then, this substrate was immersed in 100 cc of propylene glycol monomethyl ether acetate for 2 minutes, so that the coating was completely dissolved.

[0131]

Example 5

A liquid composition (R-5) was prepared to form a coating on a soda glass substrate in the same manner as

in Comparative Example 1 except that 70 parts by weight of the copolymer (B-5) (in terms of solid content) was used in place of the copolymer (β -1).

Then, this substrate was immersed in 100 cc of propylene glycol monomethyl ether acetate for 2 minutes, so that the coating was completely dissolved.

[0132]

Example 6

A liquid composition (R-6) was prepared to form a coating on a soda glass substrate in the same manner as in Comparative Example 1 except that 70 parts by weight of the copolymer (B-6) (in terms of solid content) was used in place of the copolymer (β -1).

Then, this substrate was immersed in 100 cc of propylene glycol monomethyl ether acetate for 2 minutes, so that the coating was completely dissolved.

[0133]

[Evaluation of Coating Properties]

Comparative Example 5

The liquid composition (r-1) prepared in Comparative Example 1 was applied onto a soda glass substrate, the surface on which an SiO_2 film for preventing the elution of sodium ions was formed, by a slit-nozzle type applicator for color filter TR63210S-CL (trade name) manufactured by TOKYO OHKA KOGYO CO., LTD., and then the coated substrate was left to stand at ordinary temperature for 1 hour and dried to form a coating.

Next, a slit nozzle was blow-cleaned with propylene glycol monomethyl ether acetate, and then the liquid composition (r-1) was again applied onto a new soda glass substrate by the applicator TR63210S-CL, so that it could be applied without generating foreign substances on the resulting coating.

[0134]

Comparative Example 6

The coating properties were evaluated in the same manner as in Comparative Example 5 except that the liquid composition (r-2) prepared in Comparative Example 2 was used in place of the liquid composition (r-1), so that foreign substances were generated on the coating that was again formed and a good coating could not be formed.

[0135]

Comparative Example 7

The coating properties were evaluated in the same manner as in Comparative Example 5 except that the liquid composition (r-3) prepared in Comparative Example 3 was used in place of the liquid composition (r-1), so that the liquid composition (r-3) could be applied without generating foreign substances on the resulting coating.

[0136]

Comparative Example 8

The coating properties were evaluated in the same manner as in Comparative Example 5 except that the liquid composition (r-4) prepared in Comparative Example 4 was

used in place of the liquid composition (r-1), so that foreign substances were generated on the coating that was again formed and a good coating could not be formed.

[0137]

Example 7

The coating properties were evaluated in the same manner as in Comparative Example 5 except that the liquid composition (R-1) prepared in Example 1 was used in place of the liquid composition (r-1), so that the liquid composition (R-1) could be applied without generating foreign substances on the resulting coating.

[0138]

Example 8

The coating properties were evaluated in the same manner as in Comparative Example 5 except that the liquid composition (R-2) prepared in Example 2 was used in place of the liquid composition (r-1), so that the liquid composition (R-2) could be applied without generating foreign substances on the resulting coating.

[0139]

Example 9

The coating properties were evaluated in the same manner as in Comparative Example 5 except that the liquid composition (R-3) prepared in Example 3 was used in place of the liquid composition (r-1), so that the liquid composition (R-3) could be applied without generating foreign substances on the resulting coating.

[0140]

Example 10

The coating properties were evaluated in the same manner as in Comparative Example 5 except that the liquid composition (R-4) prepared in Example 4 was used in place of the liquid composition (r-1), so that the liquid composition (R-4) could be applied without generating foreign substances on the resulting coating.

[0141]

Example 11

The coating properties were evaluated in the same manner as in Comparative Example 5 except that the liquid composition (R-5) prepared in Example 5 was used in place of the liquid composition (r-1), so that the liquid composition (R-5) could be applied without generating foreign substances on the resulting coating.

[0142]

Example 12

The coating properties were evaluated in the same manner as in Comparative Example 5 except that the liquid composition (R-6) prepared in Example 6 was used in place of the liquid composition (r-1), so that the liquid composition (R-6) could be applied without generating foreign substances on the resulting coating.

[0143]

[Evaluation of Burn-in]

Comparative Example 9

The liquid composition (r-1) prepared in Comparative Example 1 was spin-coated onto a soda glass substrate, the surface on which an SiO_2 film for preventing the elution of sodium ions was formed and an ITO (indium-tin oxide alloy) electrode was vapor-deposited in a predetermined shape, and then the coated substrate was pre-baked in a clean oven at 90°C for 10 minutes to form a coating having a film thickness of $2.0\ \mu\text{m}$.

Next, the coating was exposed with radiation having each wavelength of 365 nm, 405 nm and 436 nm at an exposure amount of $5000\ \text{J}/\text{m}^2$ not through a photomask using a high pressure mercury lamp. Then, this substrate was immersed in a developer of a 0.04 wt% aqueous solution of potassium hydroxide at 23°C for 1 minute to perform development, and rinsed with ultrapure water and air-dried. The obtained substrate was further post-baked at 250°C for 30 minutes to cure the coating, and a red pixel was formed on the substrate. The film thickness of this pixel was $1.60\ \mu\text{m}$.

Then, the substrate having this pixel formed thereon and a substrate in which an ITO electrode was only vapor-deposited in a predetermined shape were laminated with a sealing agent containing the mixed glass beads each having a diameter of 0.8 mm, and then a liquid crystal MLC 6608 (trade name) manufactured by Merck Ltd. was injected into the obtained laminate to fabricate a liquid crystal cell.

Subsequently, the obtained liquid crystal cell was placed in a thermostatic chamber at 60°C and the voltage retention of the liquid crystal cell was measured with a liquid crystal voltage retention measurement system model VHR-1A (trade name) manufactured by Toyo Technical Co., Ltd. In this case, the applied voltage was a square wave of 5.5 V and the measured frequency was 60 Hz. The term "voltage retention" as used herein refers to a value of (Potential difference of liquid crystal cell 16.7 msec after application/Voltage applied at 0 msec). As a result, the voltage retention was 91%.

When the voltage retention of a liquid crystal cell is less than 90%, the liquid crystal cell cannot retain the applied voltage at a predetermined level for a period of time of 16.7 msec, which means that the liquid crystal cannot be sufficiently orientated. Accordingly, a liquid crystal display device provided with a color filter formed using the liquid composition (r-1) has a low possibility of causing "burn-in".

[0144]

Comparative Example 10

A liquid crystal cell was fabricated in the same manner as in Comparative Example 9 except that the liquid composition (r-2) prepared in Comparative Example 2 was used in place of the liquid composition (r-1), and the voltage retention was measured to be 50%. Accordingly, a liquid crystal display device provided with a color

filter formed using the liquid composition (r-2) has a high possibility of causing "burn-in".

[0145]

Comparative Example 11

A liquid crystal cell was fabricated in the same manner as in Comparative Example 9 except that the liquid composition (r-3) prepared in Comparative Example 3 was used in place of the liquid composition (r-1), and the voltage retention was measured to be 45%. Accordingly, a liquid crystal display device provided with a color filter formed using the liquid composition (r-3) has a high possibility of causing "burn-in".

[0146]

Comparative Example 12

A liquid crystal cell was fabricated in the same manner as in Comparative Example 9 except that the liquid composition (r-4) prepared in Comparative Example 4 was used in place of the liquid composition (r-1), and the voltage retention was measured to be 92%. Accordingly, a liquid crystal display device provided with a color filter formed using the liquid composition (r-4) has a low possibility of causing "burn-in".

[0147]

Example 13

A liquid crystal cell was fabricated in the same manner as in Comparative Example 9 except that the liquid composition (R-1) prepared in Example 1 was used in place

of the liquid composition (r-1), and the voltage retention was measured to be 92%. Accordingly, a liquid crystal display device provided with a color filter formed using the liquid composition (R-1) has a low possibility of causing "burn-in".

[0148]

Example 14

A liquid crystal cell was fabricated in the same manner as in Comparative Example 9 except that the liquid composition (R-2) prepared in Example 2 was used in place of the liquid composition (r-1), and the voltage retention was measured to be 91%. Accordingly, a liquid crystal display device provided with a color filter formed using the liquid composition (R-2) has a low possibility of causing "burn-in".

[0149]

Example 15

A liquid crystal cell was fabricated in the same manner as in Comparative Example 9 except that the liquid composition (R-3) prepared in Example 3 was used in place of the liquid composition (r-1), and the voltage retention was measured to be 93%. Accordingly, a liquid crystal display device provided with a color filter formed using the liquid composition (R-3) has a low possibility of causing "burn-in".

[0150]

Example 16

A liquid crystal cell was fabricated in the same manner as in Comparative Example 9 except that the liquid composition (R-4) prepared in Example 4 was used in place of the liquid composition (r-1), and the voltage retention was measured to be 94%. Accordingly, a liquid crystal display device provided with a color filter formed using the liquid composition (R-4) has a low possibility of causing "burn-in".

[0151]

Example 17

A liquid crystal cell was fabricated in the same manner as in Comparative Example 9 except that the liquid composition (R-5) prepared in Example 5 was used in place of the liquid composition (r-1), and the voltage retention was measured to be 95%. Accordingly, a liquid crystal display device provided with a color filter formed using the liquid composition (R-5) has a low possibility of causing "burn-in".

[0152]

Example 18

A liquid crystal cell was fabricated in the same manner as in Comparative Example 9 except that the liquid composition (R-6) prepared in Example 6 was used in place of the liquid composition (r-1), and the voltage retention was measured to be 93%. Accordingly, a liquid crystal display device provided with a color filter

formed using the liquid composition (R-6) has a low possibility of causing "burn-in".

[0153]

The evaluation results were summarized together with the type of copolymers in Table 1.

In Table 1, A and B in each evaluation item mean as follows.

Immersion Test

A: Coating was completely dissolved,

B: Generation of foreign substances in a solution

Coating Properties

A: No generation of foreign substances during next application

B: Generation of foreign substances during next application

Burn-in

A: when voltage retention $\geq 90\%$, the possibility of causing "burn-in" is low,

B: when voltage retention $< 90\%$, the possibility of causing "burn-in" is high.

Here, a radiation-sensitive resin composition prepared using a red pigment was evaluated, however, the similar results could also be obtained in the case of a radiation-sensitive resin composition prepared using a blue, green, yellow or black pigment.

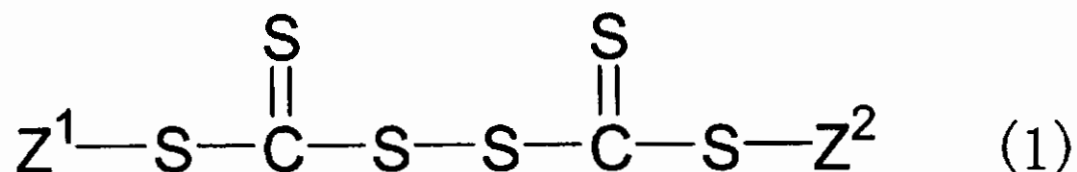
[0154]

[Table 1]

		Copolymer		Immersion test	Coating properties	Burn-in (voltage retention)
		Mw	Mw/Mn			
Comparative Example 1/5/9	β-1	5200	1.4	A	A	A (91%)
Comparative Example 2/6/10	β-2	10500	1.9	B (Generation of foreign substances)	B (Generation of foreign substances)	B (50%)
Comparative Example 3/7/11	β-3	5000	3.6	A	A	B (45%)
Comparative Example 4/8/12	β-4	14000	2.1	B (Generation of foreign substances)	B (Generation of foreign substances)	A (92%)
Example 1/7/13	B-1	5000	1.5	A	A	A (92%)
Example 2/8/14	B-2	5200	1.4	A	A	A (91%)
Example 3/9/15	B-3	5250	1.6	A	A	A (93%)
Example 4/10/16	B-4	5400	1.5	A	A	A (94%)
Example 5/11/17	B-5	5500	1.5	A	A	A (95%)
Example 6/12/18	B-6	5400	1.5	A	A	A (93%)

CLAIMS:

1. A radiation-sensitive resin composition for forming a colored layer, comprising (A) a colorant, (B) an alkali-soluble resin, (C) a polyfunctional monomer and (D) a photopolymerization initiator, wherein the alkali-soluble resin (B) comprises a copolymer produced by polymerizing a polymerizable unsaturated compound comprising (b1) at least one selected from the group consisting of polymerizable unsaturated carboxylic acids and polymerizable unsaturated carboxylic acid anhydrides in the presence of a compound represented by the following formula (1):



wherein Z^1 and Z^2 represent, independently of each other, an alkyl group having 4 to 18 carbon atoms or an optionally substituted benzyl group.

2. The radiation-sensitive resin composition for forming the colored layer according to claim 1, wherein the copolymer according to claim 1 constituting the alkali-soluble resin (B) is a copolymer produced by living radical polymerization.

3. The radiation-sensitive resin composition for forming the colored layer according to claim 1, wherein the copolymer according to claim 1 constituting the alkali-soluble resin (B) is a copolymer having a weight average molecular weight (M_w) in terms of polystyrene as measured by gel permeation chromatography (GPC) of 1,000 to 10,000 and the ratio of M_w to a number average molecular weight (M_n) in terms of polystyrene as measured by gel permeation chromatography (GPC) (M_w/M_n) of 1.0 to 2.0.

4. A color filter provided with a colored layer formed using the radiation-sensitive resin composition for forming the colored layer according to any of claims 1 to 3.

5. A color liquid crystal display device comprising the color filter according to claim 4.