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

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001]

The present invention relates to a radiation-sensitive composition for forming a coloring layer, a color filter, and a liquid crystal display device. More specifically, the present invention relates to a radiation-sensitive composition used for forming a coloring layer which is useful for a color filter used for a transmission-type or reflection-type color liquid crystal display apparatus, a color image pickup tube element, or the like, a color filter provided with the coloring layer formed by using the radiation-sensitive composition, and a color liquid crystal display device including the color filter.

2. Description of the Related Art

[0002]

Conventionally, in producing a color filter using a colored radiation-sensitive composition, a method of obtaining a pixel pattern of each color is known, involving: applying the colored radiation-sensitive composition on a substrate or on a substrate in which a light-shielding layer having a

desired pattern is previously formed followed by drying; irradiating a dried coating film in a desired pattern form (hereinafter referred to as "exposure"); and developing the resultant (for example, refer to Patent Documents 1 and 2).

[0003]

In the technical fields of color filters of recent years, there is a tendency that, in addition to the mainstream that tact time is shortened by decreasing exposure dose, the content proportion of a pigment contained in the colored radiation-sensitive composition for forming a coloring layer is further increasing in order to manage with the requirement of higher color purity with respect to color liquid crystal display devices. In those circumstances, the following problem is actually existed: at the time of producing a color filter, smudge-like color unevenness (hereinafter referred to as "water unevenness") is generated on a pixel pattern at a water-washing step performed after the development, and an inspection step performed thereafter is delayed owing to the water unevenness, thereby impairing production efficiency. However, effective means to solve the problem of the water unevenness has not been found yet.

[0004]

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

[Patent Document 2] JP-A-03-53201

SUMMARY OF THE INVENTION

Problems to be solved by the Invention

[0005]

The present invention has been made based on the above circumstances, and an object of the present invention is to provide a novel radiation-sensitive composition for forming a coloring layer which can form a pixel free from water unevenness even with low exposure dose.

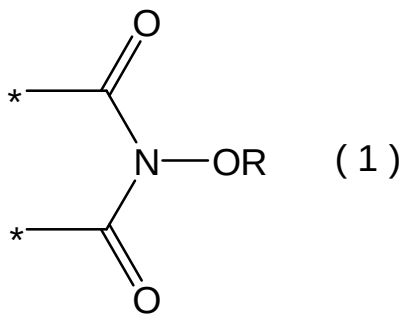
[0006]

The inventors of the present invention have conducted intensive studies, and have found that the above problem may be solved by incorporating a specific imide-based compound into a radiation-sensitive composition for forming a coloring layer. Thus, the present invention has been accomplished.

[0007]

In other words, first, the present invention provides a radiation-sensitive composition for forming a coloring layer containing: a colorant (A); an alkali-soluble resin (B); a polyfunctional monomer (C); a photopolymerization initiator (D); and a compound (E) having a structure represented by the following formula (1):

[0008]



(1)

[0009]

where: R represents a hydrogen atom, a secondary or tertiary alkyl group having 3 to 30 carbon atoms, a cyclic alkyl group having 5 to 12 carbon atoms, an allyl group, an aralkyl group having 7 to 30 carbon atoms, or an acyl group having 2 to 30 carbon atoms; and "*" represents a bond.

[0010]

Second, the present invention provides

a color filter including a coloring layer, which is formed by using the radiation-sensitive composition for forming a coloring layer.

[0011]

Third, the present invention provides

a color liquid crystal display device including the color filter.

In the present invention, "radiation" means a ray including visible light ray, ultraviolet ray, far ultraviolet ray, electron ray, or X-ray.

DETAILED DESCRIPTION OF THE INVENTION

[0012]

Hereinafter, the present invention is described in detail.

Radiation-sensitive composition for forming coloring layer

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

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

[0013]

-Colorant (A)-

The colorant (A) used in the present invention is not particularly limited, and may include organic pigments or inorganic pigments.

Examples of the organic pigments include compounds classified as pigments according to color index (C.I.; The Society of Dyers and Colourists), specifically include compounds having the following color index (C.I.) numbers:

[0014]

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

Pigment Yellow 14, C.I. Pigment Yellow 17, C.I. Pigment Yellow 20, C.I. Pigment Yellow 24, C.I. Pigment Yellow 31, C.I. Pigment Yellow 55, C.I. Pigment Yellow 83, C.I. Pigment Yellow 93, C.I. Pigment Yellow 109, C.I. Pigment Yellow 110, C.I. Pigment Yellow 138, C.I. Pigment Yellow 139, C.I. Pigment Yellow 150, C.I. Pigment Yellow 153, C.I. Pigment Yellow 154, C.I. Pigment Yellow 155, C.I. Pigment Yellow 166, C.I. Pigment Yellow 168, C.I. Pigment Yellow 180, and C.I. Pigment Yellow 211;

[0015]

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

[0016]

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

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

[0017]

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

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

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

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

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

[0018]

In the present invention, the organic pigment may be purified by a recrystallization method, a reprecipitation method, a solvent washing method, a sublimination method, a

heating under vacuum method, or a combination thereof.

[0019]

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

[0020]

In those colorants, the surface of the colorant particle may be modified with a polymer as desired. Examples of the polymer for modifying the surface of the colorant particle include a polymer described in JP-A-08-259876 and various commercially available polymers or oligomers for dispersing a pigment. The methods of coating a carbon black surface with a polymer are disclosed, for example, in JP-A-09-71733, JP-A-09-95625, and JP-A-09-124969.

The colorants may be used alone or in a mixture of two or more.

[0021]

In the case where the radiation-sensitive composition of the present invention is used for forming a pixel, because there are required high-definition color development and heat resistance for the pixel, it is preferable to use as the

colorant (A) a colorant having high color developability and high heat resistance, in particular a colorant having high resistance to thermal decomposition. Specifically an organic colorant, and in particular an organic pigment are preferred as the colorant (A).

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

[0022]

The radiation-sensitive composition of the present invention may form a pixel free from water unevenness, even in the case where the content of the colorant is 30 wt% or more with respect to the total solid content of the radiation-sensitive composition. Further, in the present invention, the upper limit of the content of the colorant is, from the viewpoint of maintaining a development property, preferably 70 wt% or less and particularly preferably 60 wt% or less with respect to the total solid content of the radiation-sensitive composition. Here, the solid content refers to a component other than the solvents to be described later.

[0023]

The colorant of the present invention may be used

together with, as desired, a dispersant and a dispersion aid.

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

[0024]

These dispersants are commercially available. Examples of the modified acrylic copolymers include Disperbyk-2000 and Disperbyk-2001 (both manufactured by BYK Japan KK); examples of the polyurethanes include Disperbyk-161, Disperbyk-162, Disperbyk-165, Disperbyk-167, Disperbyk-170, and Disperbyk-182

(all manufactured by BYK Japan KK), and Solsperse 76500 (manufactured by The Lubrizol Corporation); and examples of the cationic comb graft polymers include Solsperse 24000 and Solsperse 35100 (both manufactured by The Lubrizol Corporation), and Ajisper-PB821, Ajisper-PB822, and Ajisper-PB880 (all manufactured by Ajinomoto Fine-Techno Co., Inc.).

[0025]

The above dispersants may be used alone or in a mixture of two or more. The content of the dispersant is generally 100 parts by weight or less, preferably 0.5 to 100 parts by weight, more preferably 1 to 70 parts by weight, and particularly preferably 10 to 50 parts by weight, with respect to 100 parts by weight of the colorant (A). In this case, when the content of the dispersant exceeds 100 parts by weight, development property or the like may be impaired.

[0026]

Examples of the dispersion aid include a blue pigment derivative and a yellow pigment derivative, and a specific example thereof includes a copper phthalocyanine derivative.

[0027]

-Alkali-soluble resin (B)-

The alkali-soluble resin (B) in the present invention is not particularly limited as long as the alkali-soluble resin has solubility to an alkalin developer to be used in a

development treatment step in forming a coloring layer, and generally is a polymer having an acidic functional group such as a carboxyl group and a phenolic hydroxyl group. Of those, preferred is a polymer having a carboxyl group, and particularly preferred is a copolymer (hereinafter referred to as "carboxyl group-containing copolymer") of an ethylenic unsaturated monomer having one or more carboxyl groups (hereinafter referred to as "carboxyl group-containing unsaturated monomer") and another ethylenic unsaturated monomer which is copolymerizable with the carboxyl group-containing unsaturated monomer (hereinafter referred to as "copolymerizable unsaturated monomer").

[0028]

Examples of the carboxyl group-containing unsaturated monomer include:

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

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

mono[(meth)acryloyloxyalkyl]esters of polycarboxylic acids having at least two carboxyl groups in the molecule such as mono[2-(meth)acryloyloxyethyl]succinate, and mono[2-

(meth)acryloyloxyethyl]phthalate; and

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

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

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

[0029]

In the carboxyl group-containing copolymer, the copolymerization ratio of the carboxyl group-containing unsaturated monomer is preferably 5 to 5 wt% and more preferably 10 to 40 wt%. In this case, when the copolymerization ratio is less than 5 wt%, the solubility of the radiation-sensitive composition to be obtained to an alkalin developer tends to decrease, and on the other hand, when the copolymerization ratio exceeds 50 wt%, the solubility of the radiation-sensitive composition to be obtained to the alkalin developer tends to become excessive, with the result that a pixel tends to fall off easily from a substrate and a film on the surface of the pixel tends to get rough easily, at

the time of development with the alkalin developer.

[0030]

Further, examples of the copolymerizable unsaturated monomers include:

maleimides;

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

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

indenes such as indene and 1-methylindene;

[0031]

unsaturated carboxylates such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, i-propyl

(meth)acrylate, n-butyl (meth)acrylate, i-butyl (meth)acrylate, sec-butyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, allyl (meth)acrylate, benzyl (meth)acrylate, cyclohexyl (meth)acrylate, phenyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 2-phenoxyethyl (meth)acrylate, methoxydiethylene glycol (meth)acrylate, methoxytriethylene glycol (meth)acrylate, methoxypropylene glycol (meth)acrylate, methoxydipropylene glycol (meth)acrylate, isobornyl (meth)acrylate, tricyclo[5.2.1.$0^{2,6}$]decane-8-yl (meth)acrylate, 2-hydroxy-3-phenoxypropyl (meth)acrylate, glycerol mono(meth)acrylate, 4-hydroxyphenyl (meth)acrylate, and ethylene oxide-modified (meth)acrylate of paracumylphenol;

[0032]

unsaturated glycidyl carboxylates such as glycidyl (meth)acrylate;

vinyl carboxylates such as vinyl acetate, vinyl propionate, vinyl butyrate, and vinyl benzoate;

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

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

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

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

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

The above copolymerizable unsaturated monomers may be used alone or in a mixture of two or more.

[0033]

In the present invention, as the copolymerizable unsaturated monomer, preferred are N-substituted maleimides, aromatic vinyl compounds, unsaturated carboxylates, macromonomers having a mono(meth)acryloyl group at the terminal of a polymer molecular chain. Particularly preferred are N-phenylmaleimide, N-cyclohexylmaleimide, styrene, α-methylstyrene, p-hydroxy-α-methylstyrene, methyl (meth)acrylate, n-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, allyl (meth)acrylate, benzyl (meth)acrylate, glycerol mono(meth)acrylate, 4-hydroxyphenyl (meth)acrylate, ethylene oxide-modified (meth)acrylate of paracumylphenol, polystyrene macromonomer, and polymethylmethacrylate monomer.

[0034]

In the present invention, for example, an alkali-soluble resin copolymerized with a copolymerizable unsaturated monomer having a hydroxyl group such as 2-hydroxyethyl (meth)acrylate is reacted with an unsaturated isocyanate compound such as 2-(meth)acryloyloxyethyl isocyanate, whereby a polymerizable unsaturated bond may be introduced into a side chain of the alkali-soluble resin.

[0035]

The weight average molecular weight (hereinafter may be referred to as "Mw") in terms of polystyrene measured by gel permeation chromatography (GPC; tetrahydrofuran used as an elution solvent) in the alkali-soluble resin of the present invention is preferably 1,000 to 45,000, and particularly 3,000 to 30,000.

Further, the average molecular weight (hereinafter referred to as "Mn") in terms of polystyrene measured by gel permeation chromatography (GPC; tetrahydrofuran used as an elution solvent) in the alkali-soluble resin of the present invention is generally 1,000 to 45,000, and preferably 3,000 to 30,000.

Further, the ratio of Mw to Mn (Mw/Mn) in the alkali-soluble resin of the present invention is preferably 1 to 5, and more preferably 1 to 4.

In this case, when Mw is less than 1,000, a residual film rate or the like of a coating film to be obtained may be decreased, pattern form, heat resistance, or the like may be impaired, or electrical characteristics may become worse, and on the other hand, when Mw exceeds 45,000, definition may be decreased, pattern form may be impaired, or dry foreign matter may easily occur at the time of coating by a slit nozzle method.

[0036]

The alkali-soluble resin of the present invention may be produced by polymerizing, for example, in an appropriate solvent, an unsaturated monomer as a component of the resin in the presence of a radical polymerization initiator such as 2,2'-azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile), and 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile).

[0037]

Further, the alkali-soluble resin in the present invention may be produced by subjecting the unsaturated monomer to the radical polymerization as described above, and then purifying through a reprecipitation method which uses two or more kinds of organic solvents having different polarities. That is, the alkali-soluble resin is purified by: pouring a solution in a good solvent after the polymerization into a

large quantity (generally, 5 to 10 times the volume of the polymer solution) of precipitant (poor solvent), after the solution in the good solvent after the polymerization is subjected to filtration or centrifugal separation as required, to thereby remove insoluble impurities; and then reprecipitating the copolymer. On this occasion, of the impurities remaining in the copolymer solution, the impurities which are soluble in the precipitant remain in the liquid phase and are separated from the purified alkali-soluble resin.

Examples of the combinations of good solvents with precipitants used in the reprecipitation method include diethylene glycol monomethyl ether acetate with n-hexane, methylethylketone with n-hexane, diethylene glycol monomethyl ether acetate with n-heptane, and methylethylketone with n-heptane.

[0038]

Further, the alkali-soluble resin in the present invention may be produced, for example, by subjecting each unsaturated compound as a component of the resin to living radical polymerization in inactive solvents, at a reaction temperature of generally 0 to 150°C and preferably 50 to 120°C, in the presence of the above-mentioned radical polymerization initiators and molecular weight controlling agents, which function as iniferters such as pyrazole-1-dithiocarboxylic

acid cyano(dimethyl) methyl ester, pyrazole-1-dithiocarboxylic acid benzyl ester, tetraethylthiuram disulfide, bis(pyrazole-1-ylthiocarbonyl)disulfide, bis(3-methyl-pyrazole-1-ylthiocarbonyl) disulfide, bis(4-methyl-pyrazole-1-ylthiocarbonyl) disulfide, bis(5-methyl-pyrazole-1-ylthiocarbonyl) disulfide, bis(3,4,5-trimethyl-pyrazole-1-ylthiocarbonyl) disulfide, bis(pyrrole-1-ylthiocarbonyl) disulfide, or bisthiobenzoyl disulfide.

[0039]

In addition, the alkali-soluble resin in the present invention may be produced by subjecting each unsaturated monomer as a component of the resin to radical polymerization in an appropriate solvent in the presence of the above-mentioned radical polymerization initiator and a polyvalent thiol compound which functions as a chain transfer agent. Here, the polyvalent thiol compound refers to a compound having two or more thiol groups in one molecule. Examples of the polyvalent thiol compound include trimethylolpropane tris(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptopropionate), tetraethylene glycol bis(3-mercaptopropionate), dipentaerythritol hexakis(3-mercaptopropionate), pentaerythritol tetrakis(thioglycolate), 1,4-bis(3-mercaptobutyryloxy)butane, pentaertythritol tetrakis(3-mercaptobutyrate), and 1,3,5-tris(3-

marcaptobutyloxyethyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione.

[0040]

The alkali-soluble resin may be used alone or in a mixture of two or more.

In the present invention, the content of the alkali-soluble resin is generally 10 to 1,000 parts by weight and preferably 20 to 500 parts by weight with respect to 100 parts by weight of the colorant (A). In this case, when the content of the alkali-soluble resin is less than 10 parts by weight, for example, alkali development property may decrease, and film residue or scum may occur on the unexposed part of the substrate or on the light-shielding layer. On the other hand, when the content of the alkali-soluble resin exceeds 1,000 parts by weight, it may become difficult to achieve a target color density as a thin film, because the concentration of the pigment is relatively decreased.

[0041]

-Polyfunctional monomer (C)-

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

Examples of the polyfunctional monomer include:

di(meth)acrylates of 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 a polyalcohol having a valency of 3 or more such as glycerin, trimethylolpropane, pentaerythritol, and dipentaerythritol, or dicarboxylate-modified products thereof;

oligo(meth)acrylates such as polyester, an epoxy resin, a urethane resin, an alkyd resin, a silicone resin, and a spirane resin;

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

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

[0042]

Of those polyfunctional monomers, preferred are poly(meth)acrylates of polyhydric alcohol having a valency of 3 or more, and dicarboxylic acid modified products thereof, specifically, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, pentaerythritol triacrylate, pentaerythritol trimethacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, dipentaerythritol pentaacrylate, dipentaerythritol pentamethacrylate, dipentaerythritol hexaacrylate,

dipentaerythritol hexamethacrylate, a monoesterified product of pentaerythritol triacrylate and succinic acid, a monoesterified product of pentaerythritol trimethacrylate and succinic acid, a monoesterified product of dipentaerythritol pentaacrylate and succinic acid, and a monoesterified product of dipentaerythritol pentamethacrylate and succinic acid, and the like. Particularly preferred are trimethylol propane triacrylate, pentaerythritol triacrylate, dipentaerythritol pentaacrylate, dipentaerythritol hexaacrylate, a monoesterified product of pentaerythritol triacrylate and succinic acid, and a monoesterified product of dipentaerythritol pentaacrylate and succinic acid, because they are excellent in strength and surface smoothness of a coloring layer and hardly generate scum, film residue, or the like on the unexposed part of the substrate and on the light-shielding layer.

The polyfunctional monomers may be used alone or in a mixture of two or more.

[0043]

The content of the polyfunctional monomer in the present invention is generally 5 to 500 parts by weight and preferably 20 to 300 parts by weight with respect to 100 parts by weight of the alkali-soluble resin (B). In this case, when the amount of the polyfunctional monomer for use is less than 5 parts by

weight, strength and surface smoothness of the pixel tend to be decreased, and on the other hand, when the amount of the polyfunctional monomer for use exceeds 500 parts by weight, for example, alkali development property tends to decrease, and scum, film residue, or the like tends to occur easily on the unexposed part of the substrate or on the light-shielding layer.

[0044]

In the present invention, a part of the polyfunctional monomer may be replaced by a monofunctional monomer having one polymerizable unsaturated bond.

Examples of the monofunctional monomers include mono[(meth)acryloyloxyalkyl]esters of polycarboxylic acids having a valency of two or more such as mono[2-(meth)acryloyloxyethyl]succinate and mono[2-(meth)acryloyloxyethyl]phthalate; mono(meth)acrylates of polymers having a carboxyl group and a hydroxyl group at both terminals such as ω-carboxy polycaprolactone mono(meth)acrylate; N-vinyl nitrogen-containing heterocyclic compounds such as N-vinyl succinimide, N-vinyl pyrrolidone, N-vinyl phthalimide, N-vinyl-2-piperidone, N-vinyl-ε-caprolactam, N-vinyl pyrrole, N-vinyl pyrrolidine, N-vinyl imidazole, N-vinyl imidazolidine, N-vinyl indole, N-vinyl indoline, N-vinyl benzimidazole, N-vinyl carbazole, N-vinyl piperidine, N-vinyl

piperazine, N-vinyl morpholine, and N-vinyl phenoxazine; N-(meth)acryloylmorpholine; and, as commercially available products, M-5400 and M-5600 (trade names, manufactured by Toagosei Co., Ltd.).

Those monofunctional monomers may be used alone or in a mixture of two or more.

[0045]

The content proportion of the monofunctional monomer in the present invention is preferably 90 wt% or less and more preferably 50 wt% or less with respect to the total amount of the polyfunctional monomer and the monofunctional monomer. In this case, when the proportion of the monofunctional monomer to be used exceeds 90 wt%, strength and surface smoothness of the pixel tend to decrease.

[0046]

-Photopolymerization initiator (D)-

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

Examples of the photopolymerization initiator include acetophenone-based compounds, biimidazole-based compounds,

triazine-based compounds, O-acyloxime-based compounds, onium salt-based compounds, benzoin-based compounds, benzophenone-based compounds, α-diketone-based compounds, polynuclear quinone-based compounds, xanthone-based compounds, and diazo-based compounds.

[0047]

In the present invention, the photopolymerization initiators may be used alone or in a mixture of two or more, and as the photopolymerization initiator in the present invention, at least one kind selected from the group consisting of an acetophenone-based compound, a biimidazole-based compound, a triazine-based compound, and an O-acryloxime-based compound is preferred.

[0048]

In the present invention, the content of the photopolymerization initiator is generally 0.01 to 120 parts by weight and preferably 1 to 100 parts by weight with respect to 100 parts by weight of the polyfunctional monomer (C). In this case, when the content of the photopolymerization initiator is less than 0.01 part by weight, curing by exposure may become insufficient, with the result that it may become difficult to obtain a color filter in which a coloring layer pattern is formed in accordance with a predetermined arrangement, and on the other hand, when the content of the

photopolymerization initiator exceeds 120 parts by weight, the formed coloring layer tends to fall off easily from the substrate at the time of development.

[0049]

Of the preferable photopolymerization initiators in the present invention, specific examples of the acetophenone-based compounds include 2-hydroxy-2-methyl-1-phenylpropane-1-one, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butane-1-one, 2-(4-methylbenzyl)-2-(dimethylamino)-1-(4-morpholinophenyl)butane-1-one, 1-hydroxy cyclohexyl/phenyl ketone, 2,2-dimethoxy-1,2-diphenylethane-1-one, and 1,2-octanedione.

Of those acetophenone-based compounds, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butane-1-one, 2-(4-methylbenzyl)-2-(dimethylamino)-1-(4-morpholinophenyl)butane-1-one, and 1,2-octanedione are particularly preferable.

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

[0050]

In the present invention, in the case where the acetophenone-based compound is used as the photopolymerization initiator, the content of the acetophenone-based compound is

generally 0.01 to 80 parts by weight, preferably 1 to 70 parts by weight, and more preferably 1 to 60 parts by weight with respect to 100 parts by weight of the polyfunctional monomer (C). In this case, when the content of the acetophenone-based compound is less than 0.01 part by weight, curing by exposure may become insufficient, with the result that it may become difficult to obtain a color filter in which a coloring layer pattern is formed in accordance with a predetermined arrangement, and on the other hand, when the content of the acetophenone-based compound exceeds 80 parts by weight, the formed coloring layer tends to fall off easily from the substrate at the time of development.

[0051]

In addition, specific examples of the biimidazole-based compound include 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxycarbonylphenyl)-1,2'-biimidazole, 2,2'-bis(2-bromophenyl)-4,4',5,5'-tetrakis(4-ethoxycarbonylphenyl)-1,2'-biimidazole, 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole, 2,2'-bis(2,4-dichlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole, 2,2'-bis(2,4,6-trichlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole, 2,2'-bis(2-bromophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole, 2,2'-bis(2,4-dibromophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole, and 2,2'-bis(2,4,6-tribromophenyl)-4,4',5,5'-tetraphenyl-1,2'-

biimidazole.

[0052]

Of those biimidazole-based compounds, 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole, 2,2'-bis(2,4-dichlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole, and 2,2'-bis(2,4,6-trichlolophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole are preferred, and 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole is particularly preferred.

[0053]

Those biimidazole-based compounds have excellent solubility to a solvent and do not generate foreign matters such as undissolved matter and precipitate. In addition, the biimidazole-based compounds have high sensitivity, and hence sufficiently allowing a curing reaction to proceed with exposure of a small amount of energy, and the curing reaction does not proceed at an unexposed part. Therefore, a coating film after exposure is clearly divided into a cured part which is insoluble to a developer and an uncured part which has high solubility to the developer. Thus, a high-definition color filter may be formed, in which coloring layer pattern having no undercut is formed in accordance with a predetermined arrangement.

The biimidazole-based compounds may be used alone or in a

mixture of two or more.

[0054]

In the present invention, in the case where the biimidazole-based compound is used as the photopolymerization initiator, the content of the biimidazole-based compound is generally 0.01 to 40 parts by weight, preferably 1 to 30 parts by weight, and more preferably 1 to 20 parts by weight with respect to 100 parts by weight of the total of the polyfunctional monomers (C). In this case, when the content of the biimidazole-based compound is less than 0.01 part by weight, curing by exposure may become insufficient, with the result that it may become difficult to obtain a color filter in which a coloring layer pattern is formed in accordance with a predetermined arrangement, and on the other hand, when the content of the biimidazole-based compound exceeds 40 parts by weight, the formed coloring layer tends to fall off easily from the substrate and a film on the surface of the coloring layer tends to get rough easily, at the time of development.

[0055]

In the present invention, in the case where the biimidazole-based compounds are used as the photopolymerization initiators, the following hydrogen donor is preferably used in combination therewith in terms of further improving sensitivity.

The "hydrogen donor" as used herein refers to a compound which may donate a hydrogen atom to a radical that is generated from the biimidazole-based compounds by exposure.

Mercaptan-based compounds and amine-based compounds defined below are preferred as the hydrogen donor in the present invention.

[0056]

The mercaptan-based compounds are each a compound (hereinafter referred to as "mercaptan-based hydrogen donor") which has a benzene ring or a heterocyclic ring as a mother nucleus, and has 1 or more, preferably 1 to 3, or more preferably 1 or 2 mercapto groups which are each directly bonded to the mother nucleus.

The amine-based compounds are each a compound (hereinafter referred to as "amine-based hydrogen donor") which has a benzene ring or a heterocyclic ring as a mother nucleus, and has 1 or more, preferably 1 to 3, or more preferably 1 or 2 amino groups which are each directly bonded to the mother nucleus.

Note that those hydrogen donors may also have both the mercapto groups and the amino groups at the same time.

[0057]

Hereinafter, the hydrogen donor is described more specifically.

The mercaptan-based hydrogen donor may have one or more benzene rings or one or more heterocyclic rings, and may have both the benzene ring and the heterocyclic ring. When two or more rings are contained in the mercaptan-based hydrogen donor, the rings may or may not form a fused ring.

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

Further, any moiety other than the mercapto group in the mercaptan-based hydrogen donor may be substituted with groups such as a carboxyl group, an alkoxycarbonyl group, a substituted alkoxycarbonyl group, a phenoxycarbonyl group, a substituted phenoxycarbonyl group, or a nitrile group.

[0058]

Specific examples of the mercaptan-based hydrogen donors include 2-mercaptobenzothiazole, 2-mercaptobenzooxazole, 2-mercaptobenzoimidazole, 2,5-dimercapto-1,3,4-thiadiazole, and

2-mercapto-2,5-dimethylaminopyridine.

Of those mercaptan-based hydrogen donors, 2-mercaptobenzothiazole and 2-mercaptobenzooxazole are preferable, and 2-mercaptobenzothiazole is particularly preferable.

[0059]

The amine-based hydrogen donor may have one or more benzene rings or one or more heterocyclic rings, and may have both the benzene ring and the heterocyclic ring. When two or more rings are contained in the amine-based hydrogen donor, the rings may or may not form a fused ring.

Further, in the amine-based hydrogen donor: one or more animo groups may be substituted with an alkyl group or a substituted alkyl group; and any moiety other than the amino group may be substituted with groups such as a carboxyl group, an alkoxycarbonyl group, a substituted alkoxycarbonyl group, a phenoxycarbonyl group, a substituted phenoxycarbonyl group, or a nitrile group.

[0060]

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

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

Note that even in the case where the photopolymerization initiator is other than the biimidazole-based compounds, the amine-based hydrogen donors each have a function as a sensitizer.

[0061]

In the present invention, the hydrogen donors may be used alone or in a mixture of two or more, and it is preferred to use one or more kinds of the mercaptan-based hydrogen donors and one or more kinds of the amine-based hydrogen donors in combination, in terms of preventing the formed coloring layer from being fallen off from the substrate at the time of development and of the coloring layer having high strength and sensitivity.

Specific examples of the combination of the mercaptane-based hydrogen donor and the amine-based hydrogen donor include 2-mercaptobenzothiazole/4,4'-bis(dimethylamino)benzophenone, 2-mercaptobenzothiazole/4,4'-bis(diethylamino)benzophenone, 2-mercaptobenzooxazole/4,4'-bis(dimethylamino)benzophenone, and 2-mercaptobenzooxazole/4,4'-bis(diethylamino)benzophenone.

Examples of the more preferred combination include 2-mercaptobenzothiazole/4,4'-bis(diethylamino)benzophenone and 2-mercaptobenzooxazole/4,4'-bis(diethylamino)benzophenone. Examples of the particularly preferred combination include 2-mercaptobenzothiazole/4,4'-bis(diethylamino)benzophenone.

Further, the weight ratio of the mercaptan-based hydrogen donor to the amine-based hydrogen donor obtained when combining the mercaptan-based hydrogen donor and the amine-based hydrogen donor is generally 1:1 to 1:4, and preferably 1:1 to 1:3.

[0062]

In the present invention, when a hydrogen donor is used in combination with the biimidazole-based compound, the content of the hydrogen donor is preferably 0.01 to 40 parts by weight, more preferably 1 to 30 parts by weight, and particularly preferably 1 to 20 parts by weight with respect to 100 parts by weight of the total of the polyfunctional monomers (C). In this case, when the content of the hydrogen donor is less than 0.01 part by weight, an effect for improving sensitivity tends to decrease, and on the other hand, when the content of the hydrogen donor exceeds 40 parts by weight, the formed coloring layer tends to fall off easily from the substrate at the time of development.

[0063]

Note that in the case where the amine-based hydrogen donors are used in combination with the photopolymerization initiator other than the biimidazole-based compounds, such as the acetophenone-based compounds, the amine-based hydrogen donors may function as a sensitizer. When the amine-based hydrogen donors are used as a sensitizer, the content thereof is generally 300 parts by weight or less, preferably 200 parts by weight or less, and more preferably 100 parts by weight or less with respect to 100 parts by weight of the photopolymerization initiator other than the biimidazole-based compounds. It is desirable that the lower limit of the content be preferably 2 parts by weight and more preferably 5 parts by weight, because when the content is too small, it becomes difficult to obtain a sufficient effect.

[0064]

In addition, specific examples of the triazine-based compound include triazine-based compounds having a halomethyl group such as 2,4,6-tris(trichloromethyl)-s-triazine, 2-methyl-4,6-bis(trichloromethyl)-s-triazine, 2-[2-(5-methylfuran-2-yl)ethenyl]-4,6-bis(trichloromethyl)-s-triazine, 2-[2-(furan-2-yl)ethenyl]-4,6-bis(trichloromethyl)-s-triazine, 2-[2-(4-diethylamino-2-methylphenyl)ethenyl]-4,6-bis(trichloromethyl)-s-triazine, 2-[2-(3,4-dimethoxyphenyl)ethenyl]-4,6-bis(trichloromethyl)-s-triazine,

2-(4-methoxyphenyl)-4,6-bis(trichloromethyl)-s-triazine, 2-(4-ethoxystyryl)-4,6-bis(trichloromethyl)-s-triazine, and 2-(4-n-butoxyphenyl)-4,6-bis(trichloromethyl)-s-triazine.

[0065]

Of those triazine-based compounds, 2-[2-(3,4-dimethoxyphenyl)ethenyl]-4,6-bis(trichloromethyl)-s-triazine is particularly preferable.

The triazine-based compounds may be used alone or in a mixture of two or more.

[0066]

In the present invention, in the case where the triazine-based compound is used as the photopolymerization initiator, the content of the triazine-based compound is preferably 0.01 to 40 parts by weight, more preferably 1 to 30 parts by weight, and particularly preferably 1 to 20 parts by weight with respect to 100 parts by weight of the polyfunctional monomer (C). In this case, when the content of the triazine-based compound is less than 0.01 part by weight, curing by exposure may become insufficient, with the result that it may become difficult to obtain a color filter in which a coloring layer pattern is formed in accordance with a predetermined arrangement, and on the other hand, when the content of the triazine-based compound exceeds 40 parts by weight, the formed coloring layer tends to fall off easily from the substrate at

the time of development.

[0067]

Further, examples of the O-acyloxime-based compounds include 1,2-octanedion-1-[4-(phenylthio)phenyl]-2-(O-benzoyloxime); 1-[9-ethyl-6-benzoyl-9H-carbazol-3-yl]-nonane-1,2-nonane-2-oxime-O-benzoate; 1-[9-ethyl-6-benzoyl-9H-carbazol-3-yl]-nonane-1,2-nonane-2-oxime-O-acetate; 1-[9-ethyl-6-benzoyl-9H-carbazol-3-yl]-pentane-1,2-pentane-2-oxime-O-acetate; 1-[9-ethyl-6-benzoyl-9H-carbazol-3-yl]-octane-1-one oxime-O-acetate; 1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-ethane-1-one oxime-O-benzoate; 1-[9-ethyl-6-(1,3,5-trimethylbenzoyl)-9H-carbazol-3-yl]ethane-1-one oxime-O-benzoate; 1-[9-butyl-6-(2-ethylbenzoyl)-9H-carbazol-3-yl]-ethane-1-one oxime-O-benzoate; ethanone, 1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-, 1-(O-acetyloxime); and ethanone, 1-[9-ethyl-6-[2-methyl-4-(2,2-dimethyl-1,3-dioxolanyl)methoxybenzoyl]-9H-carbazol-3-yl]-, 1-(O-acetyloxime).

[0068]

Of those O-acyloxime-based compounds, 1,2-octanedion-1-[4-(phenylthio)phenyl]-2-(O-benzoyloxime); ethanone, 1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-, 1-(O-acetyloxime); and ethanone, 1-[9-ethyl-6-[2-methyl-4-(2,2-dimethyl-1,3-dioxolanyl)methoxybenzoyl]-9Hcarbazol-3-yl]-, 1-

(O-acetyloxime) are preferable.

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

[0069]

In the present invention, in the case where the O-acyloxime-based compound is used as the photopolymerization initiator, the content of the O-acyloxime-based compound is preferably 0.01 to 60 parts by weight, more preferably 1 to 50 parts by weight, and particularly preferably 1 to 40 parts by weight with respect to 100 parts by weight of the polyfunctional monomer (C). In this case, when the content of the O-acyloxime-based compound is less than 0.01 part by weight, curing by exposure may become insufficient, with the result that it may become difficult to obtain a color filter in which a coloring layer pattern is formed in accordance with a predetermined arrangement, and on the other hand, when the content of the O-acyloxime-based compound exceeds 60 parts by weight, the formed coloring layer tends to fall off easily from the substrate at the time of development.

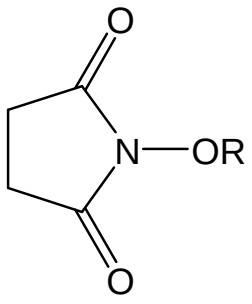
[0070]

-Component (E)-

By incorporating the component (E) into the radiation-sensitive composition of the present invention, the radiation sensitivity of the radiation-sensitive composition can be

enhanced remarkably and, in addition, the generation of water unevenness can be prevented. The component (E) is a compound having a structure represented by the formula (1), and is preferably a compound having a structure represented by any one of the following formulae (2) to (10):

[0071]



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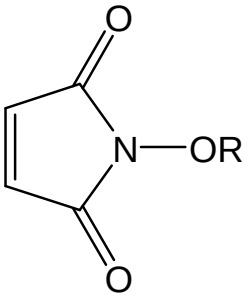

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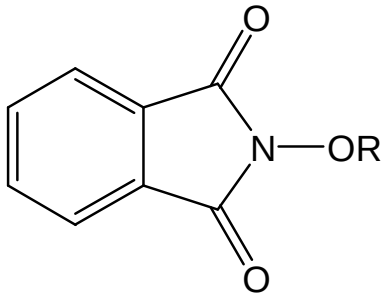

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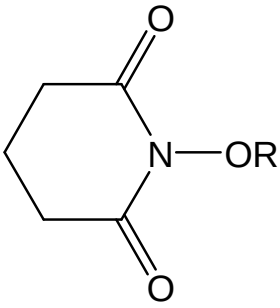

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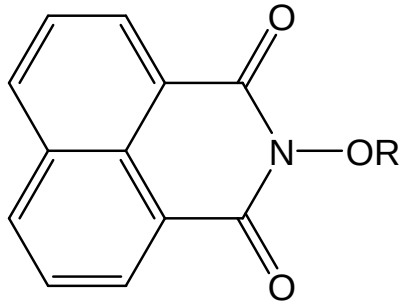

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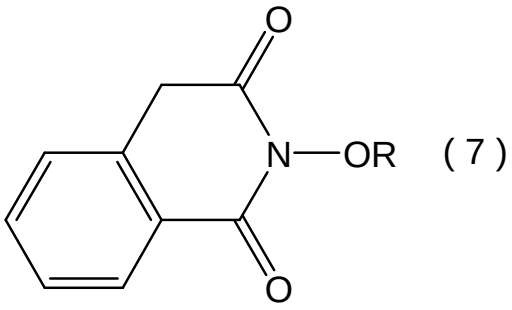

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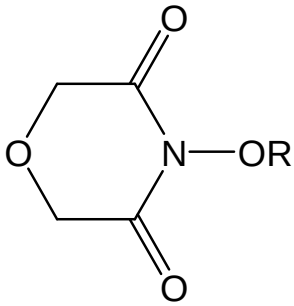

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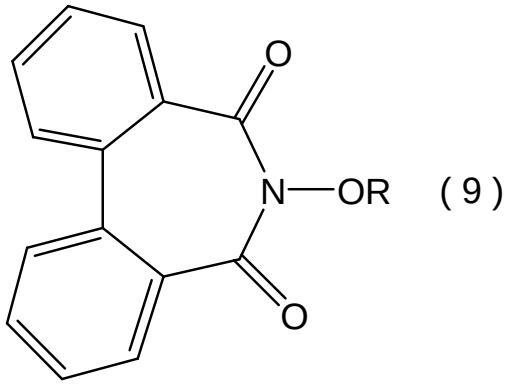

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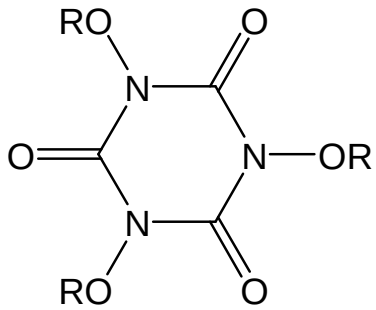


(10)

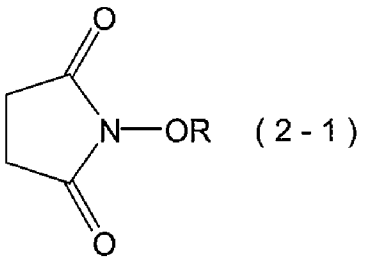
[0072]

where: R's each have the same meaning as R in the formula (1).

[0073]

Examples of the above compound include: compounds represented by the following formulae (2-1) to (2-10) as the compound having the structure represented by the formula (2); compounds represented by the following formulae (3-1) to (3-3) as the compound having the structure represented by the formula (3); compounds represented by the following formulae (4-1) to (4-7) as the compound having the structure represented by the formula (4); compounds represented by the following formulae (5-1) and (5-2) as the compound having the structure represented by the formula (5); and compounds represented by the following formulae (6-1), (7-1), (8-1), (9-1), and (10-1) as the compounds having the structure represented by the formulae (6) to (10), respectively.

[0074]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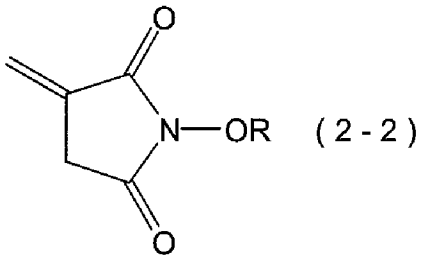
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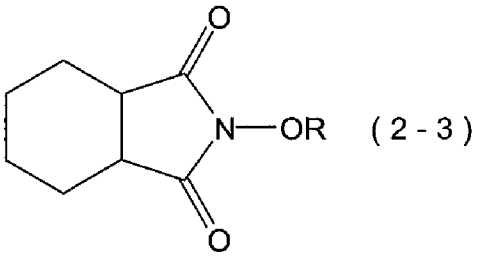
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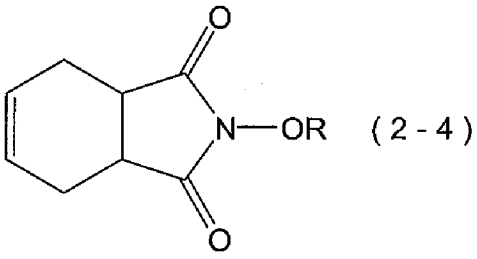
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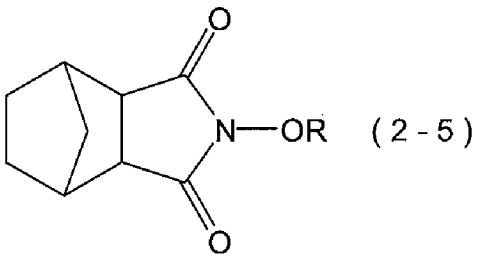
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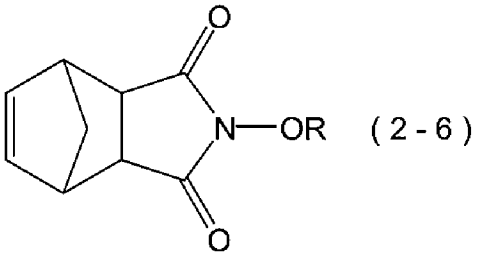
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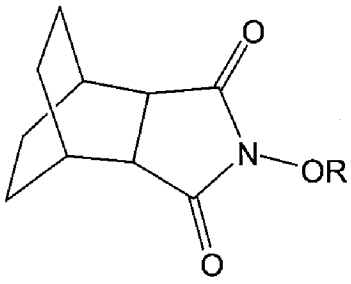
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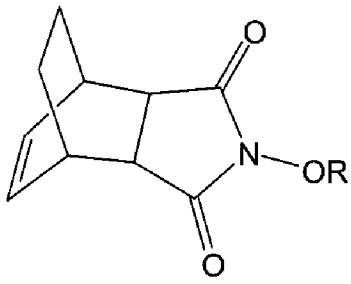
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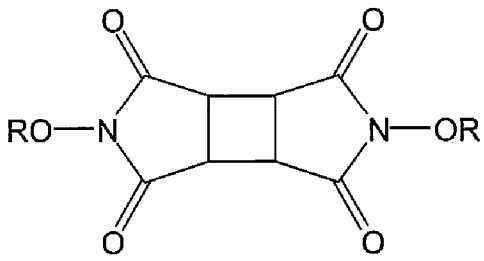
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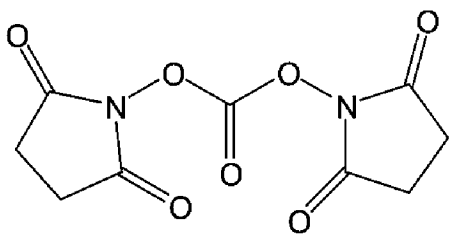
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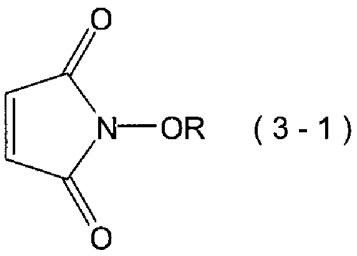
[0075]



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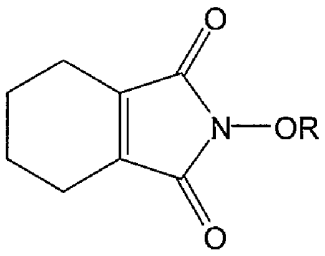

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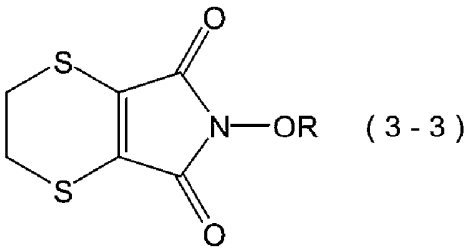

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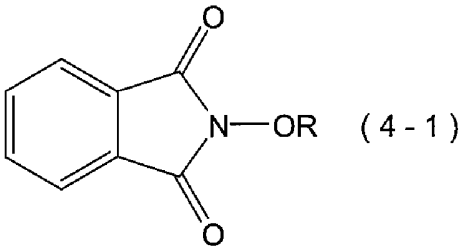

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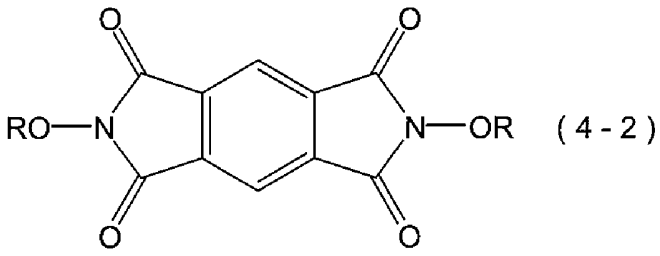

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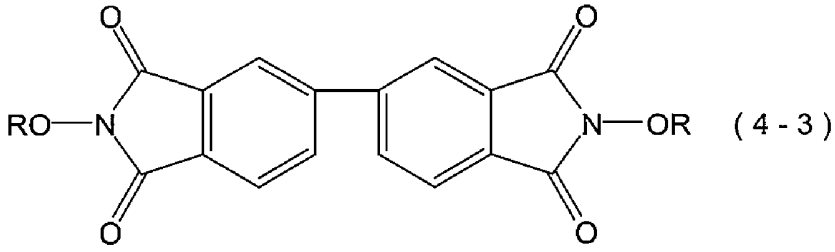

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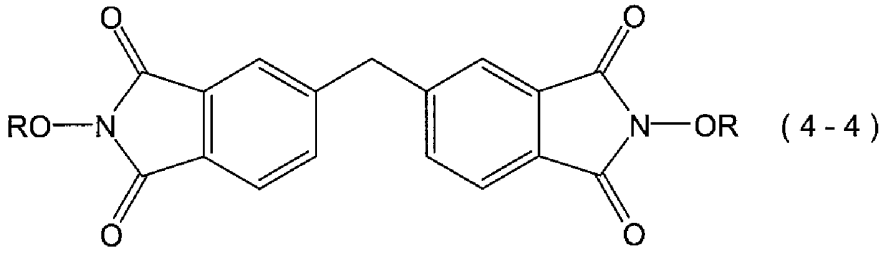

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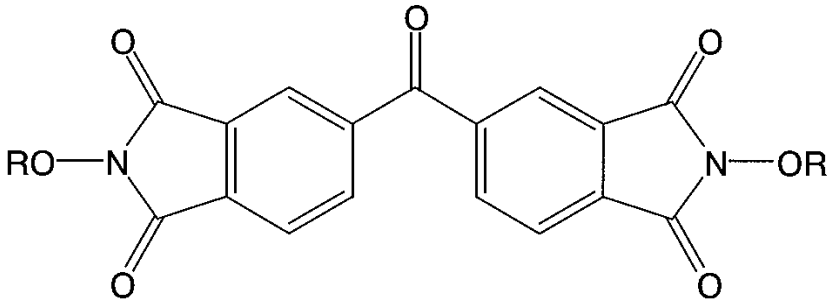

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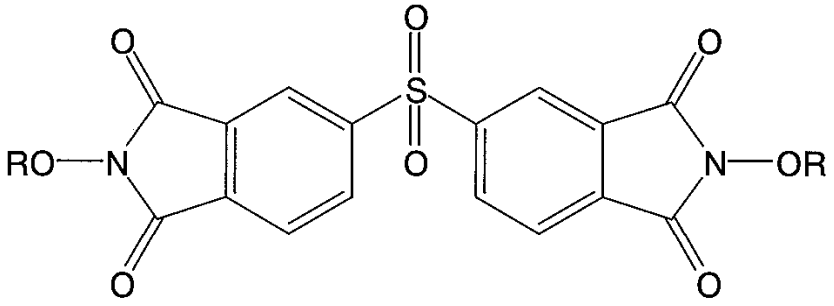

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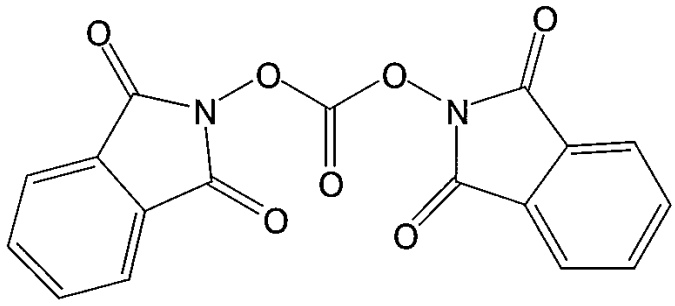

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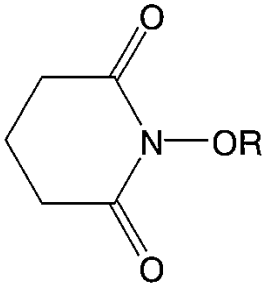

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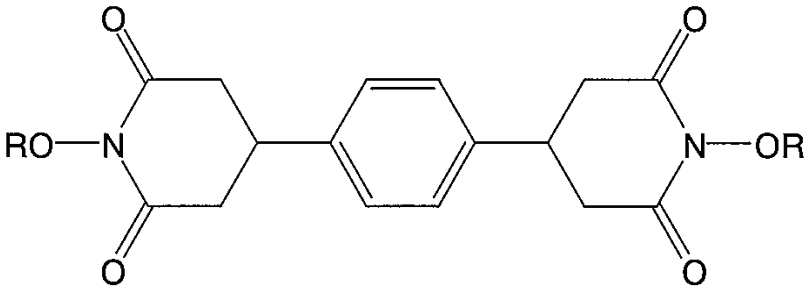

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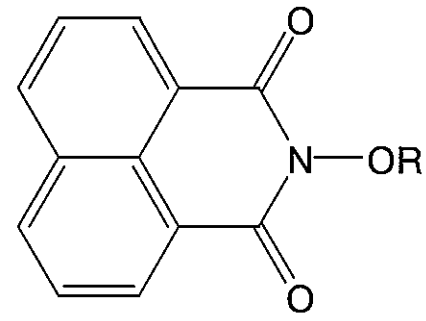
[0077]



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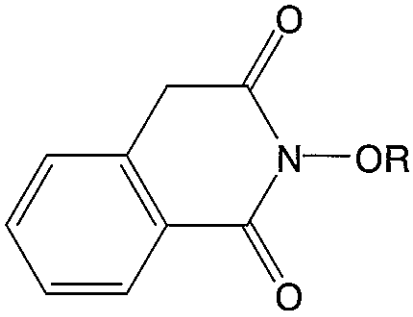

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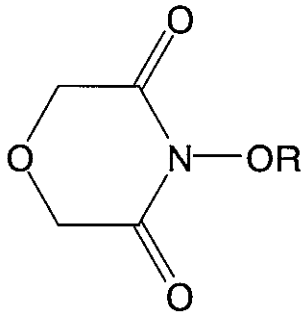

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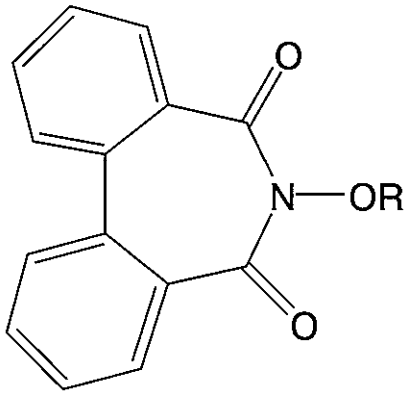

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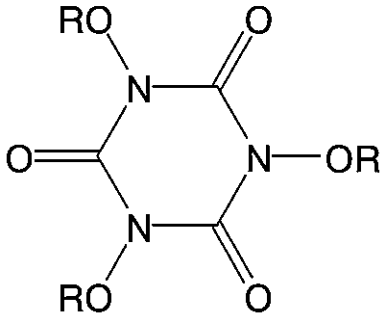


(10-1)

[0078]

where: R's each have the same meaning as R in the formula (1).

Examples of the secondary or tertiary alkyl group having 3 to 30 carbon atoms represented by R in the formula include an isopropyl group, a 2-butyl group, a t-butyl group, a 2-pentyl group, and a t-pentyl group;

examples of the cyclic alkyl group having 5 to 12 carbon

atoms represented by R in the formula include a cyclopentyl group, a cyclohexyl group, and a cyclododecyl group;

examples of the aralkyl group having 7 to 30 carbon atoms represented by R include a benzyl group, an α-methylbenzyl group, and a cinnamyl group; and

examples of the acyl groups having 2 to 30 carbon atoms represented by R include an acetyl group, a propionyl group, a butyryl group, a benzoyl group, an acetylacetyl group (acetonylcarbonyl group), a cyclohexylcarbonyl group, an acryloyl group, a methoxycarbonyl group, and a benzyloxycarbonyl group. As R in the formula, a hydrogen atom, an acetyl group, a benzoyl group, an allyl group, a benzyl group, or a t-butyl group is preferred.

[0079]

As the component (E) contained in the radiation sensitive composition of the present invention, compounds represented by the above formula (2-1), (2-5), (2-8), (4-1), (6-1), or (10-1) is preferably used. N-hydroxysuccinic imide, N-hydroxy-5-norbornene-2,3-dicarboxyimide, N-hydroxyphthal imide, N-acetoxyphthal imide, N-benzoyloxyphthal imide, N-hydroxy-1,8-naphthal imide or trihydroxyimide cyanuric acid is more preferably used, and N-hydroxysuccuinic imide, N-hydroxyphthal imide, N-acetoxyphthal imide, N-hydroxy-1,8-naphthal imide, or trihydroxyimide cyanuric acid is particularly preferred.

In the radiation-sensitive composition of the present invention, the components (E) may be used alone or in a mixture of two or more.

The content of the component (E) in the radiation-sensitive composition of the present invention is preferably 0.05 to 20 parts by weight and more preferably 0.2 to 10 parts by weight with respect to 100 parts by weight of the alkali-soluble resin (B). The component (E) is preferably used at the above proportion, because the radiation sensitivity and the water unevenness-preventing effect of the radiation-sensitive composition can be further enhanced and, in addition, the solubility of the radiation-sensitive composition to a solvent can be maintained in a suitable range.

[0080]

-Additive-

The radiation-sensitive composition of the present invention contains the above components (A) to (E) and may also contain other additives as required.

Here, examples of the other additives include: fillers such as glass and alumina; polymer compounds such as polyvinyl alcohol and poly(fluoroalkylacrylate); surfactants such as nonionic surfactants, cationic surfactants, and anionic surfactants; adhesion promoting agents such as vinyltrimethoxy silane, vinyltriethoxy silane, vinyltris(2-

methoxyethoxy)silane, N-(2-aminoethyl)-3-aminopropylmethyldimethoxy silane, N-(2-aminoethyl)-3-aminopropyltrimethoxy silane, 3-aminopropyltriethoxy silane, 3-glycidoxypropyltrimethoxy silane, 3-glycidoxypropylmethyldimethoxy silane, 2-(3,4-epoxycylohexyl)ethyltrimethoxy silane, 3-chloropropylmethyldimethoxy silane, 3-chloropropyltrimethoxy silane, 3-methacryloyloxypropyltrimethoxy silane, and 3-mercaptopropyltrimethoxy silane; antioxidants such as 2,2-thiobis(4-methyl-6-t-butylphenol) and 2,6-di-t-butylphenol; UV absorbers such as 2-(3-t-butyl-5-methyl-2-hydroxyphenyl)-5-chlorobenzotriazole, and alkoxybenzophenones; aggregation inhibitors such as sodium polacrylate; and alkali solubility improvers such as malonic acid, adipic acid, itaconic acid, citraconic acid, fumaric acid, and mesaconic acid.

[0081]

Solvent

The radiation-sensitive composition for forming a coloring layer of the present invention contains the above components (A) to (E) as essential components, and contains the above additive component as required. The radiation-sensitive composition is generally prepared as a liquid composition by compounding a solvent.

The solvent may be appropriately selected and used as

long as the solvent disperses or dissolves the components (A) to (E) and the additive component which compose the radiation-sensitive composition, does not react with those components, and has appropriate volatility.

[0082]

Examples of the solvent include:

(poly)alkylene glycol monoalkyl ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol mono-n-propyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-propyl ether, diethylene glycol mono-n-butyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol mono-n-propyl ether, propylene glycol mono-n-butyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol mono-n-propyl ether, dipropylene glycol mono-n-butyl ether, tripropylene glycol monomethyl ether, and tripropylene glycol monoethyl ether;

(poly)alkylene glycol monoalkyl ether acetates such as ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, propylene

glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, 3-methoxybutyl acetate, and 3-methyl-3-methoxybutyl acetate;

other ethers such as diethylene glycol dimethyl ether, diethylene glycol methyl ethyl ether, diethylene glycol diethyl ether, and tetrahydrofuran;

ketones such as methyl ethyl ketone, cyclohexanone, 2-heptanone, and 3-heptanone;

[0083]

lactic acid alkyl esters such as methyl lactate and ethyl lactate;

other esters such as ethyl 2-hydroxy-2-methyl-propionate, methyl 3-methoxy-propionate, ethyl 3-methoxy-propionate, methyl 3-ethoxy-propionate, ethyl 3-ethoxy-propionate, ethyl ethoxy acetate, ethyl hydroxy acetate, methyl 2-hydroxy-3-methyl butanoate, 3-methyl-3-methoxybutyl propionate, ethyl acetate, n-propyl acetate, i-propyl acetate, n-butyl acetate, i-butyl acetate, n-amyl formate, i-amyl acetate, n-butyl propionate, ethyl butyrate, n-propyl butyrate, i-propyl butyrate, n-butyl butyrate, methyl pyruvate, ethyl pyruvate, n-propyl pyruvate, methyl acetoacetate, ethyl acetoacetate, and ethyl 2-oxobutanoate;

aromatic hydrocarbons such as toluene and xylene; and

amides or lactams such as N,N-dimethyl formamide, N,N-

dimethyl acetoamide, and N-methylpyrrolidone.

[0084]

Of those solvents, from the viewpoints of solubility, pigment dispersability, and coating property, preferred are propylene glycol monomethyl ether, ethylene glycol monomethyl ether acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, 3-methoxybutyl acetate, diethylene glycol dimethyl ether, diethylene glycol methyl ethyl ether, cyclohexanone, 2-heptanone, 3-heptanone, ethyl lactate, ethyl 3-methoxy-propionate, methyl 3-ethoxy-propionate, ethyl 3-ethoxy-propionate, 3-methyl-3-methoxybutyl propionate, n-butyl acetate, i-butyl acetate, n-amyl formate, i-amyl acetate, n-butyl propionate, ethyl butyrate, i-propyl butyrate, n-butyl butyrate, and ethyl pyruvate.

The solvent may be used alone or in a mixture of two or more.

[0085]

In addition, in combination with the solvent, a solvent having a high boiling point such as benzyl ethyl ether, di-n-hexyl ether, acetonyl acetone, 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.

Those solvents each having a high boiling point may be used alone or in a mixture of two or more.

[0086]

The content of the solvent is not particularly limited, but from the viewpoint of spreadability, stability, or the like of the radiation-sensitive composition to be obtained, the total concentration of respective components excluding the solvent for the composition is 5 to 50 wt% is generally preferred, and the total concentration of respective components excluding the solvent for the composition is 10 to 40 wt% is preferably desired.

[0087]

Method of forming color filter

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

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

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

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

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

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

Hereinafter, those steps will be described sequentially.

[0088]

-Step (1)-

First, a light-shielding layer (black matrix) is formed on the surface of a substrate as required so as to mark off a portion on which a pixel is formed. The radiation-sensitive composition of the present invention which contains a colorant (A) in red color is applied, generally as a liquid composition, onto the substrate and then pre-baked to evaporate and remove a solvent, thereby forming a coating film.

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

Further, those substrates may be subjected to an appropriate pretreatment such as chemical treatment with a silane coupling agent or the like, plasma treatment, ion plating, sputtering, chemical vapor deposition, or vacuum deposition, as desired.

When the liquid composition is applied onto the substrate, there may be employed an appropriate coating method such as a

spin coating method, a cast coating method, a roll coating method, or a coating method using a slit-die coater, and the spin coating method and the coating method using a slit-die coater are preferred.

The pre-baking is performed generally at 70 to 110°C for about 2 to 4 minutes. Note that, according to the radiation-sensitive composition of the present invention, a pixel and a black matrix can be formed even when the step of pre-baking is omitted.

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

[0089]

-Step (2)-

After that, at least a part of the formed coating film is exposed to light. In this case, the film is generally exposed to light through a photomask having a predetermined pattern at the time of exposing to light a part of the coating film.

As radiation used in exposure, there may be used, for example, visible light ray, ultraviolet ray, far ultraviolet ray, electron ray, or X-ray, and radiation having a wavelength ranging from 190 to 450 nm is preferred.

The exposure dose of radiation is generally 10 to 10,000 J/m^2. According to the radiation-sensitive composition of the

present invention, there can be formed a pixel free from water unevenness even in an exposure dose of 400 J/m^2 or less.

[0090]

-Step (3)-

After that, the coating film is developed by using a developer, or preferably an alkalin developer, to thereby dissolve and remove an unexposed part of the coating film.

Examples of the alkalin developer preferably include an aqueous solution of sodium carbonate, sodium hydroxide, potassium hydroxide, tetramethyl ammonium hydrooxide, choline, 1,8-diazabicyclo-[5.4.0]-7-undecane, or 1,5-diazabicyclo-[4.3.0]-5-nonene.

The alkalin developer may be also added with a water-soluble organic solvent such as methanol or ethanol, a surfactant, or the like in an appropriate amount. It should be noted that washing is generally performed with water after alkali development. According to the radiation-sensitive composition of the present invention, there can be formed a pixel free from generating water unevenness thereon after the water washing.

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

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

[0091]

-Step (4)-

After that, the coating film after development is post-baked, to thereby obtain a substrate in which a red pixel pattern with a cured product of the radiation-sensitive composition is formed in a predetermined arrangement.

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

The film thickness of the thus formed pixel is generally 0.5 to 5.0 μm and preferably 1.0 to 3.0 μm.

[0092]

Further, a green radiation-sensitive composition which contains a colorant (A) in green color is used and the steps (1) to (4) are repeated, whereby a green pixel pattern is formed on the same substrate. In addition, a blue radiation-sensitive composition which contains a colorant (A) in blue color is used and the steps (1) to (4) are repeated, whereby a blue pixel pattern is formed on the same substrate. Thus, pixel arrays in which the pixel patterns having three primary colors of red, green, and blue are formed in a predetermined arrangement can be formed on the substrate. Note that the order of forming each color pixel can be selected

appropriately.

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

[0093]

Color filter

The color filter of the present invention includes the pixel and/or the black matrix formed from the radiation-sensitive composition of the present invention as described above.

[0094]

Color liquid crystal display device

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

Further, as one embodiment of the color liquid crystal display device of the present invention, the radiation-sensitive composition for forming a coloring layer of the present invention may be used to form the pixel and/or the black matrix on a thin film transistor substrate array as described above, thereby producing a color liquid crystal display device having outstanding properties.

Effect of the Invention

[0095]

According to the radiation-sensitive composition of the

present invention, a high-quality pixel can be formed even with low exposure dose, in which water unevenness does not occur, and also chipping or peeling in a pixel pattern at the time of development does not occur.

Therefore, the radiation-sensitive composition of the present invention may be remarkably suitably used for producing various color filters such as a color filter for a color liquid crystal display device in the electronic industry field.

EXAMPLE

[0096]

Hereinafter, the present invention will be described more specifically by way of examples. However, the present invention is not limited to the following examples.

Preperation of pigment dispersion liquid

Preparation Example 1

A pigment dispersion liquid (M-1) was prepared by mixing and dispersing for 12 hours, in a beads mill, 9 parts by weight of C.I. Pigment Green 36 and 6 parts by weight of C.I. Pigment Yellow 150 as the colorant (A), 5 parts by weight (in terms of solid content) of Solsperse 35100 (manufactured by The Lubrizol Corporation) as a dispersant, and propylene glycol monomethyl ether acetate in an amount to have a solid

concentration of 20% as a solvent.

[0097]

Preparation Example 2

A pigment dispersion liquid (M-2) was prepared by mixing and dispersing for 12 hours, in a beads mill, 9 parts by weight of C.I. Pigment Green 58 (manufactured by Dainippon Ink and Chemicals Inc.) and 6 parts by weight of C.I. Pigment Yellow 150 as the colorant (A), 5 parts by weight (in terms of solid content) of PB880 (manufactured by Ajinomoto Fine-Techno Co., Inc.) as a dispersant, and propylene glycol monomethyl ether acetate in an amount to have a solid concentration of 20% as a solvent.

[0098]

Preparation Example 3

A pigment dispersion liquid (M-3) was prepared by mixing and dispersing for 12 hours, in a beads mill, 15 parts by weight of C.I. Pigment Red 254 (manufactured by Ciba Specialty Chemicals Inc., trade name: BK-CF) as the colorant (A), 5 parts by weight (in terms of solid content) of Solsperse 76500 (manufactured by The Lubrizol Corporation) as a dispersant, and propylene glycol monomethyl ether acetate in an amount to have a solid concentration of 20% as a solvent.

[0099]

Preparation Example 4

A pigment dispersion liquid (M-4) was prepared by mixing and dispersing for 12 hours, in a beads mill, 18 parts by weight of a carbon black as the colorant (A), 2 parts by weight (in terms of solid content) of EFKA 4046 (manufactured by Ciba Specialty Chemicals Inc.) as a dispersant, and propylene glycol monomethyl ether acetate in an amount to have a solid concentration of 20% as a solvent.

[0100]

Synthesis of alkali-soluble resin (B)

Synthesis Example 1

A flask equipped with a condenser and a stirrer was fed with 3 parts by weight of 2,2'-azobisisobutyronitrile and 200 parts by weight of propylene glycol monomethyl ether acetate, and subsequently fed with 15 parts by weight of methacrylic acid, 20 parts by weight of N-phenylmaleimide, 55 parts by weight of benzyl methacrylate, 10 parts by weight of styrene, and 5 parts by weight of 2,4-diphenyl-4-methyl-1-pentene (manufactured by NOF CORPORATION, trade name: Nofmer MSD) as a molecular weight controlling agent, followed by purging with nitrogen. The reaction solution was then heated to 80°C while stirring slowly and polymerized while maintaining the temperature for 5 hours, to thereby obtain a resin solution (solid concentration=33.3 wt%). The obtained resin had Mw=12,000 and Mn=5,500. The resin solution is taken to be a

"resin solution (B-1)".

[0101]

Example 1

100 parts by weight of the pigment dispersion liquid (M-1) as the colorant (A), 10 parts by weight (in terms of solid content) of the resin solution (B-1) as the alkali-soluble resin (B), 10 parts by weight of dipentaerythritol hexaacrylate (trade name: M-402, manufactured by Toagosei Co., Ltd.) as the polyfunctional monomer (C), 3 parts by weight of 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butane-1-one (trade name: IRGACURE 369, manufactured by Ciba Specialty Chemicals Inc.) and 1 part by weight of 4,4'-bis(diethylamino)benzophenone as the photopolymerization initiator (D), 1 part by weight of N-hydroxyphthalimide as the component (E), and propylene glycol monomethyl ether acetate as a solvent were used and mixed, to thereby prepare a liquid composition (S-1) having a solid concentration of 25%.

The liquid composition (S-1) was evaluated in accordance with the following procedure. The evaluation results are shown in Table 2.

[0102]

Evaluation of development resistance

The liquid composition (S-1) was applied onto a soda glass substrate, in which an SiO_2 film for preventing a sodium

ion from being eluted was formed on the surface, by using a spin coater, and then pre-baked on a hot plate at 90°C for 4 minutes to form five coating films each having a film thickness of 2.5 μm. Next, those substrates were cooled to room temperature, and then the coating films were exposed to radiation having wavelengths of 365 nm, 405 nm, and 436 nm in exposure doses of 100, 200, 300, 500, and 800 J/m^2 through a photomask by using a high-pressure mercury lamp. Then, a shower development was performed by discharging for 80 seconds a developer of 0.04% by weight of an aqueous potassium hydroxide solution at 23°C onto those substrates under a development pressure of 1 kgf/cm^2 (nozzle size of 1 mm). After that, each of the substrates was further post-baked at 220°C for 30 minutes to form a dot pattern of 200×200 μm on the substrate.

From the results, the development resistance was evaluated, and the case where a film thickness ratio before and after the development of the dot pattern (film thickness after development × 100 / film thickness before development) was 95% or more was represented by "○", the case where the film thickness ratio before and after the development was less than 95% or the case where chipping was observed in a part of the dot pattern was represented by "△", and the case where the whole pattern was peeled off from the substrate after the

development was represented by "×".

[0103]

Evaluation of water unevenness

The liquid composition (S-1) was applied onto the surface of a glass substrate by using a spin coater, and then pre-baked on a hot plate at 90°C for 4 minutes to form a coating film having a film thickness of 1.3 μm. Next, the substrate was cooled to room temperature, and then the coating film formed on the substrate was exposed to light in an exposure dose of 400 J/m^2 through a photomask by using a high-pressure mercury lamp. Then, a shower development was performed by discharging 0.04% by weight of an aqueous potassium hydroxide solution at 23°C, until the coating film at an unexposed part was completely disappeared and the elapse of 5 seconds thereafter, onto the coating film formed on the substrates under a development pressure of 1.5 kgf/cm^2 (nozzle size of 1 mm). Next, a rinse treatment was performed by discharging ultrapure water for 60 seconds under a rinse pressure of 1.5 kgf/cm^2 (nozzle size of 1 mm), to thereby form a dot pattern of 200×200 μm.

The moisture on the surface of the substrate on which the dot pattern was formed was removed by air blowing, and after that, 20 dot patterns were observed with a light microscope. The water unevenness was evaluated, and, of those 20 dot

patterns, the case where the water unevenness was observed in 10 or more patterns was represented by "×", the case where the water unevenness was observed in 1 to 9 patterns was represented by "△", and the case where the water unevenness was not observed at all was represented by "○".

[0104]

Examples 2 to 9 and Comparative Examples 1 to 5

Liquid compositions (S-2) to (S-14) were prepared in the same manner as that in Example 1, except that types and contents of the respective components were changed as shown in Table 1.

Next, evaluations were performed in the same manner as that in Example 1, except that the liquid compositions (S-2) to (S-14) were each used instead of the liquid composition (S-1). The results are shown in Table 2.

[0105]

[Table 1]

	Liquid composition	Component (A)				Component (B)	Component (C)		Component (D)								Component (E)				
		M-1	M-2	M-3	M-4	B-1	C-1	C-2	D-1	D-2	D-3	D-4	D-5	D-6	D-7	D-8	E-1	E-2	E-3	E-4	E-5
Example 1	S-1	100	-	-	-	10	10	-	3	-	-	-	-	-	1	-	1	-	-	-	-
Example 2	S-2	100	-	-	-	10	10	-	3	-	-	-	-	-	1	-	-	1	-	-	-
Example 3	S-3	100	-	-	-	10	10	-	3	-	-	-	-	-	1	-	-	-	1	-	-
Example 4	S-4	100	-	-	-	10	10	-	3	-	-	-	-	-	1	-	-	-	-	1	-
Example 5	S-5	100	-	-	-	10	10	-	3	-	-	-	-	-	1	-	-	-	-	-	1
Example 6	S-6	100	-	-	-	10	10	-	1	-	-	-	1	1	1	-	1	-	-	-	-
Example 7	S-7	-	100	-	-	12	8	-	-	4	-	-	-	-	-	-	1	-	-	-	-
Example 8	S-8	-	-	100	-	10	10	5	-	-	3	-	-	-	-	1	1	-	-	-	-
Example 9	S-9	-	-	-	100	9	6	-	-	-	-	3	-	-	1	-	1	-	-	-	-
Comparative Example 1	S-10	100	-	-	-	10	10	-	3	-	-	-	-	-	1	-	-	-	-	-	-
Comparative Example 2	S-11	100	-	-	-	10	10	-	1	-	-	-	1	1	1	-	-	-	-	-	-
Comparative Example 3	S-12	-	100	-	-	12	8	-	-	4	-	-	-	-	-	-	-	-	-	-	-
Comparative Example 4	S-13	-	-	100	-	10	10	5	-	-	3	-	-	-	-	1	-	-	-	-	-
Comparative Example 5	S-14	-	-	-	100	9	6	-	-	-	-	3	-	-	1	-	-	-	-	-	-

[0106]

In Table 1, respective components are as follows.

C-1: dipentaerythritol hexaacrylate (trade name: M-402, manufactured by Toagosei Co., Ltd.)

C-2: a mixture of a monoesterified product of dipentaerythritol pentaacrylate and succinic acid, dipentaerythritol hexaacrylate, and dipentaerythritol pentaacrylate (trade name: TO-1382, manufactured by Toagosei Co., Ltd.)

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

D-2: 2-dimethylamino-2-(4-methylbenzyl)-1-(4-morpholine-4-yl-phenyl)-butane-1-one (trade name: IRGACURE 379, manufactured by Ciba Specialty Chemicals Inc.)

D-3: 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1-one (trade name: IRGACURE 907, manufactured by Ciba Specialty Chemicals Inc.)

D-4: ethanone, 1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-, 1-(O-acetyloxime) (trade name: IRGACURE OX02, manufactured by Ciba Specialty Chemicals Inc.)

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

D-6: 2-mercaptobenzothiazole

D-7: 4,4'-bis(diethylamino)benzophenone

D-8: 2,4-diethylthioxanthone

E-1: N-hydroxyphthalimide

E-2: N-hydroxysuccinimide

E-3: N-hydroxy-1,8-naphthalimide

E-4: N-acetoxyphthalimide

E-5: trihydroxyimide cyanuric acid

[0107]

[Table 2]

	Liquid composition	Development resistance					Water unevenness
		100 J/m^2	200 J/m^2	300 J/m^2	500 J/m^2	800 J/m^2	
Example 1	S-1	○	○	○	○	○	○
Example 2	S-2	○	○	○	○	○	○
Example 3	S-3	○	○	○	○	○	○
Example 4	S-4	○	○	○	○	○	○
Example 5	S-5	○	○	○	○	○	○
Example 6	S-6	○	○	○	○	○	○
Example 7	S-7	△	○	○	○	○	○
Example 8	S-8	○	○	○	○	○	○
Example 9	S-9	△	○	○	○	○	○
Comparative Example 1	S-10	×	×	△	○	○	×
Comparative Example 2	S-11	×	×	△	○	○	×
Comparative Example 3	S-12	×	×	△	△	○	×
Comparative Example 4	S-13	×	×	△	○	○	×
Comparative Example 5	S-14	×	×	×	△	○	×

WHAT IS CLAIMED IS:

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

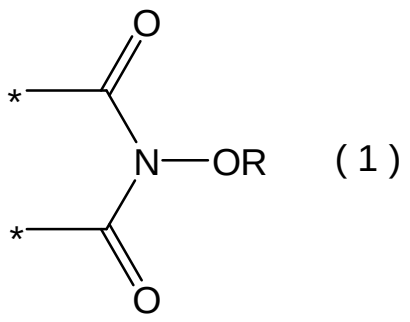
a colorant (A);

an alkali-soluble resin (B);

a polyfunctional monomer (C);

a photopolymerization initiator (D); and

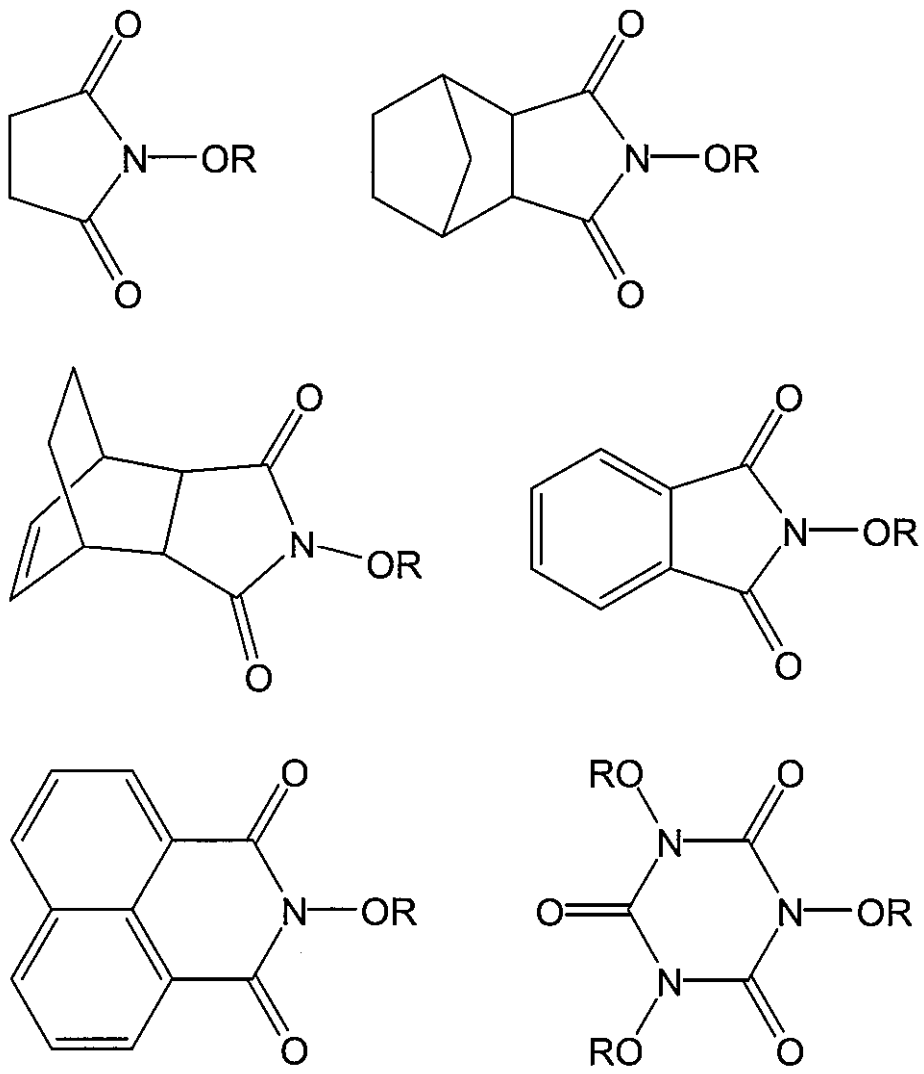
a compound (E) having a structure represented by the following formula (1):



(1)

where: R represents a hydrogen atom, a secondary or tertiary alkyl group having 3 to 30 carbon atoms, a cyclic alkyl group having 5 to 12 carbon atoms, an allyl group, an aralkyl group having 7 to 30 carbon atoms, or an acyl group having 2 to 30 carbon atoms; and "*" represents a bond.

2. The radiation-sensitive composition for forming a coloring layer according to claim 1, wherein the compound (E) is represented by any one of the following formulae:



where R's each have the same meaning as R in the formula (1).

3. The radiation-sensitive composition for forming a coloring layer according to claim 2, wherein the compound (E) comprises any one of N-hydroxysuccinimide, N-hydroxy-5-norbornene-2,3-dicarboxyimide, N-hydroxyphthalimide, N-acetoxyphthalimide, N-benzoyloxyphthalimide, N-hydroxy-1,8-

naphthalimide, and trihydroxyimide cyanuric acid.

4. A color filter comprising a coloring layer, which is formed by using the radiation-sensitive composition for forming a coloring layer according to any one of claims 1 to 3.

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