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

## Field of the Invention

The present invention relates to a radiation sensitive composition for forming a colored layer, a color filter and a color liquid crystal display device. More specifically, it relates to a radiation sensitive composition which is used to form a colored layer useful for color filters for use in transmission and reflection type color liquid crystal display devices and color image pick-up devices, a color filter having a colored layer formed from the radiation sensitive composition, and a color liquid crystal display device comprising the color filter.

## Description of the Prior Art

As means of manufacturing a color filter by using a colored radiation sensitive composition, there is known a method in which a colored radiation sensitive composition is applied to a substrate or a substrate comprising a light screening layer having a desired pattern and dried and then the dried coating film is exposed to radiation in a desired pattern (to be referred to as "exposure" hereinafter) and developed to obtain color pixels (refer to JP-A 2-144502 and JP-A 3-53201).

In the technical field of color filters, the tact time is now generally shortened by reducing the amount of exposure, and the formation of a finer pattern is strongly desired, reflecting the reduction of the pattern rule for liquid crystal display devices. However, it is difficult to obtain a satisfactory pixel pattern and black matrix pattern from the colored radiation sensitive composition of the prior art when the tact time is shortened because a missing part of the pattern edge or an undercut is apt to be produced during

development. Also, it cannot be said that the radiation sensitive composition of the prior art is satisfactory in terms of the formation of a high-definition pattern.

Further, when the concentration of a colorant contained in the colored radiation sensitive composition increases as the color purity of a color liquid crystal display device becomes higher, the residue or a stain tends to be produced on the substrate or light screening layer of an unexposed portion during development. In order to eliminate the production of the residue or a stain, it is effective to extend the development time or increase the delivery pressure of a developer. However, this causes a trouble such as the production of a missing part of the pattern edge or the removal of the pattern, thereby making it difficult to form a fine pattern. Since the pattern line width changes by the alteration of the development time, there arises a problem that a leeway such as development time during which a desired pattern line width can be obtained becomes more insufficient as the pattern becomes finer.

## Summary of the Invention

It is an object of the present invention to provide a radiation sensitive composition for forming a colored layer, which exhibits excellent developability, more specifically a radiation sensitive composition for forming a colored layer, which can provide pixels and a black matrix having an excellent high-definition pattern shape and excellent adhesion to a substrate with a small amount of exposure without producing the residue or a stain during development even when the concentration of a colorant is high, and has a sufficient leeway such as development time during which a desired pattern line width can be obtained.

It is another object of the present invention to provide a color filter having a colored layer formed from the above

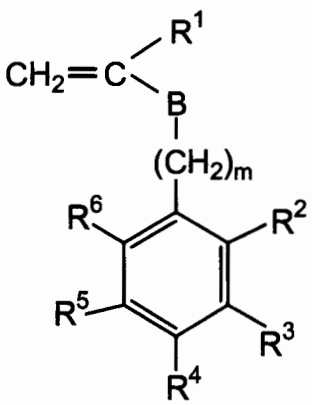
composition of the present invention and a color liquid crystal display device comprising the color filter.

Other objects and advantages of the present invention will become apparent from the following description.

According to the present invention, firstly, the above objects and advantages of the present invention are attained by 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) comprises a copolymer of an unsaturated compound represented by the following formula (1) and another copolymerizable unsaturated compound, and the another copolymerizable unsaturated compound is at least one selected from the group consisting of an N-substituted maleimide, unsaturated compound represented by the following formula (2), acidic unsaturated compound, aromatic vinyl compound, indene, macromonomer having a (meth)acryloyl group at one terminal of a polymer molecular chain, unsaturated carboxylate ester, unsaturated aminoalkyl carboxylate, unsaturated glycidyl carboxylate, vinyl cyanide compound, unsaturated amide, vinyl carboxylate, unsaturated ether and aliphatic conjugated diene.

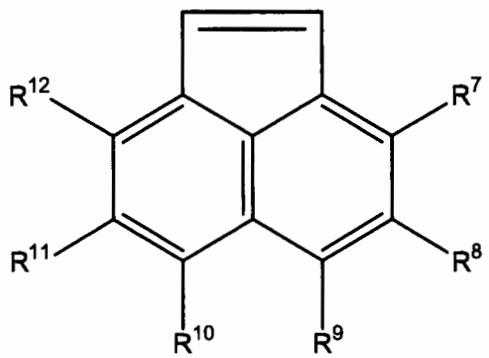
In the present invention, the colored layer means "pixels and/or a black matrix".



... (1)

(In the above formula, $R^1$ is a hydrogen atom or alkyl group

having 1 to 4 carbon atoms, $R^2$ to $R^6$ are the same or different and each a hydrogen atom, hydroxyl group, alkyl group having 1 to 6 carbon atoms or alkoxy group having 1 to 6 carbon atoms, B is -COO- or -CONH-, and m is an integer of 0 to 3, with the proviso that at least one of $R^2$ to $R^6$ is a hydroxyl group.)




(2)

(In the above formula, $R^7$ to $R^{12}$ are each independently a hydrogen atom, halogen atom, hydroxyl group, hydroxymethyl group or carboxyl group.)

According to the present invention, secondly, the above objects and advantages of the present invention are attained by a color filter having a colored layer formed from the above radiation sensitive composition for forming a colored layer of the present invention.

According to the present invention, thirdly, the above objects and advantages of the present invention are attained by a color liquid crystal display device comprising the above color filter of the present invention.

Best Mode for Carrying Out the Invention

The present invention will be described in detail hereinunder.

Radiation sensitive composition for forming a colored layer

- (A) colorant -

The colorant in the present invention is not limited to a particular color and is suitably selected according to the application purpose of the obtained color filter. It

may be a pigment, dye or natural coloring matter.

Since the development of a high-definition color and heat resistance are required for a color filter, a colorant having high color developability and high heat resistance, especially a colorant having high resistance to thermal decomposition is preferred as the colorant in the present invention. Therefore, an organic pigment or an inorganic pigment is preferably used, and an organic pigment or carbon black is particularly preferably used.

Examples of the above organic pigment are compounds classified into a group of pigments according to color index (C.I.; issued by The Society of Dyers and Colourists), specifically compounds having the following color index (C.I.) numbers:

C.I. Pigment Yellow 1, C.I. Pigment Yellow 3, C.I. Pigment Yellow 12, C.I. Pigment Yellow 13, C.I. Pigment Yellow 14, C.I. Pigment Yellow 15, C.I. Pigment Yellow 16, 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 60, C.I. Pigment Yellow 61, C.I. Pigment Yellow 65, C.I. Pigment Yellow 71, C.I. Pigment Yellow 73, C.I. Pigment Yellow 74, C.I. Pigment Yellow 81, C.I. Pigment Yellow 83, C.I. Pigment Yellow 93, C.I. Pigment Yellow 95, C.I. Pigment Yellow 97, C.I. Pigment Yellow 98, C.I. Pigment Yellow 100, C.I. Pigment Yellow 101, C.I. Pigment Yellow 104, C.I. Pigment Yellow 106, C.I. Pigment Yellow 108, C.I. Pigment Yellow 109, C.I. Pigment Yellow 110, C.I. Pigment Yellow 113, C.I. Pigment Yellow 114, C.I. Pigment Yellow 116, C.I. Pigment Yellow 117, C.I. Pigment Yellow 119, C.I. Pigment Yellow 120, C.I. Pigment Yellow 126, C.I. Pigment Yellow 127, C.I. Pigment Yellow 128, C.I. Pigment Yellow 129, C.I. Pigment Yellow 138, C.I. Pigment Yellow 139, C.I. Pigment Yellow 150, C.I. Pigment Yellow 151, C.I. Pigment Yellow 152, C.I. Pigment Yellow 153, C.I. Pigment Yellow 154, C.I.

Pigment Yellow 155, C.I. Pigment Yellow 156, C.I. Pigment Yellow 166, C.I. Pigment Yellow 168, C.I. Pigment Yellow 175, C.I. Pigment Yellow 180 and C.I. Pigment Yellow 185;

C.I. Pigment Orange 1, C.I. Pigment Orange 5, C.I. Pigment Orange 13, C.I. Pigment Orange 14, C.I. Pigment Orange 16, C.I. Pigment Orange 17, 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 51, C.I. Pigment Orange 61, C.I. Pigment Orange 63, C.I. Pigment Orange 64, C.I. Pigment Orange 71 and C.I. Pigment Orange 73;

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 Red 1, C.I. Pigment Red 2, C.I. Pigment Red 3, C.I. Pigment Red 4, C.I. Pigment Red 5, C.I. Pigment Red 6, C.I. Pigment Red 7, C.I. Pigment Red 8, C.I. Pigment Red 9, C.I. Pigment Red 10, C.I. Pigment Red 11, C.I. Pigment Red 12, C.I. Pigment Red 14, C.I. Pigment Red 15, C.I. Pigment Red 16, C.I. Pigment Red 17, C.I. Pigment Red 18, C.I. Pigment Red 19, C.I. Pigment Red 21, C.I. Pigment Red 22, C.I. Pigment Red 23, C.I. Pigment Red 30, C.I. Pigment Red 31, C.I. Pigment Red 32, C.I. Pigment Red 37, C.I. Pigment Red 38, C.I. Pigment Red 40, C.I. Pigment Red 41, C.I. Pigment Red 42, C.I. Pigment Red 48:1, C.I. Pigment Red 48:2, C.I. Pigment Red 48:3, C.I. Pigment Red 48:4, C.I. Pigment Red 49:1, C.I. Pigment Red 49:2, C.I. Pigment Red 50:1, C.I. Pigment Red 52:1, C.I. Pigment Red 53:1, C.I. Pigment Red 57, C.I. Pigment Red 57:1, C.I. Pigment Red 57:2, C.I. Pigment Red 58:2, C.I. Pigment Red 58:4, C.I. Pigment Red 60:1, C.I. Pigment Red 63:1, C.I. Pigment Red 63:2, C.I. Pigment Red 64:1, C.I. Pigment Red 81:1, C.I. Pigment Red 83, C.I. Pigment Red 88, C.I. Pigment Red 90:1, C.I. Pigment Red 97, C.I. Pigment Red 101, C.I.

Pigment Red 102, C.I. Pigment Red 104, C.I. Pigment Red 105, C.I. Pigment Red 106, C.I. Pigment Red 108, C.I. Pigment Red 112, C.I. Pigment Red 113, C.I. Pigment Red 114, C.I. Pigment Red 122, C.I. Pigment Red 123, C.I. Pigment Red 144, C.I. Pigment Red 146, C.I. Pigment Red 149, C.I. Pigment Red 150, C.I. Pigment Red 151, C.I. Pigment Red 166, C.I. Pigment Red 168, C.I. Pigment Red 170, C.I. Pigment Red 171, C.I. Pigment Red 172, C.I. Pigment Red 174, 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 188, C.I. Pigment Red 190, C.I. Pigment Red 193, C.I. Pigment Red 194, C.I. Pigment Red 202, C.I. Pigment Red 206, C.I. Pigment Red 207, C.I. Pigment Red 208, C.I. Pigment Red 209, C.I. Pigment Red 215, C.I. Pigment Red 216, C.I. Pigment Red 220, C.I. Pigment Red 224, C.I. Pigment Red 226, C.I. Pigment Red 242, C.I. Pigment Red 243, C.I. Pigment Red 245, C.I. Pigment Red 254, C.I. Pigment Red 255, C.I. Pigment Red 264 and C.I. Pigment Red 265;

C.I. Pigment Blue 15, C.I. Pigment Blue 15:3, C.I. Pigment Blue 15:4, C.I. Pigment Blue 15:6 and C.I. Pigment Blue 60;

C.I. Pigment Green 7 and C.I. Pigment Green 36;

C.I. Pigment Brown 23 and C.I. Pigment Brown 25; and

C.I. Pigment Black 1 and C.I. Pigment Black 7.

These organic pigments may be purified by sulfuric acid re-crystallization, solvent cleaning or a combination thereof before use.

Examples of the above inorganic pigment include titanium oxide, barium sulfate, calcium carbonate, zinc white, lead sulfate, yellow lead, zinc yellow, red iron oxide (red iron oxide (III)), cadmium red, ultramarine, Prussian blue, chromium oxide green, cobalt green, amber, titanium black, synthetic iron black and carbon black.

In the present invention, the above organic pigments

and inorganic pigments may be used alone or in combination of two or more, or both may be used in combination. For example, one or more organic pigments are preferably used to form pixels, and two or more organic pigments and/or carbon black are preferably used to form a black matrix.

In the present invention, the surface of the particle of the pigment may be optionally modified by a polymer before use. Examples of the polymer used to modify the surface of the particle of the pigment include polymers disclosed by JP-A 8-259876 and commercially available polymers and oligomers for dispersing a pigment.

In the present invention, optionally, the colorant may be used in conjunction with a dispersant.

The above dispersant is, for example, a cationic, anionic, nonionic, amphoteric, silicone-based or fluorine-based surfactant.

Examples of the above surfactant include polyoxyethylene alkyl ethers such as polyoxyethylene lauryl ether, polyoxyethylene stearyl ether and polyoxyethylene oleyl ether; polyoxyethylene alkylphenyl ethers such as polyoxyethylene n-octylphenyl ether and polyoxyethylene n-nonylphenyl ether; polyethylene glycol diesters such as polyethylene glycol dilaurate and polyethylene glycol distearate; sorbitan fatty acid esters; fatty acid modified polyesters; tertiary amine modified polyurethanes; and polyethylene imines; and commercially available surfactants under the trade names of KP (of Shin-Etsu Chemical, Co., Ltd.), Polyflow (of Kyoeisha Kagaku Co., Ltd.), F Top (of Tokem Products Co., Ltd.), Megafac (of Dainippon Ink and Chemicals, Inc.), Florade (of Sumitomo 3M Limited), Asahi Guard and Surflon (of Asahi Glass Co., Ltd.), BYK and Disperbyk (of BYK Chemie Japan Co., Ltd.), and Solsperse (of Seneka Co., Ltd.).

These surfactants may be used alone or in combination

of two or more.

The amount of the surfactant is preferably 50 parts or less by weight, more preferably 0 to 30 parts by weight based on 100 parts by weight of the colorant.

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

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

The solvent used for the preparation of the pigment dispersion may be identical to the solvent used for the liquid radiation sensitive composition which will be described hereinafter.

The amount of the solvent for the preparation of the pigment dispersion is preferably 200 to 1,200 parts by weight, more preferably 300 to 1,000 parts by weight based on 100 parts by weight of the pigment.

To prepare the pigment dispersion by using a bead mill, glass beads or titania beads having a diameter of about 0.5 to 10 mm are used to mix and disperse a pigment mixed solution

comprising a pigment, a solvent and a dispersant preferably while it is cooled with cooling water or the like.

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

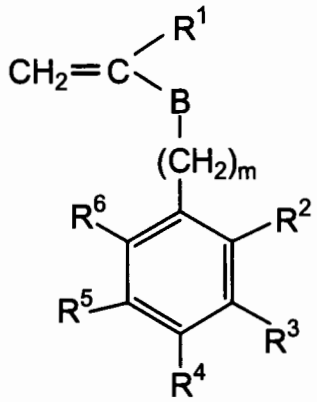
To prepare the pigment dispersion by using a roll mill, a three-roll mill or two-roll mill is used to mix and disperse the pigment mixed solution preferably while it is cooled with cooling water or the like.

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

- (B) alkali-soluble resin -

The alkali-soluble resin in the present invention is a component which comprises a copolymer (to be referred to as "copolymer (B1)" hereinafter) of a polymerizable unsaturated compound having a skeleton represented by the above formula (1) (to be referred to as "unsaturated compound (b1)" hereinafter) and another copolymerizable unsaturated compound (to be referred to as "unsaturated compound (b2)" hereinafter), serves as a binder for the colorant (A) and has solubility in an alkali developer used in the development step for forming a colored layer.

The unsaturated compound (b1) is an unsaturated compound having a phenol skeleton and radical polymerizability and represented by the following formula (1).



· · · (1)

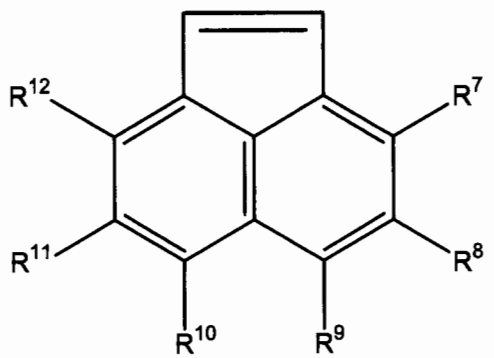
(In the above formula, $R^1$ is a hydrogen atom or alkyl group having 1 to 4 carbon atoms, $R^2$ to $R^6$ are the same or different and each a hydrogen atom, hydroxyl group, alkyl group having 1 to 6 carbon atoms or alkoxy group having 1 to 6 carbon atoms, B is -COO- or -CONH-, and m is an integer of 0 to 3, with the proviso that at least one of $R^2$ to $R^6$ is a hydroxyl group.)

The unsaturated compound (b1) is preferably N-(3,5-dimethyl-4-hydroxybenzyl)(meth)acrylamide, N-(4-hydroxyphenyl)(meth)acrylamide, 4-hydroxybenzyl (meth)acrylate or 4-hydroxyphenyl (meth)acrylate, particularly preferably 4-hydroxyphenyl (meth)acrylate. In the copolymer (B1), the above unsaturated compounds (b1) may be used alone or in combination of two or more.

In the present invention, the unsaturated compound (b2) is selected from an N-substituted maleimide, unsaturated compound represented by the following formula (2), acidic unsaturated compound, aromatic vinyl compound, indene, macromonomer having a (meth)acryloyl group at one terminal of a polymer molecular chain, unsaturated carboxylate, unsaturated aminoalkyl carboxylate, unsaturated glycidyl carboxylate, vinyl cyanide compound, unsaturated amide, vinyl carboxylate, unsaturated ether and aliphatic conjugated diene. These unsaturated compounds (b2) may be used alone or in combination of two or more.

The unsaturated compound (b2) is preferably an N-substituted maleimide or an unsaturated compound

represented by the following formula (2) (to be referred to as "acenaphthylene" hereinafter) (the N-substituted maleimide and the acenaphthylene are collectively referred to as "unsaturated compound (b2')" hereinafter).




(2)

(In the above formula, $R^7$ to $R^{12}$ are each independently a hydrogen atom, halogen atom, hydroxyl group, hydroxymethyl group or carboxyl group.)

Examples of the N-substituted maleimide include N-phenylmaleimide, N-o-hydroxyphenylmaleimide, N-m-hydroxyhpenylmaleimide, N-p-hydroxyphenylmaleimide, N-o-methylphenylmaleimide, N-m-methylphenylmaleimide, N-p-methylphenylmaleimide, N-o-methoxyphenylmaleimide, N-m-methoxyphenylmaleimide, N-p-methoxyphenylmaleimide and N-cyclohexylmaleimide.

Out of these N-substituted maleimides, N-phenylmaleimide and N-cyclohexylmaleimide are preferred, and N-phenylmaleimide is particularly preferred. In the copolymer (B1), the N-substituted maleimides may be used alone or in combination of two or more.

Examples of the acenaphthylene include acenaphthylene, 5-chloroacenaphthylene, 5-hydroxymethylacenaphthylene and 5-hydroxyacenaphthylene.

Out of these acenaphthylenes, acenaphthylene and 5-chloroacenaphthylene are preferred, and acenaphthylene is particularly preferred. In the copolymer (B1), the acenaphthylenes may be used alone or in combination of two or more.

Examples of the acidic unsaturated compound having at least one acidic functional group such as carboxyl group or phenolic hydroxyl group or at least one type of acidic functional groups in the molecule include unsaturated monocarboxylic acids such as (meth)acrylic acid, crotonic acid, α-chloroacrylic acid and cinnamic acid; unsaturated dicarboxylic acids and anhydrides thereof such as maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride and mesaconic acid; unsaturated polycarboxylic acids having three or more carboxyl groups and anhydrides thereof; mono[(meth)acryloyloxyalkyl]esters of a polycarboxylic acid having two or more carboxyl groups such as mono[2-(meth)acryloyloxyethyl]succinate and mono[2-(meth)acryloyloxyethyl]phthalate; and mono(meth)acrylates of a polymer having a carboxyl group and a hydroxyl group at both terminals such as ω-carboxypolycaprolactone mono(meth)acrylate.

The mono(2-acryloyloxyethyl)succinate and mono(2-acryloyloxyethyl)phthalate are available on the market under the trade names of Light Ester HOA-MS and Light Ester HOA-MPE (of Kyoeisha Kagaku Co., Ltd.), respectively.

Acidic unsaturated compounds other than the above 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.

Out of these acidic unsaturated compounds, (meth)acrylic acid, mono[2-(meth)acryloyloxyethyl]succinate,

ω-carboxypolycaprolactone mono(meth)acrylate and p-vinylphenol are preferred, and (meth)acrylic acid is particularly preferred.

In the copolymer (B1), the above acidic unsaturated compounds may be used alone or in combination of two or more.

Examples of the aromatic vinyl compound include styrene, α-methylstyrene, o-vinyltoluene, m-vinyltoluene, p-vinyltoluene, p-chlorostyrene, o-methoxystyrene, m-methoxystyrene, p-methoxystyrene, o-vinylbenzylmethyl ether, m-vinylbenzylmethyl ether, p-vinylbenzylmethyl ether, o-vinylbenzylglycidyl ether, m-vinylbenzylglycidyl ether and p-vinylbenzylglycidyl ether.

Examples of the indene include indene and 1-methylindene.

Examples of the macromonomer having a (meth)acryloyl group at one terminal of a polymer molecular chain include polystyrene, polymethyl (meth)acrylate, poly-n-butyl (meth)acrylate and polysiloxane.

Examples of the unsaturated carboxylate include methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, i-propyl (meth)acrylate, n-butyl (meth)acrylate, i-butyl (meth)acrylate, sec-butyl (meth)acrylate, t-butyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, allyl (meth)acrylate, benzyl (meth)acrylate, cyclohexyl (meth)acrylate, phenyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 2-phenoxyethyl (meth)acrylate, methoxydiethylene glycol (meth)acrylate, methoxytriethylene glycol (meth)acrylate, methoxypropylene glycol (meth)acrylate, methoxydipropylene glycol (meth)acrylate, isobornyl (meth)acrylate, dicyclopentadienyl (meth)acrylate,

2-hydroxy-3-phenoxypropyl (meth)acrylate and glycerol mono(meth)acrylate.

Examples of the unsaturated aminoalkyl carboxylate include 2-aminoethyl (meth)acrylate, 2-dimethylaminoethyl (meth)acrylate, 2-aminopropyl (meth)acrylate, 2-dimethylaminopropyl (meth)acrylate, 3-aminopropyl (meth)acrylate and 3-dimethylaminopropyl (meth)acrylate.

Examples of the unsaturated glycidyl carboxylate include glycidyl (meth)acrylate.

Examples of the vinyl cyanide compound include (meth)acrylonitrile, α-chloroacrylonitrile and vinylidene cyanide.

Examples of the unsaturated amide include (meth)acrylamide, α-chloroacrylamide and N-2-hydroxyethyl (meth)acrylamide.

Examples of the vinyl carboxylate include vinyl acetate, vinyl propionate, vinyl butyrate and vinyl benzoate.

Examples of the unsaturated ether include vinyl methyl ether, vinyl ethyl ether and ally glycidyl ether.

Examples of the aliphatic conjugated diene include 1,3-butadiene, isoprene and chloroprene.

In the copolymer (B1), the above unsaturated compounds may be used alone or in combination of two or more.

In the present invention, the copolymer (B1) is preferably a copolymer of (i) at least one unsaturated compound (b1) selected from the group consisting of N-(3,5-dimethyl-4-hydroxybenzyl)(meth)acrylamide, N-(4-hydroxyphenyl)(meth)acrylamide, 4-hydroxybenzyl (meth)acrylate and 4-hydroxyphenyl (meth)acrylate, (ii) at least one unsaturated compound (b2') selected from the group consisting of N-phenylmaleimide, N-cyclohexylmaleimide, acenaphthylene and 5-chloroacenaphthylene, (iii) at least one acidic unsaturated compound selected from the group consisting of (meth)acrylic acid,

mono[2-(meth)acryloyloxyethyl]succinate and ω-carboxypolycaprolactone mono(meth)acrylate, and (iv) at least one other unsaturated compound selected from the group consisting of styrene, methyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, allyl (meth)acrylate, benzyl (meth)acrylate, phenyl (meth)acrylate, glycerol mono(meth)acrylate, polystyrene macromonomer and polymethyl (meth)acrylate macromonomer.

The copolymer (B1) is particularly preferably a copolymer of (i) 4-hydroxyphenyl (meth)acrylate, (ii) at least one of N-phenylmaleimide and acenaphthylene, (iii) (meth)acrylic acid and (iv) at least one other unsaturated compound selected from the group consisting of styrene, methyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, allyl (meth)acrylate, benzyl (meth)acrylate, phenyl (meth)acrylate, glycerol mono(meth)acrylate, polystyrene macromonomer and polymethyl (meth)acrylate macromonomer.

In the copolymer (B1), the copolymerization ratio of the unsaturated compound (b1) is preferably 1 to 70 wt%, particularly preferably 1 to 40 wt%, the copolymerization ratio of the unsaturated compound (b2') is preferably 1 to 70 wt%, particularly preferably 1 to 40 wt%, the copolymerization ratio of the acidic unsaturated compound is preferably 1 to 40 wt%, particularly preferably 5 to 30 wt%, and the copolymerization ratio of the other unsaturated compound is preferably 1 to 80 wt%, particularly preferably 5 to 60 wt%.

In the present invention, when the copolymerization ratios of the unsaturated compounds in the copolymer (B1) are set to the above respective ranges, a radiation sensitive composition for forming a colored layer which exhibits excellent developability can be obtained.

In the present invention, another alkali-soluble resin may be used in combination with the copolymer (B1).

The above another alkali-soluble resin is not particularly limited as long as it serves as a binder for the colorant (A) and has solubility in an alkali developer which is used in the development step for forming a colored layer. For example, it is preferably an alkali-soluble resin having a carboxyl group (to be referred to as "another carboxyl group-containing alkali-soluble resin" hereinafter).

The another carboxyl group-containing alkali-soluble resin is preferably a copolymer of (i) an acidic unsaturated compound and (ii) another unsaturated compound, more preferably a copolymer of (i) a carboxyl group-containing unsaturated compound containing (meth)acrylic acid as an essential component and (ii) at least one other unsaturated compound selected from the group consisting of styrene, acenaphthylene, N-phenylmaleimide, N-cyclohexylmaleimide, methyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, allyl (meth)acrylate, benzyl (meth)acrylate, phenyl (meth)acrylate, glycerol mono(meth)acrylate, polystyrene macromonomer and polymethyl (meth)acrylate macromonomer.

In the present invention, a copolymerizable unsaturated bond can be introduced into the side chain of the copolymer (B1) and/or the another carboxyl group-containing alkali-soluble resin by reacting an unsaturated isocyanate compound such as 2-(meth)acryloyloxyethyl isocyanate with the copolymer (B1) obtained by copolymerizing an unsaturated compound having a hydroxyl group such as 2-hydroxyethyl (meth)acrylate and/or the another carboxyl group-containing alkali-soluble resin.

The weight average molecular weights in terms of polystyrene (to be referred to as "Mw" hereinafter) measured by gel permeation chromatography (GPC, eluting solvent: tetrahydrofuran) of the copolymer (B1) and the another

carboxyl group-containing alkali-soluble resin in the present invention are each preferably 1,000 to 45,000, more preferably 3,000 to 20,000.

The number average molecular weights in terms of polystyrene (to be referred to as "Mn" hereinafter) measured by gel permeation chromatography (GPC, eluting solvent: tetrahydrofuran) of the copolymer (B1) and the another alkali-soluble resin in the present invention are each preferably 1,000 to 45,000, more preferably 3,000 to 20,000.

When Mw is les than 1,000, the residual rate of the obtained film may lower, the pattern shape or heat resistance may be impaired, or the electric properties may deteriorate. When Mw is more than 45,000, the resolution may lower, the pattern shape may be impaired, or dry foreign matter may be produced at the time of slit-nozzle coating.

The copolymer (B1) and the another carboxyl group-containing alkali-soluble resin can be manufactured by polymerizing the unsaturated compound (b1) and the unsaturated compound (b2) in a suitable solvent 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).

The copolymer (B1) and the another carboxyl group-containing alkali-soluble resin can be purified by re-precipitation using two or more different organic solvents which differ in polarity after the radical polymerization of the polymerizable unsaturated compounds as described above. That is, insoluble impurities are optionally removed from a good solvent solution by filtration or centrifugation after polymerization and then the resulting solution is injected into a large amount, for example, 5 to 10 times the volume of the polymer solution of a precipitant, that is, a poor solvent to re-precipitate

the copolymer for purification. Out of the impurities remaining in the polymer solution, impurities soluble in the precipitant remain in a liquid phase and are separated from the purified copolymer (B1).

A combination of the good solvent and the precipitant used in this re-precipitation is, for example, a combination of diethylene glycol monomethyl ether acetate and n-hexane, a combination of methyl ethyl ketone and n-hexane, a combination of diethylene glycol monomethyl ether acetate and n-heptane, or a combination of methyl ethyl ketone and n-heptane.

The copolymer (B1) and the another carboxyl group-containing alkali-soluble resin can also be manufactured by the living radical polymerization of unsaturated compounds as their constituent components 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 control agent which serves as an inifator, such as cyano(dimethyl)methyl pyrazol-1-dithiocarboxylate, benzyl pyrazol-1-dithiocarboxylate, tetraethylthiuram disulfide, bis(pyrazol-1-ylthiocarbonyl)disulfide, bis(3-methyl-pyrazol-1-ylthiocarbonyl)disulfide, bis(4-methyl-pyrazol-1-ylthiocarbonyl)disulfide, bis(5-methyl-pyrazol-1-ylthiocarbonyl)disulfide, bis(3,4,5-trimethyl-pyrazol-1-ylthiocarbonyl)disulfide, bis(pyrol-1-ylthiocarbonyl)disulfide, bis(thiobenzoyl)disulfide, bis(n-octylsulfanylthiocarbonyl)disulfide or bis(n-dodecylsulfanylthiocarbonyl)disulfide in an inert solvent at a reaction temperature of preferably 0 to 150°C, more preferably 50 to 120°C.

In the present invention, the copolymers (B1) may be

used alone or in combination of two or more, and the same can be said of the another carboxyl group-containing alkali-soluble resin.

In the present invention, the total amount of the alkali-soluble resins is preferably 10 to 1,000 parts by weight, more preferably 20 to 500 parts by weight based on 100 parts by weight of the colorant (A). When the total amount of the alkali-soluble resins is smaller than 10 parts by weight, alkali developability may lower, or the residue or a stain may be produced on the substrate or light screening layer of an unexposed portion. When the total amount is larger than 1,000 parts by weight, the concentration of the colorant becomes relatively low, whereby it may be difficult to achieve the target color density of a thin film.

The amount of the copolymer (B1) in the alkali-soluble resin is preferably 10 to 100 wt%, particularly preferably 30 to 100 wt%. When the amount of the copolymer (B1) is smaller than 10 wt%, the desired effect of the present invention may be impaired.

- (C) polyfunctional monomer -

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

Examples of the polyfunctional monomer include di(meth)acrylates of an alkylene glycol such as ethylene glycol and propylene glycol; di(meth)acrylates of a polyalkylene glycol such as polyethylene glycol and polypropylene glycol; poly(meth)acrylates of a polyhydric alcohol having 3 or more hydroxyl groups and dicarboxylic acid modified products thereof such as glycerin, trimethylolpropane, pentaerythritol and dipentaerythritol; oligo(meth)acrylates such as polyester, epoxy resin, urethane resin, alkyd resin, silicone resin and spiran resin;

di(meth)acrylates of a polymer having a hydroxyl group at both terminals such as poly-1,3-butadiene having a hydroxyl group at both terminals, polyisoprene having a hydroxyl group at both terminals and polycaprolactone having a hydroxyl group at both terminals; and

tris[2-(meth)acryloyloxyethyl]phosphate.

Out of these polyfunctional monomers, poly(meth)acrylates of a polyhydric alcohol having 3 or more hydroxyl groups and dicarboxylic acid modified products thereof such as trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, pentaerythritol triacrylate, pentaerythritol trimethacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, dipentaerythritol pentaacrylate, dipentaerythritol pentamethacrylate, dipentaerythritol hexaacrylate and dipentaerythritol hexamethacrylate are preferred, and trimethylolpropane triacrylate, pentaerythritol triacrylate and dipentaerythritol hexaacrylate are particularly preferred because they provide a colored layer having excellent strength and surface smoothness and rarely produce the residue or a stain on the substrate or light screening layer of an unexposed portion.

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

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

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

Examples of the above monofunctional monomer include the above compounds enumerated for the N-substituted maleimide, acidic unsaturated compound or other unsaturated compounds in the above alkali-soluble resin (B), N-(meth)acryloylmorpholine, N-vinylpyrrolidone, N-vinyl-ε-caprolactam and commercially available M-5600 (of Toagosei Chemical Industry Co., Ltd.).

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

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

When the polyfunctional monomer and the monofunctional monomer are used in combination in the present invention, the total amount of the polyfunctional monomer and the monofunctional monomer is preferably 5 to 500 parts by weight, more preferably 20 to 300 parts by weight based on 100 parts by weight of the alkali-soluble resin (B). When the total amount is smaller than 5 parts by weight, the strength and surface smoothness of the colored layer may deteriorate and when the total amount is larger than 500 parts by weight, alkali developability may lower, or the residue or a stain may be produced on the substrate or light screening layer of an unexposed portion.

- (D) photopolymerization initiator -

The photopolymerization initiator in the present invention is a compound which forms active species capable

of initiating the polymerization of the above polyfunctional monomer (C) and the optionally used monofunctional monomer upon exposure to radiation such as visible radiation, ultraviolet radiation, far ultraviolet radiation, electron radiation or X-radiation.

The photopolymerization initiator is, for example, an acetophenone-based compound, biimidazole-based compound, triazine-based compound, O-acyloxime-based compound, onium salt-based compound, benzoin-based compound, benzophenone-based compound, α-diketone-based compound, polynuclear quinone-based compound, xanthone-based compound, diazo-based compound or imidosulfonato-based compound. These compounds form an active radical, an active acid or both of them upon exposure.

In the present invention, the above photopolymerization initiators may be used alone or in combination of two or more. At least one selected from the group consisting of an acetophenone-based compound, biimidazole-based compound, triazine-based compound and O-acyloxime-based compound is preferably used as the photopolymerization initiator in the present invention.

The amount of the photopolymerization initiator in the present invention is preferably 0.01 to 120 parts by weight, more preferably 1 to 100 parts by weight based on 100 parts by weight of the polyfunctional monomer (C) or the total of the polyfunctional monomer and the monofunctional monomer. When the amount of the photopolymerization initiator is smaller than 0.01 part by weight, it may be difficult to obtain a color filter having a predetermined colored layer pattern due to incomplete curing by exposure and when the amount is larger than 120 parts by weight, the formed colored layer may fall off from the substrate during development.

Examples of the acetophenone-based compound out of the preferred photopolymerization initiators in the present

invention include 2-hydroxy-2-methyl-1-phenylpropan-1-one, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one,
2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butan-1-one, 1-hydroxycyclohexyl·phenyl ketone,
2,2-dimethoxy-1,2-diphenylethan-1-one and
1,2-octanedione.

Out of these acetophenone-based compounds, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one
2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butan-1-one and 1,2-octanedione are preferred.

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

When the acetophenone-based compound is used as the photopolymerization initiator in the present invention, the amount of the acetophenone-based compound is preferably 0.01 to 80 parts by weight, more preferably 1 to 70 parts by weight, particularly preferably 1 to 60 parts by weight based on 100 parts by weight of the polyfunctional monomer (C) or the total of the polyfunctional monomer and the monofunctional monomer. When the amount of the acetophenone-based compound is smaller than 0.01 part by weight, it may be difficult to obtain a color filter having a predetermined colored layer pattern due to incomplete curing by exposure. When the amount is larger than 80 parts by weight, the formed colored layer may fall off from the substrate during development.

Examples of the above biimidazole-based 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.

Out of these biimidazole-based 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 and 2,2′-bis(2,4,6-trichlorophenyl)-4,4′,5,5′-tetraphenyl-1,2′-biimidazole are preferred, and 2,2′-bis(2,4-dichlorophenyl)-4,4′,5,5′-tetraphenyl-1,2′-biimidazole is particularly preferred.

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

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

When the biimidazole-based compound is used as the photopolymerization initiator in the present invention, the

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

When the biimidazole-based compound is used as the photopolymerization initiator in the present invention, it is preferably used in combination with the following hydrogen donor to further improve sensitivity.

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

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

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

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

These hydrogen donors may have a mercapto group and

an amino group at the same time.

A detailed description is subsequently given of these hydrogen donors.

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

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

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

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

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

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

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

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

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

The amine-based hydrogen donor serves as a sensitizer even when a photopolymerization initiator other than a biimidazole-based compound is used.

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

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

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

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

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

Examples of the above triazine-based compound include triazine-based compounds having a halomethyl group such as 2,4,6-tris(trichloromethyl)-s-triazine,
2-methyl-4,6-bis(trichloromethyl)-s-triazine,
2-[2-(5-methylfuran-2-yl)ethenyl]-4,6-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.

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

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

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

Examples of the above O-acyloxime-based compound 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-tetrahydrofuranyl benzoyl)-9.H.-carbazol-3-yl]-1-(O-acetyloxime),

ethanone-1-[9-ethyl-6-(2-methyl-4-tetrahydropyranyl benzoyl)-9.H.-carbazol-3-yl]-1-(O-acetyloxime),

ethanone-1-[9-ethyl-6-(2-methyl-5-tetrahydrofuranyl benzoyl)-9.H.-carbazol-3-yl]-1-(O-acetyloxime),

ethanone-1-[9-ethyl-6-(2-methyl-5-tetrahydropyranyl benzoyl)-9.H.-carbazol-3-yl]-1-(O-acetyloxime),

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

ethanone-1-[9-ethyl-6-(2-methyl-4-tetrahydropyranyl methoxybenzoyl)-9.H.-carbazol-3-yl]-1-(O-acetyloxime),

ethanone-1-[9-ethyl-6-(2-methyl-5-tetrahydrofuranyl methoxybenzoyl)-9.H.-carbazol-3-yl]-1-(O-acetyloxime),

ethanone-1-[9-ethyl-6-(2-methyl-5-tetrahydropyranyl methoxybenzoyl)-9.H.-carbazol-3-yl]-1-(O-acetyloxime) and

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

Out of these O-acyloxime-based 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-tetrahydrofuranyl methoxybenzoyl)-9.H.-carbazol-3-yl]-1-(O-acetyloxime) and

ethanone-1-[9-ethyl-6-{2-methyl-4-(2,2-dimethyl-1,3-dioxoranyl)methoxybenzoyl}-9.H.-carbazol-3-yl]-1-(O-acetyloxime) are particularly preferred.

The above O-acyloxime-based compounds may be used alone or in combination of two or more.

When the O-acyloxime-based compound is used as the photopolymerization initiator in the present invention, the amount of the O-acyloxime-based compound is preferably 0.01 to 80 parts by weight, more preferably 1 to 70 parts by weight, particularly preferably 1 to 60 parts by weight based on 100 parts by weight of the polyfunctional monomer (C) or the total of the polyfunctional monomer and the monofunctional monomer. When the amount of the O-acyloxime-based compound is smaller than 0.01 part by weight, it may be difficult to obtain a color filter having a predetermined colored layer pattern due to incomplete curing by exposure. When the amount is larger than 80 parts by weight, the formed colored layer may fall off from the substrate during development.

- additives -

The radiation sensitive composition for forming a colored layer of the present invention may contain various additives as required.

The above additives include an organic acid and an organic amino compound (excluding the above hydrogen donor).

The above organic acid and organic amino compound serve to further improve the solubility in an alkali developer of the radiation sensitive composition and further suppress the production of the residual undissolved product after development.

The above organic acid is preferably an aliphatic carboxylic acid or phenyl group-containing carboxylic acid having at least one carboxyl group in the molecule.

Examples of the above aliphatic carboxylic acid

include monocarboxylic acids such as formic acid, acetic acid, propionic acid, butyric acid, valeric acid, pivalic acid, caproic acid, diethylacetic acid, enanthic acid and caprylic acid; dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, brassylic acid, methylmalonic acid, ethylmalonic acid, dimethylmalonic acid, methylsuccinic acid, tetramethylsuccinic acid, cyclohexanedicarboxylic acid, itaconic acid, citraconic acid, maleic acid, fumaric acid and mesaconic acid; and tricarboxylic acids such as tricarballylic acid, aconitic acid and camphoronic acid.

The above phenyl group-containing carboxylic acid is, for example, a compound having a carboxyl group directly bonded to a phenyl group, or a carboxylic acid having a carboxyl group bonded to a phenyl group through a carbon chain.

Examples of the phenyl group-containing carboxylic acid include aromatic monocarboxylic acids such as benzoic acid, toluic acid, cuminic acid, hemellitic acid and mesitylenic acid; aromatic dicarboxylic acids such as phthalic acid, isophthalic acid and terephthalic acid; aromatic polycarboxylic acids having 3 or more carboxyl groups such as trimellitic acid, trimesic acid, mellophanic acid and pyromellitic acid; and phenylacetic acid, hydroatropic acid, hydrocinnamic acid, mandelic acid, phenylsuccinic acid, atropic acid, cinnamic acid, cinnamylidenic acid, coumaric acid and umbellic acid.

Out of these organic acids, aliphatic dicarboxylic acids are preferred, and malonic acid, adipic acid, itaconic acid, citraconic acid, fumaric acid and mesaconic acid are particularly preferred as the aliphatic carboxylic acid from the viewpoints of alkali solubility, solubility in a solvent which will be described hereinafter and the prevention of

the residue or a stain on the substrate or light screening layer of an unexposed portion. Aromatic dicarboxylic acids are preferred, and phthalic acid is particularly preferred as the phenyl group-containing carboxylic acid.

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

The amount of the organic acid is preferably 15 wt% or less, more preferably 10 wt% or less based on the total solids content of the radiation sensitive composition. When the amount of the organic acid is larger than 15 wt%, the adhesion to the substrate of the formed colored layer may lower.

The above organic amino compound is preferably an aliphatic amine or phenyl group-containing amine having at least one amino group in the molecule.

Examples of the above aliphatic amine include mono(cyclo)alkylamines such as n-propylamine, i-propylamine, n-butylamine, i-butylamine, sec-butylamine, t-butylamine, n-pentylamine, n-hexylamine, n-heptylamine, n-octylamine, n-nonylamine, n-decylamine, n-undecylamine, n-dodecylamine, cyclohexylamine, 2-methylcyclohexylamine, 3-methylcyclohexylamine, 4-methylcyclohexylamine, 2-ethylcyclohexylamine, 3-ethylcyclohexylamine and 4-ethylcyclohexylamine; di(cyclo)alkylamines such as methyl·ethylamine, diethylamine, methyl·n-propylamine, ethyl·n-propylamine, di-n-propylamine, di-i-propylamine, di-n-butylamine, di-i-butylamine, di-sec-butylamine, di-t-butylamine, di-n-pentylamine, d-n-hexylamine, methylcyclohexylamine, ethylcyclohexylamine and dicyclohexylamine; tri(cyclo)alkylamines such as dimethyl·ethylamine, methyl·diethylamine, triethylamine, dimethyl·n-propylamine, diethyl·n-propylamine, methyl·di-n-propylamine, ethyl·di-n-propylamine, tri-n-propylamine, tri-i-propylamine, tri-n-butylamine,

tri-i-butylamine, tri-sec-butylamine, tri-t-butylamine, tri-n-pentylamine, tri-n-hexylamine, dimethylcyclohexylamine, diethylcyclohexylamine, methyldicyclohexylamine, ethyldicyclohexylamine and tricyclohexylamine; mono(cyclo)alkanolamines such as 2-aminoethanol, 3-amino-1-propanol, 1-amino-2-propanol, 4-amino-1-butanol, 5-amino-1-pentanol, 6-amino-1-hexanol and 4-amino-1-cyclohexanol; di(cyclo)alkanolamines such as diethanolamine, di-n-propanolamine, di-i-propanolamine, di-n-butanolamine, di-i-butanolamine, di-n-pentanolamine, di-n-hexanolamine and di(4-cyclohexanol)amine; tri(cyclo)alkanolamines such as triethanolamine, tri-n-propanolamine, tri-i-propanolamine, tri-n-butanolamine, tri-i-butanolamine, tri-n-pentanolamine, tri-n-hexanolamine and tri(4-cyclohexanol)amine; amino(cyclo)alkanediols such as 3-amino-1,2-propanediol, 2-amino-1,3-propanediol, 4-amino-1,2-butanediol, 4-amino-1,3-butanediol, 4-amino-1,2-cyclohexanediol, 4-amino-1,3-cyclohexanediol, 3-dimethylamino-1,2-propanediol, 3-diethylamino-1,2-propanediol, 2-dimethylamino-1,3-propanediol and 2-diethylamino-1,3-propanediol; amino group-containing cycloalkane methanols such as 1-aminocyclopentane methanol, 4-aminocyclopentane methanol, 1-aminocyclohexane methanol, 4-aminocyclohexane methanol, 4-dimethylaminocyclopentane methanol, 4-diethylaminocyclopentane methanol, 4-dimethylaminocyclohexane methanol and 4-diethylaminocyclohexane methanol; and aminocarboxylic acids such as β-alanine, 2-aminobutyric acid, 3-aminobutyric acid, 4-aminobutyric acid, 2-aminoisobutyric acid, 3-aminoisobutyric acid, 2-aminovaleric acid, 5-aminovaleric acid, 6-aminocaproic acid, 1-aminocyclopropanecarboxylic acid,

1-aminocyclohexanecarboxylic acid and 4-aminocyclohexanecarboxylic acid.

The above phenyl group-containing amine is, for example, a compound having an amino group directly bonded to a phenyl group, or a compound having an amino group bonded to a phenyl group through a carbon chain.

Examples of the phenyl group-containing amine include aromatic amines such as aniline, 2-methylaniline, 3-methylaniline, 4-methylaniline, 4-ethylaniline, 4-n-propylaniline, 4-i-propylaniline, 4-n-butylaniline, 4-t-butylaniline, 1-naphthylamine, 2-naphthylamine, N,N-dimethylaniline, N,N-diethylaniline and 4-methyl-N,N-dimethylaniline; aminobenzyl alcohols such as 2-aminobenzyl alcohol, 3-aminobenzyl alcohol, 4-aminobenzyl alcohol, 4-dimethylaminobenzyl alcohol and 4-diethylaminobenzyl alcohol; and aminophenols such as 2-aminophenol, 3-aminophenol, 4-aminophenol, 4-dimethylaminophenol and 4-diethylaminophenol.

Additives other than the above additives include a dispersion aid such as a blue pigment derivative or yellow pigment derivative, e.g., a copper phthalocyanine derivative; filler such as glass or alumina; polymer compound such as polyvinyl alcohol, polyethylene glycol monoalkyl ether or poly(fluoroalkylacrylate); nonionic, cationic or anionic surfactant; adhesion accelerator such as vinyl trimethoxysilane, vinyl triethoxysilane, vinyl tris(2-methoxyethoxy)silane, N-(2-aminoethyl)-3-aminopropyl·methyl·dimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropyl·methyl·dimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 3-chloropropyl·methyl·dimethoxysilane,

3-chloropropyltrimethoxysilane, 3-methacryloyloxypropyltrimethoxysilane or 3-mercaptopropyltrimethoxysilane; antioxidant such as 2,2-thiobis(4-methyl-6-t-butylphenol) or 2,6-di-t-butylphenol; ultraviolet light absorber such as 2-(3-t-butyl-5-methyl-2-hydroxyphenyl)-5-chlorobenzo triazole or alkoxybenzophenone; cohesion inhibitor such as sodium polyacrylate; and heat radical generator such as 1,1'-azobis(cyclohexane-1-carbonitrile) or 2-phenylazo-4-methoxy-2,4-dimethylvaleronitrile.

Solvent

The radiation sensitive composition for forming a colored layer of the present invention comprises the above components (A) to (D) as essential components and optionally the above additives and is preferably mixed with a solvent to be prepared as a liquid composition.

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

Examples of the solvent include (poly)alkylene glycol monoalkyl ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol mono-n-propyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-propyl ether, diethylene glycol mono-n-butyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol mono-n-propyl ether, propylene glycol mono-n-butyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether,

dipropylene glycol mono-n-propyl ether, dipropylene glycol mono-n-butyl ether, tripropylene glycol monomethyl ether and tripropylene glycol monoethyl ether; (poly)alkylene glycol monoalkyl ether acetates such as ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether acetate and propylene glycol monoethyl ether acetate; other ethers such as diethylene glycol dimethyl ether, diethylene glycol methyl ethyl ether, diethylene glycol diethyl ether and tetrahydrofuran; ketones such as methyl ethyl ketone, cyclohexanone, 2-heptanone and 3-heptanone; alkyl lactates such as methyl lactate and ethyl lactate; other esters such as ethyl 2-hydroxy-2-methylpropionate, methyl 3-methoxypropionate, ethyl 3-methoxypropionate, methyl 3-ethoxypropionate, ethyl 3-ethoxypropionate, ethyl ethoxyacetate, ethyl hydroxyacetate, methyl 2-hydroxy-3-methylbutanoate, 3-methoxybutylacetate, 3-methyl-3-methoxybutylacetate, 3-methyl-3-methoxybutylpropionate, ethyl acetate, n-propyl acetate, i-propyl acetate, n-butyl acetate, i-butyl acetate, n-amyl formate, i-amyl acetate, n-butyl propionate, ethyl butyrate, n-propyl butyrate, i-propyl butyrate, n-butyl butyrate, methyl pyruvate, ethyl pyruvate, n-propyl pyruvate, methyl acetoacetate, ethyl acetoacetate and ethyl 2-oxobutanoate; aromatic hydrocarbons such as toluene and xylene; and amides and lactams such as N,N-dimethylformamide, N,N-dimethylacetamide and N-methylpyrrolidone.

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

methyl 3-ethoxypropionate, ethyl 3-ethoxypropionate, 3-methoxybutylacetate, 3-methyl-3-methoxybutylpropionate, n-butyl acetate, i-butyl acetate, n-amyl formate, i-amyl acetate, n-butyl propionate, ethyl butyrate, i-propyl butyrate, n-butyl butyrate and ethyl pyruvate are particularly preferred from the viewpoints of pigment dispersibility, solubility for components other than pigment and coatability.

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

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

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

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

Color filter

The color filter of the present invention has a colored layer formed from the radiation sensitive composition for forming a colored layer of the present invention.

A description is subsequently given of the method of forming a colored layer in the color filter of the present invention.

A light screening layer is optionally formed on the surface of a substrate to define a portion for forming pixels thereon, and a liquid radiation sensitive composition comprising, for example, a red pigment dispersed therein is applied to the substrate and prebaked to evaporate the solvent so as to form a coating film.

This coating film is then exposed to radiation through a photomask, developed with an alkali developer to dissolve and remove an unexposed portion of the coating film and post-baked to form a red pixel array having a predetermined pixel pattern.

Thereafter, the application, prebaking, exposure, development and post-baking of liquid radiation sensitive compositions comprising green and blue pigments dispersed therein are carried out likewise to form a green pixel array and a blue pixel array on the same substrate sequentially so as to obtain a color filter having red, green and blue pixel arrays on the substrate. The order of forming the color pixels is not limited to the above in the present invention.

A black matrix can be formed likewise by using a liquid radiation sensitive composition comprising, for example, a black pigment dispersed therein.

The substrate used to form pixels and/or a black matrix is made of glass, silicon, polycarbonate, polyester, aromatic polyamide, polyamide-imide or polyimide.

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

To apply the liquid radiation sensitive composition to the substrate, a suitable coating technique such as spray coating, roll coating, rotational coating (spin coating), slit die coating, bar coating or ink jet coating may be employed. Out of these, spin coating and split die coating

are preferred.

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

The radiation used to form pixels and/or a black matrix is selected from visible radiation, ultraviolet radiation, far ultraviolet radiation, electron radiation and X-radiation. Out of these, radiation having a wavelength of 190 to 450 nm is preferred.

The dose of the radiation is preferably 10 to 10,000 $J/m^2$.

As for prebaking conditions which differ according to the type and amount of each component, the coating film is preferably prebaked at 70 to 120°C for about 1 to 15 minutes.

To form a coating film of the radiation sensitive composition of the present invention, a dry film method may be employed. In this case, the dry film is a laminate (to be referred to as "radiation sensitive dry film" hereinafter) consisting of a base film, preferably a flexible base film and a radiation sensitive layer formed from the radiation sensitive composition of the present invention on the base film.

The above radiation sensitive dry film can be formed by applying the radiation sensitive composition of the present invention, preferably as a liquid composition, to the base film and removing the solvent to form a radiation sensitive layer. The base film of the radiation sensitive dry film is, for example, a film of a synthetic resin such as polyethylene terephthalate (PET), polyethylene, polypropylene, polycarbonate or polyvinyl chloride. The thickness of the base film is suitably 15 to 125 μm. The thickness of the obtained radiation sensitive layer is preferably about 1 to 30 μm. The removal of the solvent can be carried out by heating preferably at 80 to 150°C for about

1 to 10 minutes.

The radiation sensitive dry film can be preserved by further forming a cover film on the radiation sensitive layer when it is not used. This cover film needs to have suitable releasability so that it cannot be removed when it is not used and can be easily removed when it is used. As a cover film which satisfies the above condition may be used, for example, a film obtained by applying or baking a silicone-based release agent to the surface of a synthetic resin film such as PET film, polypropylene film, polyethylene film or polyvinyl chloride film. The thickness of the cover film is generally about 25 μm.

When the radiation sensitive composition of the present invention is used as a solution, its solids content (ratio of the weight excluding the solvent from the composition to the total weight of the composition) is preferably 15 to 80 wt%. The more preferred solids content differs according to the method of forming a coating film. The solids content is preferably 15 to 30 wt% when the coating film is formed by coating and preferably 50 to 70 wt% when the coating film is formed by the dry film method.

The above alkali developer is preferably an aqueous solution of sodium carbonate, sodium hydroxide, potassium hydroxide, tetramethylammonium hydroxide, choline, 1,8-diazabicyclo-[5.4.0]-7-undecene or 1,5-diazabicyclo-[4.3.0]-5-nonene.

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

Shower development, spray development, dip (immersion) development or puddle development may be employed. As for development conditions, the coating film is preferably developed at normal temperature for 5 to 300

sec.

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

Color liquid crystal display device

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

As an example of the color liquid crystal display device of the present invention, a color liquid crystal display device having excellent characteristic properties can be manufactured by using the radiation sensitive composition for forming a colored layer of the present invention to form pixels and/or a black matrix on a thin film transistor substrate array as described above.

As described above, the radiation sensitive composition for forming a colored layer of the present invention can provide pixels and a black matrix having an excellent high-definition pattern shape and excellent adhesion to a substrate without producing the residue or a stain during development.

Therefore, the radiation sensitive composition for forming a colored layer of the present invention can be extremely advantageously used in the manufacture of color filters including a color filter for color liquid crystal display devices in the field of the electronic industry.

Examples

The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting. "Parts" and "%" are based on weight.

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

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

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

Eluting solvent: tetrahydrofuran containing 0.5 wt% of phosphoric acid

Synthesis of alkali-soluble resin

Synthesis Example 1

5 parts of 2,2'-azobisisobutyronitrile and 200 parts of propylene glycol monomethyl ether acetate were fed to a flask equipped with a cooling tube and a stirrer, 5 parts of 4-hydroxyphenyl methacrylate, 30 parts of N-phenylmaleimide, 15 parts of methacrylic acid, 18 parts of styrene, 22 parts of benzyl methacrylate, 10 parts of 2-hydroxyethyl methacrylate and 5 parts of α-methylstyrene dimer as a chain transfer agent were then fed to the flask, and the inside of the flask was substituted by nitrogen. And then, the temperature of the obtained reaction solution was elevated to 80°C while it was stirred gently to be polymerized by maintaining that temperature for 3 hours. After the end of polymerization, the reaction solution was heated at 100°C, 0.5 part of 2,2'-azobisisobutyronitrile was added, and polymerization was further continued for 1 hour to obtain a solution of an alkali-soluble resin (solids content of 33.0 wt%).

The obtained alkali-soluble resin had an Mw of 9,000 and an Mn of 4,500. This alkali-soluble resin was designated as alkali-soluble resin (B-1).

Synthesis Example 2

4 parts of 2,2'-azobisisobutyronitrile and 200 parts

of propylene glycol monomethyl ether acetate were fed to a flask equipped with a cooling tube and a stirrer, and then 15 parts of 4-hydroxyphenyl methacrylate, 30 parts of acenaphthylene, 15 parts of methacrylic acid, 5 parts of mono[2-(meth)acryloyloxyethyl]succinate, 25 parts of benzyl methacrylate, 10 parts of 2-hydroxyethyl methacrylate and 6 parts of α-methylstyrene dimer as a chain transfer agent were fed to the flask to carry out polymerization in the same manner as in Synthesis Example 1 so as to obtain a solution of an alkali-soluble resin (solids content of 33.0 wt%).

The obtained alkali-soluble resin had an Mw of 12,000 and an Mn of 5,500. This alkali-soluble resin was designated as alkali-soluble resin (B-2).

Synthesis Example 3

4 parts of 2,2'-azobisisobutyronitrile and 200 parts of propylene glycol monomethyl ether acetate were fed to a flask equipped with a cooling tube and a stirrer, and then 30 parts of 4-hydroxyphenyl methacrylate, 30 parts of acenaphthylene, 15 parts of methacrylic acid, 15 parts of benzyl methacrylate, 10 parts of 2-hydroxyethyl methacrylate and 6 parts of α-methylstyrene dimer as a chain transfer agent were fed to the flask to carry out polymerization in the same manner as in Synthesis Example 1 so as to obtain a solution of an alkali-soluble resin (solids content of 33.0 wt%).

The obtained alkali-soluble resin had an Mw of 11,500 and an Mn of 5,000. This alkali-soluble resin was designated as alkali-soluble resin (B-3).

Synthesis Example 4

4 parts of 2,2'-azobisisobutyronitrile and 200 parts of propylene glycol monomethyl ether acetate were fed to a flask equipped with a cooling tube and a stirrer, and then 20 parts of 4-hydroxyphenyl methacrylate, 15 parts of

acenaphthylene, 15 parts of methacrylic acid, 30 parts of benzyl methacrylate, 20 parts of glycerol methacrylate and 6 parts of α-methylstyrene dimer as a chain transfer agent were fed to the flask to carry out polymerization in the same manner as in Synthesis Example 1 so as to obtain a solution of an alkali-soluble resin (solids content of 33.0 wt%).

The obtained alkali-soluble resin had an Mw of 9,700 and an Mn of 4,600. This alkali-soluble resin was designated as alkali-soluble resin (B-4).

Synthesis Example 5

5 parts of 2,2'-azobisisobutyronitrile and 200 parts of propylene glycol monomethyl ether acetate were fed to a flask equipped with a cooling tube and a stirrer, and then 30 parts of 4-hydroxyphenyl methacrylate, 15 parts of methacrylic acid, 30 parts of styrene, 15 parts of benzyl methacrylate, 10 parts of 2-hydroxyethyl methacrylate and 5 parts of α-methylstyrene dimer as a chain transfer agent were fed to the flask to carry out polymerization in the same manner as in Synthesis Example 1 so as to obtain a solution of an alkali-soluble resin (solids content of 33.0 wt%).

The obtained alkali-soluble resin had an Mw of 11,000 and an Mn of 4,700. This alkali-soluble resin was designated as alkali-soluble resin (B-5).

Synthesis Example 6

4 parts of 2,2'-azobisisobutyronitrile and 200 parts of propylene glycol monomethyl ether acetate were fed to a flask equipped with a cooling tube and a stirrer, and then 15 parts of acenaphthylene, 25 parts of N-phenylmaleimide, 15 parts of methacrylic acid, 5 parts of mono[2-(meth)acryloyloxyethyl]succinate, 15 parts of styrene, 25 parts of benzyl methacrylate and 6 parts of α-methylstyrene dimer as a chain transfer agent were fed to

the flask to carry out polymerization in the same manner as in Synthesis Example 1 so as to obtain a solution of an alkali-soluble resin (solids content of 33.0 wt%).

The obtained alkali-soluble resin had an Mw of 10,300 and an Mn of 4,700. This alkali-soluble resin was designated as alkali-soluble resin (B-6).

Example 1

<preparation of liquid composition>

8 parts of a mixture of C.I. Pigment Red 254 and C.I. Pigment Red 177 in a weight ratio of 80/20 as the colorant (A), 4 parts (solids content) of Disperbyk-2001 as a dispersant and 75 parts of propylene glycol monomethyl ether acetate as a solvent were mixed and dispersed together by a bead mill to prepare a pigment dispersion.

87 parts of the obtained pigment dispersion, 8 parts of the alkali-soluble resin (B-1) as the alkali-soluble resin (B), 2 parts of dipentaerythritol hexaacrylate and 4 parts of pentaerythritol tetraacrylate as the polyfunctional monomers (C), 3 parts of 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butan-1-one as the photopolymerization initiator (D), and 70 parts of 3-methoxybutyl acetate and 96 parts of ethyl 3-ethoxypropionate as solvents were mixed together to prepare a liquid composition (R1).

<formation of colored layer>

The liquid composition (R1) was applied to a soda glass substrate having an $SiO_2$ film for preventing the elution of sodium ions on the surface with a spin coater and prebaked on a hot plate at 90°C for 2 minutes to form a 1.2 μm-thick coating film.

Subsequently, the substrate was cooled to room temperature, and the coating film was exposed to ultraviolet

radiation having wavelengths of 365 nm, 405 nm and 436 nm through a photomask (slit width of 30 μm) with a high-pressure mercury lamp. The amount of exposure at this point was 100 $J/m^2$. This substrate was then shower developed by delivering a 0.04 wt% aqueous solution of potassium hydroxide having a temperature of 23°C at a development pressure of 2 $kgf/cm^2$ (nozzle diameter of 1 mm) for 40 seconds, rinsed with super pure water and dried with air. Thereafter, it was further post-baked in a clean oven at 230°C for 30 minutes to form a red striped pixel pattern on the substrate.

A red striped pixel pattern was formed in the same manner as above except that the shower development time was changed to 60 seconds.

<evaluation>

When the pixel array on the substrate which had been shower developed for 40 seconds was observed through an optical microscope, the development residue was not seen on the substrate of an unexposed portion (○) and a missing part was not seen at the edge of the pixel pattern.

When the section of the pixel pattern on the substrate which had been shower developed for 40 seconds was observed through a scanning electron microscope (SEM), no undercut was seen (○) and a pattern having a line width of 6 μm could be formed.

When the line widths of the pixel patterns formed on the substrate which had been shower developed for 40 seconds and the substrate which had been shower developed for 60 seconds through a photomask having a slit width of 30 μm were measured by an optical microscope, a change in the line width was 1.2 μm.

Examples 2 to 5

Liquid compositions (R2) to (R5) were prepared in the

same manner as in Example 1 except that the alkali-soluble resin was changed as shown in Table 1. Then, a red striped pixel pattern was formed on the substrate in the same manner as in Example 1 except that the liquid compositions (R2) to (R5) were used in place of the liquid composition (R1) to carry out evaluations.

The above results are shown in Table 1.

Table 1

| Examples | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Liquid composition | R1 | R2 | R3 | R4 | R5 |
| Red pigment | 8 | 8 | 8 | 8 | 8 |
| Dispersant BYK-2001 | 4 | 4 | 4 | 4 | 4 |
| Alkali-soluble resin (B-1) | 8 | | | | |
| Alkali-soluble resin (B-2) | | 8 | | | |
| Alkali-soluble resin (B-3) | | | 8 | | |
| Alkali-soluble resin (B-4) | | | | 8 | |
| Alkali-soluble resin (B-5) | | | | | 8 |
| Residue | ○ | ○ | ○ | ○ | ○ |
| Missing part of pattern | None | None | None | None | None |
| Undercut | ○ | ○ | ○ | ○ | ○ |
| Change in line width(μm) | 1.2 | 1.1 | 1.5 | 1.4 | 2.2 |
| Formable pattern(μm) | 6 | 5 | 6 | 8 | 15 |

Example 6

<preparation of liquid composition>

11 parts of a mixture of C.I. Pigment Green 36 and C.I. Pigment Yellow 150 in a weight ratio of 60/40 as the colorant (A), 4 parts (solids content) of Disperbyk-2001 as a dispersant and 75 parts of propylene glycol monomethyl ether acetate as a solvent were mixed and dispersed together by a bead mill to prepare a pigment dispersion.

90 parts of the obtained pigment dispersion, 8 parts

of the alkali-soluble resin (B-1) as the alkali-soluble resin (B), 2 parts of dipentaerythritol hexaacrylate and 4 parts of pentaerythritol tetraacrylate as the polyfunctional monomers (C), 3 parts of 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butan-1-one as the photopolymerization initiator (D), and 70 parts of 3-methoxybutyl acetate and 96 parts of ethyl 3-ethoxypropionate as solvents were mixed together to prepare a liquid composition (G1).

<formation of colored layer>

A green striped pixel pattern was formed on the substrate in the same manner as in Example 1 except that the liquid composition (G1) was used in place of the liquid composition (R1).

<evaluation>

When the pixel array on the substrate which had been shower developed for 40 seconds was observed through an optical microscope, the development residue was not seen on the substrate of an unexposed portion and a missing part was not seen at the edge of the pixel pattern.

When the section of the pixel pattern on the substrate which had been shower developed for 40 seconds was observed through a scanning electron microscope (SEM), no undercut was seen and a pattern having a line width of 6 μm could be formed.

When the line widths of the pixel patterns formed on the substrate which had been shower developed for 40 seconds and the substrate which had been shower developed for 60 seconds through a photomask having a slit width of 30 μm were measured by an optical microscope, a change in the line width was 1.1 μm.

Examples 7 to 10

Liquid compositions (G2) to (G5) were prepared in the same manner as in Example 6 except that the alkali-soluble resin was changed as shown in Table 2. A green striped pixel pattern was formed on the substrate in the same manner as in Example 1 except that the liquid compositions (G2) to (G5) were used in place of the liquid composition (R1) to carry out evaluations.

The above results are shown in Table 2.

Table 2

| Examples | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|
| Liquid composition | G1 | G2 | G3 | G4 | G5 |
| Green pigment | 11 | 11 | 11 | 11 | 11 |
| Dispersant BYK-2001 | 4 | 4 | 4 | 4 | 4 |
| Alkali-soluble resin (B-1) | 8 | | | | |
| Alkali-soluble resin (B-2) | | 8 | | | |
| Alkali-soluble resin (B-3) | | | 8 | | |
| Alkali-soluble resin (B-4) | | | | 8 | |
| Alkali-soluble resin (B-5) | | | | | 8 |
| Residue | ○ | ○ | ○ | ○ | ○ |
| Missing part of pattern | None | None | None | None | None |
| Undercut | ○ | ○ | ○ | ○ | ○ |
| Change in line width(μm) | 1.1 | 1.3 | 1.4 | 1.2 | 2.1 |
| Formable pattern(μm) | 6 | 8 | 5 | 5 | 15 |

Example 11

<preparation of liquid composition>

9 parts of a mixture of C.I. Pigment Blue 15:6 and C.I. Pigment Violet 23 in a weight ratio of 95/5 as the colorant (A), 4 parts (solids content) of Disperbyk-2001 as a dispersant and 75 parts of propylene glycol monomethyl ether acetate as a solvent were mixed and dispersed together by

a bead mill to prepare a pigment dispersion.

88 parts of the obtained pigment dispersion, 8 parts of the alkali-soluble resin (B-1) as the alkali-soluble resin (B), 2 parts of dipentaerythritol hexaacrylate and 4 parts of pentaerythritol tetraacrylate as the polyfunctional monomers (C), 3 parts of 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one as the photopolymerization initiator (D), and 70 parts of 3-methoxybutyl acetate and 96 parts of ethyl 3-ethoxypropionate as solvents were mixed together to prepare a liquid composition (B1).

<formation of colored layer>

Thereafter, a blue striped pixel pattern was formed on the substrate in the same manner as in Example 1 except that the liquid composition (B1) was used in place of the liquid composition (R1).

<evaluation>

When the pixel array on the substrate which had been shower developed for 40 seconds was observed through an optical microscope, the development residue was not seen on the substrate of an unexposed portion and a missing part was not seen at the edge of the pixel pattern.

When the section of the pixel pattern on the substrate which had been shower developed for 40 seconds was observed through a scanning electron microscope (SEM), no undercut was seen and a pattern having a line width of 5 μm could be formed.

When the line widths of the pixel patterns formed on the substrate which had been shower developed for 40 seconds and the substrate which had been shower developed for 60 seconds through a photomask having a slit width of 30 μm were measured by an optical microscope, a change in the line width

was 1.5 μm.

Examples 12 to 15

Liquid compositions (B2) to (B5) were prepared in the same manner as in Example 11 except the alkali-soluble resin was changed as shown in Table 3. A blue striped pixel pattern was formed on the substrate in the same manner as in Example 1 except that the liquid compositions (B2) to (B5) were used in place of the liquid composition (R1) to carry out evaluations.

The above results are shown in Table 3.

Table 3

| Examples | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|
| Liquid composition | B1 | B2 | B3 | B4 | B5 |
| Blue pigment | 9 | 9 | 9 | 9 | 9 |
| Dispersant BYK-2001 | 4 | 4 | 4 | 4 | 4 |
| Alkali-soluble resin (B-1) | 8 | | | | |
| Alkali-soluble resin (B-2) | | 8 | | | |
| Alkali-soluble resin (B-3) | | | 8 | | |
| Alkali-soluble resin (B-4) | | | | 8 | |
| Alkali-soluble resin (B-5) | | | | | 8 |
| Residue | ○ | ○ | ○ | ○ | ○ |
| Missing part of pattern | None | None | None | None | None |
| Undercut | ○ | ○ | ○ | ○ | ○ |
| Change in line width(μm) | 1.5 | 1.4 | 1.2 | 1.3 | 2.3 |
| Formable pattern(μm) | 5 | 8 | 6 | 8 | 15 |

Example 16

<preparation of liquid composition>

20 parts of carbon black as the colorant (A), 4 parts (solids content) of Disperbyk-2001 as a dispersant and 75 parts of propylene glycol monomethyl ether acetate as a

solvent were mixed and dispersed together by a bead mill to prepare a pigment dispersion.

99 parts of the obtained pigment dispersion, 8 parts of the alkali-soluble resin (B-1) as the alkali-soluble resin (B), 2 parts of dipentaerythritol hexaacrylate and 4 parts of pentaerythritol tetraacrylate as the polyfunctional monomers (C), 3 parts of ethanone-1-[9-ethyl-6-[2-methyl-4-(2,2-dimethyl-1,3-dioxoranyl)methoxybenzoyl]-9.H.-carbazol-3-yl]-1-(O-acetyloxime) as the photopolymerization initiator (D), and 150 parts of propylene glycol monomethyl ether acetate as a solvent were mixed together to prepare a liquid composition (BK1).

<formation of colored layer>

Thereafter, a black striped pixel pattern was formed on the substrate in the same manner as in Example 1 except that the liquid composition (BK1) was used in place of the liquid composition (R1).

<evaluation>

When the pixel array on the substrate which had been shower developed for 40 seconds was observed through an optical microscope, the development residue was not seen on the substrate of an unexposed portion and a missing part was not seen at the edge of the pixel pattern.

When the section of the pixel pattern on the substrate which had been shower developed for 40 seconds was observed through a scanning electron microscope (SEM), no undercut was seen and a pattern having a line width of 6 μm could be formed.

When the line widths of the pixel patterns formed on the substrate which had been shower developed for 40 seconds and the substrate which had been shower developed for 60

seconds through a photomask having a slit width of 30 μm were measured by an optical microscope, a change in the line width was 1.3 μm.

Examples 17 to 20

Liquid compositions (BK2) to (BK5) were prepared in the same manner as in Example 16 except the alkali-soluble resin was changed as shown in Table 4. A black striped pixel pattern was formed on the substrate in the same manner as in Example 1 except that the liquid compositions (BK2) to (BK5) were used in place of the liquid composition (R1) to carry out evaluations.

The above results are shown in Table 4.

Table 4

| Examples | 16 | 17 | 18 | 19 | 20 |
|---|---|---|---|---|---|
| Liquid composition | BK1 | BK2 | BK3 | BK4 | BK5 |
| Carbon Black | 20 | 20 | 20 | 20 | 20 |
| Dispersant BYK-2001 | 4 | 4 | 4 | 4 | 4 |
| Alkali-soluble resin (B-1) | 8 | | | | |
| Alkali-soluble resin (B-2) | | 8 | | | |
| Alkali-soluble resin (B-3) | | | 8 | | |
| Alkali-soluble resin (B-4) | | | | 8 | |
| Alkali-soluble resin (B-5) | | | | | 8 |
| Residue | ○ | ○ | ○ | ○ | ○ |
| Missing part of pattern | None | None | None | None | None |
| Undercut | ○ | ○ | ○ | ○ | ○ |
| Change in line width(μm) | 1.3 | 1.2 | 1.1 | 1.5 | 2.3 |
| Formable pattern(μm) | 6 | 5 | 8 | 5 | 15 |

Comparative Example 1

A liquid composition (CR1) was prepared in the same manner as in Example 1 except that the alkali-soluble resin

(B-1) was changed to the alkali-soluble resin (B-6). Then, a red striped pixel pattern was formed on the substrate in the same manner as in Example 1 except that the liquid composition (CR1) was used in place of the liquid composition (R1).

<evaluation>

When the pixel array on the substrate which had been shower developed for 40 seconds was observed through an optical microscope, the development residue was seen on the substrate of an unexposed portion (×) and a missing part was seen at the edge of the pixel pattern.

When the section of the pixel pattern on the substrate which had been shower developed for 40 seconds was observed through a scanning electron microscope (SEM), an undercut was seen (×) and a pattern having a line width of 35 μm could be formed.

When the line widths of the pixel patterns formed on the substrate which had been shower developed for 40 seconds and the substrate which had been shower developed for 60 seconds through a photomask having a slit width of 30 μm were measured by an optical microscope, a change in the line width was 3.7 μm.

Comparative Example 2

A liquid composition (CG1) was prepared in the same manner as in Example 6 except that the alkali-soluble resin (B-1) was changed to the alkali-soluble resin (B-6). Then, a green striped pixel pattern was formed on the substrate in the same manner as in Example 1 except that the liquid composition (CG1) was used in place of the liquid composition (R1) to carry out evaluations.

Comparative Example 3

A liquid composition (CB1) was prepared in the same manner as in Example 11 except that the alkali-soluble resin (B-1) was changed to the alkali-soluble resin (B-6). Then, a blue striped pixel pattern was formed on the substrate in the same manner as in Example 1 except that the liquid composition (CB1) was used in place of the liquid composition (R1) to carry out evaluations.

Comparative Example 4

A liquid composition (CBK1) was prepared in the same manner as in Example 16 except that the alkali-soluble resin (B-1) was changed to the alkali-soluble resin (B-6). Then, a black striped pixel pattern was formed on the substrate in the same manner as in Example 1 except that the liquid composition (CBK1) was used in place of the liquid composition (R1) to carry out evaluations.

The above results are shown in Table 5.

Table 5

| Comparative Examples | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Red pigment | 8 | | | |
| Green pigment | | 11 | | |
| Blue pigment | | | 9 | |
| Carbon black | | | | 20 |
| Dispersant BYK-2001 | 4 | 4 | 4 | 4 |
| Alkali-soluble resin (B-6) | 8 | 8 | 8 | 8 |
| Residue | × | ○ | ○ | × |
| Missing part of pattern | Seen | Seen | Seen | Seen |
| Undercut | × | × | × | × |
| Change in line width (μm)*) | 3.7 | 3.1 | 3.5 | 4.1 |
| Formable pattern (μm) | 35 | 45 | 40 | 50 |

Red pigment: a mixture of C.I. Pigment Red 254 and C.I. Pigment Red 177 in a weight ratio of 80/20

Green pigment: a mixture of C.I. Pigment Green 36 and C.I. Pigment Yellow 150 in a weight ratio of 60/40

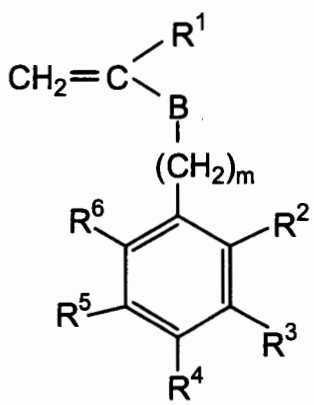
Blue pigment: a mixture of C.I. Pigment Blue 15:6 and C.I. Pigment Violet 23 in a weight ratio of 95/5

Change in line width (μm): line width after 40 seconds of shower development (μm) - line width after 60 seconds of shower development (μm)

What is claimed is:

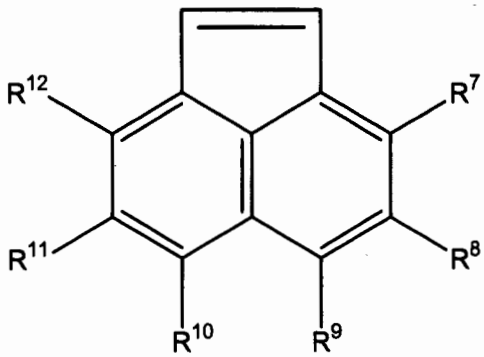
1. A radiation sensitive composition for forming a colored layer, comprising (A) a colorant, (B) an alkali-soluble resin, (C) a polyfunctional monomer and (D) a photopolymerization initiator, wherein

the alkali-soluble resin (B) comprises a copolymer of a phenol structure-containing unsaturated compound represented by the following formula (1) and another copolymerizable unsaturated compound, and the another copolymerizable unsaturated compound is at least one selected from the group consisting of an N-substituted maleimide, unsaturated compound represented by the following formula (2), acidic unsaturated compound, aromatic vinyl compound, indene, macromonomer having a (meth)acryloyl group at one terminal of a polymer molecular chain, unsaturated carboxylate, unsaturated aminoalkyl carboxylate, unsaturated glycidyl carboxylate, vinyl cyanide compound, unsaturated amide, vinyl carboxylate, unsaturated ether and aliphatic conjugated diene.



... (1)

(wherein $R^1$ is a hydrogen atom or alkyl group having 1 to 4 carbon atoms, $R^2$ to $R^6$ are the same or different and each a hydrogen atom, hydroxyl group, alkyl group having 1 to 6 carbon atoms or alkoxy group having 1 to 6 carbon atoms, B is -COO- or -CONH-, and m is an integer of 0 to 3, with the proviso that at least one of $R^2$ to $R^6$ is a hydroxyl group.)




(2)

(wherein $R^7$ to $R^{12}$ are each independently a hydrogen atom, halogen atom, hydroxyl group, hydroxymethyl group or carboxyl group.)

2. The radiation sensitive composition for forming a colored layer according to claim 1, wherein the another copolymerizable unsaturated compound is at least one selected from the group consisting of an N-substituted maleimide and an unsaturated compound represented by the above formula (2).

3. A color filter having a colored layer formed from the radiation sensitive composition for forming a colored layer of claim 1 or 2.

4. A color liquid crystal display device comprising the color filter of claim 3.

5. Use of a copolymer of a phenol skeleton-containing compound represented by the above formula (1) and another copolymerizable unsaturated compound as the alkali-soluble resin in the radiation sensitive composition for forming a colored layer.