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RADIATION SENSITIVE COMPOSITION AND
COLOR LIQUID CRYSTAL DISPLAY DEVICE



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Detailed Description of the Invention

5 The present invention relates to a radiation sensitive composition which is used to form a colored layer, preferably pigmented layer, containing pixels and/or a color black matrix for a color liquid crystal display device on a substrate for driving a thin film transistor (TFT) color
10 liquid crystal display device and to a color liquid crystal display device.

 A color liquid crystal display device comprising a thin film transistor (TFT) substrate has been produced by manufacturing a color filter substrate for displaying a color
15 image separate from a drive substrate having a thin film transistor (TFT) mounted thereon and laminating this color filter substrate with the drive substrate. However, since the positioning accuracy of this system is low at the time of lamination, the width of the black matrix must be made
20 large, thereby making it difficult to obtain a high opening rate (the rate of opening area for transmitting light).

 Meanwhile, there has been developed a new system that a colored layer is formed on a drive substrate having a thin film transistor (TFT) mounted thereon directly or through
25 a passivation film such as a silicon nitride film and this substrate having the colored layer formed thereon is laminated with a substrate having an ITO (tin doped indium oxide) electrode formed thereon by sputtering. Since the colored layer including pixels and/or a black matrix is
30 directly formed on the drive substrate in this system, the step of laminating the color filter substrate with the drive substrate becomes unnecessary and the opening rate can be drastically improved compared with the former system, thereby making it possible to obtain a bright high-definition

display.

However, when a colored layer is to be formed by the latter system, it is necessary to form an about 1 to 15 μm diameter through hole or U-shaped dent for connecting an ITO electrode formed on the colored layer by sputtering to the terminal of the drive substrate underlying the colored layer. There has been unknown a radiation sensitive composition which enables the formation of this through hole or U-shaped dent, provides a colored layer having such a shape that an ITO electrode can be formed without being broken in the ITO sputtering step after the formation of the through hole or U-shaped dent, is free from the development residue and is excellent in surface smoothness and adhesion to a drive substrate and a passivation film such as a silicon nitride film.

In the system for forming a colored layer on the surface of a drive substrate having a thin film transistor (TFT) formed thereon, it is necessary to sputter ITO over the surface of the colored layer formed on the drive substrate and to form an ITO electrode by shaping the obtained ITO layer to a pattern having a predetermined shape. The process of shaping this ITO layer to a pattern generally consists of a series of steps - the coating of a positive resist, exposure to radiation, development, the etching of the ITO layer and the removal of the positive resist. A stripping liquid is used in the step of removing the positive resist. If the colored layer swells with the stripping liquid considerably, the ITO electrode overlying the colored layer cracks, giving a great hindrance to the function of a color liquid crystal display device.

Further, in a liquid crystal display device obtained by this system, a display failure may occur when a portion to which voltage has been applied does not function accurately, or pixels to which voltage has not been applied malfunction,

which is a problem to be solved from the viewpoint of the reliability of a color liquid crystal display device.

It is therefore an object of the present invention to provide a radiation sensitive composition to be used for forming a colored layer which enables the formation of a through hole or U-shaped dent, hardly swells with a positive resist stripping liquid used to form an electrode on the surface of a colored layer, is free from a display failure caused by the breakage at the forming of an ITO film, a display failure caused by deterioration in the operation function of a portion to which voltage has been applied or a display failure caused by the malfunctioning of a portion to which voltage has not been applied, is devoid of the development residue generated at the time of development, and is excellent in surface smoothness and adhesion to a drive substrate having a thin film transistor (TFT) formed thereon and a passivation film such as a silicon nitride film.

It is another object of the present invention to provide a color liquid crystal display device having pixels of a colored layer formed from the above radiation sensitive composition.

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

Firstly, according to the present invention, the above objects and advantages of the present invention are attained by a radiation sensitive composition used to form a colored layer on a substrate for driving a thin film transistor (TFT) color liquid crystal display device, the composition comprising (A) a colorant, (B) an alkali soluble resin, (C) a polyfunctional monomer and (D) a photopolymerization initiator.

Secondly, the above objects and advantages of the present invention are attained by a thin film transistor (TFT) color liquid crystal display device having a colored layer

formed on a drive substrate directly or through a passivation film, the colored layer being formed from the above radiation sensitive composition.

The term "radiation" as used herein includes visible
5 rays, ultraviolet rays, far ultraviolet rays, electron beams, X-rays and the like.

The present invention will be described in detail hereinafter.

(A) colorant

10 The colorant in the present invention is not limited to a particular color but is suitably selected according to the application of the obtained color filter. The colorant may be a pigment, dye or natural coloring matter.

Since high-definition color development and heat
15 resistance are required of a color filter, the colorant in the present invention is preferably a colorant having high chromophoric activity and high heat resistance, particularly preferably a colorant having high resistance to thermal decomposition. A pigment is generally used, and an organic
20 pigment and/or carbon black are/is particularly preferred.

Illustrative examples of the above organic pigment include 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
25 color index (C.I.) numbers:

C.I. Pigment Yellow 83, C.I. Pigment Yellow 128, 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,
30 C.I. Pigment Yellow 156, C.I. Pigment Yellow 166, C.I. Pigment Yellow 168, C.I. Pigment Yellow 175 and C.I. Pigment Yellow 185;

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 177, 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 and C.I. Pigment Blue 15:6;
C.I. Pigment Green 7 and C.I. Pigment Green 36; and
C.I. Pigment Black 1 and C.I. Pigment Black 7.

These organic pigments may be used alone or in combination of two or more.

The above organic pigments may be purified by, for example, a sulfuric acid recrystallization method, solvent cleaning method or a combination thereof before use.

Although the colored layer formed from the radiation sensitive composition of the present invention has sufficiently high volume resistivity, the volume resistivity of the colored layer can be further improved by using an organic pigment which has been purified to reduce the contents of impurities as described above.

Inorganic pigments include, for example, titanium oxide, barium sulfate, calcium carbonate, zinc white, lead sulfate, yellow lead, zinc yellow, rouge(iron red oxide (III)), cadmium red, ultramarine blue, iron blue, chromic oxide green, cobalt green, amber, titanium black, synthetic iron black, carbon black and the like.

These inorganic pigments may be used alone or in combination of two or more.

When the radiation sensitive composition of the present invention is used to form pixels, one or more organic pigments are preferably used as colorants and when it is used to form

a black matrix, two or more organic pigments and/or carbon black are preferably used as colorants.

The colored layer formed from the radiation sensitive composition of the present invention shows a sufficiently
5 small dielectric constant value which can be further reduced by controlling the content of the colorant in the colored layer, which is related to the amounts of the components (B) to (D) and additive components used, to preferably 1 to 60 wt%, more preferably 3 to 35 wt%, much more preferably 5 to
10 15 wt%.

In the present invention, the surface of the particle of each of the above pigments may be modified with a polymer before use. Examples of the polymer for modifying the surface of the particle of the pigment include polymers
15 disclosed by JP-A 8-259876 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") and commercially available polymers and oligomers for dispersing pigments.

The colorant in the present invention may be used in
20 combination with a dispersant as desired.

The dispersant is, for example, a cation, anion, nonionic, amphoteric, silicone-based or fluorine-based surfactant.

Illustrative examples of the surfactant include
25 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
30 polyethylene glycol dilaurate and polyethylene glycol distearate; sorbitan fatty acid esters; fatty acid modified polyesters; tertiary amine modified polyurethanes; polyethylene imines; and commercial products under the trade names of KP (Shin-Etsu Chemical Co., Ltd.), Polyflow (Kyohei

Kagaku Co., Ltd.), F Top (Tokem Products Co., Ltd.), Megafac (Dainippon Ink and Chemicals, Inc.), Florade (Sumitomo 3M Limited), Asahi Guard and Surflon (Asahi Glass Co., Ltd.), Disperbyk (Bickemy Japan Co., Ltd.), Solsperse (Zeneka Co., Ltd.), EFKA (Efka Chemicals, Co., Ltd.) and the like.

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 30 parts or less by weight based on 100 parts by weight of the colorant.

(B) alkali soluble resin

Preferably, the alkali soluble resin in the present invention serves as a binder for the colorant (A) and has solubility in a developer, particularly preferably an alkali developer used in the developing step for the production of a color filter. The alkali soluble resin is, for example, a copolymer of a photopolymerizable unsaturated monomer having an acidic functional group such as a carboxyl group, phenolic hydroxyl group or sulfonic acid group and other copolymerizable unsaturated monomer (to be referred to as "copolymerizable unsaturated monomer" hereinafter).

Examples of the photopolymerizable unsaturated monomer having a carboxyl group (to be referred to as "carboxyl group-containing unsaturated monomer" hereinafter) 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 a functionality of 3 or more and anhydrides thereof; mono[(meth)acryloyloxyalkyl]esters of polycarboxylic acids having a functionality of 2 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 hydroxyl group at both terminals such as ω -carboxypolycaprolactone mono(meth)acrylate; and the like.

5 Out of these carboxyl group-containing unsaturated monomers, (meth)acrylic acid and mono[2-(meth)acryloyloxyethyl]succinate are particularly preferred.

 The above carboxyl group-containing unsaturated
10 monomers may be used alone or in combination of two or more.

 Examples of the photopolymerizable unsaturated monomer having a phenolic hydroxyl group include o-hydroxystyrene, m-hydroxystyrene, p-hydroxystyrene, o-hydroxy- α -methylstyrene, m-hydroxy- α -methylstyrene, p-
15 hydroxy- α -methylstyrene, N-o-hydroxyphenylmaleimide, N-m-hydroxyphenylmaleimide, N-p-hydroxyphenylmaleimide and the like.

 These photopolymerizable unsaturated monomers having a phenolic hydroxyl group may be used alone or in combination
20 of two or more.

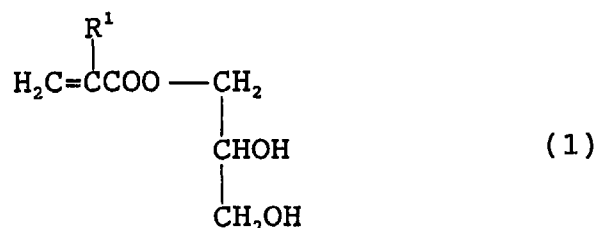
 Example of the photopolymerizable unsaturated monomer having a sulfonic acid group include isoprenesulfonic acid, p-styrenesulfonic acid and the like.

 These photopolymerizable unsaturated monomers having
25 a sulfonic acid group may be used alone or in combination of two or more.

 Examples of the copolymerizable unsaturated monomer include macromonomers having a mono(meth)acryloyl group at a terminal of a polymer molecular chain (to be simply referred
30 to as "macromonomers" hereinafter) such as polystyrene, polymethyl (meth)acrylate, poly-n-butyl (meth)acrylate and polysiloxane; N-position-substituted maleimides such as N-(substituted) arylmaleimides exemplified by N-phenylmaleimide, N-o-hydroxyphenylmaleimide, N-m-

hydroxyphenylmaleimide, N-p-hydroxyphenylmaleimide, N-o-methylphenylmaleimide, N-m-methylphenylmaleimide, N-p-methylphenylmaleimide, N-o-methoxyphenylmaleimide, N-m-methoxyphenylmaleimide and N-p-methoxyphenylmaleimide, and
 5 N-cyclohexylmaleimide; aromatic vinyl compounds such as 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,
 10 o-vinylbenzylglycidyl ether, m-vinylbenzylglycidyl ether and p-vinylbenzylglycidyl ether; indenenes such as indene and 1-methylindene; unsaturated carboxylic esters such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, 1-propyl (meth)acrylate, n-butyl
 15 (meth)acrylate, 1-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,
 20 methoxypropylene glycol (meth)acrylate, methoxydipropylene glycol (meth)acrylate, isobornyl (meth)acrylate, dicyclopentadienyl (meth)acrylate, 2-hydroxy-3-phenoxypropyl (meth)acrylate and glycerol (meth)acrylate represented by the following formula (1):

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(wherein R^1 is a hydrogen atom or methyl group); unsaturated carboxylic acid aminoalkyl esters such as 2-aminoethyl (meth)acrylate, 2-dimethylaminoethyl (meth)acrylate, 2-aminopropyl (meth)acrylate, 2-dimethylaminopropyl acrylate, 5 3-aminopropyl (meth)acrylate and 3-dimethylaminopropyl (meth)acrylate; unsaturated carboxylic acid glycidyl esters such as glycidyl (meth)acrylate; carboxylic acid vinyl esters such as vinyl acetate, vinyl propionate, vinyl butyrate and vinyl benzoate; unsaturated ethers such as 10 vinylmethyl ether, vinyl ethyl ether and allylglycidyl 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 15 dienes such as 1,3-butadiene, isoprene and chloroprene; and the like.

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

Out of the above copolymerizable unsaturated monomers, 20 macromonomers, N-position-substituted maleimides, 2-hydroxyethyl (meth)acrylate, benzyl (meth)acrylate and glycerol (meth)acrylate are preferred. Out of the macromonomers, polystyrene macromonomer and polymethyl (meth)acrylate macromonomer are particularly preferred. 25 Out of the N-position-substituted maleimides, N-phenylmaleimide and N-cyclohexylmaleimide are particularly preferred.

The alkali soluble resin in the present invention is preferably a copolymer of a carboxyl group-containing 30 unsaturated monomer and a copolymerizable unsaturated monomer (to be simply referred to as "carboxyl group-containing copolymer" hereinafter).

The carboxyl group-containing copolymer is preferably a copolymer (to be referred to as "carboxyl group-containing

copolymer (I)" hereinafter) of a monomer mixture containing (1) a carboxyl group-containing unsaturated monomer and (2) at least one selected from the group consisting of polystyrene macromonomer, polymethyl (meth)acrylate macromonomer, N-phenylmaleimide, N-cyclohexylmaleimide, 2-hydroxyethyl (meth)acrylate, benzyl (meth)acrylate and glycerol (meth)acrylate and optionally (3) at least one selected from the group consisting of styrene, methyl (meth)acrylate, allyl (meth)acrylate and phenyl (meth)acrylate, particularly preferably a copolymer (to be referred to as "carboxyl group-containing copolymer (II)" hereinafter) of a monomer mixture containing (1) a carboxyl group-containing unsaturated monomer component which comprises (meth)acrylic acid as an essential component and optionally mono[2-(meth)acryloyloxyethyl]succinate and (2) at least one selected from the group consisting of polystyrene macromonomer, polymethyl (meth)acrylate macromonomer, N-phenylmaleimide, N-cyclohexylmaleimide, 2-hydroxyethyl (meth)acrylate, benzyl (meth)acrylate and glycerol (meth)acrylate and optionally (3) at least one selected from the group consisting of styrene, methyl (meth)acrylate, allyl (meth)acrylate and phenyl (meth)acrylate.

Illustrative examples of the carboxyl group-containing copolymer (I) include (meth)acrylic acid/benzyl (meth)acrylate/polystyrene macromonomer copolymer, (meth)acrylic acid/benzyl (meth)acrylate/polymethyl (meth)acrylate macromonomer copolymer, (meth)acrylic acid/N-phenylmaleimide/benzyl (meth)acrylate/styrene copolymer, (meth)acrylic acid/mono[2-(meth)acryloyloxyethyl]succinate/N-phenylmaleimide/styrene/allyl (meth)acrylate copolymer, (meth)acrylic acid/mono[2-(meth)acryloyloxyethyl]succinate/N-phenylmaleimide/benzyl (meth)acrylate/styrene copolymer,

- (meth)acrylic acid/N-cyclohexylmaleimide/benzyl
 (meth)acrylate/styrene copolymer, (meth)acrylic
 acid/mono[2-(meth)acryloyloxyethyl]succinate/N-
 cyclohexylmaleimide/styrene/allyl (meth)acrylate copolymer,
 5 (meth)acrylic acid/mono[2-
 (meth)acryloyloxyethyl]succinate/N-
 cyclohexylmaleimide/benzyl (meth)acrylate/styrene
 copolymer, (meth)acrylic acid/benzyl
 (meth)acrylate/glycerol mono(meth)acrylate copolymer,
 10 (meth)acrylic acid/mono[2-
 (meth)acryloyloxyethyl]succinate/benzyl
 (meth)acrylate/glycerol mono(meth)acrylate copolymer,
 (meth)acrylic acid/2-hydroxyethyl (meth)acrylate copolymer,
 (meth)acrylic acid/2-hydroxyethyl (meth)acrylate/styrene
 15 copolymer, (meth)acrylic acid/2-hydroxyethyl
 (meth)acrylate/benzyl (meth)acrylate copolymer,
 (meth)acrylic acid/2-hydroxyethyl (meth)acrylate/phenyl
 (meth)acrylate copolymer, (meth)acrylic acid/2-
 hydroxyethyl (meth)acrylate/benzyl
 20 (meth)acrylate/polystyrene macromonomer copolymer,
 (meth)acrylic acid/2-hydroxyethyl (meth)acrylate/benzyl
 (meth)acrylate/polymethyl (meth)acrylate macromonomer
 copolymer, (meth)acrylic acid/N-phenylmaleimide/benzyl
 (meth)acrylate/glycerol mono(meth)acrylate/styrene
 25 copolymer and the like.

The amount of the carboxyl group-containing
 unsaturated monomer is preferably 5 to 50 wt%, more preferably
 10 to 40 wt% based on the carboxyl group-containing copolymer.
 When the amount of the carboxyl group-containing unsaturated
 30 monomer is smaller than 5 wt%, the solubility in an alkali
 developer of the obtained radiation sensitive composition
 tends to lower and when the amount is larger than 50 wt%,
 the solubility in an alkali developer becomes excessive,
 whereby the obtained sensitive radiation composition is apt

to fall off from the substrate of pixels when it is developed with an alkali developer, or it is liable to be difficult to make the surface roughness of each pixel sufficiently small.

5 The weight average molecular weight (to be referred to as "Mw" hereinafter) in terms of polystyrene measured by gel permeation chromatography (GPC, eluting solvent: tetrahydrofuran) of the alkali soluble resin in the present invention is preferably 3,000 to 300,000, more preferably
10 5,000 to 100,000.

 The number average molecular weight (to be referred to as "Mn" hereinafter) in terms of polystyrene measured by gel permeation chromatography (GPC, eluting solvent: tetrahydrofuran) of the alkali soluble resin in the present
15 invention is preferably 3,000 to 60,000, more preferably 5,000 to 25,000.

 A radiation sensitive composition having excellent developability can be obtained from an alkali soluble resin having the above specific Mw or Mn, thereby making it possible
20 to form pixels having a sharp pattern edge and making it difficult to produce the residue, stains, film remnants and the like on the substrate and light screening layer of an unexposed portion at the time of development.

 The Mw/Mn ratio of the alkali soluble resin in the
25 present invention is preferably 1 to 5, more preferably 1 to 4.

 A radiation sensitive composition having excellent developability can be obtained from an alkali soluble resin having the above specific Mw or Mn, thereby making it possible
30 to form pixels having a sharp pattern edge and to form a panel which does not cause the breakage of an ITO film at the time of forming the ITO film and in which the vertical section of an opening existent in a colored layer formed from the composition has a bottom side longer than a top side, and

making it difficult to produce the residue, stains, film remnants or the like on the substrate and light screening layer of an unexposed portion at the time of development.

In the present invention, the alkali soluble resins may
5 be used alone or in combination of two or more.

The amount of the alkali soluble resin in the present invention 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 amount of the alkali
10 soluble resin is smaller than 10 parts by weight, alkali developability may lower, or stains or film remnants may be existent on the substrate or light screening layer of an unexposed portion and when the amount is larger than 1,000 parts by weight, the concentration of the colorant decreases
15 relatively, whereby it may be difficult to attain the targeted color strength of a thin film.

(C) polyfunctional monomer

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

20 Polyfunctional monomers can be divided into a group of carboxyl group-containing polyfunctional monomers and a group of polyfunctional monomers having no carboxyl group (to be referred to as "other polyfunctional monomers" hereinafter).

25 The carboxyl group-containing polyfunctional monomers include, for example, free carboxyl group-containing polyfunctional ester compounds of a polyhydric alcohol having a functionality of two or more and a polymerizable unsaturated carboxylic acid having two or more carboxyl
30 groups and free carboxyl group-containing polyfunctional ester compounds of a dicarboxylic acid and a free hydroxyl group-containing polyfunctional ester of a polyhydric alcohol having a functionality of three or more and a polymerizable unsaturated carboxylic acid having one or more

carboxyl groups (to be referred to as "(C1) polyfunctional monomers" hereinafter); free carboxyl group-containing polyfunctional ester compounds (to be referred to as "(C2) polyfunctional monomers" hereinafter) of a polycarboxylic acid having a functionality of three or more and a polymerizable unsaturated compound having one or more hydroxyl groups; and the like.

Examples of the polyhydric alcohol having a functionality of two or more of the polyfunctional monomer (C1) include ethylene glycol, propylene glycol, polyethylene glycol, polypropylene glycol, and the like. Examples of the polymerizable unsaturated carboxylic acid having two or more carboxyl groups include maleic acid, fumaric acid, itaconic acid, citraconic acid, mesaconic acid, and the like.

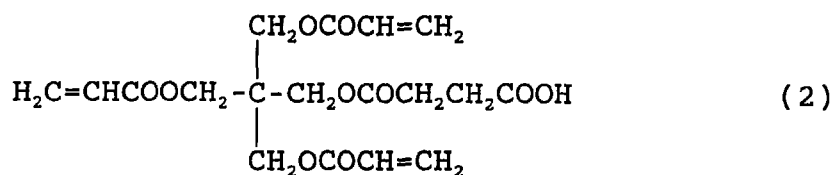
Examples of the polyhydric alcohol having a functionality of three or more of the polyfunctional monomer (C1) include glycerin, trimethylol propane, pentaerythritol, dipentaerythritol and the like. Examples of the polymerizable unsaturated carboxylic acid having one or more carboxyl groups include (meth)acrylic acid, crotonic acid, α -chloroacrylic acid, cinnamic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, mesaconic acid and the like. Examples of the dicarboxylic acid include 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, cyclohexane-1,2-dicarboxylic acid, cyclohexane-1,3-dicarboxylic acid, cyclohexane-1,4-dicarboxylic acid, phthalic acid, isophthalic acid, terephthalic acid and the like.

Examples of the polycarboxylic acid having a functionality of three or more of the polyfunctional monomer (C2) include propane-1,2,3-tricarboxylic acid

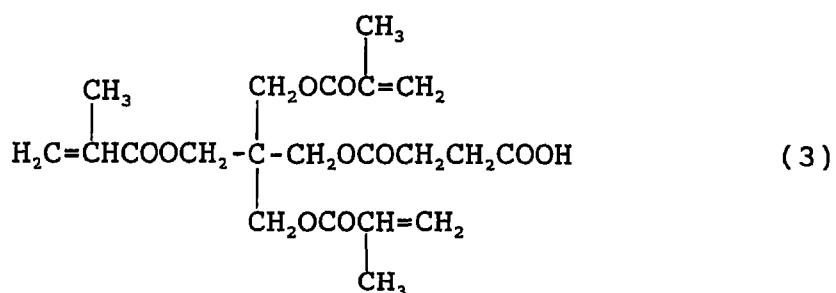
(tricarballic acid), butane-1,2,4-tricarboxylic acid, aconitic acid, camphoronic acid, cyclohexane-1,2,3-tricarboxylic acid, cyclohexane-1,2,4-tricarboxylic acid, cyclohexane-1,3,5-tricarboxylic acid, benzene-1,2,3-tricarboxylic acid, trimellitic acid, trimesic acid, mellophanic acid, pyromellitic acid and the like. Examples of the polymerizable unsaturated compound having one or more hydroxyl groups include (meth)allyl alcohol, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate and the like.

Preferred examples of the polyfunctional monomer (C1) and the polyfunctional monomer (C2) in the present invention include free carboxyl group-containing monoester compounds of a monohydroxyl group-containing oligo(meth)acrylate such as trimethylolpropane di(meth)acrylate, pentaerythritol tri(meth)acrylate or dipentaerythritol penta(meth)acrylate and a dicarboxylic acid such as malonic acid, succinic acid, glutaric acid or terephthalic acid; free carboxyl group-containing oligoester compounds of a tricarboxylic acid such as propane-1,2,3-tricarboxylic acid, butane-1,2,4-tricarboxylic acid, benzene-1,2,3-tricarboxylic acid, trimellitic acid or trimesic acid and a monohydroxyalkyl (meth)acrylate such as 2-hydroxyethyl (meth)acrylate or 2-hydroxypropyl (meth)acrylate; and the like.

Out of the above polyfunctional monomers (C1) and polyfunctional monomers (C2), a free carboxyl group-containing monoester compound of pentaerythritol triacrylate and succinic acid represented by the following formula (2) (to be referred to as "polyfunctional acrylate (1)" hereinafter) and a free carboxyl group-containing monoester compound of pentaerythritol trimethacrylate and succinic acid represented by the following formula (3) (to be referred to as "polyfunctional methacrylate (2)" hereinafter) are particularly preferred.



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Both the polyfunctional acrylate (1) and the polyfunctional methacrylate (2) can give a radiation sensitive composition which has high pixel strength and excellent pixel surface smoothness and hardly produces stains and film remnants in an area other than a portion where pixels are formed.

In the present invention, the carboxyl group-containing polyfunctional monomer serves to further improve the solubility in an alkali developer of the radiation sensitive composition and to further suppress the formation of an undissolved product after development. In this sense, the carboxyl group-containing polyfunctional monomer shows the function of an organic acid component as an additive which will be described hereinafter.

The other polyfunctional monomers include, for example, 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 functionality of three or more such as glycerin, trimethylolpropane, pentaerythritol and dipentaerythritol; oligo(meth)acrylates such as polyesters,

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epoxy resin, urethane resin, alkyd resin, silicone resin and spiran resin; di(meth)acrylates of both terminal hydroxylated polymers 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; tris[2-(meth)acryloyloxyethyl]phosphate; and the like.

Out of these other polyfunctional monomers, poly(meth)acrylates of a polyhydric alcohol having a functionality of three or more are preferred, as exemplified by trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol penta(meth)acrylate and dipentaerythritol hexa(meth)acrylate, out of which trimethylolpropane triacrylate, pentaerythritol triacrylate and dipentaerythritol hexaacrylate are particularly preferred because they have high pixel strength, excellent pixel surface smoothness and hardly produce stains, film remnants and the like on the substrate and light screening layer of an unexposed portion.

In the present invention, the polyfunctional monomers may be used alone or in combination of two or more, and a carboxyl group-containing polyfunctional monomer and other polyfunctional monomer may be used in combination. The radiation sensitive composition of the present invention has sufficient resolution as a radiation sensitive composition used to form a colored layer on a substrate for driving a thin film transistor (TFT) color liquid crystal display device and can form a through hole of a size required for the colored layer at the time of forming the colored layer. The size of the through hole can be suitably selected as fitted to the size of a pattern corresponding to a photomask by using a carboxyl group-containing polyfunctional monomer as one or all of the polyfunctional monomers.

In the present invention, the amount of the carboxyl group-containing polyfunctional monomer is preferably 5 to 95 wt%, more preferably 10 to 80 wt%, particularly preferably 10 to 50 wt% based on the total of all the polyfunctional monomers. When the amount of the carboxyl group-containing polyfunctional monomer is smaller than 5 wt%, it may be difficult to form a desired through hole according to the composition of the radiation sensitive composition if a carboxyl group-containing monofunctional monomer (E) which will be described hereinafter is not used, and when the amount is larger than 95 wt%, an alkali developer readily permeates into the colored layer with the result that the colored layer may fall off at the time of development.

The amount of the polyfunctional monomer used 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, pixel strength and surface smoothness may lower and when the amount is larger than 500 parts by weight, for example, alkali developability may deteriorate, or stains, film remnants and the like may be produced on the substrate or light screening layer of an unexposed portion.

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

Examples of the monofunctional monomer include carboxyl group-containing unsaturated monomers and copolymerizable unsaturated monomers enumerated for the alkali soluble resin (B), N-vinyl derivatives such as N-vinylsuccinimide, N-vinylpyrrolidone, N-vinylphthalimide, N-vinyl-2-piperidone, N-vinyl- ϵ -caprolactam, N-vinylpyrrole, N-vinylpyrrolidine, N-vinylimidazole, N-vinylimidazolidine, N-vinylindole, N-vinylindoline, N-

vinylbenzimidazole, N-vinylcarbazole, N-vinylpiperidine, N-vinylpiperazine, N-vinylmorpholine and N-vinylphenoxazine; N-(meth)acryloylmorpholine; and commercial products under the trade names of M-5300, M-5400 and M-5600 (trade names 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%, pixel strength, black matrix strength and surface smoothness tend to deteriorate.

(D) photopolymerization initiator

The photopolymerization initiator in the present invention is a compound which can form active species capable of initiating the polymerization of the above polyfunctional monomer (C) and the monofunctional monomer used as the case may be by the irradiation (to be referred to as "exposure" hereinafter) of radiation such as visible rays, ultraviolet rays, far ultraviolet rays, electron beams and X-rays.

Examples of the photopolymerization initiator include acetophenone compound, biimidazole compounds, triazine compounds, benzoin compounds, benzophenone compounds, α -diketone compounds, polynuclear quinone compounds, xanthone compounds, diazo compounds and the like.

These photopolymerization initiators may be used alone or in combination of two or more in the present invention. The photopolymerization initiator is preferably at least one selected from the group consisting of acetophenone compounds, biimidazole compounds and triazine compounds.

The amount of the photopolymerization initiator used in the present invention is preferably 0.01 to 80 parts by

weight, more preferably 1 to 60 parts by weight based on 100 parts by weight of the total of the polyfunctional monomer (C) and the monofunctional monomer used as the case may be. When the amount of the photopolymerization initiator is
5 smaller than 0.01 part by weight, it may be difficult to obtain an array of pixels arranged in a predetermined pattern due to incomplete curing by exposure and when the amount is larger than 80 parts by weight, the formed pixels tend to fall off from the substrate at the time of development.

10 Out of the preferred photopolymerization initiators in the present invention, the acetophenone compounds include, for example, 2-hydroxy-2-methyl-1-phenylpropan-1-one, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butanone-
15 1, 1-hydroxycyclohexyl-phenyl ketone, 2,2-dimethoxy-1,2-diphenylethan-1-one and the like.

Out of these acetophenone compounds, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1 and 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butanone-1
20 are particularly preferred. The above acetophenone compounds may be used alone or in combination of two or more.

The amount of the acetophenone compound as a photopolymerization initiator is preferably 0.01 to 80 parts by weight, more preferably 1 to 60 parts by weight, much more
25 preferably 1 to 30 parts by weight based on 100 parts by weight of the total of the polyfunctional monomer (C) and the monofunctional monomer. When the amount of the acetophenone compound is smaller than 0.01 part by weight, it may be difficult to obtain an array of pixels arranged in a
30 predetermined pattern due to incomplete curing by exposure and when the amount is larger than 80 parts by weight, the formed colored layer tends to fall off from the substrate at the time of development.

The biimidazole compounds include, for example,

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, 2,2'-bis(2,4,6-tribromophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole and the like. Out of these, 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 more preferred.

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

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

The amount of the biimidazole compound as a photopolymerization initiator is preferably 0.01 to 40 parts by weight, more preferably 1 to 30 parts by weight, much more

preferably 1 to 20 parts by weight based on 100 parts by weight of the total of the polyfunctional monomer (C) and the monofunctional monomer. When the amount of the biimidazole compound is smaller than 0.01 part by weight, it may be
5 difficult to obtain an array of pixels arranged in a predetermined pattern due to incomplete curing by exposure and when the amount is larger than 40 parts by weight, the formed colored layer tends to fall off from the substrate, or the surface of each pixel is apt to be roughened at the
10 time of development.
-hydrogen donor-

When a biimidazole compound is used as a photopolymerization initiator in the present invention, the following hydrogen donor is preferably used in combination
15 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 a biimidazole compound by exposure.

The hydrogen donor in the present invention is
20 preferably a mercaptan compound or amine compound.

The mercaptan compound is a compound having a benzene ring or heterocyclic ring as a fundamental structure and one or more, preferably 1 to 3, more preferably 1 or 2 mercapto groups directly bonded to the fundamental structure (to be
25 referred to as "mercaptan hydrogen donor" hereinafter).

The amine compound is a compound having a benzene ring or heterocyclic ring as a fundamental structure and one or more, preferably 1 to 3, more preferably 1 or 2 amino groups directly bonded to the fundamental structure (to be referred
30 to as "amino hydrogen donor" hereinafter).

These hydrogen donors may have a mercapto group and an amino group at the same time.

The hydrogen donor will be described in more detail hereinafter.

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

5 When the mercaptan hydrogen donor has two or more mercapto groups, under the condition that 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, under the condition that at least one free mercapto
10 group remains, the mercaptan hydrogen donor can have a structural unit whose two sulfur atoms are bonded together by a divalent organic group such as an alkylene group or a structural unit whose two sulfur atoms are bonded together in the form of a disulfide.

15 Further, the mercaptan hydrogen donor may be substituted by a carboxyl group, alkoxycarbonyl group, substituted alkoxycarbonyl group, phenoxycarbonyl group, substituted phenoxycarbonyl group, nitrile group or the like at a position other than mercapto groups.

20 Illustrative examples of the above mercaptan hydrogen donor include 2-mercaptobenzothiazole, 2-mercaptobenzooxazole, 2-mercaptobenzoimidazole, 2,5-dimercapto-1,3,4-thiadiazole, 2-mercapto-2,5-dimethylaminopyridine and the like.

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

30 The amine hydrogen donor can have one or more benzene rings or heterocyclic rings, or both of them. When the amine hydrogen donor has two or more benzene rings and heterocyclic rings, a fused ring may or may not be formed.

One or more amino groups of the amine hydrogen donor may be substituted by an alkyl group or substituted alkyl

group, and the amine hydrogen donor may be substituted by a carboxyl group, alkoxycarbonyl group, substituted alkoxycarbonyl group, phenoxycarbonyl group, substituted phenoxycarbonyl group, nitrile group or the like at a position
5 other than amino groups.

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

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

The amine hydrogen donor serves as a sensitizer even in the case of a photopolymerization initiator other than a biimidazole compound.

The hydrogen donors may be used alone or in combination
20 of two or more. When one or more mercaptan hydrogen donors and one or more amine hydrogen donors are used in combination, the formed colored layer hardly falls off from the substrate at the time of development and has high strength and sensitivity.

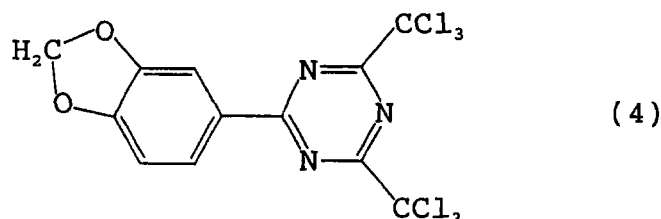
Illustrative examples of a mercaptan hydrogen donor/
25 amine hydrogen donor combination include 2-mercaptobenzothiazole/4,4'-bis(dimethylamino)benzophenone, 2-mercaptobenzothiazole/4,4'-bis(diethylamino)benzophenone,
30 2-mercaptobenzooxazole/4,4'-bis(dimethylamino)benzophenone, 2-mercaptobenzooxazole/4,4'-bis(diethylamino)benzophenone and the like. 2-mercaptobenzothiazole/4,4'-bis(diethylamino)benzophenone and 2-

mercaptobenzoxazole/4,4'-bis(diethylamino)benzophenone are preferred, and 2-mercaptobenzothiazole/4,4'-bis(diethylamino)benzophenone is particularly preferred.

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

10 The amount of the hydrogen donor used when a biimidazole compound is used in the present invention 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 total of the polyfunctional monomer (C) and the monofunctional monomer. When the amount of the hydrogen donor is smaller than 0.01 part by weight, the effect
15 of improving sensitivity tends to lower and when the amount is larger than 40 parts by weight, the formed colored layer is apt to fall off from the substrate at the time of development.

The triazine compounds as a photopolymerization
20 initiator include, for example, 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,
25 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)-
30 s-triazine, 2-(4-n-butoxyphenyl)-4,6-bis(trichloromethyl)-s-triazine, and triazine-based compounds having a halomethyl group such as a compound represented by the following formula (4) (to be referred to as "triazine compound (1)" hereinafter).



5

Out of these triazine compounds, 2-[2-(3,4-dimethoxyphenyl)ethenyl]-4,6-bis(trichloromethyl)-s-triazine and the triazine compound (1) are preferred.

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

The amount of the triazine compound as a photopolymerization initiator 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
15 parts by weight of the total of the polyfunctional monomer (C) and the monofunctional monomer. When the amount of the triazine compound is smaller than 0.01 part by weight, it may be difficult to obtain an array of pixels arranged in a predetermined pattern due to incomplete curing by exposure
20 and when the amount is larger than 40 parts by weight, the formed colored layer tends to fall off from the substrate at the time of development.

Additives

The radiation sensitive composition for a color liquid
25 crystal display device of the present invention may contain various additives as required.

The additives include an organic acid or organic amino compound (excluding the above hydrogen donor) which show the function of further improving the solubility in an alkali
30 developer of the radiation sensitive composition and the function of further suppressing the formation of an undissolved product after development.
-organic acid-

The organic acid is preferably an aliphatic carboxylic

acid or phenyl group-containing carboxylic acid having one or more carboxyl groups in the molecule and a molecular weight of 1,000 or less.

Examples of the aliphatic carboxylic acid include
5 aliphatic 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; aliphatic dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid,
10 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
15 and mesaconic acid; and aliphatic tricarboxylic acids such as tricarballylic acid, aconitic acid and camphoronic acid.

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

Illustrative examples of the phenyl group-containing carboxylic acid include aromatic monocarboxylic acids such as benzoic acid, toluic acid, cuminic acid, hemellitic acid and mesitylic acid; aromatic dicarboxylic acids such as
25 phthalic acid, isophthalic acid and terephthalic acid; aromatic polycarboxylic acids having a functionality of three or more such as trimellitic acid, trimesic acid, mellophanic acid and pyromellitic acid; phenylacetic acid, hydroatropic acid, hydrocinnamic acid, mandelic acid,
30 phenylsuccinic acid, atropic acid, cinnamic acid, cinnamylidenic acid, coumaric acid, umbellic acid and the like.

From the viewpoints of alkali solubility, solubility in a solvent which will be described hereinafter, and the

prevention of stains and film remnants on the substrate or light screening layer of an unexposed portion, out of these organic acids, aliphatic dicarboxylic acids are preferred as aliphatic carboxylic acids, out of which malonic acid, adipic acid, itaconic acid, citraconic acid, fumaric acid and mesaconic acid are particularly preferred, while aromatic dicarboxylic acids are preferred as phenyl group-containing carboxylic acids, out of which phthalic acid is particularly preferred.

10 The 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 whole radiation sensitive composition. When the amount of the organic acid is larger than 15 wt%, the adhesion of the formed colored layer to the substrate tends to lower.

-organic amino compound-

 The organic amino compound is preferably an aliphatic amine or phenyl group-containing amine having one or more amino groups in the molecule and a molecular weight of 1,000 or less.

 Illustrative examples of the aliphatic amine include mono(cyclo)alkylamines such as n-propylamine, i-propylamine, n-butylamine, i-butylamine, sec-butylamine, t-butylamine, n-pentylamine, n-hexylamine and cyclohexylamine; di(cyclo)alkylamines such as methylethylamine, diethylamine, methyl n-propylamine, ethyl n-propylamine, di-n-propylamine, di-i-propylamine, di-n-butylamine, di-i-butylamine, di-sec-butylamine and di-t-butylamine; tri(cyclo)alkylamines such as dimethylethylamine, methyldiethylamine, 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 and

tri-t-butylamine; mono(cyclo)alkanolamines such as 2-aminoethanol, 3-amino-1-propanol, 1-amino-2-propanol and 4-amino-1-butanol; di(cyclo)alkanolamines such as diethanolamine, di-n-propanolamine, di-i-propanolamine, 5 di-n-butanolamine and di-i-butanolamine; tri(cyclo)alkanolamines such as triethanolamine, tri-n-propanolamine, tri-i-propanolamine, tri-n-butanolamine and tri-i-butanolamine; amino(cyclo)alkanediols such as 3-amino-1,2-propanediol, 2-amino-1,3-propanediol, 4-amino-10 1,2-butanediol, 4-amino-1,3-butanediol, 3-dimethylamino-1,2-propanediol, 3-diethylamino-1,2-propanediol, 2-dimethylamino-1,3-propanediol and 2-diethylamino-1,3-propanediol; aminocarboxylic acids such as β -alanine, 2-aminobutyric acid, 3-aminobutyric acid, 4-aminobutyric acid, 15 2-aminoisobutyric acid and 3-aminoisobutyric acid; and the like.

The phenyl group-containing amine is, for example, a compound having an amino group directly bonded to a phenyl group, compound having an amino group bonded to a phenyl group 20 through a carbon chain, or the like.

Illustrative examples of the phenyl group-containing amine include aromatic amines such as aniline, o-methylaniline, m-methylaniline, p-methylaniline, p-ethylaniline, 1-naphthylamine, 2-naphthylamine, N,N-25 dimethylaniline, N,N-diethylaniline and p-methyl-N,N-dimethylaniline; aminobenzyl alcohols such as o-aminobenzyl alcohol, m-aminobenzyl alcohol, p-aminobenzyl alcohol, p-dimethylaminobenzyl alcohol and p-diethylaminobenzyl alcohol; aminophenols such as o-aminophenol, m-aminophenol, 30 p-aminophenol, p-dimethylaminophenol and p-diethylaminophenol; aminobenzoic acids (derivatives) such as m-aminobenzoic acid, p-aminobenzoic acid, p-dimethylaminobenzoic acid and p-diethylaminobenzoic acid; and the like.

From the viewpoints of solubility in a solvent which will be described hereinafter and the prevention of stains and film remnants on the substrate or light screening layer of an unexposed portion, out of these organic amino compounds, 5 mono(cyclo)alkanolamines and amino(cyclo)alkanediols are preferred as aliphatic amines, out of which 2-aminoethanol, 3-amino-1-propanol, 5-amino-1-pentanol, 3-amino-1,2-propanediol, 2-amino-1,3-propanediol and 4-amino-1,2-butanediol are particularly preferred. Aminophenols are 10 preferred as phenol group-containing amines, out of which o-aminophenol, m-aminophenol and p-aminophenol are particularly preferred.

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

15 The amount of the organic amino compound is preferably 15 wt% or less, more preferably 10 wt% or less based on the whole radiation sensitive composition. When the amount of the organic amino compound is larger than 15 wt%, the adhesion of the formed colored layer to the substrate tends to lower.

20 Additives other than the above include, for example, dispersion aids such as blue pigment derivatives and yellow pigment derivatives exemplified by copper phthalocyanine derivatives; fillers such as glass and alumina; polymer compounds such as polyvinyl alcohols, polyethylene glycol 25 monoalkyl ethers and poly(fluoroalkylacrylates); nonionic, cationic and anionic surfactants; adhesion accelerators such as vinyl trimethoxysilane, vinyl triethoxysilane, vinyl tris(2-methoxyethoxy)silane, N-(2-aminoethyl)-3-aminopropyl·methyl·dimethoxysilane, N-(2-aminoethyl)-3-aminopropyl trimethoxysilane, 3-aminopropyl 30 triethoxysilane, 3-glycidoxypropyl trimethoxysilane, 3-glycidoxypropyl·methyl·dimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyl trimethoxysilane, 3-chloropropyl·methyl·dimethoxysilane, 3-chloropropyl

trimethoxysilane, 3-methacryloxypropyl trimethoxysilane and 3-mercaptopropyl trimethoxysilane; antioxidants such as 2,2-thiobis(4-methyl-6-t-butylphenol) and 2,6-di-t-butylphenol; ultraviolet light absorbers such as 2-(3-t-butyl-5-methyl-2-hydroxyphenyl)-5-chlorobenzotriazole and alkoxybenzophenone; anticoagulants such as sodium polyacrylate; heat radical generating agents such as 1,1'-azobis(cyclohexane-1-carbonitrile) and 2-phenylazo-4-methoxy-2,4-dimethylvaleronitrile; and the like.

10 solvent

The radiation sensitive composition of the present invention comprises the above colorant (A), alkali soluble resin (B), polyfunctional monomer (C) and photopolymerization initiator as essential ingredients and is preferably prepared as a liquid composition by mixing a solvent.

Any solvent is acceptable if it disperses or dissolves the components (A) to (D) forming a radiation sensitive composition and additive components, does not react with these components and has appropriate volatility.

Illustrative 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
5 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
methylethyl ether, diethylene glycol diethyl ether and
10 tetrahydrofuran; ketones such as methyl ethyl ketone,
cyclohexanone, 2-heptanone and 3-heptanone; lactic acid
alkyl esters such as methyl 2-hydroxypropionate and ethyl
2-hydroxypropionate; other esters such as ethyl 2-
hydroxy-2-methylpropionate, methyl 3-methoxypropionate,
15 ethyl 3-methoxypropionate, methyl 3-ethoxypropionate, ethyl
3-ethoxypropionate, ethyl ethoxyacetate, ethyl
hydroxyacetate, methyl 2-hydroxy-3-methylbutanoate, 3-
methyl-3-methoxybutylacetate, 3-methyl-3-
methoxybutylpropionate, ethyl acetate, n-propyl acetate,
20 i-propyl acetate, n-butyl acetate, i-butyl acetate, n-pentyl
formate, i-pentyl acetate, n-butyl propionate, ethyl
butyrate, n-propyl butyrate, i-propyl butyrate, n-butyl
butyrate, methyl pyruvate, ethyl pyruvate, n-propyl pyruvate,
methyl acetoacetate, ethyl acetoacetate and ethyl 2-
25 oxybutanoate; aromatic hydrocarbons such as toluene and
xylene; amides such as N-methylpyrrolidone, N,N-
dimethylformamide and N,N-dimethylacetamide; and the like.

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

ethoxypropionate, 3-methyl-3-methoxybutylpropionate, n-butyl acetate, i-butyl acetate, n-pentyl formate, i-pentyl acetate, n-butyl propionate, ethyl butyrate, i-propyl butyrate, n-butyl butyrate and ethyl pyruvate are preferred
5 from the viewpoints of solubility, pigment dispersibility and coatability.

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

Further, a high-boiling solvent such as benzyl ethyl
10 ether, dihexyl 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
15 be used in combination with the solvent.

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

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

method of forming colored layer

25 The radiation sensitive composition of the present invention is used to form a colored layer on a drive substrate having a thin film transistor (TFT) for a thin film transistor (TFT) color liquid crystal display device formed thereon by lithography (to be referred to as "TFT liquid crystal drive
30 substrate" hereinafter). The term "colored layer" as used herein means what includes only display pixels, only a black matrix or both of them.

The method of forming the colored layer on the TFT liquid crystal drive substrate will be described

hereinafter.

A light screening layer for defining a portion where pixels are to be formed is first formed on the surface of a TFT liquid crystal drive substrate or a substrate having a passivation film such as a silicon nitride film formed on the surface of the drive substrate as required, and a liquid radiation sensitive composition containing, for example, a red pigment dispersed therein is coated on the substrate and prebaked to evaporate the solvent to form a coating film. Thereafter, the coating film is exposed to light through a photomask and developed with an alkali developer to dissolve and remove an unexposed portion of the coating film and then post-baked to form an array of red pixels arranged in a predetermined pattern. The photomask used has a pattern for forming pixels and also a pattern for forming a through hole or U-shaped dent.

Subsequently, a liquid radiation sensitive composition containing a green pigment dispersed therein and a liquid radiation sensitive composition containing a blue pigment dispersed therein are coated, prebaked, exposed, developed and post-baked in the same manner as described above to form an array of green pixels and an array of blue pixels on the same substrate sequentially, thereby making it possible to obtain a color liquid crystal display device having arrays of three primary colors, red, green and blue, disposed on the TFT liquid crystal drive substrate and a through hole or U-shaped dent formed in the drive substrate.

A black matrix may be formed in the same manner as the above pixel arrays.

The TFT liquid crystal drive substrate used to form the colored layer is made from glass, silicon, polycarbonate, polyester, aromatic polyamide, polyamideimide, polyimide or the like. The substrate may be subjected to a pretreatment such as chemical treatment with a silane coupling agent or

the like, plasma treatment, ion plating, sputtering, vapor-phase reaction, vacuum deposition or the like as desired.

To coat the liquid radiation sensitive composition on the substrate, appropriate coating such as rotational coating, cast coating or roll coating may be employed.

The thickness of coating is preferably 0.1 to 10 μm , more preferably 0.2 to 5.0 μm , particularly preferably 0.2 to 3.0 μm in terms of film thickness after drying.

The radiation used to form the colored layer is selected from visible rays, ultraviolet rays, far ultraviolet rays, electron beams, X-rays and the like but preferably has a wavelength of 190 to 450 nm.

The amount of exposure to radiation is preferably 10 to 10,000 J/m^2 .

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

An appropriate amount of a water-soluble organic solvent such as methanol or ethanol or surfactant may be added to the alkali developer. The radiation sensitive composition is generally washed in water after development with the alkali developer.

Development may be shower development, spray development, dip development, puddle development or the like. As for development conditions, development is preferably carried out at normal temperature for 5 to 300 sec.

The size of the through hole of the thus formed color liquid crystal display device is suitably selected from a range of preferably 10 μm or less, more preferably 5 μm or less, much more preferably 1 to 5 μm according to the size of a pattern corresponding to the photomask.

The vertical section of an opening present in the thus formed colored layer is such trapezoidal that the length of its bottom side is smaller than the length of its top side and that the angle formed by a straight line connecting an upper pattern edge and a lower pattern edge and the top side of the opening (to be referred to as "taper angle" hereinafter) is preferably 30 to 60°. This taper angle is more preferably 40 to 60°, much more preferably 40 to 50°.

When the taper angle is smaller than 30°, the through hole for connecting the ITO electrode to the terminal of the drive substrate underlying the colored layer may be blocked and when the taper angle is larger than 60°, a portion where the angle formed by the straight line connecting the upper pattern edge and the lower pattern edge of the section of the colored layer and the bottom side becomes larger than 90° may be formed and the ITO electrode may break in this portion.

The radiation sensitive composition of the present invention has a degree of swelling for a positive resist stripping liquid used to form an electrode, for example, an ITO electrode on the surface of the colored layer which is a cured film formed by exposing its dried coating film to form on the TFT liquid crystal drive substrate of preferably 5 % or less, more preferably 4 % or less, much more preferably 3.5 % or less.

With this degree of swelling, when the radiation sensitive composition is immersed in a stripping liquid for stripping a positive resist in the step of shaping a conductive layer pattern to form an electrode (for example, ITO electrode) on the colored layer, the swelling of the colored layer overlying the electrode pattern with the stripping liquid is suppressed, thereby eliminating the possibility that the electrode is cracked and making it possible to obtain a color liquid crystal display device

having extremely high reliability.

The term "degree of swelling" as used herein is defined by the following expression when a cured film formed from the radiation sensitive composition is immersed in a stripping liquid for a positive resist used to form an electrode on the surface of the colored layer on the TFT liquid crystal drive substrate at 60°C until the swelling of the cured film with the stripping liquid becomes saturated:

$$Sw = (Vb - Va) \times 100 / Va$$

wherein Sw is a degree of swelling (%), Va is the volume of the cured film before swelling and Vb is the volume of the cured film after swelling.

The exposure conditions for measuring the degree of swelling Sw are conditions employed when the radiation sensitive composition of the present invention is used to form the colored layer on the TFT liquid crystal drive substrate by lithography.

The stripping liquid used to measure the degree of swelling Sw is selected from:

- (1) a mixture of dimethyl sulfoxide and N-methylpyrrolidone,
- (2) a mixture of an organic solvent and dimethyl sulfoxide,
- (3) a mixture of an organic solvent and an amino compound, and
- (4) a mixture of an organic solvent, phenol and alkylbenzenesulfonic acid.

Examples of the organic solvent used as a component of the stripping liquid include aromatic hydrocarbons such as benzene, toluene, xylene, monochlorobenzene and dichlorobenzene; alkyl ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol mono-n-propyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol di-n-propyl ether, ethylene glycol di-n-butyl ether, diethylene glycol monomethyl ether,

diethylene glycol monoethyl ether. diethylene glycol mono-n-propyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol di-n-propyl ether, diethylene glycol di-n-butyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, triethylene glycol mono-n-propyl ether, triethylene glycol mono-n-butyl ether, triethylene glycol dimethyl ether, triethylene glycol diethyl ether, triethylene glycol di-n-propyl ether and triethylene glycol di-n-butyl ether; hydrocarbon halides such as perchloroethylene; and the like.

Examples of the amino compound used as a component of the stripping liquid include monoethanolamine, diethanolamine, triethanolamine, triethylamine, tri-n-butylamine, 1,8-diazabicyclo-7-undecene and the like.

Examples of the alkylbenzenesulfonic acid used as a component of the stripping liquid include p-n-octylbenzenesulfonic acid, p-n-nonylbenzenesulfonic acid, p-n-decylbenzenesulfonic acid, p-n-undecylbenzenesulfonic acid, p-n-dodecylbenzenesulfonic acid, p-n-tridecylbenzenesulfonic acid, p-n-tetradecylbenzenesulfonic acid and the like.

Illustrative examples of the stripping liquid include a mixture of dimethyl sulfoxide and N-methylpyrrolidone (weight ratio = 60/40), a mixture of diethylene glycol mono-n-butyl ether and dimethyl sulfoxide (weight ratio = 40/60), a mixture of diethylene glycol mono-n-butyl ether and monoethanolamine (weight ratio = 65/35), a mixture of o-dichlorobenzene, phenol and alkylbenzenesulfonic acid (weight ratio = 55/25/20 or 60/20/20), a mixture of perchloroethylene, o-dichlorobenzene, phenol and alkylbenzenesulfonic acid (weight ratio = 10/50/20/20) and the like.

The time elapsed before the swelling of the cured film

with the stripping liquid becomes saturated when the degree of swelling Sw is to be measured, which differs according to the composition of the radiation sensitive composition, the type of stripping liquid and the like, is preferably 5 to 60 minutes at 60°C.

The dielectric constant of the colored layer formed from the radiation sensitive composition of the present invention is preferably 10 or less, more preferably 7 or less, particularly preferably 5 or less. A thin film transistor (TFT) color liquid crystal display device having a colored layer with the above dielectric constant has high reliability without a display failure caused by deterioration in the operation function of a portion to which voltage has been applied.

The volume resistivity of the colored layer formed from the radiation sensitive composition of the present invention is preferably 10^{12} Ωcm or more, preferably 10^{13} Ωcm or more, much more preferably 10^{14} Ωcm or more. A thin film transistor (TFT) color liquid crystal display device having the above colored layer has high reliability without a display failure caused by the malfunctioning of pixels to which voltage has not been applied.

The dielectric constant and volume resistivity of the colored layer can be measured as follows, for example.

The radiation sensitive composition is coated on a substrate covered with a metal thin film of chromium or aluminum in accordance with the above method and prebaked to form a coating film. The entire coating film is exposed to light and post-baked to form a colored layer on the substrate.

Thereafter, an aluminum or other metal thin film of an appropriate size is formed on the obtained colored layer by vapor deposition to form an upper electrode. The colored layer of a portion devoid of the above upper electrode is

chipped off to expose the underlying metal thin film and make it as a lower electrode. The capacitance or resistance between the both electrodes is measured to calculate the dielectric constant and volume resistivity of the colored layer.

The red, green and blue pixels formed from the radiation sensitive composition of the present invention have excellent surface smoothness with a surface roughness of 50 Å or less.

The term "surface roughness" as used herein means Ra defined by the following expression (5):

$$Ra = \frac{1}{L} \int_0^L |y| dx \quad (5)$$

wherein Ra is the average roughness (Å) along a center line of each pixel, L is a measurement length (μm), y is the distance (Å) from the center line of the pixel to a roughness curve, and x is position coordinates in a measurement length direction.

An appropriate value may be used as the measurement length L in the above expression but preferably about 1 to 15 mm.

In the present invention, the surface roughness Ra of each pixel is preferably 40 Å or less, particularly preferably 35 Å or less. The lower limit of surface roughness Ra of each pixel in the present invention changes by such factors as the concentration of the colorant (A) in the radiation sensitive composition, the particle diameter of the pigment contained in the colorant, the amount of the photopolymerization initiator, and the ratio of the alkali soluble resin (B) to the polyfunctional monomer (C). Although it cannot be limited to a specific value unconditionally, it is preferably about 10 Å.

According to the present invention, there can be

obtained a color liquid crystal display element which can suppress bad influences such as (1) the bleeding of impurities from the colored layer into liquid crystals due to an increase in the contact area between pixels and liquid crystals and
5 (2) the poor orientation of liquid crystals caused by the roughened surfaces of pixels and which is free from a display failure such as burning or nonuniform display by controlling the surface roughness Ra of the pixels formed from the radiation sensitive composition for color filters to 50 Å
10 or less.

The thus formed color liquid crystal display device having pixels and/or a black matrix can be of a transmission type or reflection type and the radiation sensitive composition for a color liquid crystal display device of the
15 present invention is also useful for thin film transistor (TFT) color image pick-up tube elements, color sensors and the like.

The following examples are provided for the purpose of further illustrating the present invention but are in no way
20 to be taken as limiting.

Example

Example 1

100 parts by weight of a 65/35 (weight ratio) mixture of C.I. Pigment Red 177 and C.I. Pigment Red 224 as a colorant
25 (A), 70 parts by weight of a methacrylic acid/N-phenylmaleimide/benzyl methacrylate/glycerol monomethacrylate/styrene copolymer (weight ratio = 15/25/35/10/15, Mw = 30,000, Mn = 10,000) as an alkali soluble resin (B), 80 parts by weight of dipentaerythritol
30 hexaacrylate as a polyfunctional monomer (C), 50 parts by weight of 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butanone-1 as a photopolymerization initiator (D) and 1,000 parts by weight of propylene glycol monomethyl ether acetate as a solvent were mixed together

to prepare a liquid radiation sensitive composition (R1).
<formation and evaluation of pixel array>

The liquid composition (R1) was coated on the surface of a substrate produced by forming a silicon nitride film on the surface of a TFT liquid crystal drive substrate with
5 a spin coater and prebaked in a clean oven at 90°C for 10 minutes to form a 1.7 μm thick coating film.

Thereafter, this substrate was cooled to room temperature and the coating film was exposed to ultraviolet
10 rays having wavelengths of 365 nm, 405 nm and 436 nm with an exposure amount of 2,000 J/m² through a photomask using a high-pressure mercury lamp. This substrate was then developed by immersing in a 0.1 wt% aqueous solution of tetramethylammonium hydroxide at 23°C for 1 minute, washed
15 in ultra-pure water and dried with air. Thereafter, it was post-baked in a clean oven at 220°C for 25 minutes to form an array of stripe-like red pixels on the substrate.

When the obtained pixel array was observed through an optical microscope, the development residue was not observed
20 on the substrate of an unexposed portion. A 10 μm square through hole was formed and the adhesion of the obtained pixels to the substrate was excellent. When the vertical section of the opening existent in the colored layer was observed by SEM, the taper angle was 55°.

25 The surface roughness Ra of the pixel measured at a measurement length of 10 mm using a tracer type surface roughness meter (Alfastep 500 of KLA Tencall Co., Ltd.) was 25 Å. When the pixel surface was observed through an optical microscope, the roughened surface was not observed and the
30 pixel had excellent surface smoothness.

When the degree of swelling Sw of the pixel array was measured by immersing it in a mixture of dimethyl sulfoxide and N-methylpyrrolidone (weight ratio = 60/40) (of Tokyo Ohka Kogyo Co., Ltd.) at 60°C for 10 minutes, it was 3.4 %.

When a pixel array formed in the same manner as described above was used and laminated with a substrate having an ITO electrode formed thereon by sputtering to produce a panel and electricity was applied to the panel, the panel
5 showed excellent display characteristics without a display failure.

Example 2

100 parts by weight of a 65/35 (weight ratio) mixture of C.I. Pigment Red 177 and C.I. Pigment Red 224 as a colorant
10 (A), 70 parts by weight of a methacrylic acid/N-phenylmaleimide/benzyl methacrylate/glycerol monomethacrylate/styrene copolymer (weight ratio = 15/25/35/10/15, Mw = 30,000, Mn = 10,000) as an alkali soluble resin (B), 80 parts by weight of dipentaerythritol
15 hexaacrylate as a polyfunctional monomer (C), 20 parts by weight of 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1 as a photopolymerization initiator (D), 15 parts by weight of 4,4'-bis(diethylamino)benzophenone as a sensitizer and 1,000
20 parts by weight of propylene glycol monomethyl ether acetate as a solvent were mixed together to prepare a liquid radiation sensitive composition (R2).

<formation and evaluation of pixel array>

An array of stripe-like red pixels was formed on the
25 substrate and evaluated in the same manner as in Example 1 except that the liquid composition (R2) was used in place of the liquid composition (R1).

When the obtained pixel array was observed through an optical microscope, the development residue was not observed
30 on the substrate of an unexposed portion. A 10 μm square through hole and a 5 μm square through hole were formed and the adhesion of the obtained pixels to the substrate was excellent. When the vertical section of the opening existent in the colored layer was observed by SEM, the taper angle

was 40°.

The surface roughness Ra of the pixel measured in the same manner as in Example 1 was 30 Å, the roughened surface was not observed, and the pixel had excellent surface smoothness.

When the degree of swelling Sw of the pixel array was measured by immersing it in a mixture of dimethyl sulfoxide and N-methylpyrrolidone (weight ratio = 60/40) (of Tokyo Ohka Kogyo Co., Ltd.) at 60°C for 10 minutes, it was 2.9 %.

When a pixel array formed in the same manner as described above was used and laminated with a substrate having an ITO electrode formed thereon by sputtering to produce a panel and electricity was applied to the panel, the panel showed excellent display characteristics without a display failure.

Example 3

55 parts by weight of a 95/5 (weight ratio) mixture of C.I. Pigment Blue 15:6 and C.I. Pigment Violet 23 as a colorant (A), 75 parts by weight of a methacrylic acid/2-hydroxyethyl methacrylate/benzyl methacrylate copolymer (weight ratio = 15/15/70, Mw = 25,000, Mn = 10,000) as an alkali soluble resin (B), 75 parts by weight of dipentaerythritol hexaacrylate as a polyfunctional monomer (C), 6 parts by weight of 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole as a photopolymerization initiator (D), 6 parts by weight of 4,4'-bis(diethylamino)benzophenone as an amine hydrogen donor, 3 parts by weight of 2-mercaptobenzothiazole as a mercaptan hydrogen donor, and 700 parts by weight of propylene glycol monomethyl ether acetate and 300 parts by weight of cyclohexanone as solvents were mixed together to prepare a liquid radiation sensitive composition (B1).

<formation and evaluation of pixel array>

An array of stripe-like blue pixels was formed on the substrate and evaluated in the same manner as in Example 1

except that the liquid composition (B1) was used in place of the liquid composition (R1).

When the obtained pixel array was observed through an optical microscope, the development residue was not observed on the substrate of an unexposed portion. A 10 μm square through hole was formed and the adhesion of the obtained pixels to the substrate was excellent. When the vertical section of the opening existent in the colored layer was observed by SEM, the taper angle was 50°.

The surface roughness Ra of the pixel measured in the same manner as in Example 1 was 30 Å, the roughened surface of the pixel was not observed, and the pixel had excellent surface smoothness.

When the degree of swelling Sw of the pixel array was measured by immersing it in a mixture of dimethyl sulfoxide and N-methylpyrrolidone (weight ratio = 60/40) (of Tokyo Ohka Kogyo Co., Ltd.) at 60°C for 10 minutes, it was 2.7 %.

When a pixel array formed in the same manner as described above was used and laminated with a substrate having an ITO electrode formed thereon by sputtering to produce a panel and electricity was applied to the panel, the panel showed excellent display characteristics without a display failure.

Example 4

100 parts by weight of a 65/35 (weight ratio) mixture of C.I. Pigment Green 36 and C.I. Pigment Yellow 150 as a colorant (A), 75 parts by weight of a methacrylic acid/2-hydroxyethyl methacrylate/benzyl methacrylate copolymer (weight ratio = 15/15/70, Mw = 25,000, Mn = 10,000) as an alkali soluble resin (B), 75 parts by weight of dipentaerythritol hexaacrylate as a polyfunctional monomer (C), 10 parts by weight of the triazine-based compound (1) as a photopolymerization initiator (D), and 700 parts by weight of propylene glycol monomethyl ether acetate and 300

parts by weight of cyclohexanone as solvents were mixed together to prepare a liquid radiation sensitive composition (G1).

<formation and evaluation of pixel array>

5 An array of stripe-like green pixels was formed on the substrate and evaluated in the same manner as in Example 1 except that the liquid composition (G1) was used in place of the liquid composition (R1).

10 When the obtained pixel array was observed through an optical microscope, the development residue was not observed on the substrate of an unexposed portion. A 10 μm square through hole was formed and the adhesion of the obtained pixels to the substrate was excellent. When the vertical section of the opening existent in the colored layer was
15 observed by SEM, the taper angle was 50°.

 The surface roughness Ra of the pixel measured in the same manner as in Example 1 was 30 Å, the roughened surface of the pixel was not observed, and the pixel had excellent surface smoothness.

20 When the degree of swelling Sw of the pixel array was measured by immersing it in a mixture of dimethyl sulfoxide and N-methylpyrrolidone (weight ratio = 60/40) (of Tokyo Ohka Kogyo Co., Ltd.) at 60°C for 10 minutes, it was 3.1 %.

 When a pixel array formed in the same manner as described
25 above was used and laminated with a substrate having an ITO electrode formed thereon by sputtering to produce a panel and electricity was applied to the panel, the panel showed excellent display characteristics without a display failure.
 Example 5

30 A liquid radiation sensitive composition (R3) was prepared in the same manner as in Example 1 except that 10 parts by weight of the polyfunctional acrylate (1) was further used.

<formation and evaluation of pixel array>

An array of stripe-like red pixels was formed on the substrate and evaluated in the same manner as in Example 1 except that the liquid composition (R3) was used in place of the liquid composition (R1).

5 When the obtained pixel array was observed through an optical microscope, the development residue was not observed on the substrate of an unexposed portion. A 5 μ m square through hole was formed, and the adhesion of the obtained pixels to the substrate was excellent.

10 Example 6

A liquid radiation sensitive composition (B2) was prepared in the same manner as in Example 3 except that 10 parts by weight of a polyfunctional methacrylate (2) was further used.

15 <formation and evaluation of pixel array>

An array of stripe-like blue pixels was formed on the substrate and evaluated in the same manner as in Example 3 except that the liquid composition (B2) was used in place of the liquid composition (B1).

20 When the obtained pixel array was observed through an optical microscope, the development residue was not observed on the substrate of an unexposed portion. A 5 μ m square through hole was formed, and the adhesion of the obtained pixels to the substrate was excellent.

25 Example 7

A liquid radiation sensitive composition (G2) was prepared in the same manner as in Example 4 except that 10 parts by weight of the polyfunctional acrylate (1) was further used.

30 <formation and evaluation of pixel array>

An array of stripe-like blue pixels was formed on the substrate and evaluated in the same manner as in Example 3 except that the liquid composition (G2) was used in place of the liquid composition (G1).

When the obtained pixel array was observed through an optical microscope, the development residue was not observed on the substrate of an unexposed portion. A 5 μm square through hole was formed, and the adhesion of the obtained
5 pixels to the substrate was excellent.

Example 8

50 parts by weight of a 65/35 (weight ratio) mixture of C.I. Pigment Red 177 and C.I. Pigment Red 224 as a colorant (A), 140 parts by weight of a methacrylic acid/N-
10 phenylmaleimide/benzyl methacrylate/glycerol monomethacrylate/styrene copolymer (weight ratio = 15/25/35/10/15, $M_w = 30,000$, $M_n = 10,000$) as an alkali soluble resin (B), 160 parts by weight of dipentaerythritol hexaacrylate as a polyfunctional monomer (C), 50 parts by
15 weight of 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butan-1-one as a photopolymerization initiator (D) and 1,000 parts by weight of propylene glycol monomethyl ether acetate as a solvent were mixed together to prepare a liquid radiation sensitive composition (R4).

20 A colored layer was formed from the liquid composition (R4) to measure its dielectric constant and volume resistivity and a pixel array was formed separately to evaluate its display performance in the following manner.
<measurement of dielectric constant>

25 The liquid composition (R4) was coated on a chromium covered aluminum substrate (diameter of 100.2 mm, thickness of chromium film of 0.525 μm , manufactured by Asahi Glass Co., Ltd.) with a spin coater and prebaked in a clean oven at 90°C for 10 minutes to form a 1.5 μm thick coating film.

30 Thereafter, this substrate was cooled to room temperature and the entire surface of the coating film was exposed to ultraviolet rays having wavelengths of 365 nm, 405 nm and 436 nm with an exposure amount of 2,000 J/m^2 using a high-pressure mercury lamp. This substrate was then

post-baked in a clean oven at 220°C for 25 minutes to form a colored layer on the substrate.

5 Thereafter, a circular aluminum electrode having a diameter of 1 mm was formed on the obtained colored layer using a vacuum deposition apparatus (PEC-A2 of Shimadzu Corporation). A 5 mm square portion on which the aluminum electrode was not formed of the coating film was scraped off to expose the surface of chromium.

10 Subsequently, silver paste was used to attach a copper wire to the exposed surface of chromium and the capacitance of the colored layer was measured when an AC voltage of 1 V at 1 kHz was applied by setting it in a capacitance meter (trader name: LCR Meter 4284A of Hewlett Packard Co., Ltd.) to calculate the dielectric constant of the colored layer
15 from the value. As a result, the dielectric constant of the colored layer was 4.3.

<measurement of volume resistivity>

 The above formed colored layer having electrodes was set in a microcurrent meter (trader name: pA Meter 4140B of
20 Hewlett Packard Co., Ltd.) to measure a current value when a DC voltage of 0.1 V was applied and calculate the volume resistivity of the colored layer from the measurement value. As a result, the volume resistivity of the colored layer was $2.8 \times 10^{14} \Omega\text{cm}$.

25 <formation of pixel array and evaluation of display performance>

 The liquid composition (R4) was coated on the surface of a substrate produced by forming a silicon nitride film on the surface of a TFT liquid crystal drive substrate with
30 a spin coater and prebaked in a clean oven at 90°C for 10 minutes to form a 3.0 μm thick coating film.

 Thereafter, this substrate was cooled to room temperature and the coating film was exposed to ultraviolet rays having wavelengths of 365 nm, 405 nm and 436 nm with

an exposure amount of 2,000 J/m² through a photomask using a high-pressure mercury lamp. This substrate was then developed by immersing in a 0.1 wt% aqueous solution of tetramethylammonium hydroxide 23°C for 1 minute, washed in
5 ultra-pure water and dried with air. Subsequently, the substrate was post-baked in a clean oven at 220°C for 25 minutes to form an array of stripe-like red pixels on the substrate.

When a color liquid crystal display device was
10 manufactured by laminating the obtained substrate with a substrate having an ITO electrode formed thereon by sputtering and operated, a display failure did not occur.
Example 9

50 parts by weight of a 65/35 (weight ratio) mixture
15 of C.I. Pigment Red 177 and C.I. Pigment Red 224 as a colorant (A), 140 parts by weight of a methacrylic acid/N-phenylmaleimide/benzyl methacrylate/glycerol monomethacrylate/styrene copolymer (weight ratio = 15/25/35/10/15, Mw = 30,000, Mn = 10,000) as an alkali soluble
20 resin (B), 160 parts by weight of dipentaerythritol hexaacrylate as a polyfunctional monomer (C), 20 parts by weight of 1-[4-(methylthio)phenyl]-2-methyl-2-morpholinopropan-1-one as a photopolymerization initiator (D), 15 parts by weight of 4,4'-
25 bis(diethylamino)benzophenone as a sensitizer and 1,000 parts by weight of propylene glycol monomethyl ether acetate as a solvent were mixed together to prepare a liquid radiation sensitive composition (R5).

<measurement of dielectric constant, formation of pixel
30 array and evaluation of display performance>

A colored layer was formed in the same manner as in Example 8 except that the liquid composition (R5) was used in place of the liquid composition (R4) to measure its dielectric constant and volume resistivity and an array of

stripe-like red pixels was formed on the substrate to evaluate its display performance.

As a result, the colored layer had a dielectric constant of 4.5 and a volume resistivity of $2.5 \times 10^{14} \Omega\text{cm}$ and a display failure did not occur during the operation of the obtained color liquid crystal display device.

Example 10

35 parts by weight of a 95/5 (weight ratio) mixture of C.I. Pigment Blue 15:6 and C.I. Pigment Violet 23 as a colorant (A), 150 parts by weight of a methacrylic acid/2-hydroxyethyl methacrylate/benzyl methacrylate copolymer (weight ratio = 15/15/70, $M_w = 25,000$, $M_n = 10,000$) as an alkali soluble resin (B), 150 parts by weight of dipentaerythritol hexaacrylate as a polyfunctional monomer (C), 6 parts by weight of 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole as a photopolymerization initiator (D), 6 parts by weight of 4,4'-bis(diethylamino)benzophenone as an amine hydrogen donor, 3 parts by weight of 2-mercaptobenzothiazole as a mercaptan hydrogen donor, and 700 parts by weight of propylene glycol monomethyl ether acetate and 300 parts by weight of cyclohexanone as solvents were mixed together to prepare a liquid radiation sensitive composition (B3).
<measurement of dielectric constant, formation of pixel array and evaluation of display performance>

A colored layer was formed in the same manner as in Example 8 except that the liquid composition (B3) was used in place of the liquid composition (R4) to measure its dielectric constant and volume resistivity and an array of stripe-like blue pixels was formed on the substrate to evaluate its display performance.

As a result, the colored layer had a dielectric constant of 4.8 and a volume resistivity of $1.8 \times 10^{14} \Omega\text{cm}$ and a display failure did not occur during the operation of the obtained color liquid crystal display device.

Example 11

50 parts by weight of a 65/35 (weight ratio) mixture of C.I. Pigment Green 36 and C.I. Pigment Yellow 150 as a colorant (A), 150 parts by weight of a methacrylic acid/2-hydroxyethyl methacrylate/benzyl methacrylate copolymer (weight ratio = 15/15/70, $M_w = 25,000$, $M_n = 10,000$) as an alkali soluble resin (B), 150 parts by weight of dipentaerythritol hexaacrylate as a polyfunctional monomer (C), 10 parts by weight of the triazine-based compound (1) as a photopolymerization initiator (D), and 700 parts by weight of propylene glycol monomethyl ether acetate and 300 parts by weight of cyclohexanone as solvents were mixed together to prepare a liquid radiation sensitive composition (G3).

<measurement of dielectric constant, formation of pixel array and evaluation of display performance>

A colored layer was formed in the same manner as in Example 8 except that the liquid composition (G3) was used in place of the liquid composition (R4) to measure its dielectric constant and volume resistivity and an array of stripe-like green pixels was formed on the substrate to evaluate its display performance.

As a result, the colored layer had a dielectric constant of 4.7 and a volume resistivity of $4.1 \times 10^{14} \Omega\text{cm}$ and a display failure did not occur during the operation of the obtained color liquid crystal display device.

As described above, the radiation sensitive composition of the present invention enables the formation of a through hole or U-shaped dent, does not produce the development residue at the time of development and has excellent adhesion to a TFT liquid crystal drive substrate and a passivation film such as a silicon nitride film.

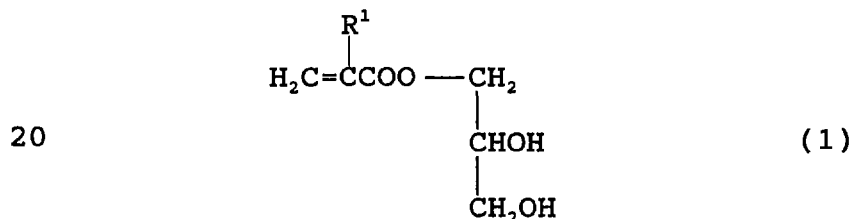
Therefore, the radiation sensitive composition of the present invention can provide a high-definition and

high-quality color liquid crystal display device with a high opening rate.

What is claimed is:

1. A radiation sensitive composition which comprises (A) a colorant, (B) an alkali soluble resin, (C) a polyfunctional monomer and (D) a photopolymerization initiator, and is used
5 to form a colored layer on a substrate for driving a thin film transistor (TFT) color liquid crystal display device.

2. The radiation sensitive composition of claim 1, wherein the alkali soluble resin (B) is a copolymer of (a) at least
10 one photopolymerizable unsaturated monomer having one or more carboxyl groups in the molecule and (b) at least one member selected from the group consisting of macromonomers having a mono(meth)acryloyl group at a terminal of a polymer molecular chain, N-position substituted maleimides, 2-
15 hydroxyethyl (meth)acrylate, benzyl (meth)acrylate and glycerol (meth)acrylate represented by the following formula (1):



wherein R^1 is a hydrogen atom or methyl group.

25 3. The radiation sensitive composition of claim 1, wherein the alkali soluble resin (B) is a carboxyl group-containing copolymer (I).

4. The radiation sensitive composition of claim 1, wherein
30 the alkali soluble resin (B) is a carboxyl group-containing copolymer (II).

5. The radiation sensitive composition of claim 1, wherein the polyfunctional monomer (C) is at least one member selected

from the group consisting of trimethylolpropane acrylate, pentaerythritol triacrylate and dipentaerythritol hexaacrylate.

- 5 6. The radiation sensitive composition of claim 1, wherein the photopolymerization initiator (D) is at least one member selected from the group consisting of an acetophenone compound, biimidazole compound and triazine compound.
- 10 7. The radiation sensitive composition of claim 1, wherein the photopolymerization initiator (D) is a biimidazole compound and further contains a hydrogen donor.
- 15 8. The radiation sensitive composition of claim 7, wherein the photopolymerization initiator (D) further contains at least one member selected from the group consisting of an acetophenone compound and triazine compound.
- 20 9. The radiation sensitive composition of claim 1 which is capable of forming a through hole as large as 10 μm or less in a colored layer at the time of forming the colored layer.
- 25 10. The radiation sensitive composition of claim 1, wherein the colored layer has a degree of swelling for a positive resist stripping liquid used to form an electrode on the surface of 5 % or less.
- 30 11. The radiation sensitive composition of claim 1, wherein the colored layer has a dielectric constant of 10 or less.
12. The radiation sensitive composition of claim 1, wherein the vertical section of an opening existent in the colored layer is such trapezoidal that the length of its bottom side

is smaller than the length of its top side and the angle formed by a straight line connecting an upper pattern edge and a lower pattern edge and the top side of the opening is 30 to 60°.

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13. The radiation sensitive composition of claim 1, wherein the colored layer has a volume resistivity of $10^{12} \Omega\text{cm}$ or more.

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14. A thin film transistor (TFT) color liquid crystal display device having a colored layer which is formed from the radiation sensitive composition of claim 1 on a drive substrate directly or on a passivation film formed on a drive substrate.

15. A method for forming a color layer for a thin film transistor color liquid crystal display device, which comprises forming a coating film from the radiation sensitive composition of claim 1 on a drive substrate directly or on a passivation film formed on a drive substrate, said drive substrate having a thin transistor for the thin film transistor color liquid crystal display; exposing the coating film to light through a photomask; developing with an alkali developer to dissolve and remove an unexposed portion of the coating film; and post-baking to form an array of red, green or blue pixels arranged in a predetermined pattern.