

RADIATION SENSITIVE COMPOSITION FOR COLOR
LIQUID DISPLAY DEVICES

Field of the Invention

5 The present invention relates to a radiation sensitive composition used to form a spacer and/or a black matrix on a drive substrate for thin film transistor (TFT) color liquid crystal display devices.

Description of the Prior Art

10 In the prior art, in order to produce a spacer and a black matrix for a color filter from a black radiation sensitive composition, a radiation sensitive composition comprising a black colorant dispersed therein is applied to a substrate and dried, and the obtained coating film is
15 exposed to radiation (to be referred to as "exposure" hereinafter) through a photomask and developed to form a desired pattern.

 Although a large amount of the black colorant must be contained in the black radiation sensitive composition to
20 improve the light screening properties of the spacer or black matrix, the radiation is absorbed by the colorant, thereby inevitably causing a phenomenon that the effective strength of the radiation in the coating film decreases gradually from the surface to the bottom of the coating film (namely, near
25 the surface of the substrate). Therefore, a curing reaction in the coating film tends to become more incomplete from the surface to the bottom, whereby a lower portion of the formed pattern is removed by a developer at the time of development and accordingly, the edge of the pattern is apt to be reversely
30 tapered in the end. However, when the edge is reversely tapered, rubbing cloth is caught by the edge portion at the time of rubbing for the orientation of crystals with the result that the pattern may peel off or the rubbing cloth may be worn away.

Further, in a system where a color filter is placed on a drive substrate for thin film transistor (TFT) color liquid crystal display devices, through holes are formed in the color filter to make an ITO (tin doped indium oxide) film and an electrode conductive with each other. When a spacer or a black matrix is formed after the formation of the color filter, the residue of the radiation sensitive composition for forming the spacer or black matrix is apt to remain in the through holes. If development conditions are made very strict to remove the residue, the erosion of the pattern will become large. Also in this case, the rubbing cloth may be caught by the pattern and the pattern may peel off. The spacer and black matrix for a color liquid crystal display device must be free from image sticking which causes a display failure.

However, these problems cannot be completely solved with the prior art radiation sensitive composition used to form a spacer or a black matrix for thin film transistor (TFT) color liquid crystal display devices.

Summary of the Invention

It is an object of the present invention to provide a radiation sensitive composition used to form a spacer and/or a black matrix on a drive substrate for thin film transistor (TFT) color liquid crystal display devices.

It is another object of the present invention to provide a radiation sensitive composition used for the above purpose characterized in that the erosion rate of a pattern formed therefrom is low, the pattern is hardly tapered reversely at the time of development, rubbing cloth caught by the pattern and the separation of the pattern can be effectively prevented, a display failure such as image sticking does not occur, the pattern has high film hardness and excellent surface smoothness, the film residue and stain are hardly produced on the substrate of an unexposed portion, and the

adhesion of the pattern to the substrate at the time of development is excellent.

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

5 According to the present invention, firstly, the above objects and advantages of the present invention are attained by a radiation sensitive composition which (1) comprises (A) a colorant containing a pigment, (B) an alkali-soluble resin, (C) a polyfunctional monomer and (D) a photopolymerization
10 initiator, (2) has an erosion rate of a 20 μm dot pattern formed therefrom of 30 % or less, and (3) is used to form a spacer and/or a black matrix on a drive substrate for thin film transistor (TFT) color liquid crystal display devices.

 The "radiation" as used herein includes visible
15 radiation, ultraviolet radiation, far ultraviolet radiation, electron beams and X-radiation.

Brief Description of the Drawings

 Fig. 1 is a diagram for explaining the method of measuring the erosion rate of a dot pattern.

20 Detailed Description of the Preferred Embodiment

 The present invention will be described in detail hereinbelow.

(A) colorant

 The colorant in the present invention is a colorant
25 which contains a pigment.

 The above pigment can be suitably selected according to the application purpose of a color liquid crystal display device and a desired color. It may be inorganic or organic and a single pigment or a mixture of two or more pigments.
30 The pigment in the present invention is preferably a pigment having high color developing properties and high heat resistance, particularly high thermal decomposition resistance, particularly preferably what contains carbon black and/or two or more organic pigments.

Examples of the carbon black include furnace blacks such as SAF, SAF-HS, ISAF, ISAF-LS, ISAF-HS, HAF, HAF-LS, HAF-HS, NAF, FEF, FEF-HS, SRF, SRF-LM, SRF-LS, GPF, ECF, N-339 and N-351; thermal blacks such as FT and MT; and acetylene
5 black.

These carbon blacks may be used alone or in combination of two or more.

Examples of the inorganic pigment other than carbon black include metal oxides such as titanium black,
10 Cu-Fe-Mn-based oxide and synthetic iron black.

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

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

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

C.I. Pigment Orange 36, C.I. Pigment Orange 43, C.I. Pigment Orange 51, C.I. Pigment Orange 61 and C.I. Pigment Orange 71;

30 C.I. Pigment Red 9, C.I. Pigment Red 97, C.I. Pigment Red 122, C.I. Pigment Red 123, C.I. Pigment Red 149, C.I. Pigment Red 168, C.I. Pigment Red 176, C.I. Pigment Red 177, C.I. Pigment Red 180, C.I. Pigment Red 209, C.I. Pigment Red 215, C.I. Pigment Red 224, C.I. Pigment Red 242 and C.I. Pigment

Red 254;

C.I. Pigment Violet 19, C.I. Pigment Violet 23 and C.I. Pigment Violet 29;

C.I. Pigment Blue 15, C.I. Pigment Blue 60, C.I. Pigment Blue
5 15:3, C.I. Pigment Blue 15:4 and C.I. Pigment Blue 15:6;
C.I. Pigment Green 7, C.I. Pigment Green 36, C.I. Pigment
Green 136 and C.I. Pigment Green 210;

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

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

 Out of these organic pigments, particularly preferably
are/is a mixture of C.I. Pigment Red 177 and C.I. Pigment
Blue 15:4 and/or a mixture of C.I. Pigment Red 177 and C.I.
15 Pigment Blue 15:6.

 The colorant of the present invention may optionally
contain an extender pigment.

 Examples of the above extender pigment include barium
sulfate, barium carbonate, calcium carbonate, silica, basic
20 magnesium carbonate, alumina white, gloss white, satin white
and hydrotalcite.

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

 The amount of the extender pigment is preferably 0 to
25 100 parts by weight, more preferably 5 to 50 parts by weight,
much more preferably 10 to 40 parts by weight based on 100
parts by weight of the total of all the pigments.

 In the present invention, the surface of the above
pigment may be modified by a polymer before use.

30 The colorant other than pigments is a dye, natural
colorant or the like.

-urethane-based dispersant-

 In the present invention, the pigment contained in the
colorant is desirably dispersed by a dispersant,

particularly preferably a dispersant having an urethane bond (to be referred to as "urethane-based dispersant" hereinafter).

A description is subsequently given of the
5 urethane-based dispersant.

The urethane bond of the urethane-based dispersant is generally represented by the formula $R-NH-COO-R'$ (R and R' are each an aliphatic, alicyclic or aromatic monovalent or polyvalent organic group which is bonded to a group having
10 an urethane bond or another group). The urethane bond may be existent in a lipophilic group and/or hydrophilic group contained in the urethane-based dispersant or in the main chain and/or side chain of the urethane-based dispersant, and further one or more urethane bonds may be existent in
15 the urethane-based dispersant. When two or more urethane bonds are existent in the urethane-based dispersant, they may be the same or different.

This urethane-based dispersant may be cationic, anionic, nonionic or amphoteric and may have a silicone-based
20 or fluorine-based structure.

This urethane-based dispersant is a reaction product between a diisocyanate and/or a triisocyanate and a polyester having a hydroxyl group at one terminal and/or a polyester having a hydroxyl group at both terminals.

25 Examples of the diisocyanate include aromatic diisocyanates such as benzene diisocyanates including benzene-1,3-diisocyanate and benzene-1,4-diisocyanate; toluene diisocyanates including toluene-2,4-diisocyanate, toluene-2,5-diisocyanate, toluene-2,6-diisocyanate and
30 toluene-3,5-diisocyanate; and xylene diisocyanates including 1,2-xylene-3,5-diisocyanate, 1,2-xylene-3,6-diisocyanate, 1,2-xylene-4,6-diisocyanate, 1,3-xylene-2,4-diisocyanate, 1,3-xylene-2,5-diisocyanate, 1,3-xylene-2,6-diisocyanate, 1,3-xylene-4,6-diisocyanate,

1,4-xylene-2,5-diisocyanate and
1,4-xylene-2,6-diisocyanate. Examples of the
triisocyanate include aromatic triisocyanates such as
benzene triisocyanates including
5 benzene-1,2,4-triisocyanate, benzene-1,2,5-triisocyanate
and benzene-1,3,5-triisocyanate; toluene triisocyanates
including toluene-2,3,5-triisocyanate,
toluene-2,3,6-triisocyanate, toluene-2,4,5-triisocyanate,
toluene-2,4,6-triisocyanate, toluene-3,4,6-triisocyanate
10 and toluene-3,5,6-triisocyanate; and xylene triisocyanates
including 1,2-xylene-3,4,6-triisocyanate,
1,2-xylene-3,5,6-triisocyanate,
1,3-xylene-2,4,5-triisocyanate,
1,3-xylene-2,4,6-triisocyanate,
15 1,3-xylene-3,4,5-triisocyanate,
1,4-xylene-2,3,5-triisocyanate and
1,4-xylene-2,3,6-triisocyanate.

These diisocyanates and triisocyanates may be used
alone or in combination of two or more.

20 Examples of the polyester having a hydroxyl group at
one terminal or the polyester having a hydroxyl group at both
terminals include polylactones having a hydroxyl group at
one terminal or both terminals such as polycaprolactone
having a hydroxyl group at one terminal or both terminals,
25 polyvalerolactone having a hydroxyl group at one terminal
or both terminals, and polypropiolactone having a hydroxyl
group at one terminal or both terminals; and polycondensation
polyesters having a hydroxyl group at one terminal or both
terminals such as polyethylene terephthalate having a
30 hydroxyl group at one terminal or both terminals and
polybutylene terephthalate having a hydroxyl group at one
terminal or both terminals.

These polyesters having a hydroxyl group at one
terminal and polyesters having a hydroxyl group at both

terminals may be used alone or in combination of two or more.

The urethane-based dispersant in the present invention is preferably a reaction product between an aromatic diisocyanate and a polylactone having a hydroxyl group at one terminal and/or a reaction product between an aromatic diisocyanate and a polylactone having a hydroxyl group at both terminals, particularly preferably a reaction product between a toluene diisocyanate and polycaprolactone having a hydroxyl group at one terminal and/or a reaction product between a toluene diisocyanate and polycaprolactone having a hydroxyl group at both terminals.

The urethane-based dispersant can be characterized by any one or more of the existence of insolubilization by a heat treatment, acid value, amine value and voltage retention.

As for the existence of insolubilization by a heat treatment, when the urethane-based dispersant is heated at preferably 150°C or more, more preferably 150 to 250°C for preferably 30 minutes or more, more preferably 30 to 90 minutes, it desirably becomes insoluble in a polar solvent such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone or γ -butyrolactone.

As for acid value and amine value, the urethane-based dispersant has desirably (i) an acid value of preferably 5 to 25 mgKOH/g, more preferably 8 to 20 mgKOH/g and an amine value of 0 mgKOH/g, or (ii) an amine value of preferably 5 to 25 mgKOH/g, more preferably 8 to 20 mgKOH/g and an acid value of 0 mgKOH/g. (i) and (ii) cannot be satisfied at the same time.

As for voltage retention, the urethane-based dispersant desirably has a voltage retention measured by the following method of 80 % or more, preferably 85 % or more. method of measuring voltage retention:

1 wt% of an urethane-based dispersant is added to a

solution prepared by dissolving the components (B), (C) and (D) in a solvent in the present invention and the resulting solution is applied to a substrate having an indium oxide (ITO) film on the surface to form a 3 μm -thick dry coating film which is then exposed and postbaked at 200 to 250°C. The voltage retention of a liquid crystal cell assembled using the obtained substrate is measured at 60°C for a retention time of 16.7 ms.

When the existence of insolubilization by a heat treatment, acid value, amine value or voltage retention of the urethane-based dispersant in the present invention satisfies the above condition, image sticking which occurs in the liquid crystal cell can be greatly reduced.

Illustrative examples of the urethane-based dispersant having at least one of the above characteristic properties include commercially available products such as EFKA-46 and 47 (EFKA Chemicals B.V.), Disperbyk (BYK Chem. Co., Ltd.) and Disparon (Kusumoto Kasei Co., Ltd.).

The weight average molecular weight in terms of polystyrene (to be abbreviated as Mw hereinafter) measured by gel permeation chromatography (GPC) of the urethane-based dispersant in the present invention is preferably 5,000 to 50,000, more preferably 7,000 to 20,000.

In the present invention, the urethane-based dispersants may be used alone or in combination of two or more.

The amount of the urethane-based dispersant is preferably 0.5 to 100 parts by weight, more preferably 1 to 70 parts by weight, much more preferably 10 to 50 parts by weight based on 100 parts by weight of the pigment contained in the colorant. When the amount of the urethane-based dispersant is smaller than 0.5 part by weight, the stability of a pigment dispersion may lower and when the amount is larger than 100 parts by weight, the property such as developability

of the obtained radiation sensitive composition may be impaired.

In the present invention, a dispersion aid may be used in conjunction with the dispersant.

5 The above dispersion aid is, for example, a copper phthalocyanine sulfonic acid compound.

Specific examples of the above copper phthalocyanine sulfonic acid compound include copper phthalocyanine sulfonic acid, copper phthalocyanine ammonium sulfonate, 10 copper phthalocyanine tetramethylammonium sulfonate, copper phthalocyanine tetraethylammonium sulfonate, copper phthalocyanine tetra-n-propylammonium sulfonate, copper phthalocyanine tetra-i-propylammonium sulfonate and copper phthalocyanine tetra-n-butylammonium sulfonate.

15 These copper phthalocyanine sulfonic acid compounds may be used alone or in combination of two or more.

The amount of the dispersion aid is preferably 20 parts or less by weight, more preferably 10 parts or less by weight, much more preferably 5 parts or less by weight based on 100 20 parts by weight of the pigment contained in the colorant.

(B) alkali-soluble resin

Any alkali-soluble resin is acceptable in the present invention if it serves as a binder for the colorant (A) and is soluble in a developer, particularly preferably an alkali 25 developer, used to form a spacer or a black matrix.

The alkali-soluble resin in the present invention is preferably a resin containing a carboxyl group, particularly preferably a copolymer (to be simply referred to as "carboxyl group-containing copolymer" hereinafter) of an 30 ethylenically unsaturated monomer having at least one carboxyl group (to be referred to as "carboxyl group-containing unsaturated monomer" hereinafter) and another copolymerizable ethylenically unsaturated monomer (to be referred to as "another unsaturated monomer"

hereinafter).

Examples of the carboxyl group-containing unsaturated monomer include unsaturated monocarboxylic acids such as acrylic acid, methacrylic acid, crotonic acid, α -chloroacrylic acid and cinnamic acid; unsaturated dicarboxylic acids (anhydrides) such as maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride and mesaconic acid; unsaturated polycarboxylic acids (anhydrides) having three or more carboxyl groups; mono(2-acryloyloxyethyl)esters or mono(2-methacryloyloxyethyl)esters of a nonpolymerizable dicarboxylic acid such as mono(2-acryloyloxyethyl)succinate, mono(2-methacryloyloxyethyl)succinate, mono(2-acryloyloxyethyl)phthalate and mono(2-methacryloyloxyethyl)phthalate; and ω -carboxypolycaprolactone monoacrylate and ω -carboxypolycaprolactone monomethacrylate.

These carboxyl group-containing ethylenically unsaturated monomers may be used alone or in combination of two or more.

Examples of the another unsaturated monomer include aromatic vinyl compounds such as styrene, α -methylstyrene, o-vinytoluene, m-vinytoluene, p-vinytoluene, p-chlorostyrene, o-methoxystyrene, m-methoxystyrene, p-methoxystyrene, p-vinylbenzylmethyl ether and p-vinylbenzylglycidyl ether; indenenes (derivatives) such as indene and 1-methylindene; unsaturated carboxylic acid esters such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-propyl acrylate, n-propyl methacrylate, i-propyl acrylate, i-propyl methacrylate, n-butyl acrylate, n-butyl methacrylate, i-butyl acrylate, i-butyl methacrylate, sec-butyl acrylate, sec-butyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate,

2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate,
3-hydroxypropyl acrylate, 3-hydroxypropyl methacrylate,
2-hydroxybutyl acrylate, 2-hydroxybutyl methacrylate,
3-hydroxybutyl acrylate, 3-hydroxybutyl methacrylate,
5 4-hydroxybutyl acrylate, 4-hydroxybutyl methacrylate, allyl
acrylate, allyl methacrylate, benzyl acrylate, benzyl
methacrylate, phenyl acrylate, phenyl methacrylate,
methoxydiethylene glycol acrylate, methoxydiethylene glycol
methacrylate, methoxytriethylene glycol acrylate,
10 methoxytriethylene glycol methacrylate, methoxydipropylene
glycol acrylate, methoxydipropylene glycol methacrylate,
glycerol monoacrylate and glycerol monomethacrylate;
unsaturated carboxylic acid aminoalkyl esters such as
2-aminoethyl acrylate, 2-aminoethyl methacrylate,
15 2-dimethylaminoethyl acrylate, 2-dimethylaminoethyl
methacrylate, 2-aminopropyl acrylate, 2-aminopropyl
methacrylate, 2-dimethylaminopropyl acrylate,
2-dimethylaminopropyl methacrylate, 3-aminopropyl acrylate,
3-aminopropyl methacrylate, 3-dimethylaminopropyl acrylate
20 and 3-dimethylaminopropyl methacrylate; unsaturated
carboxylic acid glycidyl esters such as glycidyl acrylate
and glycidyl methacrylate; carboxylic acid vinyl esters such
as vinyl acetate, vinyl propionate, vinyl butyrate and vinyl
benzoate; unsaturated ethers such as vinylmethyl ether,
25 vinylethyl ether, allylglycidyl ether and methacrylglycidyl
ether; vinyl cyanide compounds such as acrylonitrile,
methacrylonitrile, α -chloroacrylonitrile and vinylidene
cyanide; unsaturated amides such as acrylamide,
methacrylamide, α -chloroacrylamide, N-2-hydroxyethyl
30 acrylamide, N-2-hydroxyethyl methacrylamide, N-methylol
acrylamide and N-methylol methacrylamide; N-substituted
maleimides such as N-cyclohexyl maleimide, N-phenyl
maleimide, N-o-hydroxyphenyl maleimide, N-m-hydroxyphenyl
maleimide, N-p-hydroxyphenyl maleimide, N-o-methylphenyl

maleimide, N-m-methylphenyl maleimide, N-p-methylphenyl maleimide, N-o-methoxyphenyl maleimide, N-m-methoxyphenyl maleimide and N-p-methoxyphenyl maleimide; aliphatic conjugated dienes such as 1,3-butadiene, isoprene and chloroprene; and macromonomers having a monoacryloyl group or monomethacryloyl group at a terminal of the molecular chain of a polymer such as polystyrene, polymethyl acrylate, polymethyl methacrylate, poly-n-butyl acrylate, poly-n-butyl methacrylate and polysiloxane.

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

 The carboxyl group-containing copolymer is particularly preferably a copolymer (to be referred to as "carboxyl group-containing copolymer (I)" hereinafter) of
15 (1) a carboxyl group-containing unsaturated monomer containing acrylic acid and/or methacrylic acid as an essential component and optionally mono(2-acryloyloxyethyl)succinate and/or mono(2-methacryloyloxyethyl)succinate and (2) at least one
20 selected from the group consisting of styrene, methyl acrylate, methyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, benzyl acrylate, benzyl methacrylate, phenyl acrylate, phenyl methacrylate, glycerol monoacrylate, glycerol monomethacrylate,
25 N-phenylmaleimide, polystyrene macromonomer and polymethyl methacrylate macromonomer.

 Illustrative examples of the carboxyl group-containing copolymer (I) include copolymers and terpolymers (to be referred to as "carboxyl group-containing copolymers (Ia)" hereinafter) such as a copolymer of (meth)acrylic
30 acid/benzyl (meth)acrylate, terpolymer of (meth)acrylic acid/styrene/benzyl (meth)acrylate, terpolymer of (meth)acrylic acid/ benzyl (meth)acrylate/polystyrene macromonomer, and terpolymer of (meth)acrylic acid/ benzyl

(meth)acrylate/polymethyl methacrylate macromonomer; tetrapolymers (to be referred to as "carboxyl group-containing copolymers (Ib)" hereinafter) such as a tetrapolymer of (meth)acrylic acid/2-hydroxyethyl

5 (meth)acrylate/benzyl (meth)acrylate/polystyrene macromonomer, tetrapolymer of (meth)acrylic acid/2-hydroxyethyl (meth)acrylate/benzyl (meth)acrylate/polymethyl methacrylate macromonomer, tetrapolymer of (meth)acrylic acid/styrene/benzyl (meth)acrylate/N-phenyl

10 maleimide, tetrapolymer of (meth)acrylic acid/styrene/phenyl (meth)acrylate/N-phenyl maleimide, and tetrapolymer of (meth)acrylic acid/glycerol mono(meth)acrylate/styrene/N-phenyl maleimide; pentapolymers (to be referred to as "carboxyl

15 group-containing copolymers (Ic)" hereinafter) such as a pentapolymer of (meth)acrylic acid/styrene/benzyl (meth)acrylate/N-phenyl maleimide/polystyrene macromonomer, pentapolymer of (meth)acrylic acid/styrene/benzyl (meth)acrylate/N-phenyl maleimide/polymethyl methacrylate

20 macromonomer, pentapolymer of (meth)acrylic acid/styrene/phenyl (meth)acrylate/N-phenyl maleimide/polystyrene macromonomer, pentapolymer of (meth)acrylic acid/styrene/phenyl (meth)acrylate/N-phenyl maleimide/polymethyl methacrylate macromonomer,

25 pentapolymer of (meth)acrylic acid/glycerol mono(meth)acrylate/styrene/methyl (meth)acrylate/N-phenyl maleimide, pentapolymer of (meth)acrylic acid/glycerol mono(meth)acrylate/styrene/2-hydroxyethyl (meth)acrylate/N-phenyl maleimide, pentapolymer of

30 (meth)acrylic acid/glycerol mono(meth)acrylate/styrene/benzyl (meth)acrylate/N-phenyl maleimide, pentapolymer of (meth)acrylic acid/glycerol mono(meth)acrylate/styrene/phenyl (meth)acrylate/N-phenyl maleimide, pentapolymer of (meth)acrylic

acid/mono[2-(meth)acryloyloxyethyl]succinate/glycerol
mono(meth)acrylate/styrene/N-phenyl maleimide,
pentapolymer of (meth)acrylic acid, glycerol
mono(meth)acrylate/styrene/N-phenyl maleimide/polystyrene
5 macromonomer, and pentapolymer of (meth)acrylic
acid/glycerol mono(meth)acrylate/styrene/N-phenyl
maleimide/polymethyl methacrylate macromonomer; and
hexapolymers (to be referred to as "carboxyl
group-containing copolymers (Id)" hereinafter) such as a
10 hexapolymer of (meth)acrylic acid/styrene/2-hydroxyethyl
(meth)acrylate/benzyl (meth)acrylate/N-phenyl
maleimide/polystyrene macromonomer, hexapolymer of
(meth)acrylic acid/styrene/2-hydroxyethyl
(meth)acrylate/benzyl (meth)acrylate/N-phenyl
15 maleimide/polymethyl methacrylate macromonomer,
hexapolymer of (meth)acrylic acid/styrene/2-hydroxyethyl
(meth)acrylate/phenyl (meth)acrylate/N-phenyl
maleimide/polystyrene macromonomer, and hexapolymer of
(meth)acrylic acid/styrene/2-hydroxyethyl
20 (meth)acrylate/phenyl (meth)acrylate/N-phenyl
maleimide/polymethyl methacrylate macromonomer.

The copolymerization proportion of the carboxyl
group-containing unsaturated monomer to the carboxyl
group-containing copolymer is preferably 5 to 50 wt%, more
25 preferably 10 to 40 wt%. When the copolymerization
proportion of the carboxyl group-containing unsaturated
monomer is smaller than 5 wt%, the solubility in an alkali
developer of the obtained radiation sensitive composition
may lower and when the copolymerization proportion is larger
30 than 50 wt%, the formed pattern may fall off from the substrate
or the surface thereof may be roughened at the time of
development with an alkali developer.

Mw of the alkali-soluble resin in the present invention
is preferably 1,000 to 1,000,000, more preferably 5,000 to

100,000.

In the present invention, the alkali-soluble resins may 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-soluble resin is smaller than 10 parts by weight, alkali developability may lower, or a stain and the film residue may be produced in an area other than a pattern forming portion and when the amount is larger than 1,000 parts by weight, the concentration of the colorant relatively lowers, whereby it may be difficult to attain the targeted color density of a thin film.

15 (C) polyfunctional monomer

Examples of the polyfunctional monomer in the present invention include diacrylates and dimethacrylates of alkylene glycol such as ethylene glycol and propylene glycol; diacrylates and dimethacrylates of polyalkylene glycol such as polyethylene glycol and polypropylene glycol; polyacrylates and polymethacrylates of a polyhydric alcohol having 3 or more hydroxyl groups and dicarboxylic acid modified products thereof such as glycerin, trimethylolpropane, pentaerythritol and dipentaerythritol; oligoacrylates and oligomethacrylates such as polyester, epoxy resin, urethane resin, alkyd resin, silicone resin and spiran resin; diacrylates and dimethacrylates 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; and tris(2-acryloyloxyethyl)phosphate and tris(2-methacryloyloxyethyl)phosphate.

Out of these polyfunctional monomers, polyacrylates

and polymethacrylates of a polyhydric alcohol having 3 or more hydroxyl groups and dicarboxylic acid modified products thereof are preferred, as exemplified by trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, 5 pentaerythritol triacrylate, pentaerythritol trimethacrylate, succinic acid modified product of pentaerythritol triacrylate, succinic acid modified product of pentaerythritol trimethacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, 10 dipentaerythritol tetraacrylate, dipentaerythritol tetramethacrylate, dipentaerythritol hexaacrylate and dipentaerythritol hexamethacrylate. Particularly preferred are trimethylolpropane triacrylate, pentaerythritol triacrylate and dipentaerythritol 15 hexaacrylate. These polyacrylates, polymethacrylates and dicarboxylic acid modified products thereof are preferred because the strength of the obtained pattern is high, the surface smoothness of the pattern is excellent, and a stain and the film residue are hardly produced in an area other 20 than the pattern forming portion.

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

The amount of the polyfunctional monomer in the present invention is preferably 5 to 500 parts by weight, more 25 preferably 20 to 300 parts by weight based on 100 parts by weight of the alkali-soluble resin (B). When the amount of the polyfunctional monomer is smaller than 5 parts by weight, the strength and surface smoothness of the pattern may lower and when the amount is larger than 500 parts by weight, alkali 30 developability may lower, or a stain and the film residue may be produced in an area other than the pattern forming portion.

In the present invention, part of the above polyfunctional monomer may be substituted by a

monofunctional monomer.

Examples of the monofunctional monomer include carboxyl group-containing unsaturated monomers and other unsaturated monomers enumerated for the alkali-soluble resin
5 (B), 2-hydroxy-3-phenoxypropyl acrylate, 2-hydroxy-3-phenoxypropyl methacrylate and M-5300 as a commercially available product (trade name, manufactured by Toagosei Chemical Industry Co., Ltd.)

Out of these monofunctional monomers, preferred are
10 mono(2-acryloyloxyethyl)succinate, mono(2-methacryloyloxyethyl)succinate, ω -carboxypolycaprolactone monoacrylate (M-5300), ω -carboxypolycaprolactone monomethacrylate, methoxytriethylene glycol acrylate, methoxytriethylene
15 glycol methacrylate, methoxydipropylene glycol acrylate, methoxydipropylene glycol methacrylate, 2-hydroxy-3-phenoxypropyl acrylate and 2-hydroxy-3-phenoxypropyl methacrylate.

The above monofunctional monomers may be used alone or
20 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.

25 (D) photopolymerization initiator

The photopolymerization initiator in the present invention is a compound which forms active species capable of initiating the polymerization of the above polyfunctional monomer (C) and an optionally used monofunctional monomer,
30 such as a radical, anion or cation, through its decomposition or the cleavage of its bond upon exposure.

Examples of the photopolymerization initiator include biimidazole-based compounds, compounds having a benzoin bond, other optically radical generating agents and compounds

having a trihalomethyl group.

The biimidazole-based compounds include
 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis
 (4-ethoxycarbonylphenyl)-1,2'-biimidazole,
 5 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'-
 10 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,
 15 2,2'-bis(2,4-dibromophenyl)-4,4',5,5'-tetraphenyl-
 1,2'-biimidazole and
 2,2'-bis(2,4,6-tribromophenyl)-4,4',5,5'-tetraphenyl-
 1,2'-biimidazole.

These biimidazole-based compounds have excellent
 20 solubility in a solvent, do not form foreign matter such as
 an undissolved product and a precipitate, have high
 sensitivity and high contrast, fully promote a curing
 reaction by exposure with a small amount of energy and do
 not cause a curing reaction in an unexposed portion.
 25 Therefore, the 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 an excellent pattern free from
 a missing part, lost part and undercut.

30 The above compounds having a benzoin bond and other
 optically radical generating agents include
 2-hydroxy-2-methyl-1-phenylpropan-1-one,
 1-(4-i-propylphenyl)-2-hydroxy-2-methylpropan-1-one,
 4-(2-hydroxyethoxy)phenyl-(2-hydroxy-2-propyl)ketone,

1-hydroxycyclohexylphenyl ketone,
 2,2-dimethoxy-2-phenylacetophenone,
 2-methyl-(4-methylthiophenyl)-2-morpholino-1-propan-1-one,
 5 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butan-1-one, benzophenone, 3,3'-dimethyl-4-methoxybenzophenone, 2,4-diethylthioxanthone, 4-azidobenzaldehyde, 4-azidoacetophenone, 4-azidobenzalacetophenone, azidopyrene, 4-diazodiphenylamine,
 10 4-diazo-4'-methoxydiphenylamine, 4-diazo-3-methoxydiphenylamine, bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide, dibenzoyl, benzoin isobutyl ether, N-phenylthioacridone and triphenylpyrylium perchlorate.

15 The above compounds having a trihalomethyl group include 1,3,5-tris(trichloromethyl)-s-triazine, 1,3-bis(trichloromethyl)-5-(2-chlorophenyl)-s-triazine, 1,3-bis(trichloromethyl)-5-(4-chlorophenyl)-s-triazine, 1,3-bis(trichloromethyl)-5-(2-methoxyphenyl)-s-triazine
 20 and 1,3-bis(trichloromethyl)-5-(4-methoxyphenyl)-s-triazine.

Out of the compounds having a benzoin bond, other optically radical generating agents and compounds having a trihalomethyl group,
 25 2-hydroxy-2-methyl-1-phenylpropan-1-one, 2-methyl-(4-methylthiophenyl)-2-morpholino-1-propan-1-one and 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butan-1-one are preferred because the formed pattern hardly falls
 30 off from the substrate at the time of development and the strength and sensitivity of the pattern are high.

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

In the present invention, at least one selected from

the group consisting of a sensitizer, curing promoting agent and optical crosslinking agent or optical sensitizer which comprises a polymer compound (to be referred to as "polymer optical crosslinking/sensitizing agent" hereinafter) may be
5 further used in combination with the above photopolymerization initiator as required.

Examples of the above sensitizer include
4,4'-bis(dimethylamino)benzophenone,
4,4'-bis(diethylamino)benzophenone,
10 4-diethylaminoacetophenone, 4-dimethylaminopropiophenone, ethyl-4-dimethylaminobenzoate,
2-ethylhexyl-1,4-dimethylaminobenzoate,
2,5-bis(4-diethylaminobenzal)cyclohexanone,
7-diethylamino-3-(4-diethylaminobenzoyl)coumarin and
15 4-(diethylamino)chalcone.

Examples of the above curing promoting agent include chain transfer agents such as 2-mercaptobenzoimidazole, 2-mercaptobenzothiazole, 2-mercaptobenzooxazole,
2,5-dimercapto-1,3,4-thiadiazole,
20 2-mercapto-4,6-dimethylaminopyridine,
1-phenyl-5-mercapto-1H-tetrazole and
3-mercapto-4-methyl-4H-1,2,4-triazole.

Further, the above polymer optical crosslinking/sensitizing agent is a polymer compound having
25 a functional group which can function as an optical crosslinking agent and/or optical sensitizer in the main chain and/or side chain. Examples of the agent include a condensate of 4-azidobenzaldehyde and polyvinyl alcohol, condensate of 4-azidobenzaldehyde and phenol novolak resin,
30 homopolymer or copolymer of 4-acryloylphenyl cinnamoyl ester, 1,4-polybutadiene and 1,2-polybutadiene.

Out of these sensitizers, curing promoting agents and polymer optical crosslinking/sensitizing agents,
4,4'-bis(dimethylamino)benzophenone,

4,4'-bis(diethylamino)benzophenone and
2-mercaptobenzothiazole are preferred because the formed
pattern hardly falls off from the substrate at the time of
development and the strength and sensitivity of the pattern
5 are high.

The photopolymerization initiator in the present
invention is particularly preferably a combination of a
biimidazole-based compound and at least one selected from
the group consisting of a benzophenone-based compound having
10 a benzoin bond, benzophenone-based other optically radical
generating agent, benzophenone-based sensitizer and
thiazole-based curing promoting agent.

Examples of the particularly preferred combination
include combination of
15 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis
(4-ethoxycarbonylphenyl)-1,2'-biimidazole/
4,4'-bis(diethylamino)benzophenone, combination of
2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis
(4-ethoxycarbonylphenyl)-1,2'-biimidazole/
20 4,4'-bis(diethylamino)benzophenone/
2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butane-1-
one, combination of
2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis
(4-ethoxycarbonylphenyl)-1,2'-biimidazole/
25 4,4'-bis(diethylamino)benzophenone/
1-hydroxycyclohexylphenyl ketone, combination of
2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis
(4-ethoxycarbonylphenyl)-1,2'-biimidazole/
4,4'-bis(dimethylamino)benzophenone/
30 1-hydroxycyclohexylphenyl ketone/2-mercaptobenzothiazole,
combination of
2,2'-bis(2,4-dichlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-
biimidazole/4,4'-bis(diethylamino)benzophenone,
combination of

2,2'-bis(2,4-dibromophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole/4,4'-bis(diethylamino)benzophenone/2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butane-1-one, combination of

- 5 2,2'-bis(2,4-dibromophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole/4,4'-bis(diethylamino)benzophenone/
1-hydroxycyclohexylphenyl ketone, and combination of
2,2'-bis(2,4,6-trichlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole/4,4'-bis(dimethylamino)benzophenone/
10 1-hydroxycyclohexylphenyl ketone/2-mercaptobenzothiazole.

In the present invention, the total amount of the compound having a benzoin bond, other optically radical generating agent and compound having a trihalomethyl group is preferably 80 wt% or less based on the photopolymerization
15 initiator. The total amount of the sensitizer and the curing promoting agent is preferably 80 wt% or less based on the photopolymerization initiator. Further, the amount of the polymer optical crosslinking/sensitizing agent is preferably 200 parts or less by weight, more preferably 180
20 parts or less by weight based on 100 parts by weight of the biimidazole-based compound.

In the present invention, the amount of the photopolymerization initiator is preferably 0.01 to 500 parts by weight, more preferably 1 to 300 parts by weight,
25 particularly preferably 10 to 200 parts by weight based on 100 parts by weight of the total of the polyfunctional monomer (C) and an optionally used monofunctional monomer. When the amount of the photopolymerization initiator is smaller than 0.01 part by weight, curing by exposure becomes incomplete
30 with the result that part of the pattern may be missing or lost, or the pattern may be undercut. When the amount is larger than 500 parts by weight, the formed pattern may fall off from the substrate at the time of development, or a stain and the film residue may be produced in an area other than

the pattern forming portion.

Additives

The radiation sensitive composition in the present invention may optionally contain various additives.

5 The additives include a polymer compound such as polyvinyl alcohol, polyethylene glycol monoalkyl ether or poly(fluoroalkylacrylate); nonionic, cationic or anionic surfactant; adhesion accelerator such as vinyl trimethoxysilane, vinyl triethoxysilane, vinyl
10 tris(2-methoxyethoxy)silane, N-(2-aminoethyl)-3-aminopropylmethyl dimethoxysilane, N-(2-aminoethyl)-3-aminopropyl trimethoxysilane, 3-aminopropyl triethoxysilane, 3-glycidoxypropyl trimethoxysilane, 3-glycidoxypropylmethyl dimethoxysilane,
15 2-(3,4-epoxycyclohexyl)ethyl trimethoxysilane, 3-chloropropylmethyl dimethoxysilane, 3-chloropropyl trimethoxysilane, 3-methacryloxypropyl trimethoxysilane or 3-mercaptopropyl trimethoxysilane; antioxidant such as 2,2-thiobis(4-methyl-6-t-butylphenol) or
20 2,6-di-t-butylphenol; ultraviolet light absorber such as 2-(3-t-butyl-5-methyl-2-hydroxyphenyl)-5-chlorobenzotriazole or alkoxybenzophenone; and coagulation preventing agent such as sodium polyacrylate.

 The radiation sensitive composition in the present
25 invention preferably contains an organic acid to further improve the solubility in an alkali developer of a coating film formed therefrom and suppress the existence of an undissolved product after development when the alkali-soluble resin (B) is a resin having a carboxyl group.

30 The organic acid is preferably an aliphatic carboxylic acid or phenyl group-containing carboxylic acid.

 Examples of the above aliphatic carboxylic acid include monocarboxylic acids such as formic acid, acetic acid, propionic acid, butyric acid, valeric acid, pivalic acid,

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

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

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 phthalic acid, isophthalic acid and terephthalic acid; aromatic polycarboxylic acids having three or more carboxyl groups such as trimellitic acid, trimesic acid, mellophanic acid and pyromellitic acid; phenylacetic acid, hydroatropic acid, hydrocinnamic acid, mandelic acid, phenylsuccinic acid, atropic acid, cinnamic acid, cinnamylidenic acid, coumaric acid and umbellic acid.

Out of these organic acids, aliphatic dicarboxylic acids and aromatic dicarboxylic acids such as malonic acid, adipic acid, itaconic acid, citraconic acid, fumaric acid, mesaconic acid and phthalic acid are preferred from the viewpoints of alkali solubility, solubility in a solvent to be described hereinafter, and the prevention of a stain and the like in an area other than the pattern forming portion.

The above organic acids may be used alone or in

combination of two or more.

The amount of the organic acid is preferably 10 wt% or less, more preferably 1 wt% or less based on the radiation sensitive composition. When the amount of the organic acid
5 is larger than 10 wt%, the adhesion of the formed pattern to the substrate may lower.

The radiation sensitive composition in the present invention has an erosion rate measured by the following method of a 20 μm dot pattern having a thickness of 5 μm of 30 %
10 or less, preferably -60 to +30 %, more preferably -40 to +20 %, particularly preferably -30 to +10 %.

Method of measuring erosion rate;

In the dot pattern shown in Fig. 1, the width "a" of the top end and the width "b" at a position where the height
15 is 1/2 the height (L) of the pattern from the bottom are measured to calculate the erosion rate defined by the following equation.

$$\text{Erosion rate (\%)} = (a - b) \times 100/a$$

When the erosion rate of the 20 μm dot pattern having
20 a thickness of 5 μm formed from the radiation sensitive composition of the present invention satisfies the above requirement, even if development conditions are made strict to effectively remove the residue in the through holes when a color filter and a spacer and/or a black matrix are to be
25 formed on a drive substrate for a thin film transistor (TFT) color liquid crystal display device, the excessive erosion of the pattern as the spacer or the black matrix can be prevented, and the rubbing cloth caught by the pattern portion and the separation of the pattern can be effectively
30 prevented.

The optical density (OD value) of a dried film of the radiation sensitive composition of the present invention is preferably 0.5 or more, more preferably 0.6 or more, much more preferably 0.7 or more, particularly preferably 0.8 or

more per 1 μm .

Solvent

The radiation sensitive composition of the present invention comprises the above colorant (A), alkali-soluble
5 resin (B), polyfunctional monomer (C) and photopolymerization initiator (D) as essential components and the above additives as optional components. It is preferably prepared as a liquid composition by dissolving the above components except the pigment in a suitable solvent.

10 Any solvent is acceptable if it disperses or dissolves the components (A) to (D) and additive components, does not react with these components and has suitable volatility.

Illustrative examples of the solvent include (poly)alkylene glycol monoalkyl ethers such as ethylene
15 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,
20 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
25 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
30 monoethyl ether acetate, diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether acetate and propylene glycol monoethyl ether acetate; other ethers such as diethylene glycol dimethyl ether, diethylene glycol

methylethyl ether, diethylene glycol diethyl ether and tetrahydrofuran; ketones such as methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, 2-heptanone and 3-heptanone; lactic acid alkyl esters such as methyl 2-hydroxypropionate and ethyl 2-hydroxypropionate; other esters such as methyl 2-hydroxy-2-methylpropionate, ethyl 2-hydroxy-2-methylpropionate, methyl 3-methoxypropionate, ethyl 3-methoxypropionate, methyl 3-ethoxypropionate, ethyl 3-ethoxypropionate, ethyl ethoxyacetate, ethyl hydroxyacetate, methyl 2-hydroxy-3-methylbutanoate, 3-methyl-3-methoxybutylacetate, 4-methoxybutylacetate, 3-methyl-3-methoxybutylpropionate, ethyl acetate, n-propyl acetate, i-propyl acetate, n-butyl acetate, i-butyl acetate, n-amyl acetate, i-amyl acetate, n-butyl propionate, ethyl butyrate, n-propyl butyrate, i-propyl butyrate, n-butyl butyrate, methyl pyruvate, ethyl pyruvate, n-propyl pyruvate, methyl acetoacetate, ethyl acetoacetate and ethyl 2-oxybutanoate; aromatic hydrocarbons such as toluene and xylene; and carboxylic acid amides such as N-methylpyrrolidone, N,N-dimethylformamide and N,N-dimethylacetamide.

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

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

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

Out of these solvents, propylene glycol monomethyl ether, ethylene glycol monomethyl ether acetate, propylene

glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, diethylene glycol dimethyl ether, cyclohexanone, 2-heptanone, 3-heptanone, ethyl 2-hydroxypropionate, 4-methoxybutylacetate, 5 3-methyl-3-methoxybutylpropionate, ethyl 3-methoxypropionate, methyl 3-ethoxypropionate, ethyl 3-ethoxypropionate, n-butyl acetate, i-butyl acetate, n-amyl acetate, i-amyl acetate, n-butyl propionate, ethyl butyrate, i-propyl butyrate, n-butyl butyrate and ethyl 10 pyruvate are preferred from the viewpoints of solubility, pigment dispersibility and coatability. γ -butyrolactone is preferred as the high-boiling solvent.

The amount of the solvent is preferably 100 to 10,000 parts by weight, more preferably 500 to 5,000 parts by weight 15 based on 100 parts by weight of the alkali-soluble resin (B).
Method of forming spacer and black matrix

A description is subsequently given of the method of forming a spacer and a black matrix from the radiation sensitive composition of the present invention.

20 The liquid radiation sensitive composition is applied to a drive substrate for a thin film transistor (TFT) color liquid crystal display device (to be referred to as "TFT drive substrate" hereinafter) and prebaked to evaporate the solvent in order to form a coating film. Thereafter, this 25 coating film is exposed through a photomask to form a predetermined pattern, developed with an alkali developer to dissolve and remove an unexposed portion of the coating film and then preferably postbaked to form a predetermined spacer pattern.

30 To apply the liquid radiation sensitive composition to the TFT drive substrate, a suitable coating technique such as rotational coating, cast coating or roll coating may be used.

The thickness of coating is preferably 0.1 to 10 μm ,

more preferably 0.2 to 7.0 μm , much more preferably 0.5 to 6.0 μm after drying.

The thickness of the coating film after postbaking is preferably 0.5 to 10 μm , more preferably 1 to 8 μm , much more preferably 2 to 6 μm .

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

The amount of exposure energy of the radiation is preferably 10 to 10,000 J/m².

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

An appropriate amount of a water-soluble organic solvent such as methanol or ethanol, or a surfactant may be added to the above alkali developer. The coating film is preferably 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.

To form a black matrix from the radiation sensitive composition of the present invention, a TFT drive substrate having a spacer formed as described above or having no spacer is used to form a black matrix in the same manner as the spacer. When a spacer and a black matrix are to be formed on the same TFT drive substrate, the spacer may be formed before or after the black matrix or may be formed simultaneously with the black matrix.

The TFT drive substrate having a spacer and/or a black

matrix formed as described above is extremely useful for color liquid crystal display devices, color image pick-up elements, color sensors and the like.

5 Examples

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

Example 1

10 100 parts by weight of carbon black, 30 parts by weight of barium sulfate and 30 parts by weight of an urethane-based dispersant (Disperbyk-182) as colorants (A), 50 parts by weight of a tetrapolymer of methacrylic acid/2-hydroxyethyl methacrylate/benzyl methacrylate/polystyrene macromonomer
15 (weight ratio: 15/15/60/10, $M_w = 25,000$) as an alkali-soluble resin (B), 40 parts by weight of dipentaerythritol hexaacrylate as a polyfunctional monomer (C), 10 parts by weight of 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis (4-ethoxycarbonylphenyl)-1,2'-biimidazole, 10 parts by
20 weight of 4,4'-bis(diethylamino)benzophenone and 20 parts by weight of
2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butan-1-one as photopolymerization initiators (D), and 1,500 parts by weight of ethyl 3-ethoxypropionate as a solvent were mixed
25 together to prepare a liquid radiation sensitive composition (I).

 The liquid composition (I) was applied to a TFT drive substrate by a spin coater and prebaked at 90° C for 4 minutes to form a 6.7 μm -thick coating film. Thereafter, this
30 substrate was cooled to room temperature and exposed to 2,000 J/m^2 of ultraviolet radiation having a wavelength of 365 nm through a photomask using a high-pressure mercury lamp. This substrate was then immersed in a 0.04 wt% aqueous solution of potassium hydroxide at 23° C for 1 minute to develop the

coating film, washed in super pure water and dried with air. Subsequently, it was postbaked at 250°C for 30 minutes to form a 20 µm black dot spacer pattern having a thickness of 5 µm on the TFT drive substrate.

5 When a display test was made on a display panel assembled using the obtained TFT drive substrate, a display failure such as image sticking was not observed.

Further, the residue and stain were not observed on the obtained TFT drive substrate of an unexposed portion, the
10 separation of the pattern and missing and lost parts of the pattern were not observed, and yet the pattern had high film hardness and excellent surface smoothness.

When the erosion rate of the formed 20 µm black dot pattern having a thickness of 5 µm was calculated, it was
15 10 %.

The optical density (OD value) of the dry coating film formed from the liquid composition (I) was 0.67 per 1 µm.

A solution prepared by dissolving 1 wt% of the urethane-based dispersion used herein in a mixture of the
20 above components (B) to (D) and a solvent was applied to a glass substrate having an ITO film formed on the surface to a thickness after drying of 6 µm by a spin coater, prebaked at 80°C for 10 minutes, exposed to 2,000 J/m² of ultraviolet radiation having a wavelength of 365 nm and then postbaked
25 at 220°C for 1 hour. This substrate was assembled with another glass substrate having an ITO film formed on the surface and liquid crystals were injected into a space between the substrates to fabricate a liquid crystal cell which was then annealed at 100°C for 1 hour. When the voltage retention
30 of the obtained liquid crystal cell was measured at 60°C for a retention time of 16.7 ms, it was 86 %.

Example 2

140 parts by weight of C.I. Pigment Red 177, 60 parts by weight of C.I. Pigment Blue 15:4, 30 parts by weight of

barium sulfate and 60 parts by weight of an urethane-based dispersant (Disperbyk-182; Trade name) as colorants (A), 50 parts by weight of a tetrapolymer of methacrylic acid/2-hydroxyethyl methacrylate/benzyl methacrylate/polystyrene macromonomer (weight ratio: 15/15/60/10, Mw = 25,000) as an alkali-soluble resin (B), 40 parts by weight of dipentaerythritol hexaacrylate as a polyfunctional monomer (C), 10 parts by weight of 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis (4-ethoxycarbonylphenyl)-1,2'-biimidazole, 10 parts by weight of 4,4'-bis(diethylamino)benzophenone and 20 parts by weight of 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butane-1-one as photopolymerization initiators (D), and 1,500 parts by weight of ethyl 3-ethoxypropionate as a solvent were mixed together to prepare a liquid radiation sensitive composition (II).

The liquid composition (II) was applied to a TFT drive substrate by a spin coater and prebaked at 90°C for 4 minutes to form a 7.0 µm-thick coating film. Thereafter, a spacer pattern was formed in the same manner as in Example 1.

When a display test was made on a display panel assembled using the obtained TFT drive substrate, a display failure such as image sticking was not observed.

Further, the residue and stain were not observed on the obtained TFT drive substrate of an unexposed portion, the separation of the pattern and missing and lost parts of the pattern were not observed, and yet the pattern had high film hardness and excellent surface smoothness.

When the erosion rate of the formed 20 µm black dot pattern having a thickness of 5 µm was calculated, it was 5 %.

The optical density (OD value) of the dry coating film formed from the liquid composition (II) was 0.72 per 1 µm.

Example 3

A liquid radiation sensitive composition (III) was prepared in the same manner as in Example 1 except that Disperbyk-170 (trade name) was used in place of Disperbyk-182 as an urethane-based dispersant. Thereafter, a spacer pattern was formed in the same manner as in Example 1 except that the liquid composition (III) was used in place of the liquid composition (I).

When a display test was made on a display panel assembled using the obtained TFT drive substrate, a display failure such as image sticking was not observed.

Further, the residue and stain were not observed on the obtained TFT drive substrate of an unexposed portion, the separation of the pattern and missing and lost parts of the pattern were not observed, and yet the pattern had high film hardness and excellent surface smoothness.

When the erosion rate of the formed 20 μm black dot pattern having a thickness of 5 μm was calculated, it was -12 %.

When the voltage retention of the urethane-based dispersant used herein was measured in the same manner as in Example 1, it was 92 %.

Example 4

A liquid radiation sensitive composition (IV) was prepared in the same manner as in Example 1 except that Disperbyk-165 (trade name) was used in place of Disperbyk-182 as an urethane-based dispersant. Thereafter, a spacer pattern was formed in the same manner as in Example 1 except that the liquid composition (IV) was used in place of the liquid composition (I).

When a display test was made on a display panel assembled using the obtained TFT drive substrate, a display failure such as image sticking was not observed.

Further, the residue and stain were not observed on the

obtained TFT drive substrate of an unexposed portion, the separation of the pattern and missing and lost parts of the pattern were not observed, and yet the pattern had high film hardness and excellent surface smoothness.

5 When the erosion rate of the formed 20 μm black dot pattern having a thickness of 5 μm was calculated, it was -3 %.

 When the voltage retention of the urethane-based dispersant used herein was measured in the same manner as
10 in Example 1, it was 87 %.

Comparative Example 1

 A liquid radiation sensitive composition (i) was prepared in the same manner as in Example 1 except that a polyethyleneimine-polyester-based dispersant (trade name:
15 Solsperser 24000, manufactured by Zeneca Co., Ltd.) was used in place of Disperbyk-182 as a dispersant. Thereafter, a spacer pattern was formed in the same manner as in Example 1 except that the liquid composition (i) was used in place of the liquid composition (I).

20 When a display test was made on a display panel assembled using the obtained TFT drive substrate, image sticking occurred.

 When the erosion rate of the formed 20 μm black dot pattern having a thickness of 5 μm was calculated, it was
25 35 %.

 When the voltage retention of the urethane-based dispersant used herein was measured in the same manner as in Example 1, it was 71 %.

 As described above, the radiation sensitive
30 composition of the present invention is characterized in that the erosion rate of a pattern formed therefrom is low, the excessive erosion of the pattern can be prevented even under strict development conditions, the pattern is hardly tapered reversely, rubbing cloth caught by the pattern and the

separation of the pattern can be effectively prevented, a display failure such as image sticking does not occur, the pattern has high film hardness and excellent surface smoothness, the film residue and stain are hardly produced
5 on the substrate of an unexposed portion, and the adhesion of the pattern to the substrate at the time of development is excellent. Therefore, the radiation sensitive composition can be extremely advantageously used to form a spacer and/or a black matrix on a drive substrate for a thin
10 film transistor (TFT) color liquid crystal display device.

What is claimed is:

1. A radiation sensitive composition which (1) comprises (A) a colorant containing a pigment, (B) an alkali-soluble resin, (C) a polyfunctional monomer and (D) a photopolymerization initiator, (2) has an erosion rate of a 20µm dot pattern formed therefrom of 30 % or less and (3) is used to form a spacer and/or a black matrix on a drive substrate for a thin film transistor (TFT) color liquid crystal display device.
2. The radiation sensitive composition of claim 1, wherein the colorant (A) contains C.I. Pigment Red 177 and C.I. Pigment Blue 15:4 and/or C.I. Pigment Blue 15:6.
3. The radiation sensitive composition of claim 1 or 2, wherein the pigment contained in the colorant (A) is dispersed by a dispersant having an urethane bond.
4. The radiation sensitive composition of claim 3, wherein the voltage retention of the dispersant having an urethane bond is 80 % or more.
5. The radiation sensitive composition of claim 1, wherein the colorant (A) contains carbon black and/or at least two organic pigments.
6. The radiation sensitive composition of claim 3, wherein the colorant (A) further contains an extender pigment.
7. The radiation sensitive composition of claim 1, wherein the alkali-soluble resin (B) is at least one selected from the group consisting of a carboxyl group-containing copolymer (Ia), carboxyl group-containing copolymer (Ib), carboxyl group-containing copolymer (Ic) and carboxyl

group-containing copolymer (Id).

8. The radiation sensitive composition of claim 1, wherein the polyfunctional monomer (C) is at least one selected from
5 the group consisting of trimethylolpropane triacrylate, pentaerythritol triacrylate and dipentaerythritol hexaacrylate.

9. The radiation sensitive composition of claim 1, wherein
10 the photopolymerization initiator (D) is a combination of a biimidazole-based compound and at least one selected from the group consisting of a benzophenone-based compound having a benzoin bond, another benzophenone-based optically radical generating agent, a benzophenone-based sensitizer and a
15 thiazole-based curing promoting agent.

10. The radiation sensitive composition of claim 1 which has an optical density (OD value) of a dry coating film formed therefrom of 0.5 or more per 1 μm .