DESCRIPTION

RADIATION-SENSITIVE COMPOSITION FOR THE FORMATION OF COLORED LAYERS, COLOR FILTERS, AND COLOR LIQUID CRYSTAL DISPLAY

Technical Field

[0001] The subject invention relates to a radiation-sensitive composition for forming a colored layer, a color filter, and a color liquid crystal display device, and more specifically, to a radiation-sensitive composition used for forming a colored layer which is useful for a color filter used for a transmission-type or reflection-type color liquid crystal display apparatus a color image pickup tube device etc., to a color filter having the colored layer formed from the radiation-sensitive composition, and to a color liquid crystal display device comprising the color filter.

Background Art

[0002] In producing a color filter using a coloring radiation-sensitive composition, a method of obtaining a pixel in each color is known, the method involving forming a coating film of a coloring radiation-sensitive composition on a substrate or on a substrate on which a light-shielding layer having a desired pattern has been preliminarily formed, irradiating the coating film with radiation through a photomask having a predetermined pattern (hereinafter, referred to as "exposure," "exposed to light," or the like), developing the resultant to dissolve and remove unexposed part, and then post-baking the resultant (see, for example, Patent

Documents 1 and 2).

[0003] In the technical field of color filters in recent years, in addition to the fact that shortening takt time by decreasing exposure dose is mainly employed, the content ratio of a pigment in a coloring radiation-sensitive composition tends to be further increased in order to meet a demand for higher color purity with respect to color liquid crystal display devices. As the content ratio of a pigment in the coloring radiation-sensitive composition is increased such as above and the exposure dose for forming a pixel pattern is decreased, the cross-section of the pixel pattern tends to have a reverse taper (overhanging) shape. As a result, a tangible problem that the wiring of a transparent electrode formed of ITO or the like on the pixel pattern is disconnected, is occurred.

To cope with the problem that the cross-section of a pixel pattern has a reverse taper shape, for example, Patent Documents 3 and 4 propose use of a composition comprising a chain transfer agent. However, in such a method as described above, forming a pixel pattern for obtaining sufficient residual film thickness and adhesiveness has been difficult when exposure dose is decreased. Meanwhile, when the cross-section of a pixel pattern has a normal-taper shape but with too gentle taper angle, a problem that the slant portion of the pixel pattern becomes longer, producing a portion with a thinner film thickness in a pixel edge, with the result that a desired color cannot be reproduced, is occurred.

In addition, a tangible problem in the mass production process of a color filter that an inspection step stagnates because of

aggregation particle, color unevenness etc. generated in various steps, resulting in a reduction in production efficiency, is occurred.

Prior Art Documents

[0004] Patent Document 1: JP 02-144502 A

Patent Document 2: JP 03-53201 A

Patent Document 3: JP 2002-167404 A

Patent Document 4: JP 2002-287337 A

Disclosure of the Invention

Problems to be solved by the Invention

[0005] The subject invention has been made according to the above-mentioned circumstances. An object of the subject invention is to provide a novel radiation-sensitive composition for forming a colored layer which is capable of forming, even in low exposure dose, a pixel having a moderate normal-taper shape and being excellent in residual film thickness and adhesiveness.

Another object of the subject invention is to provide a color filter comprising a pixel formed from the radiation-sensitive composition for forming a colored layer, and a color liquid crystal display device comprising the color filter.

Means for solving the Problems

[0006] In view of the above-mentioned circumstances, the inventors of the subject invention have made intensive studies. As a result, the inventors have found that a radiation-sensitive

composition for forming a colored layer comprising as a polyfunctional monomer a certain amount of a compound having a caprolactone structure and two or more polymerizable unsaturated bonds in the molecules can solve the above-mentioned problems. Consequently, the subject invention has been completed.

[0007] That is, the subject invention provides a radiation-sensitive composition for forming a colored layer, comprising: a colorant (A); an alkali-soluble resin (B); a polyfunctional monomer (C); and a photopolymerization initiator (D), wherein the radiation-sensitive composition comprises 100 to 300 parts by weight of a compound having a caprolactone structure and two or more polymerizable unsaturated bonds in the molecules, as the polyfunctional monomer (C), with respect to 100 parts by weight of the alkali-soluble resin (B).

[0008] In addition, the subject invention also provides a color filter comprising a pixel formed by using the radiation-sensitive composition, and a color liquid crystal display device comprising the color filter.

Effects of the Invention

[0009] By using the radiation-sensitive composition of the subject invention, exposure dose can be decreased, leading to shortened takt time, and besides, the pixel pattern having a moderate normal-taper shape and being excellent in residual film thickness and adhesiveness can be formed even if the content ratio of a pigment in the coloring radiation-sensitive composition is high. In

addition, a color filter can be produced at high production efficiency by using the radiation-sensitive composition of the subject invention.

Thus, the radiation-sensitive composition of the subject invention can be used extremely suitably for producing color filters in the field of the electronics industry, ranging from a color filter for a color liquid crystal display device to color filters for various applications such as a color image pickup tube device and a color sensor.

Brief Description of the Drawing

[0010] FIG. 1 is a schematic view illustrating a cross-sectional shape of a pixel pattern.

Modes for carrying out the Invention

[0011] Radiation-sensitive composition for forming a colored layer

The "colored layer" used in a radiation-sensitive composition for forming a colored layer (hereinafter, may be simply referred to as "radiation-sensitive composition") of the subject invention means a layer formed of a pixel and/or a black matrix and used for a color filter.

Hereinafter, the constituent components of the radiation-sensitive composition for forming a colored layer of the subject invention are described.

[0012] -Colorant (A)-

A colorant (A) used in the subject invention is not particularly

limited and may include organic pigments or inorganic pigments.

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

[0013] C.I. Pigment Yellow 12, C.I. Pigment Yellow 13, C.I. Pigment Yellow 14, C.I. Pigment Yellow 17, C.I. Pigment Yellow 20, C.I. Pigment Yellow 24, C.I. Pigment Yellow 31, C.I. Pigment Yellow 55, C.I. Pigment Yellow 83, C.I. Pigment Yellow 93, C.I. Pigment Yellow 109, C.I. Pigment Yellow 110, C.I. Pigment Yellow 138, C.I. Pigment Yellow 139, C.I. Pigment Yellow 150, C.I. Pigment Yellow 153, C.I. Pigment Yellow 154, C.I. Pigment Yellow 155, C.I. Pigment Yellow 166, C.I. Pigment Yellow 168, and C.I. Pigment Yellow 211;

[0014] C.I. Pigment Orange 5, C.I. Pigment Orange 13, C.I. Pigment Orange 14, C.I. Pigment Orange 24, C.I. Pigment Orange 34, C.I. Pigment Orange 36, C.I. Pigment Orange 38, C.I. Pigment Orange 40, C.I. Pigment Orange 43, C.I. Pigment Orange 46, C.I. Pigment Orange 49, C.I. Pigment Orange 61, C.I. Pigment Orange 64, C.I. Pigment Orange 68, C.I. Pigment Orange 70, C.I. Pigment Orange 71, C.I. Pigment Orange 72, C.I. Pigment Orange 73, and C.I. Pigment Orange 74;

[0015] C.I. Pigment Red 1, C.I. Pigment Red 2, C.I. Pigment Red 5, C.I. Pigment Red 17, C.I. Pigment Red 31, C.I. Pigment Red 32, C.I. Pigment Red 41, C.I. Pigment Red 122, C.I. Pigment Red 123, C.I. Pigment Red 144, C.I. Pigment Red 149, C.I. Pigment Red 166, C.I. Pigment Red 168, C.I. Pigment Red 170, C.I. Pigment Red

171, C.I. Pigment Red 175, C.I. Pigment Red 176, C.I. Pigment Red 177, C.I. Pigment Red 178, C.I. Pigment Red 179, C.I. Pigment Red 180, C.I. Pigment Red 185, C.I. Pigment Red 187, C.I. Pigment Red 202, C.I. Pigment Red 206, C.I. Pigment Red 207, C.I. Pigment Red 209, C.I. Pigment Red 214, C.I. Pigment Red 220, C.I. Pigment Red 221, C.I. Pigment Red 224, C.I. Pigment Red 242, C.I. Pigment Red 243, C.I. Pigment Red 254, C.I. Pigment Red 255, C.I. Pigment Red 262, C.I. Pigment Red 264, and C.I. Pigment Red 272;

[0016] C.I. Pigment Violet 1, C.I. Pigment Violet 19, C.I. Pigment Violet 23, C.I. Pigment Violet 29, C.I. Pigment Violet 32, C.I. Pigment Violet 36, and C.I. Pigment Violet 38;

C.I. Pigment Blue 15, C.I. Pigment Blue 15:3, C.I. Pigment Blue 15:4, C.I. Pigment Blue 15:6, C.I. Pigment Blue 60, and C.I. Pigment Blue 80;

C.I. Pigment Green 7, C.I. Pigment Green 36, and C.I. Pigment Green 58;

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

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

[0017] The organic pigments may also be purified by a recrystallization method, a reprecipitation method, a solvent washing method, a sublimation method, a vacuum heating method, or a combination thereof in order to be used in the subject invention.

[0018] Further, examples of the inorganic pigments include titanium oxide, barium sulfate, calcium carbonate, zinc white, lead sulfate, yellow lead, zinc yellow, blood red (red iron oxide (III)), cadmium red, ultramarine blue, Prussian blue, chromium oxide green,

cobalt green, invar steel, titanium black, synthetic iron black, and carbon black.

[0019] The surfaces of the particles of these colorants may be modified with polymers as needed before the colorants are used. Examples of the polymers for modifying the surfaces of the particles of pigments include a polymer described in JP 08-259876 A and various commercially available polymers or oligomers for dispersing a pigment. Methods of coating a carbon black surface with a polymer are disclosed, for example, in JP 09-71733 A, JP 09-95625 A, and JP 09-124969 A.

The colorants may be used alone or as a combination of two or more kinds.

[0020] In the case where the radiation-sensitive composition of the subject invention is used for forming a pixel, preferably used as the colorant (A) is a colorant having high color developability and high heat resistance, or particularly preferably used is a colorant having high resistance to thermal decomposition, because the pixel is required to provide high-definition color development and to have heat resistance. To be specific, an organic colorant is preferably used, or an organic pigment is particularly preferably used.

On the other hand, in the case where the radiation-sensitive composition of the subject invention is used for forming a black matrix, an organic pigment or a carbon black is preferably used as the colorant (A), because the black matrix is required to have light-shielding property.

[0021] The radiation-sensitive composition of the subject invention can form a pixel having a moderate normal-taper shape and being excellent in residual film thickness and adhesiveness, even in the case where the content of the colorant is 30 wt% or more with respect to the total solid content of the radiation-sensitive composition. Further, in the subject invention, the content of the colorant is, from the viewpoint of securing development property, preferably 70 wt% or less, or particularly preferably 60 wt% or less with respect to the total solid content of the radiation-sensitive composition. Here, the solid content refers to each of the components except the solvents to be described later.

[0022] The colorant of the subject invention may be used together with, as needed, a dispersant and a dispersion aid.

Any appropriate dispersant such as a cationic dispersant, an anionic dispersant, a nonionic dispersant, or an amphoteric dispersant may be used as the above-mentioned dispersant, and a polymer dispersant is preferred. Specific examples thereof include a modified acrylic copolymer, an acrylic copolymer, a polyurethane, a polyester, an alkyl ammonium salt or a phosphate salt of a high molecular copolymer, and a cationic comb graft polymer. Here, the cationic comb graft polymer refers to a polymer having a structure in which two or more molecules of a branch polymer are graft bonded to one molecule of a trunk polymer having a plurality of basic groups (cationic functional groups). For example, a polymer in which the trunk polymer part is formed of a polyethyleneimine and the branch

polymer parts are formed of a ring-opened polymer of ε-caprolactone is given. Of these dispersants, preferred are a modified acrylic copolymer, a polyurethane, and a cationic comb graft polymer.

[0023] The above-mentioned dispersants are commercially available. Examples of the modified acrylic copolymers include Disperbyk-2000, Disperbyk-2001, BYK-LPN6919, and BYK-LPN21116 (all of which are manufactured by BYK Japan KK). Examples of the polyurethanes include Disperbyk-161, Disperbyk-162, Disperbyk-165, Disperbyk-167, Disperbyk-170, and Disperbyk-182 (all of which are manufactured by BYK Japan KK), and Solsperse 76500 (manufactured by The Lubrizol Corporation). Examples of the cationic comb graft polymers include Solsperse 24000 (manufactured by The Lubrizol Corporation), and Ajisper PB821 and Ajisper PB822 (manufactured by Ajinomoto Fine-Techno Co., Inc.).

[0024] These dispersants may be used alone or as a combination of two or more kinds. The content of the dispersant is generally 100 parts by weight or less, preferably 0.5 to 100 parts by weight, more preferably 1 to 70 parts by weight, or particularly preferably 10 to 50 parts by weight, with respect to 100 parts by weight of the colorant (A), from the viewpoint of improving development property or the like.

[0025] Examples of the dispersion aid include a blue pigment derivative and a yellow pigment derivative, and specific examples thereof include a copper phthalocyanine derivative.

[0026] -Alkali-soluble resin (B)-

An alkali-soluble resin (B) included in the

radiation-sensitive composition of the subject invention is not particularly limited as long as the alkali-soluble resin has a solubility with respect to an alkaline developer to be used in a development treatment step in forming a colored layer, and generally is a polymer having an acidic functional group such as a carboxyl group or a phenolic hydroxyl group. Of these, preferred is a resin containing a polymer having a carboxyl group, and particularly preferred is a copolymer (hereinafter referred to as "carboxyl group-containing copolymer") of an ethylenic unsaturated monomer having one or more carboxyl groups (hereinafter referred to as "carboxyl group-containing unsaturated monomer") and another copolymerizable, ethylenic unsaturated monomer (hereinafter referred to as "copolymerizable unsaturated monomer."). Note that (meth)acrylic acid herein refers to methacrylic acid or acrylic acid.

[0027] Examples of the carboxyl group-containing unsaturated monomer include:

unsaturated monocarboxylic acids such as (meth)acrylic acid, crotonic acid, α-chloroacrylic acid, and cinnamic acid;

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

mono[(meth)acryloyloxyalkyl]esters of polycarboxylic acids having a valency of two or more such as mono[2-(meth)acryloyloxyethyl]succinate, and

mono[2-(meth)acryloyloxyethyl]phthalate; and

mono(meth)acrylates of polymers having a carboxyl group and a hydroxyl group at both terminals such as ω-carboxy polycaprolactone mono(meth)acrylate.

In the subject invention, as the carboxyl group-containing unsaturated monomers, (meth)acrylic acid, mono[2-(meth)acryloyloxyethyl]succinate, and ω-carboxy polycaprolactone mono(meth)acrylate are preferred, or (meth)acrylic acid is particularly preferred.

These carboxyl group-containing unsaturated monomers may be used alone or as a combination of two or more kinds.

[0028] Further, examples of the copolymerizable unsaturated monomers include:

N- substituted maleimides such as N-phenylmaleimide, N-o-hydroxyphenylmaleimide, N-m-hydroxyphenylmaleimide, N-p-hydroxyphenylmaleimide, N-benzylmaleimide, N-cyclohexylmaleimide, N-succinimidyl-3-maleimide benzoate, N-succinimidyl-4-maleimide butyrate, N-succinimidyl-6-maleimide caproate, N-succinimidyl-3-maleimide propionate, and N-(acridinyl)maleimide;

aromatic vinyl compounds such as styrene, α-methylstyrene, o-vinyltoluene, m-vinyltoluene, p-vinyltoluene, p-chlorostyrene, o-methoxystyrene, m-methoxystyrene, p-methoxystyrene, o-vinylphenol, m-vinylphenol, p-vinylphenol, p-hydroxy-α-methylstyrene, o-vinylbenzyl methyl ether, m-vinylbenzyl methyl ether, p-vinylbenzyl methyl ether,

o-vinylbenzyl glycidyl ether, m-vinylbenzyl glycidyl ether, and p-vinylbenzyl glycidyl ether;

indenes such as indene and 1-methylindene;

[0029] unsaturated carboxylate esters such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, i-propyl (meth)acrylate, n-butyl (meth)acrylate, i-butyl (meth)acrylate, sec-butyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, allyl (meth)acrylate, benzyl (meth)acrylate, cyclohexyl (meth)acrylate, phenyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 2-phenoxyethyl (meth)acrylate, methoxy diethylene glycol (meth)acrylate, methoxy triethylene glycol (meth)acrylate, methoxy propylene glycol (meth)acrylate, methoxy dipropylene glycol (meth)acrylate, isobornyl (meth)acrylate, tricyclo[5.2.1.$0^{2,6}$]decane-8-yl (meth)acrylate, 2-hydroxy-3-phenoxypropyl (meth)acrylate, glycerol mono(meth)acrylate, 4-hydroxyphenyl (meth)acrylate, and an ethylene oxide-modified (meth)acrylate of paracumylphenol;

[0030] unsaturated glycidyl carboxylate esters such as glycidyl (meth)acrylate;

vinyl carboxylate esters such as vinyl acetate, vinyl propionate, vinyl butyrate, and vinyl benzoate;

other unsaturated ethers such as vinyl methyl ether, vinyl ethyl ether, and allyl glycidyl ether;

vinyl cyanide compounds such as (meth)acrylonitrile, α-chloroacrylonitrile, and vinylidene cyanide;

unsaturated amides such as (meth)acrylamide, α-chloroacrylamide, and N-2-hydroxyethyl (meth)acrylamide;

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

macromonomers having a mono(meth)acryloyl group at the terminal of the polymer molecular chains such as polystyrene, polymethyl (meth)acrylate, poly-n-butyl (meth)acrylate, and polysiloxane.

The above-mentioned copolymerizable unsaturated monomers may be used alone or as a combination of two or more kinds.

[0031] In the subject invention, as the copolymerizable unsaturated monomers, preferred are monomers each containing at least one kind selected from the group consisting of N- substituted maleimides, aromatic vinyl compounds, unsaturated carboxylate esters, and macromonomers having a mono(meth)acryloyl group at the terminal of the polymer molecular chains. More preferred are monomers each containing at least one kind selected from the group consisting of N-phenylmaleimide, N-cyclohexylmaleimide, styrene, α-methylstyrene, p-hydroxy-α-methylstyrene, methyl (meth)acrylate, n-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, allyl (meth)acrylate, benzyl (meth)acrylate, glycerol mono(meth)acrylate, 4-hydroxyphenyl (meth)acrylate, an ethylene oxide-modified (meth)acrylate of paracumylphenol, a polystyrene macromonomer, and a

polymethylmethacrylate macromonomer. Particularly preferred are monomers each containing at least one kind selected from the group consisting of N-phenylmaleimide, N-cyclohexylmaleimide, styrene, α-methylstyrene, methyl (meth)acrylate, n-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, benzyl (meth)acrylate, glycerol mono(meth)acrylate, and an ethylene oxide-modified (meth)acrylate of paracumylphenol.

[0032] In the subject invention, for example, an alkali-soluble resin obtained by copolymerizing copolymerizable unsaturated monomers having a hydroxyl group such as 2-hydroxyethyl (meth)acrylate may be reacted with an unsaturated isocyanate compound such as 2-(meth)acryloyloxyethyl isocyanate, to thereby introduce a polymerizable unsaturated bond into a side chain of the alkali-soluble resin.

[0033] In the carboxyl group-containing copolymer, the copolymerization ratio of the carboxyl group-containing unsaturated monomer is preferably 5 to 50 wt% or more preferably 10 to 40 wt%. When the copolymerization ratio is too low, the solubility of the radiation-sensitive composition to be obtained with respect to an alkaline developer tends to be low. On the other hand, when the copolymerization ratio is too high, the solubility of the radiation-sensitive composition to be obtained with respect to the alkaline developer tends to be excessively high, with the result that a pixel tends to be lost easily from a substrate and a film on the surface of the pixel tends to be easily roughen, at the time of development with the alkaline developer.

[0034] The weight average molecular weight (hereinafter referred to as "Mw") in terms of polystyrene measured by gel permeation chromatography (GPC; tetrahydrofuran used as an elution solvent) of the alkali-soluble resin in the subject invention is generally 1000 to 45,000 or preferably 3000 to 20,000. When Mw is too low, a survival rate of film or the like of the resultant coating film may be decreased, pattern shape, heat resistance etc. may be impaired, or electrical characteristics may be deteriorated. On the other hand, when Mw is too high, definition may be decreased, pattern shape may be impaired, or dry aggregation particle may easily be produced at the time of slit nozzle application.

Further, the number average molecular weight (hereinafter referred to as "Mn") in terms of polystyrene measured by gel permeation chromatography (GPC; tetrahydrofuran used as an elution solvent) of the alkali-soluble resin in the subject invention is generally 1,000 to 45,000, or preferably 3,000 to 20,000.

Further, the ratio of Mw to Mn (Mw/Mn) of the alkali-soluble resin in the subject invention is preferably 1.0 to 5.0, or more preferably 1.0 to 4.0.

[0035] The alkali-soluble resin in the subject invention can be produced by a known method. Structure, Mw, or Mw/Mn of the alkali-soluble resin may be controlled, for example, by a method disclosed in JP 2003-222717 A, JP 2006-259680 A, or WO 07/029871 A1.

[0036] The alkali-soluble resins may be used alone or as a combination of two or more kinds in the subject invention.

In the subject invention, the content of the alkali-soluble resin (B) is generally preferably 10 to 1000 parts by mass or particularly preferably 20 to 500 parts by mass with respect to 100 parts by mass of the colorant (A). When the content of the alkali-soluble resin is too low, for example, alkali development property may be lowered, and residue or scum may be produced on the unexposed part of a substrate or on the light-shielding layer. On the other hand, when the content of the alkali-soluble resin is too high, concentration of the colorlant is relatively decreased and as a result, achieving a desired color density of a thin film may be difficult.

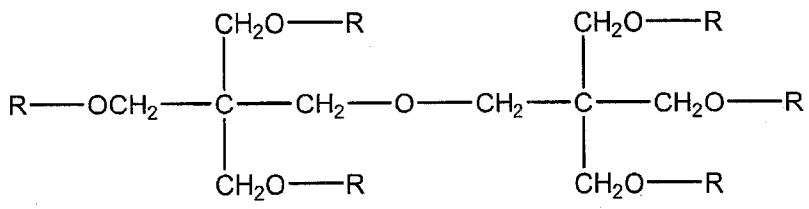
[0037] -Polyfunctional monomer (C)-

A polyfunctional monomer in the subject invention consists of a monomer having two or more polymerizable unsaturated bonds. The polyfunctional monomer includes a compound having a caprolactone structure and two or more polymerizable unsaturated bonds in the molecules (the compound may hereinafter be referred to as a "caprolactone structure-containing polyfunctional monomer") at 100 to 300 parts by weight or preferably 100 to 250 parts by weight with respect to 100 parts by weight of the alkali-soluble resin (B). When the content of the caprolactone-modified polyfunctional monomer is less than 100 parts by weight, desired effects may not be adequately provided. On the other hand, when the content is more than 300 parts by weight, the adhesiveness of a pixel pattern to a substrate may be decreased.

[0038] Examples of the caprolactone structure-containing

polyfunctional monomer include a ε-caprolactone structure-containing polyfunctional (meth)acrylate, which is obtained by esterification of a polyhydric alcohol such as trimethylolethane, ditrimethylolethane, trimethylolpropane, ditrimethylolpropane, pentaerythritol, dipentaerythritol, tripentaerythritol, glycerin, diglycerol, or trimethylolmelamine, with (meth)acrylic acid and ε-caprolactone. In particular, the caprolactone structure-containing polyfunctional monomers represented by the following formula (1) are preferred from the viewpoint of ability of forming a pixel having a moderate normal-taper shape even in low exposure dose.

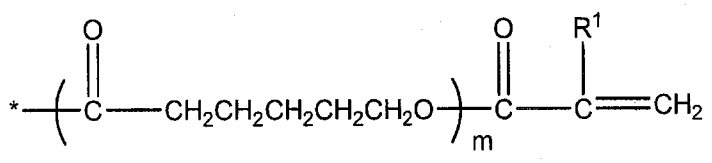
[0039]



(1)

[0040] (wherein all 6 R groups are represented by the following formula (2), or 1 to 5 R groups out of the 6 R groups are represented by the following formula (2) and the remaining R groups are represented by the following formula (3).)

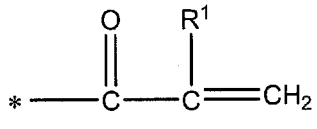
[0041]



(2)

[0042] (wherein R^1 represents a hydrogen atom or a methyl group, m represents a number of 1 or 2, and "*" represents a bond.)

[0043]



(3)

[0044] (wherein R^1 represents a hydrogen atom or a methyl group and "*" represents a bond.)

[0045] Among the compounds represented by the above-mentioned formula (1), a compound having two or more groups represented by the formula (2) is preferred, a compound having three or more groups represented by the formula (2) is more preferred, or a compound having six groups represented by the formula (2) is even more preferred.

The caprolactone structure-containing polyfunctional monomers described above are commercially available, for example, as a KAYARAD DPCA series from Nippon Kayaku Co., Ltd. Examples of the KAYARAD DPCA series include DPCA-20 (a compound represented by the above-mentioned formulas (1) to (3) wherein m is 1, the number of the groups represented by the formula (2) is 2, and all R^1 groups represent hydrogen atoms), DPCA-30 (a compound represented by the formulas (1) to (3) wherein m is 1, the number of the groups represented by the formula (2) is 3, and all R^1 groups represent hydrogen atoms), DPCA-60 (a compound represented by the formulas (1) to (3) wherein m is 1, the number of the groups represented by the formula (2) is 6, and all R^1 groups represent hydrogen atoms), and DPCA-120 (a compound represented by the formulas (1) to (3) wherein m is 2, the number of the groups represented by the formula (2) is 6, and

all R^{1}' groups represent hydrogen atoms).

In the subject invention, the caprolactone structure-containing polyfunctional monomers may be used alone or as a combination of two or more kinds.

[0046] In the subject invention, from the viewpoint of increasing the residual film thickness, the caprolactone structure-containing polyfunctional monomer is preferable to be used together with any of additional polyfunctional monomers. The caprolactone structure-containing polyfunctional monomer is more preferable to be used together with a compound having no caprolactone structure and having two or more polymerizable unsaturated bonds.

Examples of the other polyfunctional monomers include:

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

di(meth)acrylates of polyalkylene glycols such as polyethylene glycol and polypropylene glycol;

poly(meth)acrylates of polyhydric alcohols having a valency of 3 or more such as glycerin, trimethylolpropane, pentaerythritol, and dipentaerythritol, and dicarboxylic acid-modified products thereof;

oligo(meth)acrylates of any of a polyester, an epoxy resin, a urethane resin, an alkyd resin, a silicone resin, a spirane resin etc.;

di(meth)acrylates of both-terminal hydroxylated polymers such as both-terminal hydroxypoly-1,3-butadiene, both-terminal hydroxypolyisoprene, and both-terminal hydroxypolycaprolactone;

and

tris[2-(meth)acryloyloxyethyl]phosphate and ethylene oxide-modified triacrylate isocyanurate.

[0047] Among these additional polyfunctional monomers, poly(meth)acrylates of a polyhydric alcohol having a valency of 3 or more and dicarboxylic acid-modified products thereof, specifically, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, pentaerythritol triacrylate, pentaerythritol trimethacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, dipentaerythritol pentaacrylate, dipentaerythritol pentamethacrylate, dipentaerythritol hexaacrylate, dipentaerythritol hexamethacrylate, a monoesterified product of pentaerythritol triacrylate and succinic acid, a monoesterified product of pentaerythritol trimethacrylate and succinic acid, a monoesterified product of dipentaerythritol pentaacrylate and succinic acid, and a monoesterified product of dipentaerythritol pentamethacrylate and succinic acid etc. are preferable. Particularly, trimethylolpropane triacrylate, pentaerythritol triacrylate, dipentaerythritol pentaacrylate, dipentaerythritol hexaacrylate, a monoesterified product of pentaerythritol triacrylate and succinic acid, and a monoesterified product of dipentaerythritol pentaacrylate and succinic acid are preferablebecause the resultant colored layer is high in strength and excellent in surface smoothness, and scum, film residue etc. is hardly produced on the unexposed part of a substrate and on a light-shielding layer.

The other polyfunctional monomers may be used alone or as a combination of two or more kinds.

[0048] The total content of all polyfunctional monomers (C) in the subject invention is preferably 100 to 400 parts by weight or more preferably 100 to 300 parts by weight with respect to 100 parts by weight of the alkali-soluble resin (B). When the total content is too low, desired effects of the subject invention may be impaired. On the other hand, when the total content is too high, alkali development property tends to be lowered, and scum, film residue etc. tends to be produced on the unexposed part of a substrate or on a light-shielding layer.

[0049] Meanwhile, the content ratio of the caprolactone structure-containing polyfunctional monomer in all polyfunctional monomers (C) is preferably 25 to 100 wt% or more preferably 50 to 75 wt%. Using the caprolactone structure-containing polyfunctional monomer at the content ratio described as above leads to the formation of a pixel having a moderate normal-taper shape even in low exposure dose.

[0050] Further, in the subject invention, a part of the polyfunctional monomer may be replaced by a monofunctional monomer having one polymerizable unsaturated bond.

Examples of the monofunctional monomer include: mono[(meth)acryloyloxyalkyl]esters of polycarboxylic acids having a valency of two or more such as mono[2-(meth)acryloyloxyethyl] succinate and mono[2-(meth)acryloyloxyethyl] phthalate; mono(meth)acrylates of polymers having a carboxyl group and a

hydroxyl group at both terminals such as ω-carboxy polycaprolactone mono(meth)acrylate; N-(meth)acryloylmorpholine; N-vinyl pyrrolidone; N-vinyl-ε-caprolactam; and M-5600 (trade name, manufactured by Toagosei Co., Ltd.) as a commercially available product.

These monofunctional monomers may be used alone or as a combination of two or more kinds. The content ratio of the monofunctional monomer is generally 90 wt% or less or preferably 50 wt% or less with respect to the total amount of the polyfunctional monomer and the monofunctional monomer. When the content ratio of the monofunctional monomer is too high, the strength and surface smoothness of the resulting colored layer may be insufficient.

[0051] -Photopolymerization initiator (D)-

A photopolymerization initiator in the subject invention refers to a compound which generates an reactive species that may initiate polymerization of the polyfunctional monomers (C) and the monofunctional monomers to be used in some cases by exposure of radiation such as visible light rays, ultraviolet rays, far ultraviolet rays, electron rays, or X-rays.

Examples of the photopolymerization initiator include thioxanthone-based compounds, acetophenone-based compounds, biimidazole-based compounds, triazine-based compounds, O-acyloxime-based compounds, onium salt-based compounds, benzoin-based compounds, benzophenone-based compounds, α-diketone-based compounds, polynuclear quinone-based compounds, xanthone-based compounds, diazo-based compounds, and

imidosulfonate-based compounds.

[0052] In the subject invention, the photopolymerization initiators may be used alone or as a combination of two or more kinds. The photopolymerization initiator in the subject invention preferably includes at least one kind of compound selected from the group consisting of thioxanthone-based compound, acetophenone-based compound, biimidazole-based compound, triazine-based compound, and O-acyloxime-based compound.

[0053] Among the preferred photopolymerization initiators in the subject invention, specific examples of the thioxanthone-based compounds include thioxanthone, 2-chlorothioxanthone, 2-methylthioxanthone, 2-isopropylthioxanthone, 4-isopropylthioxanthone, 2,4-dichlorothioxanthone, 2,4-dimethylthioxanthone, 2,4-diethylthioxanthone, and 2,4-diisopropylthioxanthone.

[0054] Further, specific examples of the acetophenone-based compounds include 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butan-1-one, and 2-(4-methylbenzyl)-2-(dimethylamino)-1-(4-morpholinophenyl)butan-1-one.

[0055] Further, specific examples of the biimidazole-based compounds include 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'-biimid

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

[0056] In the case where the biimidazole-based compounds is used as the photopolymerization initiator, a hydrogen donor is preferably used together for improving sensitivity. The phrase "hydrogen donor" herein refers to a compound that is capable of providing a hydrogen atom to a radical generated from the biimidazole-based compound by exposure. Examples of the hydrogen donor include mercaptan-based hydrogen donor such as 2-mercaptobenzothiazole and 2-mercaptobenzoxazole, and amine-based hydrogen donor such as 4,4'-bis(dimethylamino)benzophenone and 4,4'-bis(diethylamino)benzophenone. In the subject invention, the hydrogen donor may be used alone or as a combination of two or more kinds. However, it is preferred in terms of further improving sensitivity that one or more kinds of the mercaptan-based hydrogen donor be used together with one or more kinds of the amine-based hydrogen donor.

[0057] Further, specific examples of the triazine-based compounds 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(trichloro methyl)-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.

[0058] Further, examples of the O-acyloxime-based compounds include 1,2-octanedion 1-[4-(phenylthio)phenyl]-2-(O-benzoyloxime), ethanone 1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-1-(O-acetyloxime), ethanone 1-[9-ethyl-6-(2-methyl-4-tetrahydrofuranylmethoxybenzoyl)-9H-carbazol-3-yl]-1-(O-acetyloxime), and ethanone 1-[9-ethyl-6-[2-methyl-4-(2,2-dimethyl-1,3-dioxolanyl)methoxybenzoyl]-9H-carbazol-3-yl]-1-(O-acetyloxime).

[0059] In the subject invention, in the case where compounds other than the biimidazole-based compounds, such as acetophenone-based compounds, is used as a photo radical generator, a sensitizer may also be used together. Examples of the sensitizer include 4,4'-bis(dimethylamino)benzophenone, 4,4'-bis(diethylamino)benzophenone, 4-diethylaminoacetophenone, 4-dimethylaminopropiophenone, ethyl 4-dimethylaminobenzoate, 2-ethylhexyl 4-dimethylaminobenzoate, 2,5-bis(4-diethylaminobenzal)cyclohexanone, 7-diethylamino-3-(4-diethylaminobenzoyl)cumarine, and

4-(diethylamino)chalcone.

[0060] In the subject invention, the content of the photopolymerization initiator is generally 0.01 to 120 parts by weight or preferably 1 to 100 parts by weight with respect to 100 parts by weight of the polyfunctional monomer (C). When the content of the photopolymerization initiator is too low, curing by exposure is insufficient, and hence obtaining a color filter in which patterns of colored layers are placed in accordance with a predetermined arrangement may be difficult. On the other hand, when the content of the photopolymerization initiator is too high, the formed colored layers tend to easily fall off from a substrate at the time of development.

[0061] -Additive-

The radiation-sensitive composition of the subject invention containing the above-mentioned components (A) to (D) may further contain the other additives as required.

Here, examples of the other additives include: fillers such as glass and alumina; polymer compounds such as polyvinyl alcohols and poly(fluoroalkyl acrylates); surfactants such as nonionic surfactants, cationic surfactants, and anionic surfactants; adhesion promoters such as vinyltrimethoxysilane, vinyltriethoxysilane, vinyltris(2-methoxyethoxy)silane, N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropylmethyldimethoxysilane,

2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane,

3-chloropropylmethyldimethoxysilane,

3-chloropropyltrimethoxysilane,

3-methacryloyloxypropyltrimethoxysilane, and

3-mercaptopropyltrimethoxysilane; antioxidants such as 2,2-thiobis(4-methyl-6-t-butylphenol) and 2,6-di-t-butylphenol; UV absorbers such as 2-(3-t-butyl-5-methyl-2-hydroxyphenyl)-5-chlorobenzotriazole and alkoxybenzophenones; aggregation inhibitors such as sodium polyacrylate; and alkali solubility improvers such as malonic acid, adipic acid, itaconic acid, citraconic acid, fumaric acid, and mesaconic acid.

[0062] -Solvent-

The radiation-sensitive composition for forming a colored layer of the subject invention, containing the components (A) to (D) as essential components, and containing any of the additive components as required, is generally prepared as a liquid composition by addition of a solvent.

Any kinds of solvent may be appropriately selected and used as long as the solvent can disperse or dissolve components of the radiation-sensitive composition, i.e. the components (A) to (D) and the additive components, does not react with these components, and has appropriate volatility.

[0063] 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;

[0064] (poly)alkylene glycol monoalkyl ether acetates such as ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, 3-methoxybutyl acetate, and 3-methyl-3-methoxybutyl 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;

[0065] 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-methyl-3-methoxybutyl propionate, 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 or lactams such as N,N-dimethylformamide, N,N-dimethylacetoamide, and N-methylpyrrolidone.

[0066] Among these solvents, from the viewpoints of solubility, pigment dispersability, coating property etc., propylene glycol monomethyl ether, ethylene glycol monomethyl ether acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, 3-methoxybutyl 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-methyl-3-methoxybutyl propionate, 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 preferred.

The solvents may be used alone or as a combination of two or more kinds.

[0067] In addition, in combination with these solvent, a solvent having a high boiling point, such as benzyl ethyl ether, di-n-hexyl

ether, acetonylacetone, isophorone, caproic acid, caprylic acid, 1-octanol, 1-nonanol, benzyl alcohol, benzyl acetate, ethyl benzoate, diethyl oxalate, diethyl maleate, γ-butyrolactone, ethylene carbonate, propylene carbonate, or ethylene glycol monophenyl ether acetate, may be used.

These solvents having a high boiling point may be used alone or as a combination of two or more kinds.

[0068] Although the amount of the solvent is not particularly limited, from the viewpoint of coating property, stability etc. of the radiation-sensitive composition to be obtained, the amount of the solvent is an amount wherein the total amount of these components, except the solvent, in the composition is generally 5 to 50 wt%, or preferably 10 to 40 wt%.

[0069] In the subject invention, the radiation-sensitive composition can be prepared by appropriate method. For example, the radiation-sensitive composition can be prepared by mixing the components (A) to (D) with a solvent and an additive. Preferably, the radiation-sensitive composition is prepared by pulverizing a pigment, together with part of the component (B) as required, in a solvent using, for example, a beads mill, a roll mill etc. in the presence of a dispersant and a dispersion aid added as required, by simultaneously mixing and dispersing the pigment to prepare a pigment dispersion liquid, and by mixing the obtained pigment dispersion liquid with the components (B) to (D) and, as needed, an additional solvent and additive.

[0070] -Method of forming color filter-

Next, a method of forming a color filter of the subject invention using the radiation-sensitive composition of the subject invention is described as below.

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

(1) a step of forming a coating film of the radiation-sensitive composition of the subject invention on a substrate;

(2) a step of exposure to at least a part of the coating film;

(3) a step of developing the coating film after the exposure; and

(4) a step of post-baking the coating film after the development.

Hereinafter, each of these steps is described.

[0071] Step (1)

First, a light-shielding layer (black matrix) is formed on a surface of a substrate, as required, so as to mark off a portion on which a pixel is formed. The radiation-sensitive composition of the subject invention, usually as a liquid composition, containing, for example, a red color colorant (A), is coated onto the substrate and is then pre-baked for evaporation and removal of a solvent, thereby forming a coating film.

Examples of the substrate to be used in this step include glass, silicon, a polycarbonate, a polyester, an aromatic polyamide, a polyamide-imide, a polyimide, and a polyether sulfone, and further include a ring-opened polymer of cyclic olefins and a hydrogenated product thereof.

Further, these substrates may be subjected to, as needed, an appropriate pretreatment such as chemical treatment with a silane coupling agent or the like, plasma treatment, ion plating, sputtering, a gas-phase reaction method, or vacuum deposition.

An appropriate coating method such as a spin coating method, a cast coating method, a roll coating method, or a coating method using a slit-die coater may be employed for coating the substrate with the liquid composition, among them, spin coating method and coating method using a slit-die coater are preferable.

Condition of the pre-baking is generally at 70 to 110°C for about 2 to 4 minutes. By using the radiation-sensitive composition of the subject invention, a pixel and a black matrix can be formed even if the step of the pre-baking is omitted.

The thickness of the coating is, as a film thickness after removal of the solvent, generally 1.0 to 10 μm, preferably 1.0 to 6.0 μm, or particularly preferably 1.0 to 4.0 μm.

[0072] Step (2)

Next, at least a part of the formed coating film is exposed to light. In the case of only the part of the coating film is exposed to light, the film is usually exposed through a photomask having a predetermined pattern.

For example, visible light rays, ultraviolet rays, far ultraviolet rays, electron rays, or X-rays may be used as radiation used for the exposure, and the wavelength of the radiation is preferably ranging from 190 to 450 nm.

The exposure dose of radiation is usually 10 to 10,000 J/m^2.

By using the radiation-sensitive composition of the subject invention, forming a pixel having a moderate normal-taper shape and being excellent in residual film thickness and adhesiveness, by exposure dose of 800 J/m^2 or less, preferably by exposure dose of 600 J/m^2 or less, is possible. Further, the lower limit of the exposure dose is preferably 200 J/m^2 or more from the viewpoint of the controllability of a light source when a high illuminance light source is employed.

[0073] Step (3)

Next, the coating film is developed by using a developer, or preferably an alkaline developer, and unexposed part of the coating film is dissolved and removed.

Examples of preferable alkaline developer include aqueous solutions of any of sodium carbonate, sodium hydroxide, potassium hydroxide, tetramethyl ammonium hydroxide, choline, 1,8-diazabicyclo-[5.4.0]-7-undecene, and 1,5-diazabicyclo-[4.3.0]-5-nonene.

For example, a water-soluble organic solvent such as methanol or ethanol or a surface active agent may be added to the alkaline developer in an appropriate amount.

For example, a shower development method, a spray development method, a dip (immersion) development method, or a paddle (liquid heap) development method may be applied as a treatment for development.

The condition of the development is preferably at normal temperature for about 10 to 300 seconds.

[0074] Step (4)

Next, after the development step, the coating film is post-baked to thereby yield a substrate on which a red pixel pattern formed of a cured product of the radiation-sensitive composition is placed in a predetermined arrangement.

The condition of the post-baking is preferably at 180 to 230°C for about 20 to 40 minutes.

The thickness of the formed pixel is usually 0.5 to 5.0 μm, or preferably 1.0 to 3.0 μm.

[0075] Further, a green radiation-sensitive composition containing a green color colorant (A) is used and the steps (1) to (4) are repeated, to thereby form a green pixel pattern on the same substrate. In addition, a blue, radiation-sensitive composition containing a blue color colorant (A) is used and the steps (1) to (4) are repeated, to thereby form a blue pixel pattern on the same substrate. Thus, pixel arrays in which the pixel patterns of each of the three primary colors, consisting of red, green, and blue, are placed in a predetermined arrangement can be formed on the substrate. The order of forming the pixel patterns of these respective colors may be optionally selected.

A black matrix can be formed by using a green radiation-sensitive composition containing a colorant (A) in black color and by performing the steps (1) to (4).

[0076] Color filter

A color filter of the subject invention comprises the above-described pixel and/or the black matrix formed from the

radiation-sensitive composition of the subject invention.

[0077] Color liquid crystal display device

A color liquid crystal display device of the subject invention comprises the color filter of the subject invention.

On the color filter formed as described above, a protective film is formed as required and a transparent conductive film is then formed by sputtering. Examples of the transparent conductive film include an ITO film consisting of indium oxide-tin oxide and an IZO film consisting of indium oxide-zinc oxide. The cross-section of the pixel pattern formed by using the radiation-sensitive composition of the subject invention is a normal-taper shape, and hence the wiring of a transparent electrode is not disconnected. In addition, the angle of the taper is not too gentle, and hence a pixel edge does not have a portion having a thinner film thickness. As a result, a color liquid crystal display device having high quality which is excellent in electric characteristics and chromaticity characteristics can be produced.

Further, as one embodiment of the color liquid crystal display device of the subject invention, the radiation-sensitive composition for forming a colored layer of the subject invention can be used to form a pixel and/or a black matrix as described above on a thin film transistor substrate array, thereby producing a color liquid crystal display device having particularly excellent characteristics is possble.

Example 1

[0078] Hereinafter, detailed embodiments of the subject

invention are described in below Examples. However, the subject invention is not limited to the following Examples.

[0079] Preparation of pigment dispersion liquid

Preparation Example 1

20 parts by weight of a mixture of C.I. Pigment Red 254, C.I. Pigment Red 177, and C.I. Pigment Yellow 150 at a ratio of 20/70/10 (weight ratio) were used as a colorant (A), 5 parts by weight (in terms of solid content) of Disperbyk-2001 (manufactured by BYK Japan KK) were used as a dispersant, and propylene glycol monomethyl ether acetate was used as a solvent to adjust a solid concentration to 25%, followed by treatment with a beads mill, to thereby prepare a pigment dispersion liquid (R1).

[0080] Preparation Example 2

20 parts by weight of C.I. Pigment Red 254 were used as a colorant (A), 5 parts by weight (in terms of solid content) of Disperbyk-2001 (manufactured by BYK Japan KK) were used as a dispersant, and propylene glycol monomethyl ether acetate was used as a solvent to adjust a solid concentration to 25%, followed by treatment with a beads mill, to thereby prepare a pigment dispersion liquid (R2).

[0081] Preparation Example 3

20 parts by weight of a mixture of C.I. Pigment Red 254, C.I. Pigment Red 242, and C.I. Pigment Yellow 139 at a ratio of 30/60/10 (weight ratio) were used as a colorant (A), 5 parts by weight (in terms of solid content) of Disperbyk-2001 (manufactured by BYK Japan KK) were used as a dispersant, and propylene glycol monomethyl ether acetate was used as a solvent to adjust a solid concentration to

25%, followed by treatment with a beads mill, to thereby prepare a pigment dispersion liquid (R3).

[0082] Preparation Example 4

20 parts by weight of a mixture of C.I. Pigment Green 36 and C.I. Pigment Yellow 150 at a ratio of 50/50 (weight ratio) were used as a colorant (A), 5 parts by weight (in terms of solid content) of Disperbyk-2001 (manufactured by BYK Japan KK) were used as a dispersant, and propylene glycol monomethyl ether acetate was used as a solvent to adjust a solid concentration to 25%, followed by treatment with a beads mill, to thereby prepare a pigment dispersion liquid (G1).

[0083] Preparation Example 5

20 parts by weight of a mixture of C.I. Pigment Green 58 and C.I. Pigment Yellow 150 at a ratio of 60/40 (weight ratio) were used as a colorant (A), 5 parts by weight (in terms of solid content) of Disperbyk-2001 (manufactured by BYK Japan KK) were used as a dispersant, and propylene glycol monomethyl ether acetate was used as a solvent to adjust a solid concentration to 25%, followed by treatment with a beads mill, to thereby prepare a pigment dispersion liquid (G2).

[0084] Preparation Example 6

20 parts by weight of a mixture of C.I. Pigment Green 36 and C.I. Pigment Yellow 150 at a ratio of 60/40 (weight ratio) were used as a colorant (A), 5 parts by weight (in terms of solid content) of Disperbyk-2001 (manufactured by BYK Japan KK) were used as a dispersant, and propylene glycol monomethyl ether acetate was used

as a solvent to adjust a solid concentration to 25%, followed by treatment with a beads mill, to thereby prepare a pigment dispersion liquid (G3).

[0085] Preparation Example 7

20 parts by weight of C.I. Pigment Blue 15:6 were used as a colorant (A), 5 parts by weight (in terms of solid content) of Disperbyk-2001 (manufactured by BYK Japan KK) were used as a dispersant, and propylene glycol monomethyl ether acetate was used as a solvent to adjust a solid concentration to 25%, followed by treatment with a beads mill, to thereby prepare a pigment dispersion liquid (B1).

[0086] Preparation Example 8

20 parts by weight of a mixture of C.I. Pigment Blue 15:6 and C.I. Pigment Violet 23 at a ratio of 80/20 (weight ratio) were used as a colorant (A), 5 parts by weight (in terms of solid content) of Disperbyk-2001 (manufactured by BYK Japan KK) were used as a dispersant, and propylene glycol monomethyl ether acetate was used as a solvent to adjust a solid concentration to 25%, followed by treatment with a beads mill, to thereby prepare a pigment dispersion liquid (B2).

[0087] Preparation Example 9

20 parts by weight of a mixture of C.I. Pigment Blue 15:6 and C.I. Pigment Violet 23 at a ratio of 60/40 (weight ratio) were used as a colorant (A), 5 parts by weight (in terms of solid content) of Disperbyk-2001 (manufactured by BYK Japan KK) were used as a dispersant, and propylene glycol monomethyl ether acetate was used

as a solvent to adjust a solid concentration to 25%, followed by treatment with a beads mill, to thereby prepare a pigment dispersion liquid (B3).

[0088] Synthesis of alkali-soluble resin

Synthesis Example 1

3 parts by weight of 2,2'-azobisisobutyronitrile and 200 parts by weight of propylene glycol monomethyl ether acetate were loaded into a flask equipped with a cooling tube and a stirrer. Then, 15 parts by weight of methacrylic acid, 35 parts by weight of benzyl methacrylate, 19 parts by weight of N-phenylmaleimide, 10 parts by weight of glycerol methacrylate, 11 parts by weight of styrene, 10 parts by weight of ω-carboxy polycaprolactone monoacrylate, and 5 parts by weight of 2,4-diphenyl-4-methyl-1-pentene (chain transfer agent) were loaded, followed by replacement by nitrogen gas. After that, while gently stirring, the temperature of the reaction solution was raised to 80°C. Polymerization was carried out while the temperature was kept for 3 hours, to thereby yield a copolymer solution. Mw, Mn and solid concentration of the resultant resin was 11,000, 5000 and 33.0%. The copolymer is defined as an "alkali-soluble resin (B-1)."

[0089] Synthesis Example 2

153 parts by weight of propylene glycol monomethyl ether acetate, 15 parts by weight of methacrylic acid, 35 parts by weight of benzyl methacrylate, 11 parts by weight of N-phenylmaleimide, 20 parts by weight of 2-acryloyloxyethyl succinate, 19 parts by weight of styrene, and 5 parts by weight of

2,4-diphenyl-4-methyl-1-pentene (chain transfer agent) were loaded into a flask equipped with a cooling tube and a stirrer. Next, a solution obtained by dissolving 3 parts by weight of 2,2'-azobisisobutyronitrile into 47 parts by weight of propylene glycol monomethyl ether acetate was loaded, followed by replacement by nitrogen gas. After that, while gently stirring, the temperature of the reaction solution was raised to 80°C. Polymerization was carried out while the temperature was kept for 4 hours. After that, a solution obtained by dissolving 0.5 part by weight of 2,2'-azobisisobutyronitrile into 9.5 parts by weight of propylene glycol monomethyl ether acetate was loaded. Then, the temperature of the reaction solution was raised to 100°C, and polymerization was further carried out while the temperature was kept for 1 hour, to thereby yield a copolymer solution. Mw, Mn and solid concentration of the resultant resin was 10,000, 6000 and 30.0%. The copolymer is defined as an "alkali-soluble resin (B-2)."

[0090] Synthesis Example 3

5 parts by weight of 2,2'-azobisisobutyronitrile and 200 parts by weight of propylene glycol monomethyl ether acetate were loaded into a flask equipped with a cooling tube and a stirrer. Then, 15 parts by weight of methacrylic acid, 35 parts by weight of benzyl methacrylate, 25 parts by weight of N-phenylmaleimide, 10 parts by weight of glycerol methacrylate, 15 parts by weight of styrene, and 7.5 parts by weight of 2,4-diphenyl-4-methyl-1-pentene (chain transfer agent) were loaded, followed by replacement by nitrogen gas. After that, while gently stirring, the temperature of the

reaction solution was raised to 80°C. Polymerization was carried out while the temperature was kept for 3 hours, to thereby yield a copolymer solution. Mw, Mn and solid concentration of the resultant resin was 7000, 3500 and 32.0%. The copolymer is defined as an "alkali-soluble resin (B-3)."

[0091] Example 1

100 parts by weight of the pigment dispersion liquid (R1), 10 parts by weight (in terms of solid content) of the alkali-soluble resin (A-1) as an alkali-soluble resin (B), 15 parts by weight of a mixture of KAYARAD DPCA-60 (a compound represented by the formula (1) where m is 1 in the formula (2) and the number of the groups represented by the formula (2) is 6) manufactured by Nippon Kayaku Co., Ltd. and dipentaerythritol hexaacrylate at a ratio of 50/50 (weight ratio) as a polyfunctional monomer (C), 5 parts by weight of 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butan-1-one (trade name: IRGACURE 369, manufactured by Ciba Specialty Chemicals Inc.) as a photopolymerization initiator (D), and propylene glycol monomethyl ether acetate as a solvent were mixed to adjust a solid concentration to 25%, to thereby prepare a liquid composition (S-1).

[0092] The liquid composition (S-1) was evaluated in accordance with the following procedure. Table 2 shows the results of the evaluation.

[0093] Evaluation of sensitivity

The liquid composition (S-1) was coated onto a surface of a glass substrate by using a spin coater, and the glass substrate with the liquid composition (S-1) was then pre-baked on a hot plate

at 90°C for 4 minutes to form a coating film having a thickness of 1.3 μm. Next, the substrate was cooled to room temperature, and the coating film on the substrate was exposed to light by using a high-pressure mercury lamp in an exposure dose of 400 J/m^2 through a photomask. Then, a shower development was performed by discharging an aqueous solution of 0.04 wt% potassium hydroxide at 23°C onto the coating film on the substrate for 60 seconds under a development pressure of 1 kgf/cm^2 (nozzle diameter of 1 mm). After that, the coating film on the substrate was further post-baked at 220°C for 30 minutes to form a dot pattern of 200×200 μm.

The dot pattern on the substrate obtained in the formation of the pattern was observed with a scanning electron microscope to measure its film thickness, followed by calculation of a residual film thickness ((film thickness after post-baking)×100/1.3). The higher the residual film thickness of a composition is, the composition the better the sensitivity is.

[0094] Evaluation of adhesiveness

The liquid composition (S-1) was coated onto a surface of a glass substrate by using a spin coater, and the glass substrate with the liquid composition (S-1) was then pre-baked on a hot plate at 90°C for 4 minutes to form a coating film having a thickness of 1.3 μm. Next, the substrate was cooled to room temperature, and the coating film on the substrate was then exposed to light by using a high-pressure mercury lamp in an exposure dose of 400 J/m^2. Then, a shower development was performed by discharging an aqueous solution of 0.04 wt% potassium hydroxide at 23°C onto the coating film for

60 seconds under a development pressure of 1 kgf/cm^2 (nozzle diameter of 1 mm). After that, the coating film was further post-baked at 220°C for 30 minutes.

Subsequently, the resultant cured film was cross cut into 100 pieces like a grid pattern to perform the evaluation of adhesiveness in accordance with the JIS K5400 standard. In the evaluation, if no grid piece peeling off was observed, the evaluation was represented as "○". If 1 to 10 grid pieces peeling off was observed, the evaluation was represented by "Δ". If more than 10 grid pieces peeling off was observed, the evaluation was represented by "×".

[0095] Evaluation of cross-sectional shape and development resistance

The liquid composition (S-1) was coated onto a surface of a glass substrate by using a spin coater, and the glass substrate with the liquid composition (S-1) was then pre-baked on a hot plate at 90°C for 4 minutes to form a coating film having a thickness of 1.3 μm. Next, the substrate was cooled to room temperature, and the coating film on the substrate was then exposed to light by using a high-pressure mercury lamp in an exposure dose of 400 J/m^2 through a photomask. Then, a shower development was performed by discharging an aqueous solution of 0.04 wt% potassium hydroxide at 23°C onto the coating film on the substrate for 60 seconds under a development pressure of 1.5 kgf/cm^2 (nozzle diameter of 1 mm). After that, the coating film was post-baked at 220°C for 30 minutes to form a stripe-shaped pixel pattern of 90 μm on the substrate.

Subsequently, the resultant stripe-shaped pixel pattern was

observed with an optical microscope in order to see the presence or absence of the chipping of a pattern edge.

Further, the cross-sectional shape of the resultant pixel pattern was observed with a scanning electron microscope (SEM) to measure the taper angle as illustrated in FIG. 1. When the taper angle is 80° or more, the wiring of a transparent electrode film may be disconnected. On the other hand, when the taper angle is 20° or less, the slant portion of the pixel pattern becomes longer, producing a portion with a thinner film thickness in a pixel edge. An ideal taper angle is 30 to 70°.

[0096] Examples 2 to 12 and Comparative Examples 1 to 11

Liquid compositions (S-2) to (S-23) were prepared in the same manner as that in Example 1, except that the types and amounts of the respective components in the liquid compositions were changed as shown in Table 1.

Next, evaluations were performed in the same manner as that in Example 1, except that each of the liquid compositions (S-2) to (S-23) was used instead of the liquid composition (S-1). The results are shown in Table 2.

[0097] [Table 1]

	Liquid composition	Pigment dispersion liquid		Component (B)		Component (C)		Component (D)	
		Type	Part by weight	Type	Part by weight	Type	Part by weight	Type	Part by weight
Example 1	S-1	R1	100	B-1	15	C-4	15	D-1/D-5	5/2
Example 2	S-2	R2	100	B-2	10	C-2/C-3	5/15	D-2/D-5	5/2
Example 3	S-3	R3	100	B-3	10	C-1/C-3	7/23	D-2/D-4/D-5/D-6	5/0.1/0.4/0.1
Example 4	S-4	R3	100	B-3	10	C-1/C-3	2/28	D-2/D-4/D-5/D-6	5/0.1/0.4/0.1
Example 5	S-5	R3	100	B-3	10	C-1/C-5	7/23	D-2/D-4/D-5/D-6	5/0.1/0.4/0.1
Example 6	S-6	R3	100	B-3	10	C-1/C-6	7/23	D-2/D-4/D-5/D-6	5/0.1/0.4/0.1
Example 7	S-7	G1	100	B-1	12	C-4	12	D-1/D-4/D-5/D-6	5/1/1/0.5
Example 8	S-8	G2	100	B-2	12	C-3	12	D-1/D-3/D-4/D-5/D-6	4/1/1/1/0.5
Example 9	S-9	G3	100	B-3	12	C-1/C-3	5/15	D-1/D-2/D-4/D-5/D-6	4/1/1/1/0.5
Example 10	S-10	B1	100	B-1	15	C-1/C-3	5/15	D-2/D-4/D-5/D-6	5/1/1/0.5
Example 11	S-11	B2	100	B-2	12	C-3	18	D-2/D-4/D-5/D-6	5/1/1/0.5
Example 12	S-12	B3	100	B-3	12	C-1/C-3	5/15	D-2/D-4/D-5/D-6	5/1/1/0.5
Comparative Example 1	S-13	R1	100	B-1	20	C-4	10	D-1/D-5	5/2
Comparative Example 2	S-14	R1	100	B-1	16	C-4	14	D-1/D-5	5/2
Comparative Example 3	S-15	R1	100	B-1	7	C-4	23	D-1/D-5	5/2
Comparative Example 4	S-16	R2	100	B-2	15	C-2/C-3	5/10	D-2/D-5	5/2
Comparative Example 5	S-17	R3	100	B-3	10	C-1/C-3	25/5	D-2/D-4/D-5/D-6	5/0.1/0.4/0.1
Comparative Example 6	S-18	G1	100	B-1	14	C-4	10	D-1/D-4/D-5/D-6	5/1/1/0.5
Comparative Example 7	S-19	G2	100	B-2	16	C-3	8	D-1/D-3/D-4/D-5/D-6	4/1/1/1/0.5
Comparative Example 8	S-20	G3	100	B-3	12	C-1	20	D-1/D-2/D-4/D-5/D-6	4/1/1/1/0.5
Comparative Example 9	S-21	B1	100	B-1	16	C-1/C-3	5/14	D-2/D-4/D-5/D-6	5/1/1/0.5
Comparative Example 10	S-22	B2	100	B-2	20	C-3	10	D-2/D-4/D-5/D-6	5/1/1/0.5
Comparative Example 11	S-23	B3	100	B-3	12	C-1	20	D-2/D-4/D-5/D-6	5/1/1/0.5

[0098] In Table 1, respective components are as follows.

C-1: dipentaerythritol hexaacrylate

C-2: pentaerythritol tetramethacrylate

C-3: a compound represented by the above-mentioned formulas (1) to (3) where m is 1, the number of the groups represented by the formula (2) is 6, and all R^1's represent hydrogen atoms (trade name: KAYARAD DPCA-60, manufactured by Nippon Kayaku Co., Ltd.)

C-4: a compound represented by the above-mentioned formulas (1) to (3) where m is 2, the number of the groups represented by the formula (2) is 6, and all R^1's represent hydrogen atoms (trade name: KAYARAD DPCA-120, manufactured by Nippon Kayaku Co., Ltd.)

C-5: a compound represented by the above-mentioned formulas (1) to (3) where m is 1, the number of the groups represented by the formula (2) is 2, and all R^1's represent hydrogen atoms (trade name: KAYARAD DPCA-20, manufactured by Nippon Kayaku Co., Ltd.)

C-6: a compound represented by the above-mentioned formulas (1) to (3) where m is 1, the number of the groups represented by the formula (2) is 3, and all R^1's represent hydrogen atoms (trade name: KAYARAD DPCA-30, manufactured by Nippon Kayaku Co., Ltd.)

D-1:

2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butan-1-one (trade name: IRGACURE 369, manufactured by Ciba Specialty Chemicals Inc.)

D-2:

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

(trade name: IRGACURE 907, manufactured by Ciba Specialty Chemicals Inc.)

D-3: ethanone, 1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-, 1-(O-acetyloxime) (trade name: IRGACURE OXE02, manufactured by Ciba Specialty Chemicals Inc.)

D-4: 2,2'-bis(2-chlorophenyl)-4,5,4',5'-tetraphenyl-1,2'-biimidazole

D-5: 4,4'-bis(diethylamino)benzophenone

D-6: 2-mercaptobenzothiazole

[0099] [Table 2]

	Liquid composition	Sensitivity	Adhesiveness	Taper angle (°)	Pattern chipping
Example 1	S-1	78%	○	50	Absent
Example 2	S-2	81%	○	65	Absent
Example 3	S-3	84%	○	55	Absent
Example 4	S-4	86%	○	50	Absent
Example 5	S-5	82%	○	35	Absent
Example 6	S-6	80%	○	40	Absent
Example 7	S-7	77%	○	50	Absent
Example 8	S-8	80%	○	60	Absent
Example 9	S-9	84%	○	65	Absent
Example 10	S-10	85%	○	55	Absent
Example 11	S-11	82%	○	60	Absent
Example 12	S-12	84%	○	60	Absent
Comparative Example 1	S-13	73%	○	10	Present
Comparative Example 2	S-14	77%	○	25	Present
Comparative Example 3	S-15	80%	×	75	Absent
Comparative Example 4	S-16	76%	○	85	Absent
Comparative Example 5	S-17	81%	○	100	Absent
Comparative Example 6	S-18	74%	○	20	Present
Comparative Example 7	S-19	70%	○	10	Absent
Comparative Example 8	S-20	82%	○	105	Absent
Comparative Example 9	S-21	81%	○	85	Absent
Comparative Example 10	S-22	72%	○	20	Absent
Comparative Example 11	S-23	83%	○	105	Absent

[0100] Table 2 shows that in the case where a radiation-sensitive composition for forming a colored layer comprising 100 to 300 parts by weight of a compound having a caprolactone structure, as the polyfunctional monomer with respect to 100 parts by weight of the alkali-soluble resin, and having two or more polymerizable unsaturated bonds in the molecules was used

(Examples 1 to 12), a pixel pattern having an ideal, normal-taper shape was formed and the pixel pattern was excellent in adhesiveness.

On the other hand, Table 2 shows that in the case where a radiation-sensitive composition for forming a colored layer which did not include, as the polyfunctional monomer, a compound having a caprolactone structure and two or more polymerizable unsaturated bonds in the molecules was used (Comparative Examples 8 and 11), a pixel pattern having a reverse taper shape formed. Meanwhile, Table 2 shows that in the case where the amount of a compound having a caprolactone structure and two or more polymerizable unsaturated bonds in the molecules was less than 100 parts by weight with respect to 100 parts by weight of the alkali-soluble resin (Comparative Examples 1, 2, 4 to 7, 9, and 10), a pixel pattern having an ideal, normal-taper shape was not formed, and chipping in the pixel pattern were simultaneously occurred in some cases, and shows that in the case where the amount was more than 300 parts by weight (Comparative Example 3), the resultant pixel pattern was inferior in adhesiveness.

CLAIMS

1. A radiation-sensitive composition for forming a colored layer, comprising:

a colorant (A);

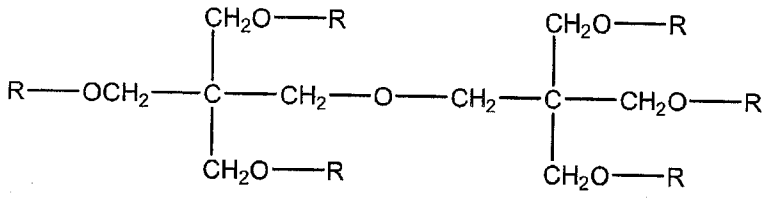
an alkali-soluble resin (B);

a polyfunctional monomer (C); and

a photopolymerization initiator (D),

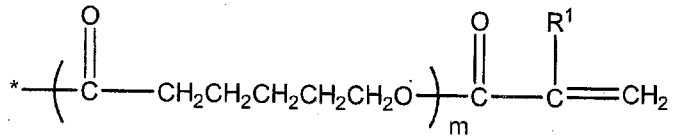
wherein the radiation-sensitive composition comprises 100 to 300 parts by weight of a compound having a caprolactone structure and two or more polymerizable unsaturated bonds in the molecules, as the polyfunctional monomer (C), with respect to 100 parts by weight of the alkali-soluble resin (B).

2. The radiation-sensitive composition for forming a colored layer according to claim 1, wherein the compound having a caprolactone structure and two or more polymerizable unsaturated bonds in the molecules is a compound represented by the following formula (1),



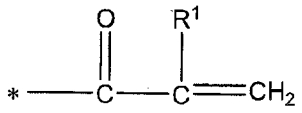
(1)

wherein all 6 R groups are groups represented by the following formula (2), or 1 to 5 R groups out of the 6 R groups are groups represented by the following formula (2) and the remaining R groups are groups represented by the following formula (3),



(2)

wherein R^1 represents a hydrogen atom or a methyl group, m represents a number of 1 or 2, and "*" represents a bond,



(3)

wherein R^1 represents a hydrogen atom or a methyl group and "*" represents a bond.

3. The radiation-sensitive composition for forming a colored layer according to claim 2, wherein the compound having a caprolactone structure and two or more polymerizable unsaturated bonds in the molecules is a compound represented by the above-mentioned formula (1) where the all 6 R groups are the groups represented by the above-mentioned formula (2).

4. The radiation-sensitive composition for forming a colored layer according to any one of claims 1 to 3, wherein the radiation-sensitive composition further comprises a compound having no caprolactone structure and having two or more polymerizable unsaturated bonds as the polyfunctional monomer (C).

5. The radiation-sensitive composition for forming a colored layer according to any one of claims 1 to 4, wherein the composition forms a colored layer in an exposure dose of 800 J/m^2 or less.

6. A color filter, comprising a colored layer formed by using the radiation-sensitive composition for forming a colored layer according to any one of claims 1 to 5.

7. A color liquid crystal display device, comprising the color filter according to claim 6.

8. A method of producing a color filter, comprising a step of forming a colored layer in an exposure dose of 800 J/m^2 or less by using the radiation-sensitive composition for forming a colored layer according to any one of claims 1 to 5.