RADIATION-SENSITIVE COMPOSITION FOR FORMING COLORED LAYER, COLOR FILTER AND COLOR LIQUID CRYSTAL DISPLAY DEVICE

BACKGROUND OF THE INVENTION

Field of the Invention

[0001]

The present invention relates to a radiation-sensitive composition for forming a colored layer, a color filter and a color liquid crystal display device, and more specifically, to a radiation-sensitive composition used in the formation of a colored layer which is useful 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 by using the radiation-sensitive 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 composition, a method including forming a coating of a colored radiation-sensitive 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 with an alkali developer to dissolve and remove unexposed portions, and then performing post-baking by using a clean oven or a hot plate to obtain pixels of colors (see, for example, JP-A-2-144502 and JP-A-3-53201) is known.

Since the size of a substrate used for forming a color filter has been increased in recent years, a coating method of a radiation-sensitive 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 with a smaller diameter for applying a radiation-sensitive composition. In the latter slit-nozzle system, a radiation-sensitive composition remains on the periphery of a nozzle tip end in many cases after completing the coating due to the small diameter (narrowness) of the liquid ejection portion, and when this composition is dried, it drops on a color filter as a dry foreign substance 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, but deterioration of the quality of the color filter due to dry foreign substances can not yet be effectively prevented, which becomes a main factor of reduction in product yield.

Accordingly, in order to cope with such a problem, a radiation-sensitive composition for a color filter 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, when the concentration of a colorant contained in a colored radiation-sensitive composition is increased with the increasing color purity of a color liquid crystal display device, there is a tendency that the solubility of a coating in an alkali developer is significantly decreased. Therefore, during developing by a shower development method, a coating on unexposed portions which was once stripped and removed cannot be completely dissolved, and the coating floats in a developing tank and is redeposited on a color filter as a foreign substance, which becomes a main factor of reduction in product yield.

[0004]

Furthermore, it has been recently required for a color liquid crystal display 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, and is a phenomenon where an image which should not be displayed is displayed on a screen, or black or white "haze" is overlappingly displayed on an image to be displayed. It is considered

that such a phenomenon is 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", but there is also a possibility that impurities are derived from components other than pigments in a colored radiation-sensitive composition, and therefore it cannot be always said that it is sufficient to only increase the pigment purity.

Therefore, the development of a further improved colored radiation-sensitive 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.

SUMMARY OF THE INVENTION

[0005]

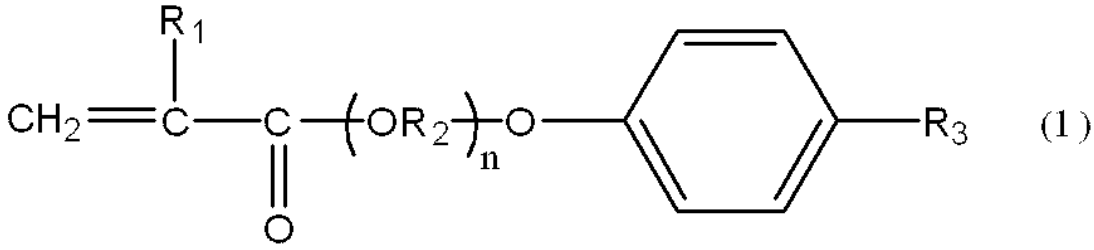
An object of the present invention is to provide a radiation-sensitive composition for forming a colored layer which can form a color filter not causing "burn-in" at a high product yield, and can form a coating having

high solubility in a cleaning solvent even after drying and high solubility in an alkali developer, and the like.

[0006]

Firstly, the present invention provides a radiation-sensitive 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) is a copolymer of an unsaturated compound (hereinafter, referred to as "copolymer (B1)") containing (b1) one selected from the group consisting of unsaturated carboxylic acids and acid anhydrides thereof, and unsaturated phenol compounds, (b2) a maleimide substituted at N-position, and (b3) an unsaturated compound represented by the following formula (1).

[0007]



(1)

[0008]

wherein R_1 represents a hydrogen atom or a methyl group; R_2 represents an alkylene group having 2 to 4 carbon atoms; R_3 represents a hydrogen atom, an alkyl group having 1 to 20 carbon atoms or an aralkyl group having 7

to 20 carbon atoms; and n represents an integer of 1 to 10.

[0009]

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

[0010]

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

Fourthly, the present invention provides a copolymer (B1).

[0011]

The radiation-sensitive composition for forming the colored layer of the present invention 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, and therefore is also suitable, for example, for application with a slit nozzle. In addition, even when the concentration of a colorant contained in the colored radiation-sensitive composition is high, the solubility of a coating in an alkali developer is high and therefore is also suitable, for example, for development by a shower development method.

The copolymer (B1) of the invention is useful as an alkali soluble resin for use in the radiation-sensitive composition for forming the colored layer.

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

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0012]

Hereinafter, the present invention will be described in detail.

Radiation-sensitive Composition for Forming Colored Layer

- (A) Colorant -

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

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

[0013]

C.I. Pigment Yellow 12, C.I. Pigment Yellow 13, C.I. Pigment Yellow 14, C.I. Pigment Yellow 17, C.I. Pigment

Yellow 20, C.I. Pigment Yellow 24, C.I. Pigment Yellow 31, C.I. Pigment Yellow 55, C.I. Pigment Yellow 83, C.I. Pigment Yellow 93, C.I. Pigment Yellow 109, C.I. Pigment Yellow 110, C.I. Pigment Yellow 138, C.I. Pigment Yellow 139, C.I. Pigment Yellow 150, C.I. Pigment Yellow 153, C.I. Pigment Yellow 154, C.I. Pigment Yellow 155, C.I. Pigment Yellow 166, C.I. Pigment Yellow 168, and C.I. Pigment Yellow 211;

[0014]

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;

[0015]

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;

[0016]

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.

[0017]

Among these organic pigments, at least one selected from 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 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 is preferred.

The above organic pigments can be used alone or as a mixture of two or more thereof, and although the organic pigment and carbon black can also be mixed for use, the 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.

[0018]

The radiation-sensitive composition for forming the colored layer of the present invention can form a coating having high solubility in an alkali developer even when the content of a colorant is 30 wt% or more in the total solid content of the composition. Further, in the present invention, the upper limit of the colorant content is preferably 70 wt% or less, and particularly preferably 60 wt% or less in the total solid content of the radiation-sensitive composition, from the viewpoint of achieving developability. The term "solid content" as used herein refers to components except solvents later described.

[0019]

When the colorant is a pigment in the composition of 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, with 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.

[0020]

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

The above urethane bond is generally represented by the formula R-NH-COO-R_4 (wherein, R and R_4 each independently represent a monovalent or polyvalent, aliphatic, alicyclic or aromatic organic group, and the polyvalent organic group is further bound 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 the 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.

[0021]

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 the both ends.

Examples of the diisocyanates include 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.

[0022]

Examples of the triisocyanates include 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 alone or as a mixture of two or more thereof.

[0023]

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

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

[0024]

As the urethane-based dispersant in the present invention, reaction products of aromatic diisocyanates with polylactones having a hydroxyl group at one end and/or polylactones having hydroxyl groups at the 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 the both ends are particularly 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)), and Disperon (produced by Kusumoto Chemicals, Ltd.).

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 alone or as a mixture of two or more thereof.

[0025]

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 alone or as a mixture of two or more thereof.

[0026]

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 particularly preferably 10 to 50 parts by weight, based on 100 parts

by weight of a pigment. In this case, 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 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.

[0027]

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

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 with a roll mill, the preparation can be preferably

performed by treating, for example, with a three roll mill or a two roll mill, a pigment mixed solution while cooling with cooling water or the like.

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.

[0028]

- (B) Alkali-Soluble Resin -

The alkali-soluble resin in the present invention contains a copolymer (B1) containing (b1) at least one selected from the group consisting of unsaturated carboxylic acids and acid anhydrides thereof, and unsaturated phenol compounds (hereinafter, these compounds are collectively referred to as "unsaturated compound (b1)"), (b2) a maleimide substituted at N-position (hereinafter, referred to as "unsaturated compound (b2)"), and (b3) an unsaturated compound represented by the above formula (1) (hereinafter, referred to as "unsaturated compound (b3)"), and is a component soluble in an alkali developer used in the developing treatment process when forming a colored layer.

[0029]

Examples of the unsaturated carboxylic acids and acid anhydrides thereof in 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 at the both ends such as ω-carboxypolycaprolactone mono(meth)acrylate.

Among these unsaturated carboxylic acids and acid anhydrides thereof, mono(2-acryloyloxyethyl) succinate and mono(2-acryloyloxyethyl) phthalate are commercially available under the respective trade names Light Ester HOA-MS and Light Ester HOA-MPA (all produced by KYOEISHA CHEMICAL CO., LTD.).

[0030]

Further, examples of the unsaturated phenol compounds include:

unsaturated phenols such as o-vinylphenol, m-vinylphenol, p-vinylphenol, 2-methyl-4-vinylphenol, 3-

methyl-4-vinylphenol, o-isopropenylphenol, m-isopropenylphenol and p-isopropenylphenol; and

unsaturated naphthols such as 2-vinyl-1-naphthol, 3-vinyl-1-naphthol, 1-vinyl-2-naphthol, 3-vinyl-2-naphthol, 2-isopropenyl-1-naphthol and 3-isopropenyl-1-naphthol.

[0031]

In the present invention, as the unsaturated compound (b1), (meth)acrylic acid, p-vinylphenol and the like are preferred, and (meth)acrylic acid is particularly preferred.

[0032]

Examples of the unsaturated compound (b2) include:

N-phenylmaleimide, N-o-hydroxyphenylmaleimide, N-m-hydroxyphenylmaleimide, N-p-hydroxyphenylmaleimide, N-benzylmaleimide, N-cyclohexylmaleimide, N-succinimidyl-3-maleimide benzoate, N-succinimidyl-4-maleimide butyrate, N-succinimidyl-6-maleimide caproate, N-succinimidyl-3-maleimide propionate, and N-(acridinyl)maleimide.

Among these maleimides substituted at N-position, N-phenylmaleimide, N-cyclohexylmaleimide and the like are preferred, and N-phenylmaleimide is particularly preferred.

In the copolymer (B1), the unsaturated compound (b2) can be used alone or as a mixture of two or more thereof.

[0033]

In the present invention, a radiation-sensitive composition for forming a colored layer which can form a

coating having high solubility in a cleaning solvent even after drying and high solubility in an alkali developer can be obtained by copolymerizing an unsaturated compound (b3) represented by the above formula (1) in an alkali-soluble resin.

[0034]

In the formula (1), examples of the alkyl group having 1 to 20 carbon atoms of R_3 include linear, branched or cyclic alkyl groups such as a methyl group, an ethyl group, an n-propyl group, an i-propyl group, an n-butyl group, an i-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, an n-dodecyl group, a cyclopentyl group and a cyclohexyl group.

Further, in the formula (1), examples of the aralkyl group having 7 to 20 carbon atoms of R_3 include phenyl C_{1-6} alkyl groups such as a benzyl group, a phenetyl group, an α-methylbenzyl group and a 2-phenylpropane-2-yl group.

[0035]

In the formula (1), R_3 is preferably the aralkyl group having 7 to 20 carbon atoms, and particularly preferably a 2-phenylpropane-2-yl group.

Further, in the formula (1), examples of the alkylene group having 2 to 4 carbon atoms of R_2 include an ethylene group, a propylene group, a trimethylene group, a butylene group and a tetramethylene group, but

an ethylene group and a propylene group are particularly preferred.

Furthermore, in the formula (1), n is preferably 1 to 6, and particularly preferably 1 to 4.

[0036]

Examples of the unsaturated compound (b3) include phenol ethylene oxide (EO)-modified (meth)acrylate, paracumylphenol EO-modified (meth)acrylate, and nonylphenol EO-modified (meth)acrylate or nonylphenol propylene oxide (PO)-modified (meth)acrylate.

Among these unsaturated compounds (b3), phenol EO-modified acrylate is commercially available under the trade names Aronix M-101A (n=about 2) and M-102 (n=about 4), paracumylphenol EO-modified acrylate is commercially available under the trade name Aronix M-110 (n=about 1), nonylphenol EO-modified acrylate is commercially available under the trade names Aronix M-111 (n=about 1) and M-113 (n=about 4), and nonylphenol PO-modified acrylate is commercially available under the trade name Aronix M-117 (all produced by TOAGOSEI CO., LTD.).

[0037]

In the present invention, unsaturated compounds used for synthesis of the copolymer (B1) can further contain, in addition to the unsaturated compound (b1), the unsaturated compound (b2) and the unsaturated compound (b3), other unsaturated compounds copolymerizable with

these compounds (hereinafter, referred to as "unsaturated compounds (b4)").

Examples of the unsaturated compounds (b4) include:

aromatic vinyl compounds such as styrene, α-methylstyrene, 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;

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

[0038]

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 and glycerol (meth)acrylate;

[0039]

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.

[0040]

Among these unsaturated compounds (b4), styrene, macromonomers, methyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, 2-hydroxylethyl (meth)acrylate, allyl (meth)acrylate, benzyl (meth)acrylate, cyclohexyl (meth)acrylate, phenyl (meth)acrylate, isobornyl (meth)acrylate, tricyclo[5.2.1.$0^{2,6}$]decane-8-yl (meth)acrylate, glycerol mono(meth)acrylate and the like are preferred, and among the macromonomers, polystyrene macromonomer and polymethyl (meth)acrylate macromonomer are particularly preferred.

In the copolymer (B1), the unsaturated compound (b4) can be used alone or as a mixture of two or more thereof.

[0041]

In the copolymer (B1), the copolymerization ratio of the unsaturated compound (b1) is preferably 10 to 40 wt%, and particularly preferably 10 to 25 wt%, the copolymerization ratio of the unsaturated compound (b2) is preferably 10 to 50 wt%, and particularly preferably 15 to 40 wt%, the copolymerization ratio of the unsaturated compound (b3) is preferably 5 to 50 wt%, and particularly preferably 10 to 40 wt%, and the copolymerization ratio of the unsaturated compound (b4) is preferably 5 to 70 wt%, and particularly preferably 10 to 60 wt%.

In the present invention, a radiation-sensitive composition for forming a colored layer which is excellent in sensitivity, adhesion to a substrate, cleaning performance by an organic solvent, solubility in an alkali developer and the like can be obtained by setting the copolymerization ratio of each of the unsaturated compounds in the copolymer (B1) in the above range.

[0042]

In the present invention, other alkali-soluble resins can be used together with the copolymer (B1).

The other alkali-soluble resins are not particularly limited as long as they are soluble in an alkali developer used in the developing treatment process when forming a colored layer, but examples thereof include a copolymer of at least one selected from the group consisting of the above unsaturated compounds (b1) with at least one selected from the group consisting of the above unsaturated compounds (b2) and the above unsaturated compounds (b4).

[0043]

In the present invention, the copolymer (B1) and other alkali-soluble resin each have a Mw of preferably 1,000 to 25,000, more preferably 3,000 to 20,000, and particularly preferably 3,000 to 12,000.

Further, the copolymer (B1) and other alkali-soluble resin each have a Mw/Mn of preferably 1.0 to 2.2, more

preferably 1.0 to 2.0, and particularly preferably 1.0 to 1.8.

In the present invention, the copolymer (B1) having the specific Mw and/or Mw/Mn is used, or the copolymer (B1) and the other alkali-soluble resin having the specific Mw and/or Mw/Mn can be used in combination to thereby obtain a radiation-sensitive composition excellent in developability. Thereby, a pixel or a black matrix having a sharp pattern edge can be formed, and simultaneously high production yield can be realized without causing dry foreign substances during the production of a color filter due to high cleaning performance of an organic solvent, and "burn-in" of a color filter can be more effectively prevented.

[0044]

Further, according to the present inventors, when an unsaturated compound (b3) represented by the above formula (1) is copolymerized into an alkali-soluble resin (B), the polymerization conversion tends to be reduced. When the polymerization conversion is reduced and an unreacted unsaturated compound remains, electrical characteristics of the colored layer obtained may be deteriorated, and therefore it is necessary to control this unreacted unsaturated compound. In the production of the copolymer (B1), the polymerization conversion is preferably 80 wt% or more, and more preferably 90 wt% or more, and particularly preferably 95 wt% or more. The

term "polymerization conversion" as used herein refers to a ratio of the weight of a copolymer (B1) obtained by polymerization reaction to the total weight of each component constituting a copolymer (B1) subjected to the polymerization reaction.

[0045]

A production method in which the Mw, Mn and polymerization conversion of a copolymer (B1) are controlled within the above range includes, for example, living radical polymerization. The living radical polymerization can be performed by polymerizing each unsaturated compound in the presence of a radical polymerization initiator such as 2,2'-azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile) or 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), and a molecular weight controlling agent which acts as an iniferter such as cyano(dimethyl)methyl pyrazole-1-dithiocarboxylate, benzyl pyrazole-1-dithiocarboxylate, tetraethylthiuram disulfide, bis(pyrazole-1-ylthiocarbonyl) disulfide, bis(3-methyl-pyrazole-1-ylthiocarbonyl) disulfide, bis(4-methyl-pyrazole-1-ylthiocarbonyl) disulfide, bis(5-methyl-pyrazole-1-ylthiocarbonyl) disulfide, bis(3,4,5-trimethyl-pyrazole-1-ylthiocarbonyl) disulfide, bis(pyrrole-1-ylthiocarbonyl) disulfide, bisthiobenzoyl disulfide, bis(n-octylmercapto-thiocarbonyl) disulfide, bis(n-dodecylmercapto-thiocarbonyl) disulfide, or

bis(benzylmercapto-thiocarbonyl) disulfide (appended), in an inert solvent at a reaction temperature of usually 0 to 150°C, and preferably 50 to 120°C.

[0046]

In the present invention, the copolymer (B1) can be used alone or as a mixture of two or more thereof, and other alkali-soluble resins can also be similarly used.

In the present invention, the total amount of alkali-soluble resins 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). In this case, when the total amount of alkali-soluble resins used is less than 10 parts by weight, for example, alkali developability may be deteriorated, and/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 exceeds 1,000 parts by weight, it may become difficult to achieve color density to be aimed as a film since the colorant concentration relatively decreases.

Further, the ratio of the copolymer (B1) used in the alkali-soluble resins is preferably 10 to 100 wt%, and particularly preferably 30 to 100 wt%. In this case, when the ratio of the copolymer (B1) used is less than 10 wt%, expected effect of the present invention may be impaired.

[0047]

- (C) Polyfunctional Monomer -

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

Examples of the polyfunctional monomer include:

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

di(meth)acrylates of polyalkylene glycols such as polyethylene glycol and 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 such as polyesters, epoxy resins, urethane resins, alkyd resins, silicone resins and spirane 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.

[0048]

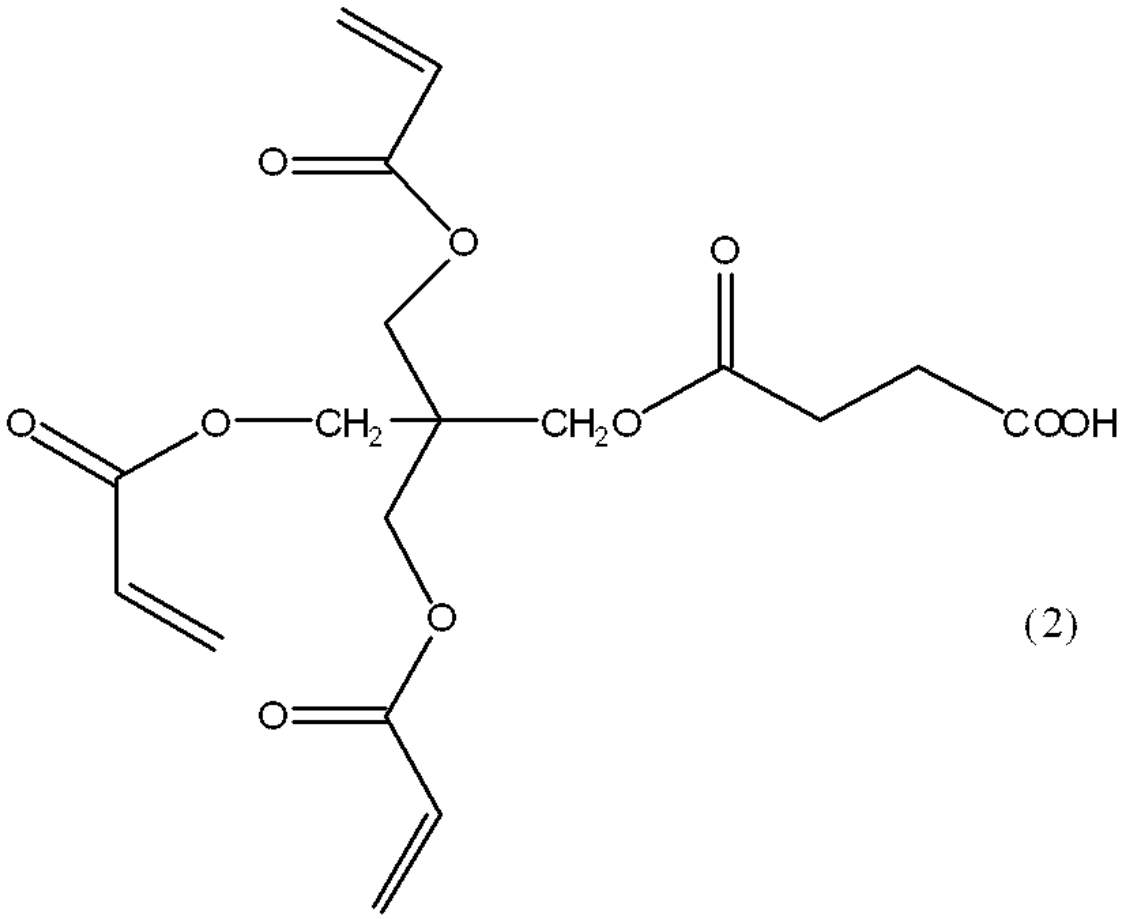
Among these polyfunctional monomers, poly(meth)acrylate of polyhydric alcohols having three or more valences and the dicarboxylic acid-modified compounds thereof are preferred. Specifically, preferred

examples thereof include trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, pentaerythritol triacrylate, pentaerythritol trimethacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, dipentaerythritol pentaacrylate, dipentaerythritol pentamethacrylate, dipentaerythritol hexaacrylate, dipentaerythritol hexamethacrylate;

[0049]

a compound represented by the following formula (2):

[0050]

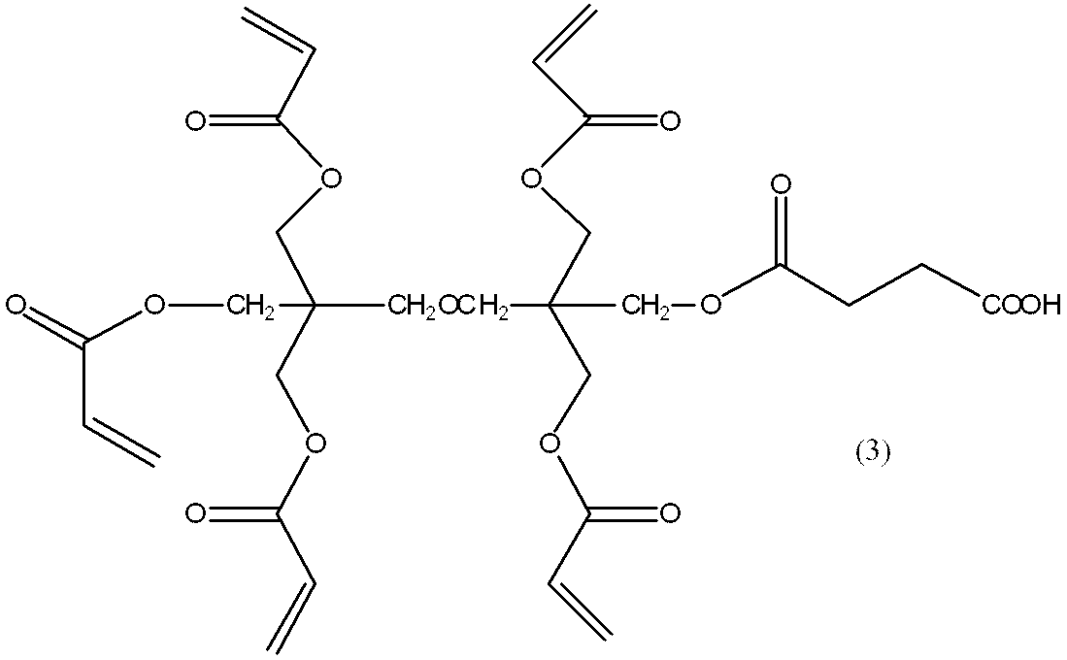


(2)

[0051]

and a compound represented by the following formula (3):

[0052]



(3)

[0053]

Particularly preferred are trimethylolpropane triacrylate, pentaerythritol triacrylate and dipentaerythritol hexaacrylate because the colored layer has high strength and excellent surface smoothness, and scumming, film residues and the like are hard to occur on the unexposed portions of a substrate and on a light shielding layer.

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

[0054]

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 alkali-soluble resin (B). In this case, when the amount of the polyfunctional monomer used is too small, the strength or surface smoothness of the colored layer may be deteriorated. On the other hand, when the amount is too large, for example, alkali developability may be deteriorated, or scumming, film residues and the like may occur on the unexposed portions of a substrate and on a light shielding layer.

[0055]

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 polyfunctional monomer include M-5600 (trade name, produced by TOAGOSEI CO., LTD.) as a commercial product in addition to those same as the compounds exemplified by the unsaturated compounds (b1) or the unsaturated compounds (b4) in the alkali-soluble resin (B), N-(meth)acryloylmorpholine, N-vinylpyrrolidone, N-vinyl-ε-caprolactam.

These monofunctional monomers can be used alone 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. In this case, when the ratio of the monofunctional monomers used is too large, the strength or surface smoothness of the obtained colored layer may be insufficient.

[0056]

The total amount of a polyfunctional monomer and a monofunctional 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 alkali-soluble resin (B). In this case, when the total amount used is too small, the strength or surface smoothness of the colored layer may be deteriorated. On the other hand, when the total amount is too large, for example, alkali developability may be deteriorated, or scumming, film residues and the like may occur on the unexposed portions of a substrate and on a light shielding layer.

[0057]

- (D) Photopolymerization Initiator -

The photopolymerization initiator (D) in the present invention is a compound which generates active species which can start polymerization of the above 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, O-acyloxime compounds, onium salt compounds, benzoin compounds, benzophenone compounds, α-diketone compounds, multinuclear quinone compounds, xanthone compounds, diazo compounds and imide sulfonate compounds. These compounds are components which generate active radicals or active acids, or both thereof by exposure.

[0058]

In the present invention, a photopolymerization initiator can be used alone or as a mixture of two or more thereof, but as the photopolymerization initiator in the present invention, at least one selected from the group consisting of acetophenone compounds, biimidazole compounds, triazine compounds and O-acyloxime compounds is preferred.

[0059]

In the present invention, the general amount of the photopolymerization initiator used is usually 0.01 to 120 parts by weight and preferably 1 to 100 parts by weight, based on 100 parts by weight of the total of a polyfunctional monomer (C) and a monofunctional monomer. In this case, when the amount of the photopolymerization initiator used is too small, curing by exposure becomes insufficient, it may be difficult to obtain a color filter in which a colored layer pattern is arranged

according to a predetermined pattern. On the other hand, when the amount is too large, the formed colored layer may easily fall off from a substrate during development.

[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-morpholinopropan-1-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butan-1-one, 1-hydroxycyclohexyl phenyl ketone and 2,2-dimethoxy-1,2-diphenylethane-1-one and 1,2-octanedione.

Among these acetophenone compounds, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butane-1-one, 1,2-octanedione and the like are particularly preferred.

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

[0061]

In the present invention, when an acetophenone compound is used as a photopolymerization initiator, the amount used is usually 0.01 to 80 parts by weight, preferably 1 to 70 parts by weight and more preferably 1 to 60 parts by weight, based on 100 parts by weight of the total of a polyfunctional monomer (C) and a monofunctional monomer. In this case, when the amount of the acetophenone compound used is too small, curing by

exposure becomes insufficient, it may be difficult to obtain a color filter in which a colored layer pattern is arranged according to a predetermined pattern. On the other hand, when the amount is too large, the formed colored layer may easily fall off from a substrate during development.

[0062]

Further, specific examples of the above 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.

[0063]

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 particularly preferred.

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

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

[0064]

In the present invention, when a biimidazole compound is used as a photopolymerization initiator, the amount used is usually 0.01 to 40 parts by weight, preferably 1 to 30 parts by weight and 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. In this case, when the amount of the biimidazole compound used is too small, curing by exposure becomes insufficient, and it may become

difficult to obtain a color filter in which a colored layer pattern is arranged according to a predetermined pattern. On the other hand, when the amount is too large, the formed colored layer may easily fall off from a substrate and film roughness may easily occur on the colored layer surface during development.

[0065]

In the present invention, when a biimidazole compound is used as a photopolymerization initiator, the following hydrogen donors are preferably used together with it because 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.

[0066]

The above mercaptan compound includes 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 above amine compound includes 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 at the same time.

[0067]

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 thereof, 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 at least one free mercapto group remains, one or more of the remaining mercapto group(s) may be substituted with an alkyl, aralkyl or aryl group, and further as long as at least one free mercapto group remains, 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.

[0068]

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 particularly preferred.

[0069]

Further, the amine hydrogen donor can have one or more benzene rings or heterocyclic rings, and can have both thereof, 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 phenoxycarbonyl group, a nitrile group or the like.

[0070]

Specific examples of such an amine hydrogen donor include 4,4'-bis(dimethylamino)benzophenone, 4,4'-

bis(diethylamino)benzophenone, 4-diethyl aminoacetophenone, 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 particularly preferred.

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

[0071]

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

Specific examples of the combination of the mercaptan hydrogen donor and the 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 particularly preferred combination is 2-mercaptobenzothiazole/4,4'-bis(diethylamino)benzophenone.

In the combination of the mercaptan hydrogen donor and the 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.

[0072]

In the present invention, when the hydrogen donor is used together with a biimidazole compound, the amount used is preferably 0.01 to 40 parts by weight, more preferably 1 to 30 parts by weight and particularly 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. In this case, when the amount of the hydrogen donor used is too small, the effect of improving the sensitivity tends to decrease. On the other hand, when the amount is too large, the formed colored layer may easily fall off from a substrate during development.

[0073]

Further, specific examples of the above triazine compounds include triazine compounds each 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.

[0074]

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

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

[0075]

In the present invention, when a triazine compound is used as a photopolymerization initiator, the amount used is preferably 0.01 to 40 parts by weight, more preferably 1 to 30 parts by weight and particularly 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. In this case, when the amount of the triazine compound used is too small, curing by exposure becomes insufficient, and it may become

difficult to obtain a color filter in which a colored layer pattern is arranged according to a predetermined pattern. On the other hand, when the amount is too large, the formed colored layer may easily fall off from a substrate during development.

[0076]

Further, specific examples of the above O-acyloxime compounds include 1-[4-(phenylthio)phenyl]-heptane-1,2-dione 2-(O-benzoyloxime), 1-[4-(phenylthio)phenyl]-octane-1,2-dione 2-(O-benzoyloxime), 1-[4-(benzoyl)phenyl]-octane-1,2-dione 2-(O-benzoyloxime), 1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-ethanone 1-(O-acetyloxime), 1-[9-ethyl-6-(3-methylbenzoyl)-9H-carbazol-3-yl]-ethanone 1-(O-acetyloxime), 1-(9-ethyl-6-benzoyl-9H-carbazol-3-yl)-ethanone 1-(O-acetyloxime), ethanone-1-[9-ethyl-6-(2-methyl-4-tetrahydrofuranylbenzoyl)-9H-carbazol-3-yl]-1-(O-acetyloxime), ethanone-1-[9-ethyl-6-(2-methyl-4-tetrahydropyranylbenzoyl)-9H-carbazol-3-yl]-1-(O-acetyloxime), ethanone-1-[9-ethyl-6-(2-methyl-5-tetrahydrofuranylbenzoyl)-9H-carbazol-3-yl]-1-(O-acetyloxime), ethanone-1-[9-ethyl-6-(2-methyl-5-tetrahydropyranylbenzoyl)-9H-carbazol-3-yl]-1-(O-acetyloxime), ethanone-1-[9-ethyl-6-{2-methyl-4-(2,2-dimethyl-1,3-dioxolanyl)benzoyl}-9H-carbazol-3-yl]-1-(O-acetyloxime), ethanone-1-[9-ethyl-6-(2-methyl-4-tetrahydrofuranylmethoxybenzoyl)-9H-carbazol-3-yl]-1-(O-

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

[0077]

Among these O-acyloxime compounds, 1-[4-(phenylthio)phenyl]-octane-1,2-dione 2-(O-benzoyloxime), 1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-ethanone 1-(O-acetyloxime), ethanone-1-[9-ethyl-6-(2-methyl-4-tetrahydrofuranylmethoxybenzoyl)-9H-carbazol-3-yl]-1-(O-acetyloxime), and ethanone-1-[9-ethyl-6-{2-methyl-4-(2,2-dimethyl-1,3-dioxolanyl)methoxybenzoyl}-9H-carbazol-3-yl]-1-(O-acetyloxime) are particularly preferred.

The above O-acyloxime compounds can be used alone or as a mixture of two or more thereof.

[0078]

In the present invention, when an O-acyloxime compound is used as a photopolymerization initiator, the amount used is preferably 0.01 to 80 parts by weight, more preferably 1 to 70 parts by weight and particularly preferably 1 to 60 parts by weight, based on 100 parts by weight of the total of a polyfunctional monomer (C) and a

monofunctional monomer. In this case, when the amount of the O-acyloxime compound used is too small, curing by exposure becomes insufficient, and it may become difficult to obtain a color filter in which a colored layer pattern is arranged according to a predetermined pattern. On the other hand, when the amount is too large, the formed colored layer may easily fall off from a substrate during development.

[0079]

- Other Additives -

The radiation-sensitive composition for forming the colored layer of the present invention contains the above components (A) to (D) as essential 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; and

residual improvers such as moronic acid, adipic acid, itaconic acid, citraconic acid, fumaric acid and mesaconic acid.

[0080]

Preparation of Liquid Composition

The radiation-sensitive 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 composition and other additive components and does not react with these components and has moderate volatility.

[0081]

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, ethylene glycol mono-n-propyl ether acetate, ethylene glycol mono-n-butyl 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, dipropylene glycol monoethyl ether acetate and 3-methoxybutyl 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;

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;

[0082]

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-methoxypropanoate, methyl 3-ethoxypropionate, ethyl 3-ethoxypropanoate, 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.

[0083]

Among these solvents, propylene glycol monomethyl ether, propylene glycol monoethyl ether, ethylene glycol monomethyl ether acetate, ethylene glycol mono-n-propyl ether acetate, ethylene glycol mono-n-butyl 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 above solvents can be used alone or as a mixture of two or more thereof.

[0084]

Further, high boiling point solvents 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 above solvents.

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

[0085]

The amount of the solvent used is not particularly 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 particularly preferably 10 to 40 wt%, from the viewpoints of coating properties and stability of the liquid composition to be obtained.

[0086]

Method For Forming Color Filter

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

[0087]

– 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 composition for forming a 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 a substrate, but the radiation-sensitive composition in the present invention has high solubility in a cleaning solvent even after drying, and therefore coating with a slit nozzle is preferred.

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.

[0088]

– 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.

Visible rays, ultraviolet rays, far-ultraviolet rays, electron beams and X-rays, for example, can be used as radiation used for this step, but 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/m^2.

[0089]

– 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 above 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 above alkali developer, for example. 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, but the radiation-sensitive composition in the present invention has high solubility in an alkali developer, and therefore development by a shower developing method is preferred.

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

[0090]

– Step (4) –

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

Post-baking is preferably performed under the condition of 180 to 230℃ 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.

[0091]

Further, green and blue pixel patterns are formed on the same substrate by repeating the above steps (1) to (4) using a liquid composition of the radiation-sensitive 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 composition for forming the colored layer containing a black pigment is used.

[0092]

Color Filter

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

[0093]

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 significantly improved and therefore a color liquid crystal device which is bright and has high definition can be obtained.

[Examples]

[0094]

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

[0095]

Synthesis of Alkali-Soluble Resin

Synthesis Example 1

A flask equipped with a cooling tube and a stirrer was charged with 2 parts by weight of 2,2'-azobisisobutyronitrile, 4 parts by weight of cyano(dimethyl)methyl pyrazole-1-dithiocarboxylate and 200 parts by weight of dipropylene glycol dimethyl ether, and subsequently with 20 parts by weight of methacrylic acid, 30 parts by weight of N-phenylmaleimide, 30 parts by weight of paracumylphenol EO-modified acrylate (Aronix M-110 produced by TOAGOSEI CO., LTD.) and 20 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 maintained at this temperature to perform polymerization for 2 hours. Then, the reaction solution was heated to 100°C and 1 part by weight of 2,2'-azobisisobutyronitrile was added thereto. Polymerization was continued for another 2 hours, and

thereby a copolymer solution (polymerization conversion = 99%) was obtained. This copolymer had a Mw of 6,000 and a Mw/Mn of 1.4. This copolymer was designated as "copolymer (S-1)".

The term "polymerization conversion" used herein indicates a ratio of the amount of the components consumed by polymerization reaction to the amount of the components except solvents which are subjected to polymerization reaction, and the polymerization conversion was specifically calculated by the following equation.

Polymerization conversion (%) = Solid content concentration of copolymer solution (%) × Total weight of all charged components/Total weight of charged components except solvents

The solid content concentration of a copolymer solution was determined as follows. That is, the copolymer solution was weighed into an aluminum pan and heated on a hot plate at 180℃ for 1 hour. Before and after the heating, the weights were measured and the value of (Weight after heating × 100/Weight before heating) was calculated.

[0096]

Synthesis Example 2

A flask equipped with a cooling tube and a stirrer was charged with 3.5 parts by weight of 2,2'-azobisisobutyronitrile, 200 parts by weight of

dipropylene glycol dimethyl ether, and subsequently with 20 parts by weight of methacrylic acid, 30 parts by weight of N-phenylmaleimide, 30 parts by weight of paracumylphenol EO-modified acrylate, 20 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 maintained at this temperature to perform polymerization for 2 hours. Then, the reaction solution was heated to 100°C and 1.5 parts by weight of 2,2'-azobisisobutyronitrile was added thereto. Polymerization was continued for another 2 hours, and thereby a copolymer solution (polymerization conversion = 87%) was obtained. This copolymer had a Mw of 17,000 and a Mw/Mn of 2.1. This copolymer was designated as "copolymer (S-2)".

[0097]

Synthesis Example 3

A flask equipped with a cooling tube and a stirrer was charged with 3.5 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, 30 parts by weight of N-phenylmaleimide, 30 parts by weight of paracumylphenol EO-modified acrylate, 20 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 maintained at this temperature to perform polymerization for 2 hours. Then, the reaction solution was heated to 100°C and 3.5 parts by weight of 2,2'-azobisisobutyronitrile was added thereto. Polymerization was continued for another 2 hours, and thereby a copolymer solution (polymerization conversion = 92%) was obtained. This copolymer had a Mw of 22,000 and a Mw/Mn of 1.9. This copolymer was designated as "copolymer (S-3)".

[0098]

Synthesis Example 4

A flask equipped with a cooling tube and a stirrer was charged with 2 parts by weight of 2,2'-azobisisobutyronitrile, 4 parts by weight of cyano(dimethyl)methyl pyrazole-1-dithiocarboxylate and 200 parts by weight of dipropylene glycol dimethyl ether, and subsequently with 20 parts by weight of methacrylic acid, 30 parts by weight of N-phenylmaleimide, 30 parts by weight of benzyl (meth)acrylate and 20 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 maintained at this temperature to perform polymerization for 2 hours. Then, the reaction solution was heated to 100°C and 1 part by weight of 2,2'-azobisisobutyronitrile was added thereto. Polymerization was continued for another 2 hours, and thereby a

copolymer solution (polymerization conversion = 99%) was obtained. This copolymer had a Mw of 6,500 and a Mw/Mn of 1.5. This copolymer was designated as "copolymer (S-4)".

[0099]

Synthesis Example 5

A flask equipped with a cooling tube and a stirrer was charged with 2 parts by weight of 2,2'-azobisisobutyronitrile, 4 parts by weight of cyano(dimethyl)methyl pyrazole-1-dithiocarboxylate and 200 parts by weight of dipropylene glycol dimethyl ether, and subsequently with 20 parts by weight of methacrylic acid, 30 parts by weight of benzyl methacrylate, 30 parts by weight of paracumylphenol EO-modified acrylate (Aronix M-110 produced by TOAGOSEI CO., LTD.) and 20 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 maintained at this temperature to perform polymerization for 2 hours. Then, the reaction solution was heated to 100°C and 1 part by weight of 2,2'-azobisisobutyronitrile was added thereto. Polymerization was continued for another 2 hours, and thereby a copolymer solution (polymerization conversion = 99%) was obtained. This copolymer had a Mw of 7,000 and a Mw/Mn of 1.5. This copolymer was designated as "copolymer (S-5)".

[0100]

Synthesis Example 6

A flask equipped with a cooling tube and a stirrer was charged with 7 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, 30 parts by weight of N-phenylmaleimide, 30 parts by weight of benzyl methacrylate, 20 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 maintained at this temperature to perform polymerization for 2 hours. Then, the reaction solution was heated to 100°C and 3 parts by weight of 2,2'-azobisisobutyronitrile was added thereto. Polymerization was continued for another 2 hours and a copolymer solution (polymerization conversion = 99%) was obtained by this operation. This copolymer had a Mw of 6,300 and a Mw/Mn of 2.3. This copolymer was designated as "copolymer (S-6)".

[0101]

Synthesis Example 7

A flask equipped with a cooling tube and a stirrer was charged with 3.5 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, 30 parts by

weight of N-phenylmaleimide, 30 parts by weight of benzyl methacrylate, 20 parts by weight of styrene and 5 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 maintained at this temperature to perform polymerization for 2 hours. Then, the reaction solution was heated to 100°C and 1.5 parts by weight of 2,2'-azobisisobutyronitrile was added thereto. Polymerization was continued for another 2 hours and a copolymer solution (polymerization conversion = 99%) was obtained by this operation. This copolymer had a Mw of 16,000 and a Mw/Mn of 2.0. This copolymer was designated as "copolymer (S-7)".

[0102]

[Developer Immersion Test]

Example 1

A mixed solution containing 160 parts by weight of a mixture having a 50/50 weight ratio of C.I. Pigment Red 254 and C.I. Pigment Yellow 138 as a pigment (A), 40 parts by weight of Disperbyk 2001 (in terms of solid content) as a dispersant and 800 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, 600 parts by weight of this pigment dispersion fluid, 70 parts by weight of the copolymer (S-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)butane-1-one as a photopolymerization initiator (D) and 800 parts by weight of propylene glycol monomethyl ether acetate and 200 parts by weight of ethylene glycol mono-n-butyl 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 SiO_2 film for preventing the elution of sodium ions was formed, and then the coated substrate was pre-baked in a clean oven at 80°C for 10 minutes to form a coating having a film thickness of 3.0 μm on the substrate.

Then, this substrate was immersed in 1000 cc of a developer of a 0.04 wt% aqueous solution of potassium hydroxide which was being stirred with a magnetic stirrer for 2 minutes, so that the coating was completely dissolved.

[0103]

Example 2

A liquid composition (r-2) was prepared to form a coating on a soda glass substrate in the same manner as

in Example 1 except that 70 parts by weight of the copolymer (S-2) (in terms of solid content) was used in place of the copolymer (S-1).

Next, this substrate was immersed in 1000 cc of a developer of a 0.04 wt% aqueous solution of potassium hydroxide for 2 minutes in the same manner as in Example 1, so that the coating was completely dissolved.

[0104]

Example 3

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

Next, this substrate was immersed in 1000 cc of a developer of a 0.04 wt% aqueous solution of potassium hydroxide for 2 minutes in the same manner as in Example 1, so that the coating was completely dissolved.

[0105]

Comparative Example 1

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

Next, this substrate was immersed in 1000 cc of a developer of a 0.04 wt% aqueous solution of potassium

hydroxide for 2 minutes in the same manner as in Example 1, so that the coating was not completely dissolved and a large amount of the mass of insoluble matter was observed in the developer.

[0106]

Comparative Example 2

A liquid composition (r-5) was prepared to form a coating on a soda glass substrate in the same manner as in Example 1 except that 70 parts by weight of the copolymer (S-5) (in terms of solid content) was used in place of the copolymer (S-1).

Next, this substrate was immersed in 1000 cc of a developer of a 0.04 wt% aqueous solution of potassium hydroxide for 2 minutes in the same manner as in Example 1, so that the coating was completely dissolved.

[0107]

Comparative Example 3

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

Next, this substrate was immersed in 1000 cc of a developer of a 0.04 wt% aqueous solution of potassium hydroxide for 2 minutes in the same manner as in Example 1, so that the coating was not completely dissolved and a

large amount of the mass of insoluble matter was observed in the developer.

[0108]

Comparative Example 4

A liquid composition (r-7) was prepared to form a coating on a soda glass substrate in the same manner as in Example 1 except that 70 parts by weight of the copolymer (S-7) (in terms of solid content) was used in place of the copolymer (S-1).

Next, this substrate was immersed in 1000 cc of a developer of a 0.04 wt% aqueous solution of potassium hydroxide for 2 minutes in the same manner as in Example 1, so that the coating was not completely dissolved and a large amount of the mass of insoluble matter was observed in the developer.

As is apparent from Examples 1 to 3 and Comparative Examples 1 to 4, a coating having high solubility in a developer can be formed by copolymerizing an unsaturated compound represented by the above formula (1) in an alkali-soluble resin (B).

[0109]

[Solvent Immersion Test]

Example 4

The liquid composition (r-1) was spin-coated onto a soda glass substrate having a diameter of 4 inches, the surface on which an SiO_2 film for preventing the elution of sodium ions was formed, and then the coated substrate

was left standing in a clean room at 23°C for 12 hours and dried to thereby 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.

[0110]

Example 5

A solvent immersion test was performed in the same manner as in Example 4 except that the liquid composition (r-2) was used in place of the liquid composition (r-1), so that the coating was completely dissolved.

[0111]

Example 6

A solvent immersion test was performed in the same manner as in Example 4 except that the liquid composition (r-3) was used in place of the liquid composition (r-1), so that the coating was not completely dissolved and foreign substances were slightly observed.

[0112]

Comparative Example 5

A solvent immersion test was performed in the same manner as in Example 4 except that the liquid composition (r-4) was used in place of the liquid composition (r-1), so that the coating was completely dissolved.

[0113]

Comparative Example 6

A solvent immersion test was performed in the same manner as in Example 4 except that the liquid composition (r-5) was used in place of the liquid composition (r-1), so that the coating was completely dissolved.

[0114]

Comparative Example 7

A solvent immersion test was performed in the same manner as in Example 4 except that the liquid composition (r-6) was used in place of the liquid composition (r-1), so that the coating was completely dissolved.

[0115]

Comparative Example 8

A solvent immersion test was performed in the same manner as in Example 4 except that the liquid composition (r-7) was used in place of the liquid composition (r-1), so that the coating was not completely dissolved and a large amount of foreign substances were observed.

As is apparent from Examples 5, 6 and Comparative Example 8, it can be seen that the radiation-sensitive composition for forming the colored layer after drying has an effect of improving the solubility in a cleaning solvent by copolymerizing an unsaturated compound represented by the above formula (1) in an alkali-soluble resin (B).

[0116]

[Evaluation of Voltage Holding Ratio]

Example 7

The liquid composition (r-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 μm.

Next, the coating was exposed to radiation having each wavelength of 365 nm, 405 nm and 436 nm at an exposure amount of 5000 J/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, 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 1.6 μm.

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 holding ratio of the liquid crystal cell was measured with a liquid crystal voltage holding ratio 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 holding ratio" as used herein refers to a value of (Potential difference of liquid crystal cell after 6.7 msec/ Voltage applied at 0 msec). As a result, the voltage holding ratio was 95%.

When the voltage holding ratio 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) may hardly cause "burn-in".

[0117]

Example 8

A liquid crystal cell was fabricated in the same manner as in Example 7 except that the liquid composition (r-2) was used in place of the liquid composition (r-1), and the voltage holding ratio was measured to be 90%. 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".

[0118]

Example 9

A liquid crystal cell was fabricated in the same manner as in Example 7 except that the liquid composition (r-3) was used in place of the liquid composition (r-1), and the voltage holding ratio was measured to be 93%. Accordingly, a liquid crystal display device provided with a color filter formed using the liquid composition (r-3) may hardly cause "burn-in".

[0119]

Comparative Example 9

A liquid crystal cell was fabricated in the same manner as in Example 7 except that the liquid composition (r-4) was used in place of the liquid composition (r-1), and the voltage holding ratio was measured to be 95%. Accordingly, a liquid crystal display device provided with a color filter formed using the liquid composition (r-4) may hardly cause "burn-in".

[0120]

Comparative Example 10

A liquid crystal cell was fabricated in the same manner as in Example 7 except that the liquid composition (r-5) was used in place of the liquid composition (r-1), and the voltage holding ratio was measured to be 95%. Accordingly, a liquid crystal display device provided

with a color filter formed using the liquid composition (r-5) may hardly cause "burn-in".

[0121]

Comparative Example 11

A liquid crystal cell was fabricated in the same manner as in Example 7 except that the liquid composition (r-6) was used in place of the liquid composition (r-1), and the voltage holding ratio was measured to be 47%. Accordingly, a liquid crystal display device provided with a color filter formed using the liquid composition (r-6) has a high possibility of causing "burn-in".

[0122]

Comparative Example 12

A liquid crystal cell was fabricated in the same manner as in Example 7 except that the liquid composition (r-7) was used in place of the liquid composition (r-1), and the voltage holding ratio was measured to be 91%. Accordingly, a liquid crystal display device provided with a color filter formed using the liquid composition (r-7) has a low possibility of causing "burn-in".

[0123]

As is apparent from Examples 1 to 3 and Comparative Examples 1 to 4, it can be seen that voltage holding ratio is improved by controlling the Mw, Mw/Mn and polymerization conversion of the alkali-soluble resin (B).

[0124]

[Evaluation of Developability]

Example 10

The liquid composition (r-1) was applied using a spin coater on a soda glass substrate having a diameter of 4 inches, the surface on which an SiO_2 film for preventing the elution of sodium ions was formed, and then the obtained substrate was pre-baked on a hot plate at 90°C for 2 minutes to form a coating having a film thickness of 2.5 μm. Subsequently, the substrate was cooled to room temperature, and then the coating was exposed to ultraviolet rays having each wavelength of 365 nm, 405 nm and 436 nm through a photomask (slit width: 90 μm) using a high pressure mercury lamp. The exposure amount in this case was 100 J/m^2. Then, a 0.04 wt% aqueous solution of potassium hydroxide at 23°C was injected onto the coating at a development pressure of 1 Kgf/cm^2 (nozzle diameter: 1 mm) to thereby perform shower development. Then, this substrate was post-baked at 220°C for 30 minutes, and thereby a red stripe pixel pattern was formed on the substrate.

The pixel array on the substrate was observed with an optical microscope, so that no development residue was observed on the unexposed portions of the substrate and no chipping was observed on the edges of the pixel pattern.

[0125]

Example 11

The evaluation of developability was performed in the same manner as in Example 10 except that the liquid composition (r-2) was used in place of the liquid composition (r-1), so that no development residue was observed on the unexposed portions of the substrate and no chipping was observed on the edges of the pixel pattern.

[0126]

Example 12

The evaluation of developability was performed in the same manner as in Example 10 except that the liquid composition (r-3) was used in place of the liquid composition (r-1), so that no development residue was observed on the unexposed portions of the substrate and no chipping was observed on the edges of the pixel pattern.

[0127]

Comparative Example 13

The evaluation of developability was performed in the same manner as in Example 10 except that the liquid composition (r-4) was used in place of the liquid composition (r-1), so that no development residue was observed on the unexposed portions of the substrate and no chipping was observed on the edges of the pixel pattern.

[0128]

Comparative Example 14

The evaluation of developability was performed in the same manner as in Example 10 except that the liquid composition (r-5) was used in place of the liquid composition (r-1), so that development residue was observed on the unexposed portions of the substrate and chipping was observed on the edges of the pixel pattern.

[0129]

Comparative Example 15

The evaluation of developability was performed in the same manner as in Example 10 except that the liquid composition (r-6) was used in place of the liquid composition (r-1), so that no development residue was observed on the unexposed portions of the substrate and no chipping was observed on the edges of the pixel pattern.

[0130]

Comparative Example 16

The evaluation of developability was performed in the same manner as in Example 10 except that the liquid composition (r-7) was used in place of the liquid composition (r-1), so that no development residue was observed on the unexposed portions of the substrate and no chipping was observed on the edges of the pixel pattern.

As is apparent from Examples 10 to 12 and Comparative Examples 13 to 16, a radiation-sensitive composition for forming a colored layer having excellent

developability can be obtained by copolymerizing a maleimide substituted at N-position in an alkali-soluble resin (B).

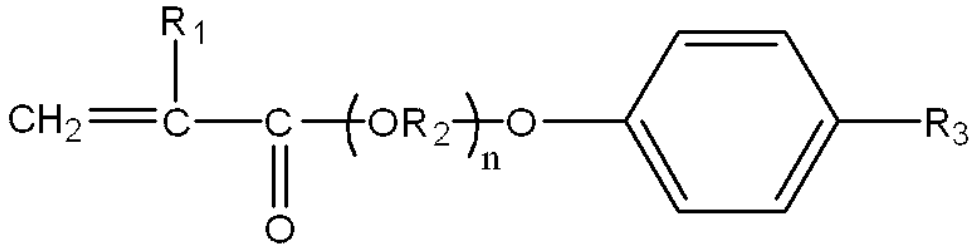
Here, the evaluation was performed for a radiation-sensitive composition using a red pigment, but similar results were also obtained in the case of a radiation-sensitive composition using a blue, green, yellow or black pigment.

[0131]

As is apparent from (1) Developer Immersion Test, (2) Solvent Immersion Test, (3) Evaluation of Voltage Holding Ratio and (4) Evaluation of Developability described above, it proved that a composition obtained by blending a copolymer containing (b1), (b2) and (b3) as an alkali-soluble resin (B) has good results in all these evaluations, and is a radiation-sensitive composition for forming a colored layer which can form a color filter not causing "burn-in" at a high product yield and can form a coating having high solubility in a cleaning solvent even after drying and high solubility in an alkali developer.

What is claimed is:

1. A radiation-sensitive 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) is a copolymer of an unsaturated compound comprising (b1) one selected from the group consisting of unsaturated carboxylic acids and acid anhydrides thereof, and unsaturated phenol compounds, (b2) a maleimide substituted at N-position, and (b3) an unsaturated compound represented by the following formula (1):



(1)

wherein R_1 represents a hydrogen atom or a methyl group; R_2 represents an alkylene group having 2 to 4 carbon atoms; R_3 represents a hydrogen atom, an alkyl group having 1 to 20 carbon atoms or an aralkyl group having 7 to 20 carbon atoms; and n represents an integer of 1 to 10.

2. The radiation-sensitive composition according to claim 1, wherein the copolymer constituting the alkali-soluble resin (B) is a copolymer having a weight average

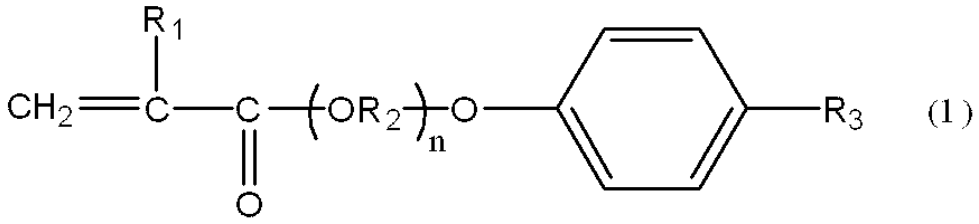
molecular weight (Mw) in terms of polystyrene as measured by gel permeation chromatography (GPC) of 1,000 to 25,000 and a ratio of Mw to a number average molecular weight (Mn) in terms of polystyrene as measured by gel permeation chromatography (GPC) (Mw/Mn) of 1.0 to 2.2.

3. The radiation-sensitive composition according to claim 2, wherein the alkali-soluble resin (B) is a copolymer obtained by living radical polymerization.

4. A color filter formed by using the radiation-sensitive composition according to any one of claims 1 to 3.

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

6. A copolymer of an unsaturated compound, comprising (b1) one selected from the group consisting of unsaturated carboxylic acids and acid anhydrides thereof, and unsaturated phenol compounds, (b2) a maleimide substituted at N-position, and (b3) an unsaturated compound represented by the following formula (1):



(1)

wherein R_1 represents a hydrogen atom or a methyl group; R_2 represents an alkylene group having 2 to 4 carbon atoms; R_3 represents a hydrogen atom, an alkyl group having 1 to 20 carbon atoms or an aralkyl group having 7 to 20 carbon atoms; and n represents an integer of 1 to 10.